

Role of Disorder in the Conduction Mechanism of Polyanilines

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We present the first theoretical calculations of the electronic structure of long (200 rings) linear chains of polyaniline, ranging in composition from leucoemeraldine to emeraldine, allowing for compositional disorder in that the sequence of quinoid-benzenoid groups is random. We show that random protonation of the disordered polymers may induce p -type conductivity: This process pulls the Fermi energy down into the valence band, past localized band tails, to extended states. The effect is only seen if disorder is taken into account.

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The interest in polyanilines stems from the fact that a dramatic increase in conductivity^{1,2} (up to 10 Scm^{-1}) can be gained by acidic treatment (decreasing of the pH of the medium) or by electrochemical oxidation, or both.³ The name polyaniline encompasses a family of compounds where nitrogen atoms connect six-membered carbon rings of benzenoid or quinoid character. The relative proportion of these groups may range from the totally reduced variety leucoemeraldine [Fig. 1(a)] where only benzenoid structures exist, through emeraldine [Fig. 1(b)] with 1:3 proportions of quinoid to benzenoid rings, to the unstable form pernigraniline with equal amounts of quinoid and benzenoid groups. Acidic treatment is usually associated³ with protonation of the chain, rough-

ly preserving the oxidation state (i.e., number of electrons per "unit cell"), whereas electrochemical reactions may be thought to both oxidize and protonate the material.⁴ Simple chemical intuition tells us that the preferential site for proton addition should be the nitrogen lone-pair orbital; furthermore, this site should be most active in the ($-\text{N}=\text{}$) situation with the nitrogen orbital in the "aza hybridization." Accordingly, it is found that acidic treatment of leucoemeraldine has no significant impact on conductivity, while spectacular effects are detected for emeraldine.³

Evidence of metallic behavior for protonated chains comes from direct measurements of conductivity and Pauli susceptibility.² Optical-absorption experiments in the visible and ultraviolet regions set the fundamental absorption edge of leucoemeraldine at $\approx 4 \text{ eV}$; for oxidized (protonated) material two new absorption bands appear, at ≈ 1.5 and $\approx 3 \text{ eV}$ with the band at $\approx 1.5 \text{ eV}$ presenting a shift to higher energies with electrochemical potential (protonation dose).⁴⁻⁶ Oxidation and protonation of emeraldine also promotes absorption in the far infrared.⁷

The electronic structure of these chains has been investigated theoretically, through sophisticated techniques, by several authors.⁸⁻¹⁴ These studies, however, treat either small oligomers⁸⁻¹¹ or infinite ordered polymers¹¹⁻¹⁴ (with the smallest possible unit cell, e.g., four rings for emeraldine). We show that an essential feature in the description of these systems is *disorder*: We will use the term "disorder" here to mean that the sequence of quinoid-benzenoid groups is random.

We use simple π -electron theory in order to treat very long (200 rings) chains. It is known¹² that in the polymers the dihedral angle between rings is of the order of 30° (but with planar arrangement of nitrogen atoms). We find, however, by investigating dimers through the

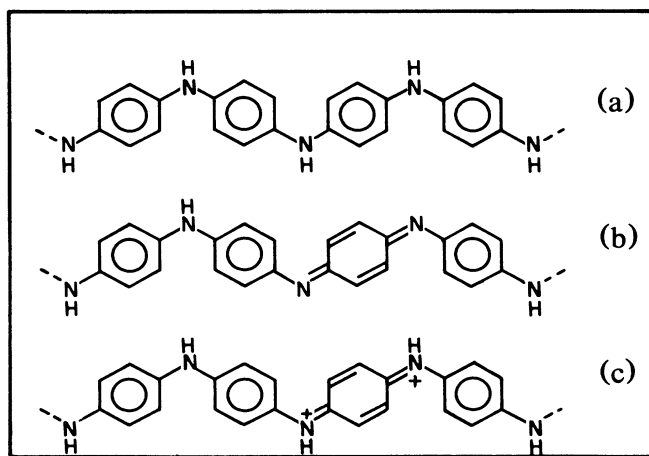


FIG. 1. Scheme of the chemical conformation in (a) leucoemeraldine, (b) emeraldine, and (c) protonated emeraldine in the "bipolaron" model (a "polaron" would consist of a single protonated site).

intermediate neglect of differential overlap (INDO) technique, that the higher occupied molecular orbitals are mostly formed from carbon- P_z and nitrogen- P_z atomic orbitals; furthermore, electronic structure results do not show a very strong dependence on the value of dihedral angle.¹¹ Hückel theory is hence used for studying small finite oligomers, and for obtaining¹⁵ the band structure of infinite ordered chains in the Bloch limit. The same parametrization used in Hückel theory is also used to study long disordered polymer chains, coupled to the negative factor counting (NFC) method. The NFC method was originally proposed by Dean¹⁶ for the study of vibrational spectra of linear chains, and later extended^{17,18} to the study of the electronic structure. We use the extended NFC method within a tight-binding formulation¹⁹ to obtain the density of states of long disordered chains. The charge distribution of individual states is then obtained through the inverse iteration method¹⁸ for energies of interest—thus yielding a clear differentiation between localized and extended states at, e.g., the Fermi energy.

This scheme allows us to study long chains with up to 200 rings in real space, and we are thus able to treat *disordered* chains ranging in composition from leucoemeraldine to emeraldine; upon such disordered chains protonation may be randomly distributed among ($-N=$) groups.

Our band-structure results agree qualitatively with published data:¹¹⁻¹⁴ Leucoemeraldine is found to be insulating with a gap of $\approx 1.2\beta$ (Ref. 15) (the resonance energy), and a reasonably delocalized uppermost valence band as may be seen in the density of states (DOS) shown in Fig. 2(a). Ordered emeraldine has a doubled unit cell compared to leucoemeraldine, with two less electrons: An unoccupied band splits off from the valence band into the gap as shown in Fig. 2(b). The

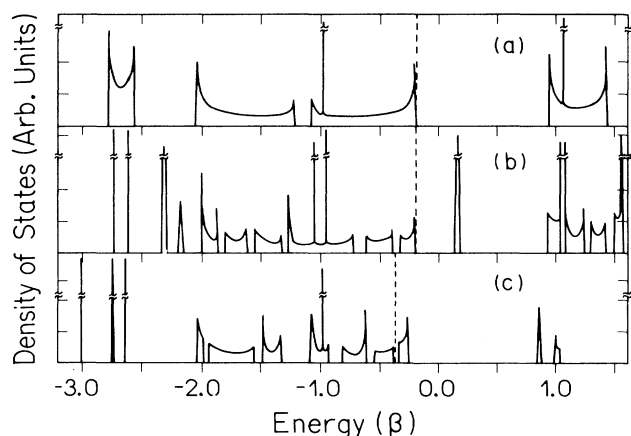


FIG. 2. Density of states obtained with Hückel theory in the Bloch limit for (a) leucoemeraldine, (b) emeraldine, and (c) fully protonated emeraldine. Energies in units of β (Ref. 15). Dashed line marks the Fermi energy.

material is now a semiconductor. Complete protonation of ordered emeraldine brings about an almost rigid downward shift of the bands which, as shown in Fig. 2(c), is so strong that it pulls the first conduction band to an energy below that corresponding to the top of the valence states of the unprotonated compound. (This strong shift of one-electron levels is also found through the INDO technique for studies on dimers, and on tetramers²⁰.) The material remains, however, a semiconductor: There is no crossing of bands at the Fermi energy.

Similar results, obtained through the more sophisticated valence effective Hamiltonian (VEH) technique, led Stafstrom *et al.*¹⁴ to postulate a “polaron lattice” in protonated emeraldine to account for the metallic behavior. Such a lattice, where “protonation” is distributed evenly among ($-N=$) and ($-NH-$) groups, would have a two-ring unit cell again, leucoemeraldinelike, with a semioccupied valence band. However, analysis of optical data strongly point to the existence of bipolaron structures.⁵

What we show next is that the “semiconducting properties” of protonated emeraldine are artificially produced by the unrealistic assumption of an ordered polymer. As a first step we analyze the results (Fig. 3) of gradual oxidation of leucoemeraldine obtained through the real-

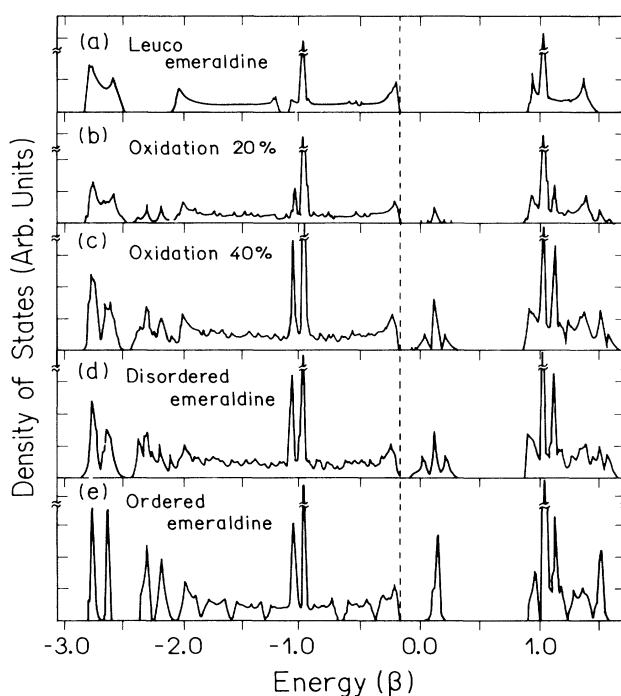


FIG. 3. Density of states obtained with the NFC method for the process of oxidation of polyaniline from the leucoemeraldine extreme in (a) to emeraldine in (d), in the disordered state. The effect of artificial ordering of emeraldine can be seen in (e) to reproduce band-structure results. Energies in units of β (Ref. 15). Dashed line marks the Fermi energy.

space scheme for chains of 200 rings. For that, we introduce quinoid groups (always between benzenoid rings) at random in the chains, according to the degree of oxidation. We may follow the formation of the first conduction band of emeraldine by the splitting, from the valence band of leucoemeraldine, of empty acceptors. While at first localized, these states finally merge into a more extended band seen as the structured peak in the DOS of disordered emeraldine, Fig. 3(d), at $\approx 0.4\beta$ from the top of the valence band. Comparison with Fig. 3(e), where ordered emeraldine is studied through the same scheme, and with Fig. 2(b), underlines the fact that the width and the structure of the peak, seen in optical absorption⁴⁻⁷ at ≈ 1.5 eV, are due to disorder effects. During the oxidation process the Fermi energy remains virtually unaffected, but we point out that states at the top of the valence band are localized, band-tail states; the material has amorphous semiconductor properties.

Now we take disordered emeraldine and start the protonation process by randomly distributing pairs of $(-N=)^+$ groups, thus creating "bipolarons." [We have also performed studies with the introduction of isolated $(-N=)^+$ groups—"polarons"—only, and of both polarons and bipolarons. The main conclusions of this work are not affected. We have chosen to present these particular results to stress that *disordered* bipolaron lattices may also be compatible with experimental data.]

The results of gradual protonation of emeraldine are depicted in the DOS curves of Fig. 4. *What we find is that protonation of the chain pulls the Fermi energy down through the localized states of the valence-band tail.* This effect immediately leads to a weak hole-mediated conductivity and Pauli susceptibility;¹⁻³ also as a consequence, the optical absorption at 0.4β will shift to higher energies.⁴⁻⁶ We draw attention to the appearance of new states in the "gap" of leucoemeraldine, close to the conduction band, which could be responsible for the absorption seen at 3 eV.⁴⁻⁶

We monitor the charge distribution of states close to the Fermi energy, and as protonation reaches $\approx (10-15)\%$ of the chain, *we find the observed transition to metallic conductivity, as the Fermi energy crosses into extended states.* This model does not exclude the possibility of single polarons—in fact it is probable that such defects exist^{2,21}—but if bipolarons are not present at all the Fermi energy is moved at a much lower rate.

As the protonation dose is increased, the absorption at $\approx 0.4\beta$ characteristic of emeraldine not only moves to higher energies but also decreases in amplitude⁶ and eventually disappears for the fully protonated compound, as expected from band-structure results [compare Figs. 4(e) and 2(c)]. In the disordered compound, however, there is no semiconductor gap even in this limit.

We thus conclude from our study of ordered and disordered polyaniline chains that the intuitive bipolaron-doping model may indeed be responsible for

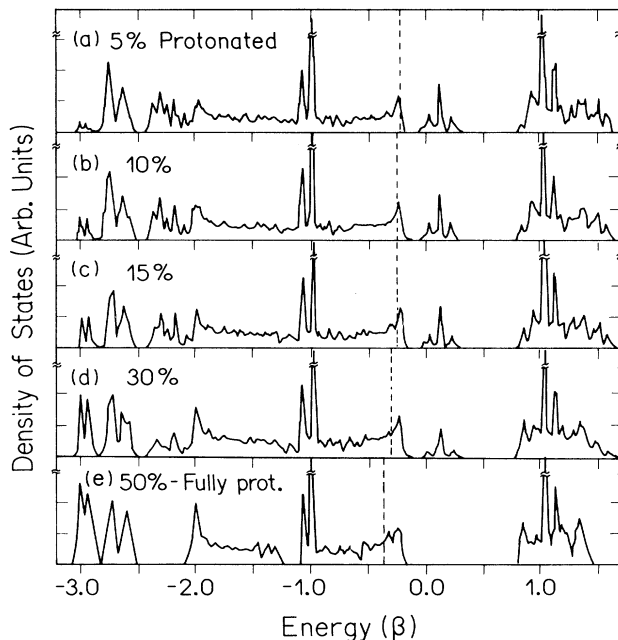


FIG. 4. Density of states obtained with the NFC method for the process of random protonation of *disordered emeraldine* (bipolaron model). The degree of protonation varies from 5% of the $(-N=)$ groups in (a) to the fully protonated chain in (e). Energies in units of β (Ref. 15). Dashed line marks the Fermi energy, and can be seen to move into the band.

the dramatic rise in (*p*-type) conductivity detected for the material upon oxidation and protonation, *if disorder effects are taken properly into account.*

In spite of the simplicity of the model (e.g., the use of the π -electron approximation, and the neglect of stacking and interchain coupling) we obtain a qualitative picture that explains several features observed experimentally for polyanilines: the insulating character of leucoemeraldine, the optical absorption behavior seen for emeraldine, and the behavior of conductivity upon protonation of emeraldine. The use of Hückel theory in the crystalline limit parallel to the use of the tight-binding NFC method allows us to discern clearly the effects of disorder: These results show, furthermore, that these procedures should be very effective in other systems where disorder is expected to play a role.

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¹⁹Details of the technique will be published elsewhere.

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