

Polarons, Bipolarons, and Solitons in Conducting Polymers

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In the last decade the discovery that it is possible to control the electrical conductivity of polymers over the range from insulating to metallic has led to substantial efforts to prepare conducting polymers for technological applications. Conducting polymers have also presented a strong fundamental scientific challenge which has been taken up by a diverse community of chemists, physicists, materials scientists, and theoreticians both in academia and in industry. The close interaction between these scientists with very different backgrounds has been a significant factor in the discovery of much of the new exciting chemistry and physics in the field of conducting polymers.¹ In this Account, we describe *from a chemist's perspective* the models recently proposed to explain the mechanisms of doping and conductivity in organic polymers, which are too often expressed in terms foreign to most chemists.

A key discovery in the development of conducting polymers was the finding in 1973 that the inorganic polymer polysulfur nitride, (SN)_x, is a metal.² The room-temperature conductivity of (SN)_x is of the order of 10³ (Ω·cm)⁻¹, to be compared with ~6 × 10⁵ (Ω·cm)⁻¹ for copper and ~10⁻¹⁴ (Ω·cm)⁻¹ for polyethylene. Below a critical temperature of about 0.3 K, (SN)_x becomes a superconductor.³ These discoveries were of particular importance because they proved the existence of highly conducting polymers and stimulated the enormous amount of work necessary to synthesize other polymeric conductors. It must be stressed that the metallic character of (SN)_x is an intrinsic property of the material, related with the presence of one unpaired electron for each S–N unit. As a result, the highest occupied electronic levels (i.e., valence band) are only half-occupied. Since there is no forbidden gap between the highest occupied and lowest unoccupied levels, the unpaired electrons can readily move under the application of an electrical field giving rise to electrical conductivity. Unlike (SN)_x, most other polymeric materials correspond to closed-shell systems where all the electrons are paired; such an electronic configuration leads to dielectric polymers.

Although its other physical properties, such as its explosive nature, prevented it from becoming commercially important, (SN)_x provided the field with the insight that eventually led to the discovery of an en-

tirely new class of conducting polymers. In 1976–1977, it was observed that the room-temperature conductivity of (SN)_x can be enhanced by an order of magnitude following exposure to bromine and similar oxidizing agents.⁴ The conducting entity is now no longer a neutral polymer but a polymeric cation, charge neutrality being preserved by incorporating into the material the reduced form of the oxidizing agent (such as Br₃⁻ in the case of exposure to bromine).

The major breakthrough in the area of conducting plastics occurred later in 1977 when the same redox chemistry was applied to an intrinsically insulating organic polymer, polyacetylene. It was discovered that polyacetylene, which has an intrinsic conductivity much lower than 10⁻⁵ (Ω·cm)⁻¹, could be made highly conducting, ~10³ (Ω·cm)⁻¹, by exposing it to oxidizing or reducing agents.⁵ This process is often referred to as "doping" by analogy with the doping of inorganic semiconductors. This is a rather misleading analogy, however, and the process is best viewed as a redox reaction. The insulating neutral polymer is converted into an ionic complex consisting of a polymeric cation (or anion) and a counterion which is the reduced form of the oxidizing agent (or the oxidized form of the reducing agent). In solid-state physics terminology, the use of an oxidizing agent corresponds to p-type doping and that of a reducing agent to n-type doping. An important criterion in selecting potentially conducting polymers is therefore the ease with which the system can be oxidized or reduced. This accounts in part for the choice of π-bonded unsaturated polymers which, like polyacetylene, have small ionization potentials and/or large electron affinities. Electrons of π character can be relatively easily removed or added to form a polymeric ion without much disruption of the σ bonds which are primarily responsible for holding the polymer together.

Following polyacetylene, this basic principle has been applied with success to an increasingly large number of other organic polymers.¹ The structures of the

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(1) For comprehensive overviews of the field of conducting polymers and its recent developments, see, e.g.: (a) Proceedings of the International Conference on Conducting Polymers, *J. Phys. (Les Ulis Fr.)*, **44**, C3 (1983); (b) Proceedings of the Workshop on Synthetic Metals, *Synth. Met.*, **9**, 129–346 (1984); (c) Proceedings of the International Conference on Synthetic Metals, *Mol. Cryst. Liq. Cryst.*, **117–121**, (1985). (d) "Handbook on Conducting Polymers"; T. J. Skotheim, Ed.; Marcel Dekker; New York, in press. (e) W. D. Gill, T. C. Clarke, and G. B. Street, *Appl. Phys. Commun.*, **2**, 211 (1982).

(2) V. V. Walatka, M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.*, **31**, 1139 (1973).

(3) R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **34**, 577 (1975).

(4) W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, *Phys. Rev. Lett.*, **38**, 1305 (1977).

(5) C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. McDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).

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polymer		maximum conductivity	type of doping
polyacetylene		200-1000	n, p
polyparaphenylene		500	n, p
polyparaphenylene sulfide		3-300	p
polyparaphenylene vinylene		1-1000	p
polypyrrole		40-200	p
polythiophene		10-100	p
polyisothianaphthene		1-50	p

Figure 1. Structure, maximum conductivities (in $\Omega^{-1} \text{ cm}^{-1}$), and type of doping (n or p) for some of the more important conducting polymers.

principal conducting polymer systems are displayed in Figure 1. Note that the maximum dopant concentrations are typically of the order of several mole percent per repeat unit of the chain backbone, for instance up to 20% in the case of polyacetylene doped by iodine, $([\text{CH}]\text{I}_{0.2})_x$.

In some cases, oxidation or reduction of the polymer can be achieved electrochemically by subjecting the neutral polymer to the appropriate oxidizing or reducing voltage in an electrochemical cell. The charge appearing on the polymer chain is then neutralized by a counterion from the electrolyte solution. An interesting group of conducting polymers consists of those prepared by the electrochemical oxidation and simultaneous polymerization of some monomer which reacts at the anode of an electrochemical cell. This group includes polypyrrole, polythiophene, and their derivatives.¹

Nature of the Charges Appearing on the Polymer Chains upon Doping

In a polymer, just as in a crystal, the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands. The highest occupied electronic levels constitute the valence band (VB) and the lowest unoccupied levels, the conduction band (CB). The width of the forbidden band, or bandgap (E_g), between the VB and CB determines the intrinsic electrical properties of the material. For all the organic conjugated polymers we have discussed so far, the bandgap is larger than 1.5 eV so that these materials are intrinsically insulating.

Initially, the high conductivity increase observed upon doping organic polymers was thought to result

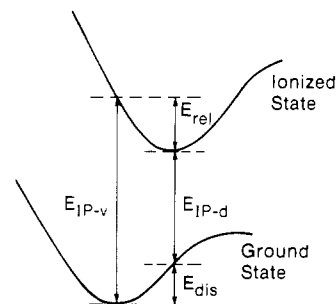


Figure 2. Illustration of the energies involved in a molecular ionization process. $E_{\text{IP-v}}$ is the vertical ionization energy, E_{rel} , the relaxation energy gained in the ionized state, E_{dis} , the distortion energy to be paid in the ground state in order that the molecule adopts the equilibrium geometry of the ionized state, and $E_{\text{IP-d}}$, the ionization energy of the distorted molecule.

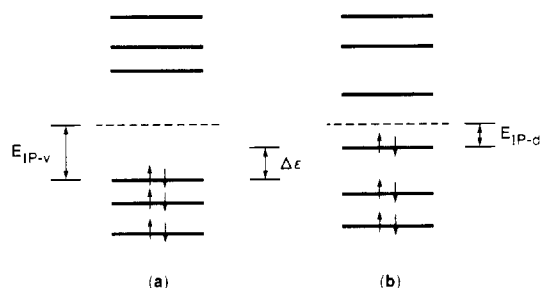


Figure 3. Schematic illustration of the one-electron energy levels for an organic molecule (e.g., biphenyl) in its ground-state electronic configuration adopting: (a) the equilibrium geometry of the ground state; (b) the equilibrium geometry of the first ionized state.

from the formation of unfilled electronic bands. It was simply assumed that upon p-type or n-type doping, electrons were respectively, removed from the top of the VB or added to the bottom of the CB, in analogy to the mechanism of generation of charge carriers in doped inorganic semiconductors. This assumption was however quickly challenged by the discovery that polyacetylene (PA),⁶ polyparaphenylene (PPP),⁷ and polypyrrole (PPy)⁸ can display conductivity which does not seem to be associated with unpaired electrons but rather with spinless charge carriers.

In organic molecules, it is usually the case that the equilibrium geometry in the ionized state is different from that in the ground state, e.g., the geometry of neutral biphenyl is benzenoid-like but becomes quinoid-like in the ionized state, for example, in the Rb^+ (biphenyl)⁻ complex.⁹ The energies involved in the ionization process of a molecule are schematically depicted in Figure 2. A vertical, Franck-Condon like ionization process costs an energy $E_{\text{IP-v}}$. If a geometry relaxation then takes place in the ionized state, we gain back a relaxation energy E_{rel} . Conceptually, going from the ground state to the relaxed ionized state can also be thought of in the following way. The geometry of the molecule is first distorted in the ground state in

(6) S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M. A. Drury, A. Sivak, A. J. Heeger, and A. G. McDiarmid, *Phys. Rev. Lett.*, **45**, 423 (1980).

(7) M. Peo, S. Roth, K. Dransfeld, B. Tiede, J. Hocker, H. Gross, A. Grupp, and H. Sixl, *Solid State Commun.*, **35**, 119 (1980).

(8) (a) J. C. Scott, M. Krounbi, P. Pfluger, and G. B. Street, *Phys. Rev. B: Condens. Matter*, **28**, 2140 (1983); (b) J. C. Scott, J. L. Brédas, P. Pfluger, K. Yakushi, and G. B. Street, *Synth. Met.*, **9**, 165 (1984); (c) J. C. Scott, J. L. Brédas, J. H. Kaufman, P. Pfluger, G. B. Street, and K. Yakushi, *Mol. Cryst. Liq. Cryst.*, **118**, 163 (1985).

(9) R. H. Baughman, J. L. Brédas, R. R. Chance, R. L. Elsenbaumer, and L. W. Shacklette, *Chem. Rev.*, **82**, 209 (1982).

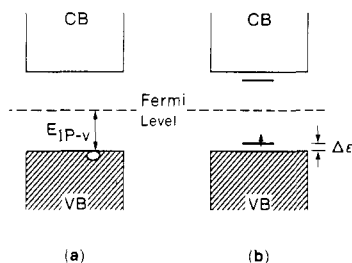


Figure 4. Illustration of the band structure of a polymeric chain in the case of (a) a vertical ionization process and (b) the formation of a polaron. The chemical potential, or Fermi level, is taken as reference level.

such a way that the molecule adopts the equilibrium geometry of the ionized state. This costs a distortion (elastic) energy E_{dis} (Figure 2). If we consider the one-electron energy levels of the molecule, this distortion leads to an upward shift $\Delta\epsilon$ of the highest occupied molecular orbital (HOMO) and a downward shift of the lowest unoccupied molecular orbital (LUMO), as illustrated in Figure 3. If we then proceed to the ionization of the distorted molecule, it requires an energy $E_{\text{IP-d}}$.

From Figure 2, it is clear that it is energetically favorable to have a geometry relaxation in the ionized state when the quantity $E_{\text{IP-v}} - E_{\text{IP-d}}$ (which actually corresponds to $\Delta\epsilon$ as can be inferred from Figure 3) is larger than the distortion energy E_{dis} ; or, in other words, when the reduction $\Delta\epsilon$ in ionization energy upon distortion is larger than the energy E_{dis} required to make that distortion.

In a polymer, or any solid, a vertical ionization process $E_{\text{IP-v}}$ results in creating a hole on top of the valence band; see Figure 4a. In this case, three remarks can be made. First, by the very definition of the process, no geometry relaxation (lattice distortion) takes place on the chain. Second, the positive charge on the chain is *delocalized* over the whole polymer chain. Third, the presence of a hole (unfilled level) on top of the VB leads, as we discussed above, to the appearance of a metallic character. This situation corresponds to the initial assumption made about the conduction mechanism in doped organic polymers.

However, in an *organic polymer chain*, it can be energetically favorable to *localize* the charge that appears on the chain and to have, around the charge, a local distortion (relaxation) of the lattice. This process causes the presence of localized electronic states in the gap due to a local upward shift $\Delta\epsilon$ of the HOMO and downward shift of the LUMO (Figure 4b). Considering the case of oxidation, i.e., the removal of an electron from the chain, we lower the ionization energy by an amount $\Delta\epsilon$. If $\Delta\epsilon$ is larger than the energy E_{dis} necessary to distort the lattice locally around the charge, this charge localization process is favorable relative to the band process. We then obtain the formation of what condensed-matter physicists call a polaron.¹⁰ In chemical terminology, the polaron is just a radical ion (spin $1/2$) associated with a lattice distortion and the presence of localized electronic states in the gap referred to as polaron states. The ability of a charge to significantly

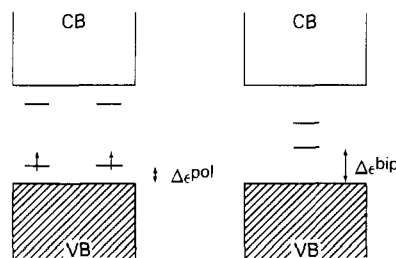


Figure 5. Band structure of a polymer chain containing: (a) two polarons; (b) one bipolaron.

deform the lattice around it is the manifestation of a strong electron-phonon coupling.

The quantity $\Delta\epsilon - E_{\text{dis}}$ ($= E_{\text{rel}}$) corresponds to the polaron binding energy. Our calculations (based on Hückel theory with σ bond compressibility) have indicated that polaron formation is energetically favorable in all the organic conjugated polymers we have studied. The polaron binding energy is of the order of 0.05 eV in PA,^{10b,11} 0.03 eV in PPP,¹¹ and 0.12 eV in PPy.¹² It must be stressed that in the case of polaron formation, the VB remains full and the CB empty. There is no appearance of metallic character since the half-occupied level is localized in the gap (Figure 4b).

Next, we consider what happens when a second electron is removed from the polymer chain: Is it more favorable to take the second electron from the polaron or from anywhere else on the chain (in which case we have two polarons)? In the former case, we have bipolaron formation.^{10b,c,11} A bipolaron is defined as a pair of like charges (here a dication) associated with a strong local lattice distortion. The bipolaron can be thought of as analogous to the Cooper pair in the BCS theory of superconductivity,¹³ which consists of two electrons coupled through a lattice vibration, i.e., a phonon. The formation of a bipolaron implies that the energy gained by the interaction with the lattice is larger than the Coulomb repulsion between the two charges of same sign confined in the same location.¹⁴

The electronic band structure corresponding to the presence of two polarons and that of one bipolaron is depicted in Figure 5. Since the lattice relaxation around two charges is stronger than around only one charge, E_{dis} for the bipolaron is larger than E_{dis} for the polaron and the electronic states appearing in the gap for a bipolaron are further away from the band edges than for a polaron.

If we compare the creation energy of a bipolaron relative to that of two polarons, our calculations for PA, PPP, and PPy indicate that the distortion energy E_{dis} to form one bipolaron is roughly equal to that to form two polarons.^{11,12} On the other hand, the decrease in ionization energy is much more important in the bipolaron case ($2\Delta\epsilon^{\text{bip}}$) than for two polarons ($2\Delta\epsilon^{\text{pol}}$); see Figure 5. This is the reason why one bipolaron is thermodynamically more stable than two polarons in these systems despite the Coulomb repulsion between two similar charges. Furthermore, the latter is also largely screened by the presence of dopants (counter-

(10) (a) W. P. Su and J. R. Schrieffer, *Proc. Natl. Acad. Sci. U.S.A.*, **77**, 5626 (1980); (b) A. R. Bishop, D. K. Campbell, and K. Fesser, *Mol. Cryst. Liq. Cryst.*, **77**, 253 (1981); (c) S. A. Brazovskii and N. Kirova, *JETP Lett.*, **33**, 4 (1981).

(11) J. L. Brédas, R. R. Chance, and R. Silbey, *Mol. Cryst. Liq. Cryst.*, **77**, 319 (1981); *Phys. Rev. B: Condens. Matter*, **26**, 5843 (1982).

(12) J. L. Brédas, J. C. Scott, K. Yakushi, and G. B. Street, *Phys. Rev. B: Condens. Matter*, **30**, 1023 (1984).

(13) J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.*, **108**, 1175 (1957). See also: ref 18, chapter 10.7.

(14) P. W. Anderson, *Phys. Rev. Lett.*, **34**, 953 (1975).

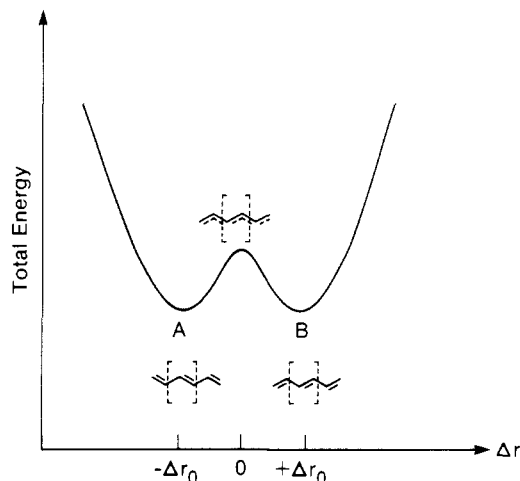


Figure 6. Total energy curve for an infinite *trans*-polyacetylene chain as a function of the degree of bond length alternation Δr . The optimal absolute value for Δr , Δr_0 , is experimentally ~ 0.08 Å ($r_{C=C} \approx 1.36$ Å; $r_{C-C} \approx 1.44$ Å).^{17b}

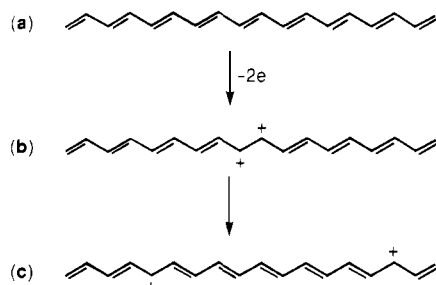


Figure 7. Illustration of the formation of two charged solitons on a chain of *trans*-polyacetylene.

ions) with opposite charges. The bipolaron binding energy [$= (2\Delta\epsilon^{\text{bip}}) - E_{\text{dis}}^{\text{bip}} - E_{\text{dis}}^{\text{bip}}$] is calculated to be larger than that of two polarons by about 0.45 eV in PPy and 0.34 eV in PPP.^{11,12}

In case of p- (n-) type doping, the bipolaron levels in the gap are empty (fully occupied); see Figure 5b. The bipolarons are thus *spinless*. The presence of bipolarons on polymer chains result in the possibility of two optical transitions below the bandgap transition: for p-type doping, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level. The oscillator strength for the lowest energy optical bipolaron transition has been calculated to be much larger than for the highest energy one.¹⁵ In the case of polarons, a third absorption is possible below the gap, corresponding to an optical transition between the two polaron levels (Figure 5a).

trans-Polyacetylene is unique so far among conducting polymers because it possesses a degenerate ground state,¹⁶ i.e., two geometric structures corresponding exactly to the *same* total energy (Figure 6). The two structures differ from one another by the exchange of the carbon-carbon single and double bonds. Experimentally, the degree of bond length alternation Δr (i.e., the difference between the length of a single and a double bond) is ~ 0.08 Å.¹⁷

(15) K. Fesser, A. R. Bishop, and D. K. Campbell, *Phys. Rev. B: Condens. Matter*, **27**, 4804 (1983).

(16) W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979).

(17) (a) C. R. Fincher, C. E. Chen, A. J. Heeger, A. G. McDiarmid, and J. B. Hastings, *Phys. Rev. Lett.*, **48**, 100 (1982); (b) C. S. Yannoni and T. C. Clarke, *Phys. Rev. Lett.*, **51**, 1191 (1983).

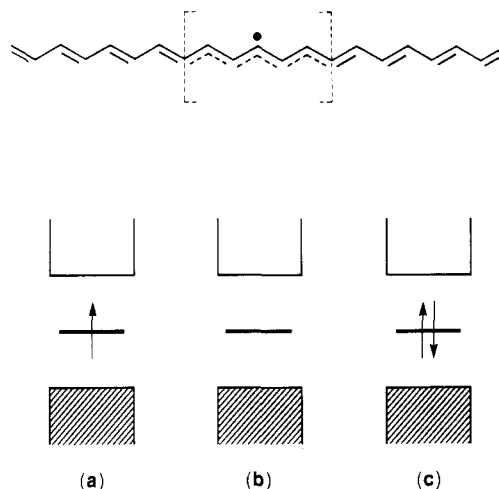


Figure 8. Top: schematic illustration of the geometric structure of a neutral soliton on a *trans*-polyacetylene chain. Bottom: band structure for a *trans*-polyacetylene chain containing (a) a neutral soliton, (b) a positively charged soliton, and (c) a negatively charged soliton.

As a result of the degeneracy, the two charges forming a would-be bipolaron in *trans*-PA can readily separate (Figure 7). This process is favorable because there is no increase in distortion energy when the two charges separate, since the geometric structure that appears between the two charges has the same energy as the geometric structure on the other sides of the charges.

From Figures 6 and 7, it is apparent that an isolated charge on a *trans*-PA chain constitutes a boundary between a segment of the chain adopting the geometric structure corresponding to one of the potential wells and a segment adopting the structure corresponding to the other well. Analogy can be made with a magnetic domain wall marking the separation between two Bloch domains in a ferromagnetic material.¹⁸ In physics terminology, such a charge associated with a boundary or domain wall is called a soliton, because it has the properties of a solitary wave which can propagate without deformation and dissipation.¹⁹ A soliton can also be viewed as an excitation of the system that leads from one potential well to another well of the *same energy* (Figure 6).¹⁹ A neutral soliton occurs in pristine *trans*-PA when a chain contains an odd number of conjugated carbons, in which case there remains an unpaired π electron, a radical, which corresponds to a soliton (Figure 8). In a long chain, the spin density in a neutral soliton (or charge density in a charged soliton) is not localized on one carbon but spread over several carbons,^{16,20,21} which gives the soliton a width. Starting from one side of the soliton, the double bonds become *gradually* longer and the single bonds shorter, so that arriving at the other side, the alternation has completely reversed. This implies that the bond lengths do equalize in the middle of a soliton. The presence of a soliton leads to the appearance of a localized electronic level at mid-gap, which is half-occupied in the case of a neutral soliton and empty (doubly occupied) in the case of a positively (negatively) charged soliton (Figure

(18) See, for instance: M. A. Omar, "Elementary Solid State Physics", Addison-Wesley, Reading, 1978, Chapter 9.11.

(19) C. Rebbi, *Sci. Am.*, **240**, 92 (1979).

(20) D. S. Boudreaux, R. R. Chance, J. L. Brédas, and R. Silbey, *Phys. Rev. B: Condens. Matter*, **28**, 6927 (1983).

(21) H. Thomann, L. R. Dalton, Y. Tomkiewicz, N. S. Shiren, and T. C. Clarke, *Phys. Rev. Lett.*, **50**, 533 (1983).

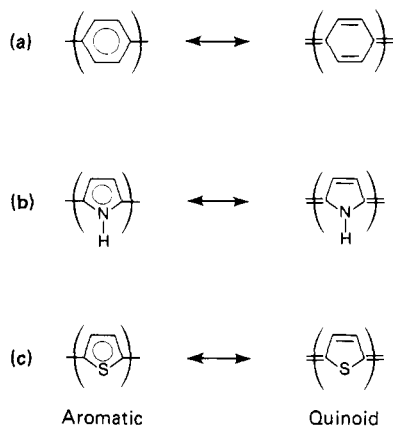


Figure 9. Aromatic (ground-state) and quinoid-like geometric structures for (a) polyparaphenylene, (b) polypyrrole, and (c) polythiophene.

8). Compared to a polaron, the soliton has unusual spin-charge relationships: since a neutral soliton is a radical, it has a spin $1/2$ whereas a charged soliton is spinless.¹⁶

The photogeneration process of these charged defects in *trans*-PA has attracted much interest. An elegant discussion of the photogeneration mechanism has been recently published.²²

Unlike *trans*-PA, systems such as PPP, PPy, or polythiophene (PT) possess a nondegenerate ground state since their ground state corresponds to a single geometric structure which, in their case, is aromatic-like. A quinoid-like resonance structure can be envisioned but has a higher total energy (Figure 9). We have performed *ab initio* calculations which show that the quinoid structure has a lower ionization potential and a larger electron affinity than the aromatic structure.²³ This explains why, on doping, the chain geometry in these compounds relaxes locally around the charges toward the quinoid structure which has a larger affinity for charges.²³

Evolution of the Electronic and Transport Properties at High Dopant Concentration

Experimental and theoretical investigations of the evolution of the electronic and transport properties as a function of doping level were conducted initially on polyacetylene²⁴⁻²⁷ and more recently on polypyrrole,^{8,12,23} poly- β,β' -dimethylpyrrole,²⁸ polythiophene,^{23,29} and polyparaphenylene.^{11,23,30} For the sake of our discussion, we take the example of polypyrrole and will then compare it to the other systems.

(22) J. Orenstein, Z. Vardeny, G. L. Baker, and S. Etemad, *Phys. Rev. B: Condens. Matter*, **30**, 786 (1984).

(23) J. L. Brédas, B. Thémans, J. G. Fripiat, J. M. André, and R. R. Chance, *Phys. Rev. B: Condens. Matter*, **29**, 6761 (1984).

(24) D. Moses, A. Denenstien, J. Chen, A. J. Heeger, P. McAndrew, T. Woerner, A. G. McDiarmid, and Y. W. Park, *Phys. Rev. B: Condens. Matter*, **25**, 7652 (1982).

(25) E. J. Mele and M. J. Rice, *Phys. Rev. B: Condens. Matter*, **23**, 5397 (1981).

(26) J. Dong and J. R. Schrieffer, to be submitted for publication.

(27) A. J. Epstein, H. Rommelmann, R. W. Bigelow, H. W. Gibson, D. M. Hoffman, and D. B. Tanner, *Phys. Rev. Lett.*, **51**, 2020 (1983); A. J. Epstein, R. W. Bigelow, A. Feldblum, H. W. Gibson, D. M. Hoffman, and D. B. Tanner, *Synth. Met.*, **9**, 155 (1984).

(28) K. Yakushi, L. J. Lauchlan, G. B. Street, and J. L. Brédas, *J. Chem. Phys.*, **81**, 4133 (1984).

(29) T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, *Phys. Rev. B: Condens. Matter*, **30**, 702 (1984).

(30) G. Crecelius, M. Stamm, J. Fink, and J. J. Ritsko, *Phys. Rev. Lett.*, **50**, 1498 (1983).

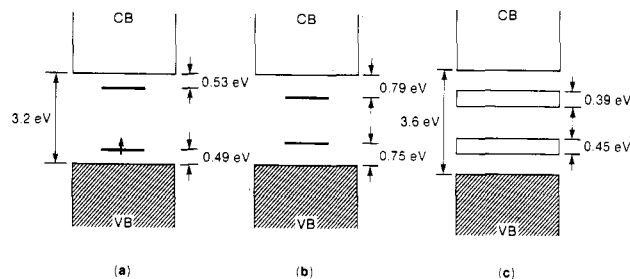


Figure 10. Evolution of the polypyrrole band structure upon doping: (a) low doping level, polaron formation; (b) moderate doping level, bipolaron formation; (c) high (33 mol %) doping level, formation of bipolaron bands.

Theoretical studies of the evolution of the PPy electronic band structure as a function of doping level have been performed by using methods ranging from highly sophisticated *ab initio* techniques to simple Hückel theory with σ compressibility. They all converge toward the same picture.^{12,23} In the undoped state, the PPy bandgap is 3.2 eV. Taking an electron out of the chain leads to the formation of a polaron whose associated quinoid-like geometry relaxation extends over about four pyrrole rings. The polaron levels are about 0.5 eV away from the band edges (Figure 10a). The polaron binding energy is 0.12 eV, constituting the difference between the 0.49 eV decrease in ionization energy and the 0.37 eV $\pi + \sigma$ energy needed for the change in geometry.

When a second electron is taken out of the chain, the energetically favorable species is a bipolaron which also extends over four pyrrole rings. The geometry relaxation is stronger than in the polaron case (i.e., the geometry within the bipolaron is more quinoid-like than within the polaron), so that the empty bipolaron electronic levels in the gap are ~ 0.75 eV away from the band edges (Figure 10b). The bipolaron binding energy is 0.69 eV meaning that a bipolaron is favored over two polarons by 0.45 (0.69 - 2 \times 0.12) eV. This evolution is supported by ESR measurements on oxygen-doped PPy.^{8a} At low doping, the ESR signal grows, in accord with the fact that polarons with spin $1/2$ are formed. At intermediate doping, the ESR signal saturates and then decreases, consistent with polarons recombining to form spinless bipolarons. At high doping, in electrochemically cycled samples, *no ESR signal is observed* although the system is highly conducting, indicating that the charge carriers in that regime are spinless. Analysis of the Pauli contribution to the susceptibility indicates that the density of states at the Fermi level is vanishingly small, <0.03 states eV^{-1} per monomer.

The band structure for a doping level of 33 mol % (per polymer repeat unit), which is usually achieved in the electrochemically grown PPy films, is displayed in Figure 10c. The overlap between the bipolaron states leads to the formation of two ~ 0.4 eV wide bipolaron bands in the gap. The bandgap has widened from 3.2 eV in the neutral state to 3.6 eV in the 33% doped state. This is due to the fact that the bipolaron states coming in the gap are taken from the VB and CB edges. This band structure supports the fact that, upon application of an electric field, the spinless bipolarons (which carry two charges) could become mobile at high dopant concentrations, where the Coulomb attraction with the counterions is largely screened. The spinless bipolarons could be the spinless charge carriers suggested by the

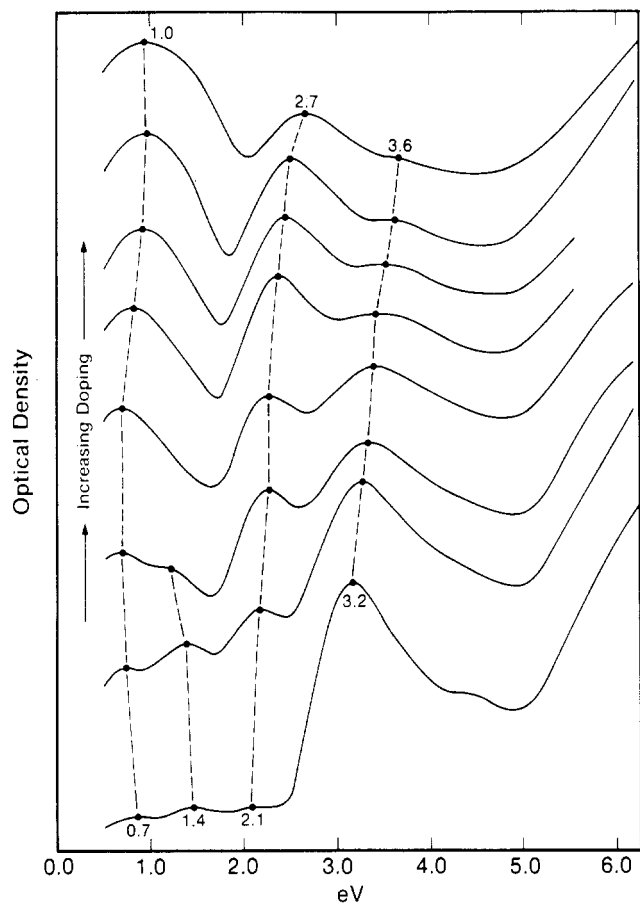


Figure 11. Optical absorption spectra of ClO_4 -doped polypyrrole as a function of dopant concentration. The dopant level increases from the bottom curve (almost neutral polypyrrole) to the top curve (33 mol % doping level) (after ref 12).

absence of any ESR signal in the highly conducting regime of the as grown films. This conduction mechanism would be highly unusual in the sense that all bands are either totally filled or empty (as shown in the band structure in Figure 10c) and that mobile bipolarons, not electrons, transport the current.⁸ A similar conduction mechanism based on the collective motion of bipolarons has also been recently proposed in vanadium bronzes.³¹ The complete elucidation of the transport mechanism remains one of the major goals to be pursued in the field of conducting polymers.

The whole band structure evolution reproduces very well the evolution of the optical spectra upon doping in polypyrrole perchlorate (Figure 11).¹² At low doping, three absorptions are present below the gap at 0.7, 1.4, and 2.1 eV, attributable, as discussed before, to the presence of polarons. At intermediate doping, the 1.4-eV absorption associated with transitions between the polaron levels in the gap disappears. It also disappears at low doping if one observes its evolution as a function of time.³² Very importantly, in this latter experiment, ESR measurements have shown a correlation between the appearance of additional spins and the presence of the 1.4-eV peak.³² This is strong experimental evidence that the 1.4-eV peak is related to polarons which eventually recombine into thermodynam-

ically more stable spinless bipolarons. At very high doping, two wide optical absorptions peaking at 1.0 and 2.7 eV are present below the gap, in agreement with the existence of two bipolaron bands. The bandgap transition has shifted to higher energies, 3.6 eV, in excellent agreement with the calculated value.

The bipolaron model for PPy is thus consistent with the evolution of the ESR data upon doping, time- and doping-dependent behavior of the optical data, and also electron-energy-loss spectroscopic data indicating that the optical transitions in the gap at high doping are due to transitions to ~ 0.5 eV wide electronic bands.³³

In poly- β,β -dimethylpyrrole,²⁸ polythiophene,²⁹ and polyparaphenylene,³⁰ the evolution of the optical data as a function of doping level is very similar to that in PPy. However, at low doping levels (~ 1 mol %), only two absorptions (and not three) arise in the gap. Since these compounds are less disordered than PPy, polarons can presumably more readily recombine to form bipolarons and only bipolaron absorptions are observed.

In the case of polythiophene, evidence has been presented that, at very high p-doping levels, the transport properties become those of a metal.²⁹ Theoretically, this can be understood by considering that the broadening of the bipolaron states in the gap upon increasing the dopant concentration eventually leads to the merging of the lower and upper bipolaron bands with the VB and the CB, respectively.²³ For p-type doping, this results in a new unfilled VB and the possibility of a conventional metallic-like conduction mechanism. Because the intrinsic bandgap in the pyrrole polymers (~ 3.2 eV) or PPP (3.5 eV) is significantly larger than in PT (2.0 eV) this merging process can occur in the former systems only at extremely high dopant concentrations (theoretically estimated around or larger than one dopant per every other monomer unit).²³ Such doping levels are not experimentally achieved in the pyrrole compounds.

The evolution of the transport properties in *trans*-polyacetylene is actually similar to that in polythiophene if one considers charged solitons rather than bipolarons. At low doping levels, charged solitons are formed either directly from existing neutral solitons or as the result of recombination among polarons. Upon increasing the doping level, soliton states at midgap start overlapping and form a soliton band. Between ~ 0.1 –1% and ~ 6 –7% doping level, a high conductivity is observed which is associated with a vanishingly small Pauli susceptibility, suggesting that the charge carriers have no spin.^{6,24,27} However, there is still controversy as to whether the conduction process is really based on mobile charged solitons^{26,34} or is due to disorder-induced bandtailing effects, which would make it possible for electrons on top of the VB to hop among soliton states and be the charge carriers.^{25,27,35,36} This is one of the most important aspects that still await a better understanding. Above 7% dopant concentration, metallic-like conductivity appears as a result of the merging of the soliton band with the VB and CB.²⁴

(33) J. J. Ritsko, J. Fink, and G. Crecelius, *Solid State Commun.*, **46**, 477 (1983).

(34) T. C. Chung, F. Moraes, J. D. Flood, and A. J. Heeger, *Phys. Rev. B: Condens. Matter*, **29**, 2341 (1984).

(35) S. Kivelson and A. J. Epstein, *Phys. Rev. B: Condens. Matter*, **29**, 3336 (1984).

(36) K. Ehinger, S. Summerfield, W. Bauhofer, and S. Roth, *J. Phys. C*, **17**, 3753 (1984).

(31) Y. Kanai, S. Kagoshima, and H. Nagasawa, *Synth. Met.*, **9**, 369 (1984).

(32) J. H. Kaufman, N. Colaneri, J. C. Scott, and G. B. Street, *Phys. Rev. Lett.*, **53**, 1005 (1984).

Two aspects remained to be stressed. First, in polymeric materials, the charge carriers have not only to move along the chains but also to jump from chain to chain. The latter process is likely to be the rate-limiting step which determines the conductivity observed macroscopically. Interchain interactions are thus of prime importance.³⁷ Models for the interchain hopping of solitons or bipolarons have been proposed.³⁸ Second, these materials are rather amorphous and inhomogeneous. Disorder effects (the importance of which can be determined from resonant raman scattering experiments)³⁹ need therefore to be properly taken into account.

Conclusions and Outlook

Many efforts and currently devoted toward developing organic polymers which would be intrinsically better conductors, i.e., which would have smaller bandgaps. Encouraging progress has already been reported, as exemplified by the synthesis of polyisothianaphthene.⁴⁰

(37) G. Wegner, in "Contemporary Topics in Polymer Science", Vol. 5, E. J. Van der Berg, Ed., Plenum Press, New York, 1984, pp 281-319.

(38) S. Kivelson, *Phys. Rev. Lett.*, **46**, 1344 (1981); R. R. Chance, J. L. Brédas, and R. Silbey, *Phys. Rev. B: Condens. Matter*, **29**, 4991 (1984).

(39) Z. Vardeny, E. Ehrenfreund, O. Brafman, and B. Horovitz, *Phys. Rev. Lett.*, **54**, 975 (1985).

Polyisothianaphthene is a polythiophene derivative in which all thiophene rings are fused to a benzene ring along the β - β' thiophene bond. As a result of the presence of the benzene ring, which stabilizes some quinoid contribution into the ground-state geometry of polyisothianaphthene,⁴¹ the bandgap is found to be of the order of 1 eV, i.e., half that of the parent polymer. Upon doping, polyisothianaphthene becomes a transparent highly conducting material.⁴⁰ Once more, the ultimate success of obtaining an intrinsically metallic plastic will come from close interactions between synthetic chemists, physicists, and theoreticians.

There has been speculation that organic polymeric conductors could become superconductor, as is the case for polysulfur nitride and some organic molecular crystals. The similarities between bipolarons and Copper pairs in the BCS theory of superconductivity makes this prospect even more interesting. In the light of the wealth of unanticipated discoveries that the field of polymeric conductors has witnessed in the last 10 years, the scientific and technological future of conducting plastics has to be viewed optimistically.

(40) F. Wudl, M. Kobayashi, N. Colaneri, M. Boysel, and A. J. Heeger, *Mol. Cryst. Liq. Cryst.*, **118**, 199 (1985).

(41) J. L. Brédas, *J. Chem. Phys.*, **82**, 3808 (1985).