Electrical and optical properties of FeCl₃-doped polyparaphenylene $[(p-C_6H_4)_x]$

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The results of an experimental study of dc and microwave electrical conductivities, electron-spin resonance, optical reflection, and infrared absorption in FeCl₃-doped polyparaphenylene (PPP) are presented. In low-conducting PPP, the conductivity is described by interpolaron hopping processes among the polaron and bipolaron states induced by the doping. Further evidence for these states is obtained from the ir and ESR results in doped PPP. The new infrared modes due to doping and the behavior of the spin density as a function of the dopant concentration can be accounted for by the formation of polarons and spinless bipolarons. The pronounced plasma edge in the reflection spectra of heavily doped samples points to an inhomogeneous material and the existence of strands with high charge-carrier concentrations, whereas the dc conductivity can be well described by variable-range hopping processes occurring within the regions between the strands.

I. INTRODUCTION

polyacetylene¹ Conducting polymers such as $[(-C_2H_2-)_x, \text{ or PA}], \text{ poly } (p-\text{phenylene})^2 [(-C_6H_4-)_x, \text{ or PA}]$ PPP], poly (*p*-phenylene sulfide)³ [($-S-C_6H_4-)_x$, or PPS], and polypyrrole⁴ [($-C_4H_3N-)_x$, or PPy] are attracting extensive interest at present, academic as well as industrial. This is due to the unusual combination of electrical, magnetic, and optical properties of these materials: an enhancement of the conductivity by doping of the intrinsically insulating polymers by 9 to 18 orders of magnitude up to metallic levels, a coexistence of a low Pauli susceptibility and high electrical conductivity found in, e.g., AsF₅-doped trans-PA (Ref. 5) and SbF₅-doped PPP (Ref. 6) implying spinless charge carriers, an intense and narrow electron-spin resonance (ESR) signal which decreases with increasing doping⁵ and which in undoped PA is coupled with the Overhauser effect in electron-nuclear double resonance (ENDOR) experiments,⁷ a strong midgap optical absorption⁸ in PA, doping-induced intense infrared (ir) modes in, e.g., PA (Ref. 9) and PPP (Ref. 10), etc.

Among the conducting polymers PA, which is the simplest fully conjugated polymer, has been the most studied so far. In PA the soliton model of Su, Schrieffer, and Heeger¹¹ and others¹² has been the most successful one to account for most of the novel features observed in the material. The model, however, has not been universally accepted. Alternatively, Tomkiewicz et al.¹³ proposed on the basis of magnetic susceptibility χ and dc conductivity measurements a highly inhomogeneous doping, forming metallic islands in a low-conductivity matrix. In this picture the soliton doping mechanism plays no role and the semiconductor-to-metal transition observed at a doping concentration $\sim 7 \mod \%$ in PA is related to a threshold for percolation between the islands. The main drawback of the model is its inability to account for the χ data of Ref. 5 and subsequent studies¹⁴ of the magnetic properties of trans-PA.

The electrical¹⁰ and magnetic⁶ properties of doped PPP are similar to those of trans-PA. Since PPP does not possess a degenerate ground state as does PA,¹¹ it is not expected to accommodate single solitons. Brédas et al.15 have shown, however, that soliton-antisoliton pairs in the form of polarons and bipolarons could be stable in doped PPP. This could be one of the reasons for the similarity between the transport properties of doped PPP and PA. In lightly doped trans-PA Kivelson's intersoliton-hopping model¹⁶ explains quantitatively the temperature, pressure, and frequency dependences of the electrical conductivity.^{17,18} Later Kivelson¹⁹ proposed that the same conduction process might be expected to be important also in other materials which have solitonlike excitations. Indeed, in this paper we show that in low-conductivity PPP the dc and microwave conductivities can be described by Kivelson's model when slightly modified for correlated defect pairs such as polarons and bipolarons.

PPP has certain advantages over PA for studying transport properties. In PPP there are no isomerization processes due to doping, and in addition it is more stable when exposed to air. On the other hand, a detailed characterization of PPP is more difficult since it is obtained as a semicrystalline powder, which may contain imperfections such as cross-links and halogen-substituted phenyl units. Further, a precise control of the doping levels is not as straightforward as in PA.

In PPP there are still a lot of open questions concerning the doping mechanism, the nature of the defect states, the dominant conduction processes, the effect of nonuniform doping, and unintentional impurities. The electrical conductivity in PPP has been previously studied by Shacklette *et al.*¹⁰ for heavily AsF₅-doped material and by Pron *et al.*²⁰ for heavily FeCl₃-doped material. In the latter paper, however, only a room-temperature value for the dc conductivity was reported.

In this paper we report the first detailed results of measurements of the dc and microwave conductivities, ir ab-

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sorption, optical reflection, and ESR in both lightly and heavily FeCl₃-doped PPP. Further, we test the applicability of isoenergetic hopping and variable-range hopping models for the electrical transport in doped PPP. FeCl₃ was chosen as a dopant partly because it has been reported to give the most stable material, an aspect of importance when considering applications. Brief preliminary reports on ESR and conductivity results were given in Ref. 21.

II. EXPERIMENTAL TECHNIQUES

A. Sample preparation and characterization

PPP used in the present study was prepared by oxidative cationic polymerization of benzene following the method of Kovacic et al.²² A low reaction temperature of 30-32 °C was employed and the material was purified by repeated washings in hot HCl. The resulting powder with a grain size of 0.1–0.3 μ m was a light brown color. The samples studied in the present work and listed in Table I are from two independent growth runs (hereafter called A and B). In series A material x-ray fluorescence measurements revealed 0.5-4 wt. % Al, 0.08-0.4 wt. % Cu, 0.06-0.2 wt. % Fe, 0.06-0.5 wt. % Ti, 0.03-0.2 wt. % Si, and 0.01-0.1 wt. % S, all other impurities being of lower concentration. The chlorine content determined gravimetrically by titration was 1.5 wt. % Cl. In comparison with this the series B material²³ had significantly smaller impurity contents of 0.03 wt. % Al, 0.03 wt. % Cu, 0.04 wt. % Fe (as determined by atomic absorption), and 1 wt. % Cl. The two lots still show similar electrical properties.

The chain length was determined using ir spectroscopy where the ratio of mono (765 cm⁻¹) to para (805 cm⁻¹) substitution peak absorptions is linearly related to the ratio of mono and para rings.¹⁰ This method gave typical chain lengths of 14 to 16 rings.

FeCl₃ doping was accomplished using the method described by Pron *et al.*²⁰ PPP powder was added to a solution of FeCl₃ in nitromethane where the latter two were dried. The reaction was performed in Ar atmosphere using vigorous stirring. Excess FeCl₃ was washed

off the powder with nitromethane. For most of the measurements the powdered reaction product was compressed into pellets. In comparison with the doping of a readily prepared pellet, which is liable to cause gradients normal to the surface, the above procedure assures homogeneity down to the scale of the individual grain.

The dopant concentration was determined by a combination of atomic absorption (measuring the Fe concentration) and ir methods. Concerning the dopant it is meaningful to consider the concentration of electrically active dopant molecules, i.e., those interacting with the polymer chain in a way contributing to the conductivity. Mass uptake and atomic absorption have proven less reliable, although they give an upper limit to the concentration. These techniques indicate the total amount of dopant or Fe, respectively, regardless of whether it is electrically active. An ir method has been useful in this connection. A measure of the electrically active dopant concentration is found in the intensity ratio of the absorptions of the dopant-induced peak at 1180 cm^{-1} and the intrinsic peak at 805 cm^{-1} (see Sec. IV A). This ratio correlates consistently with $\sigma_{\rm dc}$ yielding a calibration curve from which the electrically active dopant concentration corresponding to a certain conductivity can be determined. The method is applicable below the saturation point around 6 mol %. Since the doped material is not stable in air the samples were held in an argon atmosphere or in a vacuum. We found that σ_{dc} and the ESR signal decayed slowly by about a factor of 10 during three months of exposure to humid air.

X-ray diffractometry showed that the crystallinity of PPP was increased from about 40% to about 60% by annealing. With increasing dopant concentration, however, the crystallinity decreases and in heavily doped PPP there is hardly any crystallinity left.

B. dc and microwave conductivity measurements

The dc conductivity measurements were performed on pressed (pressure 800 MPa) cylindrical pellets having a di-

Sample	FeCl ₃ doping (mol %) ^a	RT dc conductivity σ_{dc} $(\Omega^{-1} cm^{-1})$	Activation energy of $\sigma_{\rm dc}(300 \text{ K})$ (eV)	
A 1	0	< 10 ⁻¹⁰	n pantananan menerakan kana dara serakan di serakan di serakan di serakan di serakan di serakan dari serakan k	
A 2	0.1 ^b	2×10^{-7}	0.36	
A 3	1 ^b	5×10^{-4}	0.28	
A 4	2.7	1×10^{-3}		
A 5	13.9	1		
A 6	17.5	3	0.068	
A 7	15.7	7	0.052	
B 1	0	< 10 ⁻¹⁰		
<i>B</i> 2	0.8	2×10^{-6}		
B 3	1.3	7×10^{-5}		
<i>B</i> 4	5.4	2		
<i>B</i> 5	5.6	0.5		

TABLE I. Samples studied in the ir, ESR, optical reflection, and conductivity measurements.

^aFrom atomic absorption measurements.

^bFrom ir measurements.

ameter of 0.8 cm and thickness in the range 0.2–0.5 mm. Four collinear gold electrodes were evaporated onto the pellets with a spacing of 1 mm. The size of the contacts which all showed ohmic behavior was $1 \times 2 \text{ mm}^2$. At sample resistances $R > 10^8 \Omega$, a two-point method, which gave consistent results with the four-point method for $R < 10^8 \Omega$, was utilized. The currents employed were always less than 1 mA. The σ_{dc} values given were obtained directly from the measured resistance, sample dimensions, and contact geometry. No corrections were made for the density.

Measurements of the microwave conductivity $\sigma_{\rm mw}$ and dielectric constant ϵ_r , were performed using the cavity perturbation technique,²⁴ where the complex permittivity is determined from the changes in the quality factor and resonance frequency of the cavity caused by a sample. The oscillation mode of the cavity was TM₀₁₀. The resonance frequency of the empty cavity at room temperature was 24.73 GHz (K band) and the corresponding unloaded quality factor 3200. Small needle-shaped samples were compressed of the same doped powders of which the samples for $\sigma_{\rm dc}$ measurements were made and thus the dopant concentrations are the same. The sample volume and depolarization factor were determined from the sample dimensions. In highly conducting samples the cavity perturbation method could not be used due to the small skin depth.

C. ESR, ir, and optical reflectivity measurements

The ESR measurements were performed on powdered as well as pressed samples with a Varian Associates E-109 spectrometer, which was used at 9.1 or 9.5 GHz (X band) for determining spin densities N_s . For calibration a 10^{-3} M toluene solution of 2,2,6,6,-tetramethylpiperidinyloxyl radical standard with a g factor of 2.0055 and known number of spins was utilized.

The ir spectra were measured between 400 and 4000 cm^{-1} using a Perkin Elmer 983 spectrometer. Samples were made by the KBr method mixing 1 mg PPP with 300 mg KBr. The change in the PPP spectrum upon doping was studied.

Optical reflectivity measurements in the range $550-30\,000$ cm⁻¹ for samples A were performed with a Perkin Elmer double-prism-grating monochromator using unpolarized light. The infrared part, 400-5000 cm⁻¹ for samples B, was detected using an ir spectrometer (Perkin Elmer 983) and the reflectivity in the range $5000-25\,000$ cm⁻¹ using a double-prism monochromator with an optical fiber as a light guide. The computer-aided reflectivity measurements were performed at room temperature.

III. EXPERIMENTAL RESULTS

The experimental results from the σ_{dc} measurements on lightly and heavily doped PPP are summarized in Fig. 1



FIG. 1. dc conductivity $\log_{10}\sigma_{dc}\sqrt{T}$ vs $T^{-1/4}$. Numbers 2–7 refer to samples A2-A7, respectively (Table I).

where $\log_{10}(\sigma_{dc}\sqrt{T})$ is plotted versus $(1/T)^{1/4}$. In sample A6 with the highest conductivity a linear behavior can be seen. The doping causes a dramatic increase in σ_{dc} and a strong decrease in the activation energy of $\sigma_{dc}(T)$ (Table I). The rather strong T dependence and the order of magnitude of σ_{dc} indicate that the true metallic state has not been achieved even in the most heavily doped samples. The highest value $\sigma_{dc}(300 \text{ K}) = 7 \ \Omega^{-1} \text{ cm}^{-1}$ is nearly two orders of magnitude smaller than the values reported¹⁰ for AsF₅-doped PPP but an order of magnitude larger than reported²⁰ earlier for FeCl₃-doped PPP. A similar difference has been found in AsF₅ and FeCl₃-doped PA.²⁰

 $\sigma_{\rm dc}$ and $\sigma_{\rm mw}$ versus 1/T in the lightly doped samples A2 and A3 are shown in Fig. 2. In sample A2 with the lowest $\sigma_{\rm dc}$ there is a large difference of more than three orders of magnitude between $\sigma_{\rm dc}$ and $\sigma_{\rm mw}$. Notice the rather strong T dependence of $\sigma_{\rm mw}$ in sample A2.

Figure 3 shows ir transmission spectra of undoped and FeCl₃-doped PPP. The principal polymer bands in undoped PPP in the 400-4000 cm⁻¹ range have been as-



FIG. 2. dc (circles) and microwave (triangles) conductivities vs reciprocal temperature 1000/T. Numbers 2 and 3 refer to samples A2 and A3, respectively (Table I).



FIG. 3. Infrared spectra of undoped (a) and FeCl_3 -doped (b), (c), and (d) PPP. Here (b), (c), and (d) refer to samples B3, B4, and B5, respectively (Table I). The new ir absorption modes induced by doping are indicated by arrows.

signed^{25,10} as a C-H stretching mode of aromatic rings at 3030 cm⁻¹, C-C stretching modes of phenyl rings at 1480 and 1400 cm⁻¹, a C-C stretching mode of parasubstituted phenyl rings at 1000 cm⁻¹, a C-H out-of-plane deformation mode of parasubstituted phenyl rings at 805 cm⁻¹, and C-H out-of-plane deformation modes of monosubstituted phenyl rings at 765 and 695 cm⁻¹.

The ir transmission decreases with increasing doping in the whole frequency range studied, due likely to free or weakly bound charge carriers. New absorption peaks appear in the doped polymer at 1530, 1275, 1180, and 990 cm⁻¹ with an absorption increasing with doping (Fig. 3). These are not present in the spectra of undoped PPP. It is interesting to note that Shacklette *et al.*¹⁰ found dopantinduced peaks at exactly the same wave numbers in AsF₅-doped PPP.

Figure 4 shows the reflection spectra of undoped and FeCl₃-doped PPP. The plasma edge, i.e., a strong increase in the reflectivity $R(\hbar\omega)$ at photon energies $\hbar\omega=0.4-1.1$ eV, is clearly seen in heavily doped samples. This is a typical feature of $R(\hbar\omega)$ in the case of free-carrier absorp-



FIG. 4. Reflection spectra of undoped and FeCl₃-doped PPP. Numbers 1–7 refer to samples A1-A7 (Table I). The dashed curve shows the fit of Eq. (1) with parameters $\omega_p = 15\,000$ cm⁻¹, $\tau = 10^{-15}$ s, and $\epsilon(\infty) = 3.5$.

tion at infrared frequencies. Similar results have been obtained, e.g., in AsF₅ and I-doped PA (Ref. 26) and in PPy (Ref. 27). The plasma edges appear at rather high frequencies implying a large charge-carrier concentration and seem to shift to higher frequencies with increasing dopant concentration y. This is consistent with the decrease in ir transmission (Fig. 3) with increasing y. The optical gap²⁸ of PPP is $E_g = 3.5$ eV and thus the increase in R at photon energies $\hbar \omega > 3.4$ eV both in undoped and doped PPP can be related to the interband transition.

The concentration N_s of Curie-law spins obtained from the ESR measurements is shown versus dopant concentration y for powdered as well as pressed samples in Fig. 5. In all cases N_s first increases by an order of magnitude with increasing doping for $y \le 1\%$, whereafter it strongly decreases typically below $10^{16}g^{-1}$ in heavily doped samples. A strong decrease in N_s with increasing y has previously been found in PA by Ikehata *et al.*⁵ The g factor, room-temperature peak-to-peak linewidth $\Delta B_{\rm pp}$, asymmetry of the ESR linewidth, i.e., the ratio between the maximum and the minimum values of the derivative of the ESR signal, and the concentrations and linewidths of Fe³⁺ ions for all samples are listed in Table II.

The g factor of undoped PPP is close to the values reported by Lerner and Jones *et al.*²⁹ The ESR linewidths in Table II are also typical of PPP.^{29,30} In doped samples $(y \ge 1\%) \Delta B_{\rm pp}(300 \text{ K})$ is smaller than in undoped materi-

Sample	Doping (mol %)	g factor	$\Delta B_{\rm pp}^{\rm PPP}$ (G)	ESR signal asymmetry	$\frac{\Delta B_{\rm pp}^{\rm Fe^{3+}}}{\rm (G)}$	Fe ³⁺ spin concentration
A 1	0	2.0032	4.8	0.99		
A 2	0.1	2.0024	6.0	0.82		
A 3	1	2.0011	4.3	0.88		
A 5	13.9	1.9995	4.5	0.93	550	5.4×10^{19}
A7	15.7				740	3.6×10^{20}
B 1	0	2.0032	5.1	0.96		
<i>B</i> 2	0.8	2.0028	4.1	0.97	750	2.1×10^{20}
B 3	1.3	2.0024	3.5	0.98	910	2.8×10^{20}
B 4	5.4	2.0021	4.9	0.89	530	$1.6 imes 10^{20}$
B 5	5.6	2.0027	3.5	0.93	505	8.4×10 ²⁰

TABLE II. ESR properties of FeCl₃-doped PPP.



FIG. 5. Spin density vs dopant concentration in powdered (solid curves) and pressed (dashed curve) samples. Letters A and B refer to sample growth runs (Table I).

al. Similar results have been obtained by Peo *et al.*⁶ in SbF₅-doped PPP. In undoped PPP $\Delta B_{pp}(T)$ is temperature independent in agreement with earlier results, whereas in doped PPP $\Delta B_{pp}(T)$ increases with decreasing temperature.

The ESR line shape in doped samples is slightly asymmetric (Table II), each half being Lorentzian. In contrast to the Dysonian line shape typically found in well conducting samples thicker than the skin depth, the asymmetry in doped PPP consists of an increased high-field part of the derivative of the ESR signal. This is the behavior previously found by Vansco and Rockenbauer³¹ in AsF₅-doped PA and Peo *et al.*⁶ in SbF₅-doped PPP.

In heavily FeCl-doped PPP we found an additional strong absorption peak, $\Delta B_{\rm pp}(300 \text{ K}) = 500-900 \text{ G}$ with $g = 2.04 \pm 0.03$. The spin concentration related to this broad absorption peak increases with doping (Table II) and this additional absorption is most likely due to Fe ions (Fe³⁺) in the dopant molecules.

IV. DISCUSSION

A. ir transmission and optical reflection

The most interesting results in the measured ir spectra of FeCl₃-doped PPP are the new intense ir absorption modes at 1530, 1275, 1180, and 990 cm⁻¹. Using the same arguments as in the case of polyacetylene⁹ we can state that since the same modes are observed for AsF₅ and FeCl₃ doping, these new modes are not due to specific vibrations of the dopant molecules or between the molecules and the polymer chain, but are intrinsic vibrations of the chain in the doped material. According to Racovics *et al.*³² a mode at 1298 cm⁻¹ close to our measured 1275 cm⁻¹ is related to the quinoid structure of doped PPP. Thus, the new ir modes may be evidence for local deformations of the benzoid structure of PPP towards a quinoid one due to doping. On the other hand, the quinoid structure in PPP is typical of the polaron and bipolaron defect states¹⁵ to which we shall relate the conduction mechanism in lightly doped PPP (see Sec. IV C).

The sharp plasma edge in conducting solids is typically regarded as an indication of large free-carrier concentrations or the existence of metallic regions in the material. The reflectivity of a conductor at frequency ω can be expressed by the well-known equation^{33,34}

$$\boldsymbol{R}(\omega) = \frac{1 + |\boldsymbol{\epsilon}(\omega)| - \{2[|\boldsymbol{\epsilon}(\omega)| + \boldsymbol{\epsilon}_{1}(\omega)]\}^{1/2}}{1 + |\boldsymbol{\epsilon}(\omega)| + \{2[|\boldsymbol{\epsilon}(\omega)| + \boldsymbol{\epsilon}_{1}(\omega)]\}^{1/2}}, \quad (1)$$

where

$$|\epsilon(\omega)| = [\epsilon_1^2(\omega) + \epsilon_2^2(\omega)]^{1/2}, \qquad (2)$$

 $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ being the real and imaginary parts of the complex permittivity $\epsilon(\omega)$, which is given by

$$\epsilon(\omega) = \epsilon(\infty) - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} , \qquad (3)$$

where

$$\omega_p^2 = \frac{ne^2}{m^* \epsilon(\infty)} \tag{4}$$

is the plasma frequency. $\epsilon(\infty)$ is the real part of the permittivity at high frequencies ($\omega \tau \gg 1$) and τ the relaxation time of the charge carriers whose concentration is *n* and effective mass m^* . Equation (1) has been fitted to the measured reflectivity in Figs. 4 and 6. In Fig. 4 the fit is good with unique values of the parameters, whereas in Fig. 6 we may only determine the lower and upper bounds for ω_p and τ . In any case we can estimate the order of magnitude of the high-frequency conductivity from the plasma frequency and the relaxation time

$$\sigma_{\rm opt} = \omega_p^2 \epsilon(\infty) \tau \approx 10^3 \ \Omega^{-1} \,\mathrm{cm}^{-1} \ . \tag{5}$$



FIG. 6. Observed (solid curve) and calculated (dashed and dash-dotted curves) reflection spectra for sample B4 (Table I). The dashed curve has been calculated from Eq. (1) with the parameters $\omega_p = 13500 \text{ cm}^{-1}$, $\tau = 6 \times 10^{-16}$ s, and $\epsilon(\infty) = 3.5$ and the dash-dotted curve with parameters $\omega_p = 6000 \text{ cm}^{-1}$, $\tau = 10^{-15}$ s, and $\epsilon(\infty) = 3.5$.

This value is more than two orders of magnitude larger than the RT dc conductivity indicating that σ_{dc} is dominated by low-conductivity regions between the strands with high charge-carrier concentrations. Similar results have been obtained in AsF₅- and I-doped PA (Ref. 26) and in PPy (Ref. 26).

If m^* is estimated from the tight-binding result, $m^* = 2\hbar^2 / Wa_0^2$ using the values³⁵ 3.2 eV and 4.3 Å for the π -band width W and lattice constant a_0 in PPP along the chain, respectively, one obtains for the mobility $\mu = e\tau/m^* \approx 4 \text{ cm}^2/\text{V}$ s. This value is what one expects in a disordered metal. It is smaller than $\mu = 60 \text{ cm}^2/\text{V} \text{ s}$ estimated for PA.³⁶ The difference can partly be accounted for by the smaller bandwidth in PPP. Estimating the charge-carrier concentration from the plasma frequency by using Eq. (4) one obtains $n \approx 10^{21}$ cm⁻³, which is of the same order of magnitude as the values estimated from the dopant concentrations of the heavily doped samples when a complete charge transfer is assumed. So, the simple Drude model for reflectivity seems to account for the observed behavior in heavily doped PPP, especially in sample A7, Fig. 4. Further, the large difference between the dc and high-frequency conductivities points to a highly inhomogeneous material.

B. ESR results

The origin of unpaired spins in undoped PPP has remained open to some extent. In a recent paper Froyer *et al.*³⁰ accounted for the spins by structural defects such as macrocycles [Fig. 7(a)] which are created during the polymerization process, especially in the Kovacic method. The principal source of line broadening is an unresolved proton hyperfine structure.

Since the g factor, linewidth, and T dependence of $\Delta B_{pp}(T)$ are different in undoped and doped PPP we propose that the origin of the unpaired spins is also different



FIG. 7. (a) Paramagnetic defects (Ref. 30) in undoped PPP. (b) Paramagnetic polarons and spinless bipolarons (Ref. 15) in doped PPP.

in undoped and doped samples. In trans-PA the strong decrease in the spin density N_s due to doping has been explained⁵ by dopant-induced charged solitons which are spinless. Since single solitons do not exist in PPP due to the lack of degeneracy, the soliton doping mechanism as such is excluded. However, Brédas et al.¹⁵ have recently shown that in doped PPP soliton-antisoliton pair formation in the form of polarons and bipolarons [Fig. 7(b)] is possible. The observed doping dependence of N_s (Fig. 5) may thus be accounted for by these defects. At low doping levels N_s increases due to formation of polarons which carry a spin [Fig. 7(b)]. At higher levels the spin-less bipolarons dominate¹⁵ leading to a strong reduction in N_s . This interpretation is in agreement with our assignment of the new ir modes induced by doping (Sec. IVA) and also with the proposal of Brédas et al.¹⁵ that the exceptionally small Pauli susceptibility⁶ in highly conducting PPP is due to spinless bipolarons.

Since the polarons are charged defects¹⁵ and hence bound to dopant molecules, the observed shift in the *g* factor (Table II) due to doping could be caused by a spinorbit interaction between the polaron and the dopant molecule. This is in contrast to the *trans*-PA case where the neutral solitons which are not bound to the dopants are responsible for the ESR signal. Hence, in PA the spins preserve completely their π character and no shift in *g* is observed.³⁷

C. Conductivity in lightly doped PPP

In the following we shall look for an explanation for the observed conductivity behavior in lightly doped PPP, which would be compatible with our interpretation of the ESR and ir data in terms of the polaron and bipolaron defects. Attempts to analyze quantitatively conductivity data for the low conductivity samples A2 and A3 by using conventional models for disordered semiconductors such as Mott's variable-range hopping (VRH) model [see Sec. IV D, Eqs. (11)-(17)], always resulted in quite unreasonable values for Mott's parameters, in contrast to the heavily doped case. A search for new conduction mechanisms was thus motivated.

Kivelson¹⁶ has recently proposed a novel conduction mechanism in lightly doped PA, i.e., phonon-assisted hopping between soliton bound states. This intersoliton hopping is a three-dimensional conduction process occurring between a neutral and a charged soliton in the vicinity of dopants. Since the total number of neutral and charged solitons does not change in the process, the activation energy for hopping can be arbitrarily small if the neutral soliton happens to be near an impurity. On the other hand, this condition yields a factor $1/N \ll 1$ to the transition rate at which an electron hops between a pair of solitons, N being the number of carbon atoms in a chain. Even so, the conductivity can be moderately large at low dopant concentrations. The calculated values¹⁶ of the dc and ac conductivities, thermoelectric power, and transverse spin-diffusion constant compare favorably with the experimental results obtained on trans-PA.

Later Kivelson¹⁹ pointed out that a similar conduction process might also be relevant in other quasi-one-

dimensional semiconductors which have solitonlike excitations or even in systems with slightly nondegenerate ground states, such as *cis*-PA. In this case the hopping would occur between bound soliton-antisoliton pairs such as polarons and bipolarons. Since we have interpreted our ir and ESR results on doped PPP with the aid of polaron and bipolaron defects induced by doping, it is consistent to try to describe the electrical conductivity in terms of the same defects. In the following we shall slightly modify Kivelson's model and apply it to conduction processes between polaron and bipolaron states. Note that in this model hopping processes are isoenergetic, i.e., the distribution of site energies is narrow. This qualitatively agrees with doping-induced soliton-antisoliton pairs in lightly doped PPP where the overlap of the pairs is small.

In Kivelson's model for PA the temperature dependence of $\sigma_{dc}(T)$ results from the coupling of solitons to the optical phonons which modulate the dimerization. Since the quinoid structure in PPP is also strongly modulated by the optical phonons, the temperature dependence of the interpolaron hopping processes is expected to be similar to that proposed by Kivelson, $\sigma_{dc}(T) \sim T^n$, where *n* is a constant ~ 10 . As in the intersoliton hopping process the activation energy for interpolaron hopping is small since the total number of polarons and bipolarons is not changed in the hopping process. However, in interpolaron hopping the jump rate is not reduced by the factor $1/N \ll 1$ as in the soliton case. This is due to the fact that both polarons and bipolarons are charged [Fig. 7(b)] and thus bound to impurities. When this modification is taken into account Kivelson's equations for the dc and ac electrical conductivities read, in the case of interpolaron hopping,

$$\sigma_{\rm dc}(T) = \frac{Ae^2\gamma(T)}{k_B T} \left[\frac{\xi}{R_0^2}\right] \frac{Y_p Y_{bp}}{(Y_p + Y_{bp})^2} e^{-2BR_0/\xi}, \quad (6)$$

$$\sigma_{\rm ac}(T) = \sigma_{\rm dc}(T) + \frac{e^2}{384\hbar} \left[\frac{C_{\rm imp}^2}{k_B T}\right] \frac{Y_p Y_{bp}}{(Y_p + Y_{bp})^2}$$

$$\times \xi_{||}^3 \xi_1^2 \hbar \omega \left[\ln\left[\frac{2\omega}{\Gamma_0}\right]\right]^4. \quad (7)$$

Here A = 0.45, B = 1.39, Y_p and Y_{bp} are the concentrations of polarons and bipolarons, respectively, and $R_0 = (3/4\pi C_{\rm imp})^{1/3}$ is the typical separation between impurities whose concentration is $C_{\rm imp}$. $\xi = (\xi_{||}\xi_{\perp}^2)^{1/3}$ is the average decay length of a polaron or bipolaron wave function, $\xi_{||}$ and ξ_{\perp} being the decay lengths parallel and perpendicular to the polymer chain, respectively. According to the calculations of Brédas *et al.*¹⁵ the extension of the defect should be the same for polarons and bipolarons, ~5 phenyl rings in PPP. We have

$$\Gamma_0 = Y_p Y_{bp} / (Y_p + Y_{bp})^2 \gamma(T) ,$$

where

$$\gamma(T) = \gamma_0 [T/(300 \text{ K})]^{n+1}$$

(8)

FIG. 8. dc conductivity $\log_{10}\sigma_{dc}$ vs $\log_{10}T$ in samples A2 and A3 (Table I).

is the transition rate of an electron between polaron and bipolaron states.

According to Eqs. (6) and (8) the plotting of σ_{dc} versus T on a log-log scale should give a straight line, if the measured $\sigma_{dc}(T)$ is dominated by interpolaron hopping. This behavior is indeed observed as shown in Fig. 8 from which a value n = 13.7 is obtained for sample A2. If this plot is compared with $\sigma_{dc}(T)$ in Fig. 1 one may state that the measured $\sigma_{dc}(T)$ in lightly doped samples follows slightly better the behavior predicted by Eqs. (6) and (8) than Mott's $T^{-1/4}$ law.

Equations (6) and (7) are fitted to the measured dc and microwave conductivities of sample A2 in Fig. 9. The prefactor $\gamma_0 = 1.2 \times 10^{17} \text{ s}^{-1}$ in Eq. (8) was determined from the T dependence of the microwave conductivity $\sigma_{\rm mw}$ and it is of the same order of magnitude as γ_0 estimated by Kivelson¹⁶ for *trans*-PA. The order of magnitude of $\sigma_{\rm dc}$ was adjusted with the impurity concentration $C_{\rm imp}$, which actually was the only fitting parameter. The other parameters were $\xi_{||}=10.6 \text{ Å}$ $(2\xi_{||}\approx 5 \text{ phenyl})$ rings¹⁵) and $Y_p = 10^{18} \text{ cm}^{-3} = \text{spin density obtained from}$



the ESR measurements. The value of the out-of-chain wave-function decay length ξ_{\perp} , which depends on the interchain resonance energy and the interchain distance b = 6.6 Å, is not known for PPP and it was estimated from the relation $\xi_{\perp} \approx b/2$ valid for *trans*-PA.¹⁶ Since the spin density is two orders of magnitude smaller than the dopant concentration, we assume that the rest of the dopants induce spinless bipolarons and thus $Y_{bp} \approx C_{imp}$.

The value of $C_{\rm imp}$ found in the fitting was $C_{\rm imp} = 0.033\%$, which is one third of the dopant concentration Y but still of the same order of magnitude. The calculated $\sigma_{\rm mw}$ remains slightly smaller than the measured one. This difference could partially be accounted for by impurity centers or clusters which do not contribute to the dc hopping conduction but do contribute to the ac hopping processes in which it is sufficient for a charge carrier to hop back and forth between two impurities. Note that the observed rather strong T dependence of $\sigma_{\rm mw}$ in sample A2 can be accounted for by Kivelson's model whereas, e.g., Mott's VRH model³⁸ predicts a weaker T dependence, $\sigma_{\rm ac} \sim T$.

The ratio between the ac and dc conductivities versus dopant concentration is shown in Fig. 10. As in the case of trans-PA (Refs. 39 and 40) the decrease in $\sigma_{\rm ac}/\sigma_{\rm dc}$ with increasing doping-a behavior in agreement with Kivelson's model-seems to exclude the metallic island model¹³ in lightly doped PPP since the model predicts the opposite behavior.⁴¹ Since our results were obtained on pressed samples one should of course be very cautious when interpreting the results by using an idealized model such as that of Kivelson. Especially, the potential barriers due to the grain boundaries are expected to influence the transport properties. However, the situation in the pressed PPP pellets is not so different from the one in PA where the barriers between fibrils dominate the dc conductivity in heavily doped samples, but in lightly doped ones Kivelson's model still fits well. Since σ_{dc} is large in our heavily doped samples the potential barriers must be very thin and, hence, in samples with low enough dopant concentration the resistance of the regions between the barriers can be larger than barrier resistance justifying the



neglect of barrier effects-as is done, e.g., in Kivelson's model.

D. Conductivity in heavily doped PPP

Recently Kivelson and Epstein⁴² have found by studying the frequency response of various hopping systems that the charge-transport mechanism seems to change from isoenergetic hopping in undoped PA to variablerange hopping in more heavily doped PA. This is in agreement with the intersoliton electron hopping in lightly doped PA and with the proposed variable-range hopping among pinned solitons in moderately doped PA. In our PPP samples a similar change seems to occur upon doping. In contrast to the lightly doped PAPP the dc conductivity (Fig. 1) in heavily doped samples follows well Mott's $T^{-1/4}$ law for VRH conduction:³⁸

$$\sigma_{\rm dc}(T) = \sigma_0(T) \exp[-(T_0/T)^{1/4}] . \tag{9}$$

The constants T_0 and σ_0 read⁴³

$$T_0 = \frac{\lambda \alpha^3}{k_B N(E_F)} \tag{10}$$

and

$$\sigma_0(T) = e^2 R^2(T) v_0 N(E_F) , \qquad (11)$$

where

$$R(T) = \left[\frac{9}{8\pi \alpha k_B T N(E_F)}\right]$$
(12)

is the hopping distance, v_0 a jump rate prefactor, k_B Boltzmann's constant, α the inverse rate of falloff of the wave function, and $N(E_F)$ the density of states at the Fermi level E_F . λ is a dimensionless constant having a value⁴³ ~ 18.1. Simultaneous solution of Eqs. (10)-(12) yields⁴³

$$\alpha = (2.122 \times 10^6 / v_0) (\sigma_0 \sqrt{T} \sqrt{T_0}) m^{-1}$$
(13)

and

$$N(E_F) = (1.996 \times 10^{48} / v_0^3) [(\sigma_0 \sqrt{T})^3 (T_0)^{1/2}], \quad (14)$$

in units of cm⁻³ eV⁻¹, where $\sigma_0 \sqrt{T}$ and T_0 are obtained from the experimental conductivity data. The average hopping energy W can be estimated if the hopping distance R and the density of states $N(E_F)$ are known,

$$W = \left| \frac{3}{4\pi R^3 N(E_F)} \right| \,. \tag{15}$$

The only unknown parameter in Eqs. (13) and (14) is the jump-rate prefactor v_0 . When v_0 is estimated from an optical phonon frequency $v_{\rm ph} \sim 10^{13} \, {\rm s}^{-1}$, quite unreasonable values for $N(E_F)$ and α have been obtained³⁵ in amorphous semiconductors. An increase in v_0 by a factor 10^3 to 10^6 is typically^{44,45} needed to get reasonable values. Colson and Nagels⁴⁶ have suggested that $v_0 = v_{\rm ph} \exp(2\alpha R)$. We found that in heavily doped PPP a value $v_0 = 10^{16} \, {\rm s}^{-1}$, which is typical for disordered semiconductors,⁴⁴ gives reasonable values for $N(E_F)$ and α , which are listed in Table III for samples A6 and A7.



Sample	Doping (mol %)	$T_0 \times 10^6 \text{ K}$	$\frac{N(E_F)}{(\mathrm{cm}^{-3}\mathrm{eV}^{-1})}$	α^{-1} (Å)	<i>R</i> (Å)	<i>W</i> (eV)
A 6	17.5	2.24	1.27×10 ²²	1.94	6.78	0.060
A 7	15.7	3.92	3.41×10^{20}	5.39	21.6	0.070

TABLE III. Mott's parameters for heavily FeCl₃-doped PPP ($v_0 = 10^{16} \text{ s}^{-1}$).

As mentioned earlier attempts to apply Eqs. (13) and (14) to the lightly doped PPP were unsuccessful, i.e., the obtained $N(E_F)$ and α^{-1} were quite unreasonable for any value of v_0 . This leads us to a similar conclusion as in the case⁴² of PA: In lightly doped PPP isoenergetic hopping, where the distribution of site energies is narrow on the scale of $k_B T$, seems to dominate and $\sigma_{dc}(T)$ and $\sigma_{ac}(T)$ can be described by Kivelson's model when properly modified for polarons and bipolarons bound to charged impurities. In heavily doped PPP the bipolaron states are broadened and a VRH conduction, in which the distribution of site energies is much broader than $k_B T$, seems to dominate.

V. SUMMARY

In this paper we have shown that in lightly FeCl₃doped PPP the results from electrical conductivity, ir absorption, and ESR measurements can consistently be accounted for by soliton-antisoliton—like defect pairs induced by doping. This also explains most of the similarities between the properties of PPP and *trans*-PA, in which the soliton model has successfully been applied. Kivelson's hopping model slightly modified and applied to bound polaron and bipolaron states accounts for the observed dc and microwave conductivity behavior. Further,

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the observed decrease in $\sigma_{\rm ac}/\sigma_{\rm dc}$ and the increase in the concentration of unpaired spins with increasing dopant concentration exclude the metallic island model in lightly doped material as the model predicts the opposite behavior.

The results in heavily doped PPP support a change in the charge-transport mechanism upon doping. The large difference between the high-frequency and dc conductivities indicates that potential barriers, which separate the doped metallic regions, determine the dc conductivity. Within the barriers VRH hopping among broadened bipolaron states is proposed since—in contrast to the lightly doped case— $\sigma_{dc}(T)$ can be well described by Mott's VRH model with reasonable values of Mott's parameters.

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