

Conductivity of polymer chains: A tunneling approach

P. A. Schulz* and D. S. Galvão

Instituto de Física, Universidade Estadual de Campinas, Caixa Postal 6165, Campinas, São Paulo, Brazil

M. J. Caldas

*Instituto de Física, Universidade de São Paulo, Caixa Postal 20516,
01498 São Paulo, São Paulo, Brazil*

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We investigate the effect of disorder in the conductivity of polyaniline chains. We adopt a tunneling approach coupled to a simplified Hamiltonian, in which we model the ring-structured polymer as a linear chain of pseudoatoms. To adjust the Hamiltonian parameters, we rely on previously published data on the electronic structure for such chains. Our results agree with available data on the behavior of conductivity with protonation dose, and thus give support to the disordered-chain model of polyanilines.

I. INTRODUCTION

Much work has been devoted in recent years to the study of transport properties of polymer chains. Among these systems polyanilines are of special interest, since a remarkable increase in conductivity may be achieved by acidic treatment, or electrochemical oxidation, or both.¹ Indeed, there are evidences of insulator-metal transitions associated to acidic treatment coupled to protonation of the polymer chains.¹

Polyaniline is a general name for a family of pseudo-linear compounds where nitrogen atoms connect six-membered carbon rings of benzenoid or quinoid character. We consider here two of these compounds (Fig. 1), defined by the relative proportion of benzenoid and quinoid carbon rings. The first one is the totally reduced variety *leucoemeraldine* where only benzenoid rings exist, connected as indicated in the figure by amine nitrogen

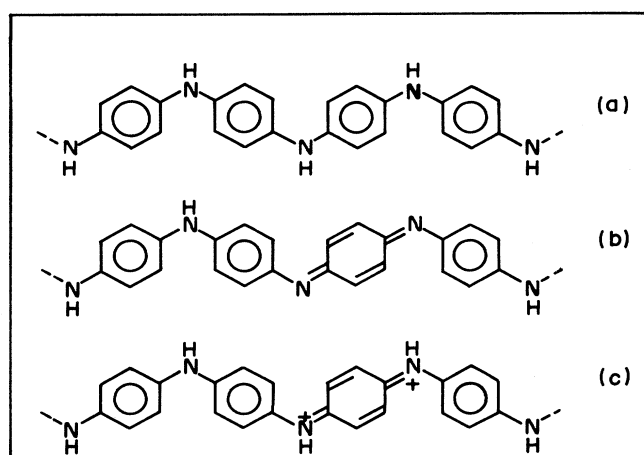


FIG. 1. Scheme of the chemical conformation in (a) leucoemeraldine, (b) emeraldine, and (c) protonated emeraldine in the "bipolaron" model (a "polaron" would consist of a single protonated site).

atoms; and the second is the *emeraldine* form with 1:3 proportions of quinoid and benzenoid rings. We also consider protonated emeraldine, where protons (H^+) are added at the imine-nitrogen sites.

In a recent paper, Galvão *et al.*² studied the electronic structure of polyanilines: Their results indicate that leucoemeraldine is an insulator, while emeraldine behaves as a semiconductor. The protonation of this last compound further reduces the gap, but no insulator-metal transition is seen in these materials when ordered. Nevertheless, the protonation of disordered emeraldine pulls the Fermi energy down, through band-tail localized states, into extended states in the valence band, which would explain the dramatic increase of conductivity seen for such systems as a function of protonation.

Disorder effects are then of paramount importance in understanding the transport properties of polyanilines. Disorder here means that the sequence of quinoid-benzenoid groups is random, subject to the constraint that a quinoid ring cannot be first neighbor to another quinoid ring in the polymer chain.

The aim of the present work is to study the effect of this kind of disorder on the transmission probabilities for carriers through such chains. The connection between the changes in the electronic structure introduced by disorder with the actual transport properties is then discussed.

II. MODEL

We recall the complexity of the actual problem we are trying to simulate: measurement of conductivity in a polymer compound. To do that, we build the simplest possible model of a polymer-like chain sandwiched between semi-infinite metallic chains. The metallic portions would then act as contacts for the measurements, while the polymer would provide the barrier for the carriers. The polyaniline structure, with its sequence of rings connected through bonds with nitrogen atoms, is substituted for a *linear chain of fictitious atomic orbitals* with suitable tight-binding Hamiltonian parameters.

The model polyaniline chain is characterized by two different “atomic” energies, E_b and E_q , representing two different kinds of ring units, benzenoid-amine nitrogen and quinoid-imine nitrogen, respectively. The bonding between the units is represented in turn by three hopping parameters: V_{bb} , for the connection of two benzenoid units; V_{bq} , a benzenoid and a quinoid unit; and V_{bq}^+ , when a benzenoid and a quinoid ring are connected through a protonated nitrogen atom. We work within the nearest-neighbor approximation, so there remain only two more parameters to be set, the energy and hopping parameters for the metallic contact chains E_m and V_m .

For the model Hamiltonian

$$H = \sum_n (E_n |n\rangle \langle n| + V_{n,n+1} |n\rangle \langle n+1| + V_{n+1,n} |n+1\rangle \langle n|), \quad (1)$$

where n is the atomic site index, the problem of transmission through the central chain segment can be exactly solved numerically, using the transfer matrix technique. We apply the Hamiltonian above to the total wave function, which yields, in principle, an infinite set of equations relating the local projections (of the wave function) on site n to the first-neighbor sites. From these, a new set of equations may be generated relating directly the projection on a site l on the left of the chain, to the projection on a site r to the right:

$$(E - E'_l) |l\rangle = V'_l |r\rangle + V_{mm} |l-1\rangle, \quad (2)$$

$$(E - E'_r) |r\rangle = V'_r |l\rangle + V_{mm} |r+1\rangle,$$

where E is the energy and primed quantities are obtained from the solution for the polymer subset. The complete set of equations is kept finite by defining⁴ transfer matrices for the contacts, $|l-1\rangle = T_l |l\rangle$ and $|r+1\rangle = T_r |r\rangle$. In this case, $|l\rangle$ is an incoming plus a reflected wave, and $|r\rangle$ is the transmitted wave.

To establish the comparison between the so-obtained transmission probabilities and the electronic structure of the chain, we evaluate Green’s functions $G(E)$ from which the local density of states at a given site n of the chain is obtained:³

$$\rho_n(E) = -\frac{1}{\pi} \text{Im}[G(E + i\theta^+)] \quad (3)$$

where E is again the electron energy and θ^+ an infinitesimal imaginary part added to the energy. These Green’s functions are obtained by solving the following set of equations:³

$$\sum_k \langle k | H - E | \sum_m | m \rangle \langle m | G | n \rangle - \langle n | n \rangle = 0. \quad (4)$$

Here H is the Hamiltonian given by Eq. (1). This set of equations is kept finite by the use of transfer matrices for the semi-infinite contact chains, as in the calculation of the transmission probabilities.

Disorder is introduced in a straightforward way by considering many different chains, where the quinoid and benzenoid sites are randomly assigned, according to the constraints of proportion and ring neighborhood men-

tioned above. An average over these many chains is undertaken, in order to minimize spurious features that could arise due to a particular configuration of a finite chain.³ For the results shown in the present paper, the number of chains taken for the averaging procedure was 250. Once the model is thus established, we calibrate the tight-binding parameters in such a way that the density of states behaves according to the results of Ref. 2. We remark that one of the major implications of that work is that conductivity is p type, that is, the relevant carriers are holes. The above model gives for the totally reduced form, leucoemeraldine, the description of a linear chain of identical atoms which, with one orbital per site, results in a single band. This band is, however, completely filled since each benzenoid-amine unit (benzene ring plus nitrogen) would contribute two electrons for the *site orbital*. We have then in this case an insulating behavior: there are no possible carriers. Taking now the case of ordered emeraldine chains we have only $\frac{1}{2}$ of the total amount of “electrons” we had for the equivalent leucoemeraldine chain. The band splits in four by symmetry (see Fig. 2), and the two lower bands are occupied, the two higher empty. Keeping in mind this charge accounting, our model preserves its consistency all the way from leucoemeraldine to emeraldine although, of course, the model is too rough for comparing the density of states (DOS) ob-

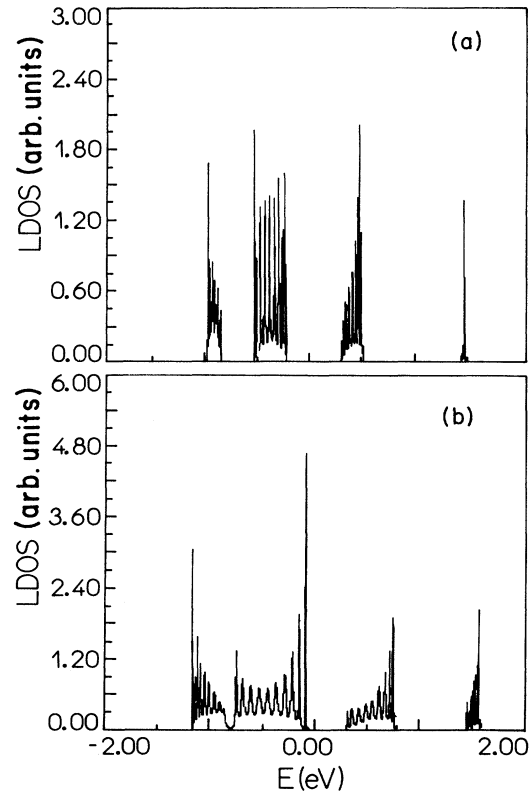


FIG. 2. Local density of states at a quinoid-group-like site at the center of (a) an unprotonated, ordered “emeraldine” chain; and (b) a protonated, ordered “emeraldine” chain. Tight-binding parameters are given in Table I. The chain is 81 sites long.

TABLE I. Values of tight-binding parameters for the diagonal atomic energies E_b and E_q , for benzenoid-amine and quinoid-imine units, respectively; and for the hopping parameters V_{bb} , V_{bq} , and V_{bq}^+ , for bonding between benzenoid units, a benzenoid and a quinoid unit, and a benzenoid and a *protonated* quinoid unit, respectively. Also the diagonal and hopping parameters for the metallic contact chains, E_m and V_m .

E_b	E_q	Model polyaniline chains			Metallic chains	
		V_{bb}	V_{bq}	V_{bq}^+	E_m	V_m
0.3	-0.3	0.8	0.3	0.5	0.0	1.0

tained here to a true DOS as in Ref. 2. In what follows we will thus discuss the behavior of the system for carriers at the gap between the second and third bands.

III. RESULTS AND DISCUSSION

We show in Fig. 2 the local density of states (LDOS) at a quinoid site at the center of an 81-site emeraldinlike ordered chain, for the nonprotonated and fully protonated structures, respectively, in 2(a) and 2(b); the oscillations seen in the LDOS are due to quantum interference with the contact chains. The parameters we used to obtain the results shown are displayed in Table I. We note that protonation brings about a reduction of the gaps between the bands, but no other strong effect. Our main

focus here, however, is not the (admittedly oversimplified) DOS, but to analyze the transmission probability which we show in Fig. 3, again for the nonprotonated [3(a)] and protonated [3(b)] structures. We can check the effect of gap narrowing, but nevertheless the protonated ordered emeraldine chain still acts as a barrier between the metallic contacts: the transmission probability drops down in the gap region by 12 orders of magnitude. In fact, there are no clear distinctions in behavior from the nonprotonated to the protonated chain.

On the other hand, the inclusion of compositional disorder for the emeraldine chain, that is, random distribution of quinoid-imine units between benzenoid-amine units, completely changes the electronic properties of the system. This may be seen from Fig. 4, where we show the transmission probabilities for the disordered counterpart of the ordered cases in Fig. 3. In Fig. 4(a) we show the transmission bands for disordered unprotonated chains, with the results for the ordered system indicated. Almost all features seen in the electronic structure of the ordered chain are lost. The transmission probability falls down orders of magnitude in the regions formerly occupied by transmission bands. Only the gap between the second and third bands of the ordered structure still shows a strong signature, indicated in Fig. 4 by an arrow. On the other hand, exactly in this gap region the transmission probability is five orders of magnitude higher than in the ordered case. While for the ordered case this gap remains, keeping its characteristics, in the disordered chains it is reduced and filled up with states following protonation, till its complete disappearance in the disordered fully protonated chain. This can be seen in Fig. 4(b), where the transmission probability for the disordered fully protonated chain is shown: now the gap region indicated by the arrow shows only a very weak feature.

In an actual system the semiconducting or insulating polymer acts as a barrier for electronic transport when a contact-polymer-contact structure is formed. If there is an insulator-metal transition in the polymer, it will not behave anymore as a barrier but the conductivity will still be affected by the disorder of the system. In the present model an insulator-metal-like transition due to protonation occurs with the vanishing of the gap in the disordered protonated emeraldine chain, with the Fermi level lying now within a band. This is in our model equivalent to the result obtained by Galvão *et al.*,² where the Fermi level is pulled down through the calculated valence band.

There remains an open question concerning the actual Fermi-level alignment in a real contact-polymer-contact structure, and whether the Fermi level moves to energies

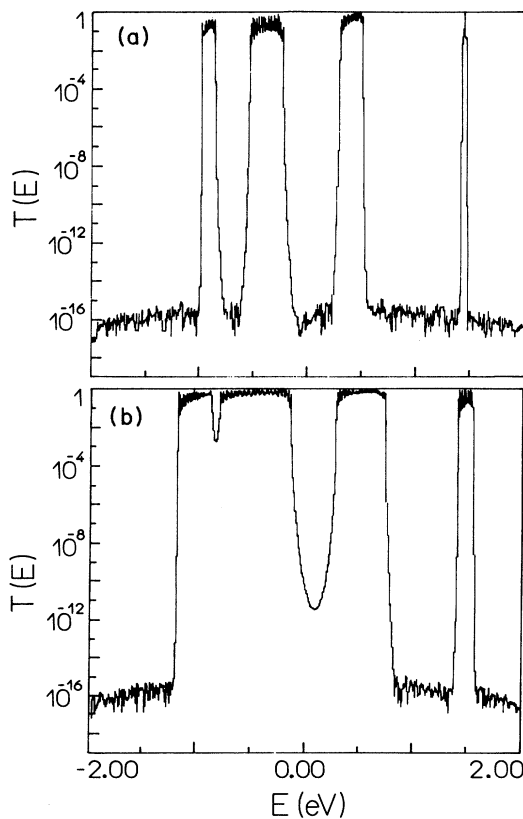


FIG. 3. Transmission probability as a function of energy: (a) for the same structure as Fig. 2(a), and (b) for the structure of Fig. 2(b).

for which the localization length is greater than the polymer chain length. This can be discussed by taking the relation between transmission probability and localization length l , given by⁵

$$l(E) = -\frac{2L}{\ln[T(E)]} \quad (5)$$

where L is the length of the chain and $T(E)$ the transmission probability. At the energy indicated by the arrow in Fig. 4(b), we have $l(E) = 30$ atomic sites, which is in fact of the same order of magnitude as the chain length, $L = 81$ sites. We can also see that finite disordered one-dimensional chains may have effectively delocalized states: here localization lengths reach $l(E) > 100$ for the energy range between the dashed lines in Fig. 4(b), which is larger than the length of the chain itself. (This effective delocalization can also be seen in the LDOS at the center of the disordered fully protonated emeraldinelike chain, which shows well-resolved interference oscillations due to the presence of the metallic semi-infinite chains, that is,

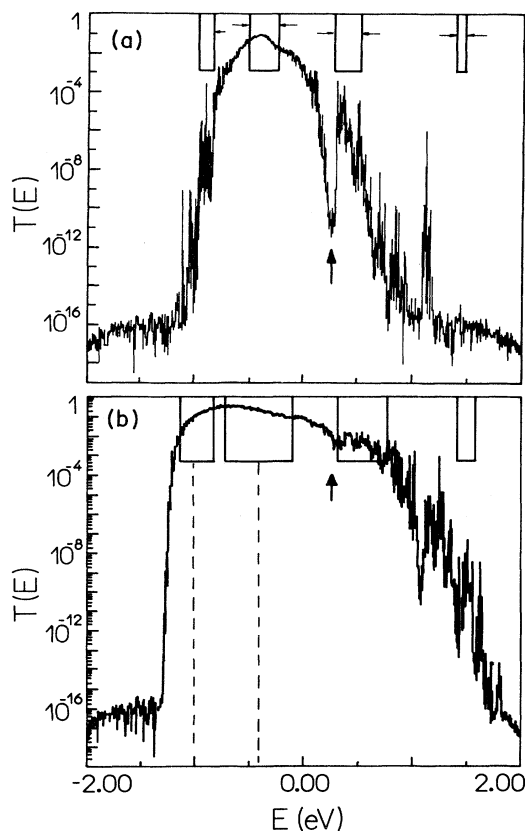


FIG. 4. Transmission probability as a function of energy: (a) for the *disordered unprotonated* emeraldine chain; and (b) for the *disordered protonated* emeraldine chain. The arrows indicate the gap features still discernible with disorder; the boxes show the position of the transmission bands for ordered structures (Fig. 3); the dashed lines delimit the region where the localization length for electronic states is of the order of the length of the chain itself.

there are energies for which the corresponding wave functions extend throughout the entire polymer chain.)

The transmission probability increases with protonation for the complete range of energies in the disordered case. In Fig. 5 we follow the transmission probability as a function of protonation, at the energy indicated by the arrow in Fig. 4. At the end points we also place the values for the ordered polymers. We see that the transmission probability is more than four orders of magnitude higher for the disordered structures; the qualitative behavior agrees with what is established for the conductivity of emeraldine as a function of protonation.⁶

The relation between $T(E)$ and the conductance of one-dimensional conductors depends strongly on how the measurement to be compared with is done.⁷ The conductance σ should be directly proportional to $T(E)$ if σ is measured between points well inside the charge reservoirs connected to the contact-polymer-contact structure. If measured between points in the contacts near the polymer, then $\sigma \sim T/(1-T)$. From the information available on actual polymer systems it is difficult to decide between these models for the conductance. Nevertheless, for the particular value of energy chosen, $T(E) \ll 1$ so both equations for the conductance yield the same numerical result, and the transmission probability as a function of protonation in Fig. 5 should be proportional to the conductance of the chain.

IV. SUMMARY AND CONCLUSIONS

We develop here a model to study the effect of disorder on the transport properties of polyanilines; for that, the electronic properties of actual polyanilines are modeled in a very simple way, but in general accordance with more sophisticated calculations. It should be stressed that the model is not dependent on the nature of the car-

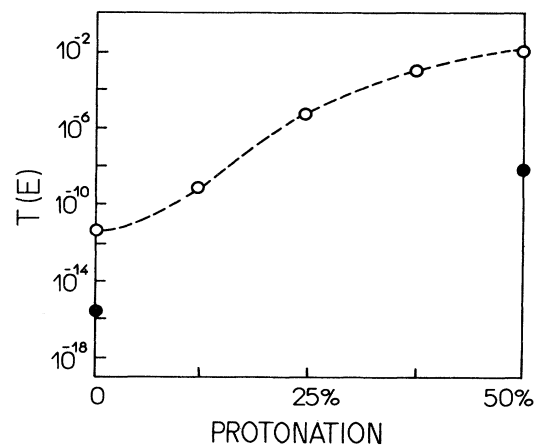


FIG. 5. Transmission probability as a function of protonation for the energy indicated by the arrows in Fig. 4. Open circles are for the disordered chains and the dark circles at the extremes for the ordered chains; 50% protonation corresponds to complete protonation of the imine nitrogen atoms.

riers, electron or holes, so that a comparison with the interpretation given by Galvão *et al.*² is valid.

Our model polyaniline goes through an insulator-metal transition following protonation if the emeraldinelike chain is disordered, in the sense that the Fermi level ends up inside a band by the closing of a gap. A real insulator-metal transition occurs when this Fermi level is located in an energy range where the electronic states are extended. Our results show that *there are effectively delocalized states in a one dimensional finite system with the*

kind of disorder considered. Recent calculations by Dunlap, Wu, and Phillips⁸ on a quinoid defect in a benzenoid chain also point to the presence of these states, which following their results would lie close to—but not directly at—the valence-band edge. Our model is too simple to allow any quantitative estimate of the Fermi-level shift through extended states in real systems. Nevertheless, the behavior of conductivity with protonation dose for real emeraldine chains^{1,6} is fairly reproduced here (Fig. 5) in our conductance calculations.

*Present address: Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Germany.

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