Conducting Organic Materials

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Summary. Some of the current directions of scientific research on electrically conducting organic solids are reviewed. Both molecular charge transfer salts and polymers are included, with emphasis on the present level of understanding of the novel solid-state properties of these materials in terms of their chemistry and structure. For the charge transfer salts the various types of metal-to-insulator phase transitions which dominate the properties of most of these materials are discussed. Also described are the superconducting and magnetic states which have been found recently. In the case of the polymers the chemistry and physics of the conduction mechanism is examined and contrasted with that of their classical inorganic counterparts.

Conducting organic materials have attracted the interest of scientists for about 20 years. The past 10 years have seen the level of activity grow rapidly as new and unanticipated phenomena were observed which were not found in nonconducting organic materials and were found only rarely in inorganic materials. The prediction that superconductivity (the complete absence of electrical resistance) might occur in organic solids at a technologically useful temperature (for instance, room temperature) also provided a stimulus for this field. So far, this prediction has not been fulfilled, although some organic materials have been found to be superconductors at very low temperatures ($T < 5$ K). The field is highly interdisciplinary involving chemists, materials scientists, and theoretical and experimental physicists, whose interaction has led to much new chemistry and physics.

The bulk of the research has been on three broad classes of materials: the crystalline charge transfer complexes or salts, polymers, and graphite and its intercalation compounds. The charge transfer (CT) salts and the conducting polymers have many features in common and therefore we shall limit our discussion to these two classes of materials. For example, they both exhibit anisotropic, quasi–one-dimensional properties; that is, the conductivity is much greater in one direction than in others. In conducting polymers the conductivity is greatest along the chain direction, whereas in the CT salts the anisotropy is determined by the stacking of the molecules in the crystal structure. Another common feature of these materials is that in the conducting state they are ionic. In the case of the polymers charge is transferred between the polymer chain and a dopant, and in the case of the CT salts charge is transferred between the donor and acceptor components of the complex. In spite of the similarities between these two classes of materials, most of their novel properties are different and therefore we shall discuss them separately in this article.

It would be impossible to cover all the significant work that has been done on conducting organic materials in the space available for this review. Many other reviews and several books have been devoted to this topic. Some of the most recent reviews and conference proceedings are cited in (*1–6*), and an exhaustive bibliography of all the known reviews up to 1982 is given in (*3*). It is our intent here to give a brief introduction to the properties of the two main classes of conducting organic solids and to give an impression of some of the current active areas of research.

Charge Transfer Salts

The first stable organic materials which could conduct electricity like a metal were discovered in the early 1960's. They are materials in which charge is transferred between donor (cation) molecules (such as TTF) and acceptor (anion) molecules (such as TCNQ) to form a charge transfer compound (TTF-TCNQ). A few examples of donor and acceptor molecules which produce organic "metals" are shown in Fig. 1. A description of all the molecules which form the important conducting CT salts is given in (*2*). The electrical conduction arises because in the crystalline compound the large planar molecules can stack on top of each other like pancakes, which allows the transferred charge to move easily along the separate donor and acceptor stacks. In the language of solid-state physics, a conduction band is formed from the overlap of π orbitals on neighboring molecules along the stack. The partial filling of this band with electrons by charge transfer from donor to acceptor leads to the metallic levels of conductivity observed. The CT salts are quasi–one-dimensional metals because the orbital overlap is greater along the stacks of molecules and less between them, which makes the conductivity greater along the stack than in other directions. The best organic conductors have a conductivity of order 2000 ohm^{-1} cm^{-1} at room temperature, or about three orders of magnitude smaller than that of copper. Below room temperature, the metallic conduction is usually interrupted by a transition to an insulating state; in other words, a metal-insulator phase transition occurs. One of the major results of research on CT salts has been the elucidation of the nature of this metal-insulator phase transition as well as the development of chemical and physical techniques to suppress the transition in order to retain the metallic state to near absolute zero in temperature. An elementary review of this work which includes a historical perspective is given in (*1*).

Metal-insulator phase transitions. To understand the nature of the metal-insulator transition, we need to discuss some properties of one-dimensional metals. Physics in one dimension is different from that in higher dimensions and has been studied theoretically for many years. However, the synthesis of real materials (such as the CT salts) with quasi–one-dimensional properties has led to further understanding of one-dimensional metals. Consider a chain of molecules, separated by a distance "a," with one electron in the highest unoccupied orbital (Fig. 2a). If separation "a" is small enough to allow overlap of the

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molecular wave functions, the electrons can move freely along the stack and a metallic state is obtained. However, this one-dimensional metallic state is unstable against a variety of distortions which lead to metal-insulator phase transitions. These are shown in Fig. 2, b to d. When the electrons interact with the lattice vibrations it can become energetically favorable for the chain of molecules to distort so that the molecules dimerize, as shown in Fig. 2b. This gives rise to two electrons in the highest occupied orbital of each dimer and consequently to completely filled bands and an insulating state. This was first shown theoretically by R. Peierls and has since become known as a Peierls distortion. Sometimes the Coulombic repulsion between electrons on the chain of molecules is greater than their interaction with the lattice. This repulsion causes the electrons to be confined to their individual molecules with their spins ordered in the alternating fashion shown in Fig. 2c, and one finds an insulating magnetic state. This state is sometimes called a spin density wave (SDW) state. Finally, the presence of an ordered array of anions with a periodicity "2a," shown in Fig. 2d, will cause a doubling of the original lattice (analogous to the situation represented by Fig. 2b), and this too can lead to an insulating state. In a strictly one-dimensional system, these phase transitions can occur only at absolute zero in temperature. However, the CT salts are three-dimensional crystals rather than single-chain filaments and therefore there is some electronic coupling between neighboring chains (hence the label quasi–one-dimensional materials). In this case, any phase transition will occur at a temperature (T_c) given roughly by the average of two energies, $T_\parallel$ and $T_\perp$, where $T_\perp$ characterizes the strength of the interchain interactions and $T_\parallel$ characterizes the intrachain interactions driving the phase transition. In the temperature region between $T_\parallel$ and T_c one expects to observe precursor (or fluctuation) effects associated with the transition.

Recent results. The synthesis of the CT salt TTF-TCNQ (Fig. 1) in the early 1970's led to a dramatic increase in the research on organic metals. This CT salt was much more conducting than the previously known CT salts and was one of the first clear examples of a Peierls transition. Attempts to eliminate this Peierls transition, which occurred at ~54 K, and thereby maintain the metallic state to lower temperatures, were unsuccessful. During the later 1970's many analogous conducting compounds were found. A study of their properties and those of TTF-TCNQ led to a deeper understanding of the physical processes in quasi–one-dimensional materials (*2–5*).

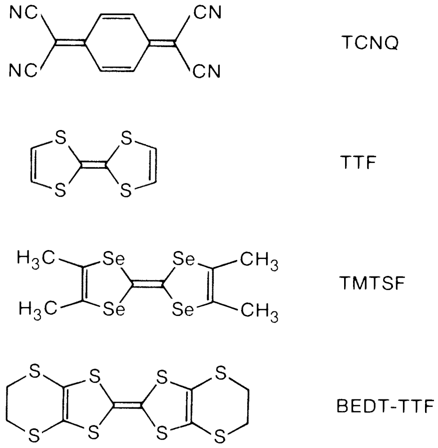


Fig. 1. A few important donor and acceptor molecules are tetracyanoquinodimethane (TCNQ), tetrathiafulvalene (TTF), tetramethyltetraselenafulvalene (TMTSF), and bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF).

In 1980, Bechgaard *et al.* (*7*) synthesized compounds of the form $(TMTSF)_2X$, where X is an inorganic anion such as PF_6^-, AsF_6^-, FSO_3^-, ReO_4^-, or ClO_4^-. These materials have given several significant new results and have accounted for 90 percent of the research activity on CT compounds since 1980. The major discoveries were the observation of superconductivity at low temperatures, the observation of SDW and anion-ordered insulating states, and the observation of a unique phase transition upon application of a magnetic field. Thus the $(TMTSF)_2X$ compounds and their derivatives exhibit a variety of physical properties that are not found in other organic metals. These materials have metal-insulator transitions between 10 and 200 K but under hydrostatic pressure become superconductors. A notable exception is the ClO_4^- salt, which is a superconductor (T_c ~ 1.2 K) at ambient pressure. The isostructural sulfur compounds $(TMTTF)_2X$ have lower conductivity and do not exhibit superconductivity. In contrast, the sulfur-containing molecule BEDT-TTF (Fig. 1) in the stoichiometry $(BEDT\text{-}TTF)_2X$ does show superconductivity (*8*) for X = ReO_4^- and X = I_3^-. The latter compound has the highest transition temperature (T_c ~ 2.5 K) observed at ambient pressure in an organic solid. Salts with different stoichiometries or crystal structures have metal-insulator transitions but no superconductivity. Magnetism (Fig. 2c) is found in salts with symmetrical anions (PF_6^-, AsF_6^-, and so on), while anion ordering (Fig. 2d) is found with nonsymmetrical anions (such as ReO_4^-). Why the magnetic (SDW) state is favored over the Peierls state in these materials is not well understood. The application of modest levels of hydrostatic pressure eliminates the metal-insulator transition and leads to a metallic state with superconductivity appearing at a low temperature. A typical pressure phase diagram is shown in Fig. 3. An understanding of exactly how pressure suppresses the metal-insulator transition is also lacking at present. The simplest explanation is that pressure squeezes the molecules closer together, increasing the interchain interaction to the point at which the metallic state is more energetically favorable and the system becomes an anisotropic three-dimensional metal (*9*). Since superconductivity is a common property of three-dimensional metals, its occurrence in the $(TMTSF)_2X$ salts would then not be surprising. A different idea has been proposed by researchers in France (*3*). In their view, the $(TMTSF)_2X$ salts are highly one-dimensional, have a high $T_\parallel$, and exhibit superconducting fluctuations at temperatures up to 40 K. Since the measured T_c for superconductivity is no more than 2.5 K, this proposal would suggest that by increasing the interchain coupling ($T_\perp$) one could obtain organic superconductors with transition temperatures comparable to or higher than those of the best superconductors known to date (Nb_3Ge has the highest known T_c, about 23 K). Unfortunately, almost all the experimental and theoretical evidence to date suggests that the organic superconductors are two- or three-dimensional rather than one-dimensional in their properties (*9*).

The third unusual property of the $(TMTSF)_2X$ salts is the occurrence of a magnetic field–induced transition at low temperature. The phase diagram for this transition (as determined by many different experiments) is shown in Fig. 4. The system, in this case $(TMTSF)_2ClO_4$, goes from a metallic, nonmagnetic state to a semimetallic, magnetic state as the magnetic field is increased. To our knowledge, there is no other solid (organic or inorganic) which has such a phase transition. This transition was first discovered in the PF_6^- salt in 1981 (*10*) and its possible origin is just now being clarified. The theory assumes that in the low-temperature metallic state the motion of the electrons is two-dimensional, that is, the electrons can move easily along the molecular stacks and can hop readily from stack to stack in one plane. When a magnetic field is applied along the third direction, the motion along the stack is not affected but the stack-to-stack motion is reduced until finally the electron is confined to a single stack. At this point, the electron motion is truly one-dimensional and a magnetic (SDW) instability can occur. This explains the essential physics of the transition but leaves out many subtle points, which cannot be discussed here but can be discovered by the interested reader (*11*). At magnetic fields and temperatures above the transition, unusual electronic properties are found, very similar to the quantum Hall effect observed in two-dimensional metals (*12*). The study of this magnetic field–induced state is now one of the most active areas of research in CT materials.

Future issues. Many conducting CT salts have been synthesized since the early 1960's [see (*2*) for a summary] but only a few of these have had properties sufficiently different to stimulate a detailed study. Through research on some of these, such as TTF-TCNQ, $(TMTSF)_2X$, and now the $(BEDT\text{-}TTF)_2X$ compounds, much has been learned about the properties of organic metals. However, there are still many gaps in our knowledge. It is not possible, in general, to predict or design the physical (or chemical) properties of a new CT crystal. The relation between crystal structure, stoichiometry, and molecular properties and the actual physical properties of the crystal are at best understood in a phenomenological way. The discovery of new materials with interesting properties is empirical in nature and depends more on the intuition of the materials scientist than on hard facts. Many other important issues are unresolved and will be the focus of future research. These include determining the interactions responsible for the superconductivity; attempting to raise the transition temperature to the level of good inorganic superconductors; understanding why the SDW is favored over the Peierls transition in the $(TMTSF)_2X$ salts; understanding the influence of the Coulomb interaction on the properties of the CT salts; determining which concepts of one-dimensional physics are relevant to the observed physical properties; and understanding in more detail the state of these materials at high magnetic fields and low temperatures, that is, above the phase transition shown in Fig. 4. Considerable effort will be required to make progress on resolving these still quite fundamental questions.

Conducting Polymers

In contrast to the CT salts, the widespread fascination with conducting polymers is clearly motivated by their perceived technological potential (*13–15*). However, as in the case of the CT salts, these materials have also presented a strong scientific challenge. This challenge has attracted a diverse community of chemists, physicists, and materials scientists who have not previously been actively interested in polymer science. The resulting involvements and contributions have gone a long way toward contradicting the view of some scientists that "there is no science in polymers." This prejudice has been nurtured by the difficulty in defining the structure of polymers with the precision associated with more crystalline materials. In reviewing the current status of the field of conducting polymers, we will emphasize the progress which has been made despite the difficulties in understanding the chemistry and physics of these materials. This progress has been achieved both in the understanding of the physics of electrical conductivity and in the control over the physical properties of the polymers. Because of their excellent physical and mechanical properties, plastics have pervaded most areas of our lives, replacing many other materials in a multitude of applications. However, because typical plastics are electrically insulating, they have not yet made an impact on the electronics industry except as dielectrics. In fact, electrically conducting or semiconducting applications remain the last great challenge for polymeric materials, although organic polymers, it should be pointed out, have been important as photoconductors for many years (*13*).

Poly(sulfur nitride): An intrinsically conducting polymer. A key development in the evolution of conducting polymers as we know them today was the discovery (*16*) that the inorganic polymer poly(sulfur nitride), $(SN)_x$, is a metal (that is, its electrical conductivity decreases with increasing temperature) and at low temperature becomes superconducting. This discovery was important because it provided an existence theorem for highly conducting polymers and stimulated the enormous amount of work necessary to synthesize other polymeric conductors. The metallic conductivity observed for $(SN)_x$ crystals is an intrinsic property of the crystals, arising from the presence of one unpaired electron associated with each sulfur-nitrogen unit; this unpaired electron can move under the effect of an applied field, carrying charge

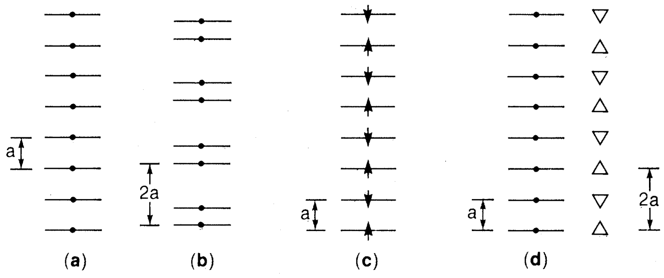
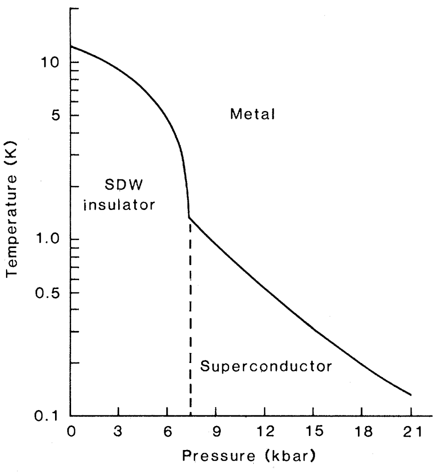


Fig. 2. Several possible configurations of a linear chain of molecules with one electron (●) in the highest orbital: (a) metal with uniform spacing of lattice constant "a"; (b) insulator with dimerization caused by Peierls transition; (c) SDW insulator with spin (↑) periodicity caused by Coulomb interactions; (d) insulator with periodicity caused by ordering of nonsymmetric anions (△).



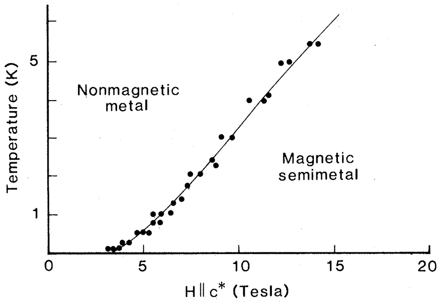


Fig. 3 (left). Pressure-temperature phase diagram of typical $(TMTSF)_2X$ salt showing the boundaries between the metallic, superconducting, and insulating states. Fig. 4 (right). Phase diagram of $(TMTSF)_2ClO_4$ at ambient pressure for magnetic field (H) applied perpendicular to conducting plane.

and giving rise to electrical conductivity.

Though the electronic properties of $(SN)_x$ were very exciting, its other physical properties did not lend themselves to commercialization (for instance, it was explosive and synthesized from explosive intermediates). However, $(SN)_x$ did provide the field with further insight which proved significant in the development of an entirely new class of conducting polymers. It was observed that the conductivity of $(SN)_x$ could be increased by reaction with bromide (*15*) (and similar oxidizing agents) to give an even more conducting polymer where the conducting entity was no longer a neutral polymer but a polymeric cation, charge neutrality being maintained by incorporating Br_3^- anions (formed by reduction of the Br_2) into the structure, as shown below.

$$(SN)_x + 3/2\, yBr_2 \rightarrow (SN)_x^{y+} + yBr_3^-$$

This has provided a model for all of the nonintrinsically conducting polymers which have been discovered subsequently.

Polyacetylene and the nonintrinsically conducting polymers. With the exception of $(SN)_x$, most polymeric systems are closed-shell systems with all of their electrons paired. Such an electronic configuration leads, as expected, to dielectric polymers. However, as was first demonstrated in the case of polyacetylene [often referred to as $(CH)_x$], an insulating polymer can be made to conduct by partial oxidation, which removes electrons from the system and facilitates conductivity (*17*). This process is referred to as doping by analogy with the doping of inorganic semiconductors. As we shall discuss later, this is a rather misleading analogy. Essentially, we are chemically converting the insulating neutral polymer into an ionic compound consisting of a polymeric cation and a counterion which is the reduced form of the oxidizing agent (Br_3^- in the case of bromine). In this sense, the doped polymers are similar to the CT salts discussed earlier.

In selecting potentially conducting polymer systems, it is important to choose a polymer which can be readily oxidized and which forms a cation rather than undergoing other chemistry. This accounts in part for the choice of π-bonded unsaturated polymers like $(CH)_x$. The π electrons can be relatively easily removed to give a polymeric cation without breaking the σ bonds which are primarily responsible for holding the polymer together. In contrast, with saturated polyethylene oxidation would remove σ electrons and lead to bond breaking and chemical decomposition. Even with π-bonded polymers, it is important to choose mild oxidizing agents which do not cause other disruptive chemistry such as addition across the carbon-carbon double bond. The latter reaction tends to be a problem when oxidizing $(CH)_x$ with Br_2.

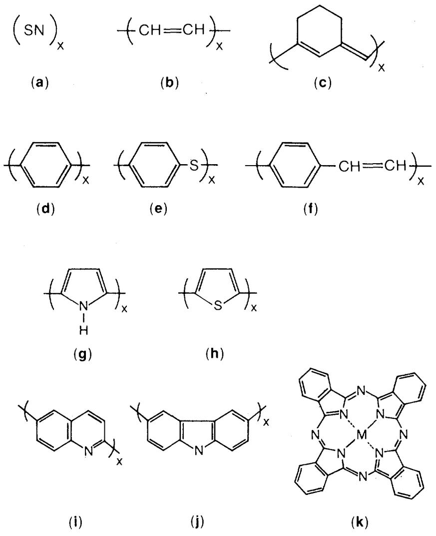


Fig. 5. The principal conducting polymers: (a) poly(sulfur nitride) or poly(thiazyl); (b) polyacetylene; (c) poly(1,6-heptadiene); (d) poly(*p*-phenylene); (e) poly(*p*-phenylene sulfide); (f) poly(*p*-phenylene vinylene); (g) polypyrrole; (h) polythiophene; (i) polyquinoline; (j) polycarbazole; (k) metallo-phthalocyanine.

Although $(CH)_x$ is clearly the most extensively studied and understood of the conducting organic polymers (*18*), this basic principle has been applied with success to an increasingly large number of other polymer systems. Conductivity is usually achieved by oxidation, but several polymer systems can also be reduced to give conducting polymeric anions. (Again, charge neutrality is preserved by incorporation of the cation derived from the reducing agent, for example, Li^+ in the case of reduction by Li.) Thus, both n-type (conduction by negative charge carriers) and p-type (conduction by positive charge carriers) materials can be prepared.

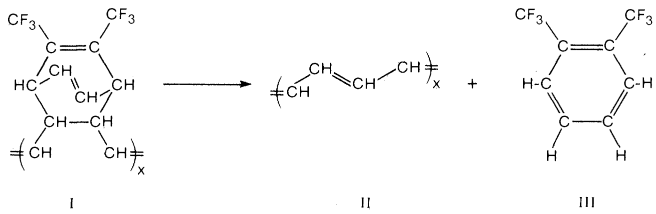
$$(CH)_x + 3/2\, yBr_2 \rightarrow (CH)_x^{y+} + yBr_3^-$$

$$(CH)_x + yLi \rightarrow (CH)_x^{y-} + yLi^+$$

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 (*19*). The charge on the polymer is then neutralized by a counterion from the electrolyte solution. Figure 5 shows the principal polymers which are or can be made to be electrically conducting. An important subgroup of nonintrinsically conducting polymers consists of those prepared by the electrochemical oxidation of some monomer which polymerizes at the anode of an electrochemical cell. These include polypyrrole, polythiophene, polyazulene, and polymers derived from other aromatic heterocyclic precursors (*20*).

Advantages of nonintrinsically conducting polymers. There are several attractive features of nonintrinsic conducting polymers. Their conductivity can be controlled in many cases by varying the extent of doping so that one system can span the whole conductivity range from insulator to semiconductor to metal. In some systems, doping can be achieved with more precision with electrochemical doping techniques, which also enable the conductivity of these systems to be switched between the conducting and insulating states by application of the appropriate voltage. This switching is usually accompanied by a color change, leading to efforts to develop electrochromic displays with conducting polymers (*21*). This electroactivity of conducting polymers is also the basis of the much more significant efforts which have gone into the development of batteries having conducting polymers as one or both of the electrodes. In the case of a $(CH)_x$ battery, where the polymer is used for both electrodes (*22*), the discharge reaction involves, for example, the reduction of polyacetylene perchlorate to neutral polyacetylene at one electrode and at the other electrode the oxidation of the lithium salt of the reduced form of polyacetylene to give neutral polyacetylene. In battery applications, the fibrous nature of $(CH)_x$ is advantageous in giving high current densities.

Advantage can also be taken of the counterion present in the nonintrinsically conducting systems to modify the physical properties of the parent polymer. For instance, the mechanical properties of polypyrrole are significantly improved by the incorporation of toluenesulfonate as the anion (*23*). Specific anions have also been incorporated into polypyrrole to prepare catalysts (*24*). The technological potential has led to considerable efforts to improve the mechanical properties and stability of conducting polymer systems. Currently, this has been most successful for polymers derived from aromatic heterocycles, especially the polyphthalocyanines (*25, 26*) and polypyrroles. Polyphthalocyanines, in particular, have been used as fillers in the high-strength polymer Kevlar to give conducting fiber composites of encouraging mechanical strength and stability (*25*). The polypyrroles can be made into tough, flexible plastics either by the appropriate choice of anion (as mentioned



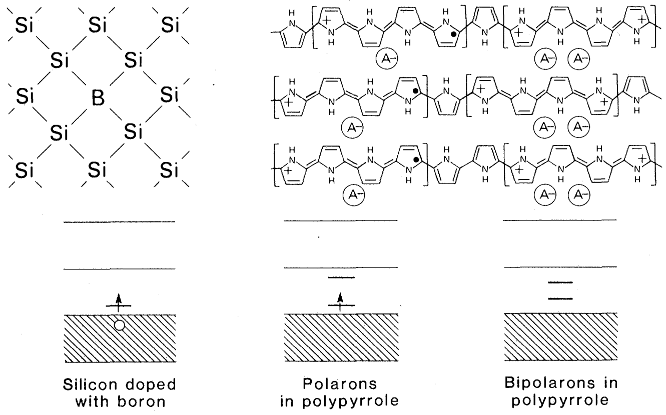


Fig. 6 (left). Feast synthesis of polyacetylene from a soluble prepolymer: I, soluble prepolymer; II, polyacetylene; III, leaving group. Fig. 7 (right). Comparison of acceptor doping of silicon and polypyrrole showing polaron and bipolaron formation.

above), by forming graft copolymers, or by electrochemically depositing the polymer in the matrix of a swellable polymer such as polyvinyl alcohol or polyvinyl chloride (*27*).

The intense efforts to understand the chemistry and physics of conducting polymers have been hampered by the insolubility and limited crystallinity of these materials, characteristics which have made traditional methods of polymer characterization difficult. Progress has begun to be made toward solution-processible conducting polymers. Conducting films of poly(*p*-phenylene sulfide) (PPS) hexafluoroarsenate have been cast from an AsF_3-AsF_5 solvent (*28*). Several polymers which are soluble in their insulating state, such as PPS or polycarbazole (*29*), become insoluble when oxidized to a conducting state. Perhaps the most significant progress along these lines has been the Feast synthesis (*30*) of polyacetylene outlined in Fig. 6. This synthesis involves the formation of a soluble prepolymer from which polyacetylene can be prepared by heating. By applying a stress to the prepolymer film during the thermal conversion, it has been possible to obtain films of $(CH)_x$ which are extremely highly crystalline and close to theoretical density, with the $(CH)_x$ chain oriented parallel to the direction of stress (*31*). Previous films of $(CH)_x$ were much less crystalline; thus these highly ordered films will be of great importance in resolving some of the problems associated with the characterization of polyacetylene. Highly oriented films of poly(*p*-phenylene vinylene) have also been prepared from stressed prepolymers (*32*).

Carrier generation in conducting polymers: Polarons, bipolarons, and solitons. It was initially assumed that the generation of charge carriers in nonintrinsically conducting polymers was analogous to that in classical inorganic semiconductors such as silicon or germanium. However, this assumption was challenged by the discovery that doped conducting polymers could display conductivity which was not associated with unpaired electron spins (*33*).

The generation of charge carriers in inorganic semiconductors is achieved by doping, for instance, silicon with part-per-million quantities of elements such as boron or lithium which are appropriate in size to fit into the silicon lattice either substitutionally or interstitially (Fig. 7). This process involves removing a neutral atom of silicon and substituting for it a neutral atom of, for example, boron which fits on the lattice site vacated by the silicon atom (*34*). Whereas the silicon atom had four valence electrons, the boron has only three, leading to the appearance of empty energy levels associated with the boron atoms slightly above the top of the silicon valence band. Electrons can be thermally transferred from the silicon to the boron levels, producing holes in the silicon valence band and giving rise to unpaired electrons, which can be detected by electron spin resonance (ESR) techniques.

The situation is very different when it comes to generation of charge carriers by doping of conjugated polymers. Doping of polymers is more appropriately seen as chemical modification because it involves incorporating into the polymer several percent of an oxidizing agent (acceptor) or a reducing agent (donor). The dopant perturbs the polymer extensively not only because of its large physical size, which does not allow it to fit substitutionally into the polymer lattice, but also because of the extensive charge transfer which takes place between the polymer chain and the dopant, causing both to become ionic and leading to changes in the geometry of the chain. In the case of acceptor doping, such as iodine doping, the polymer becomes a cation and the iodine becomes an anion, I_3^-. The levels corresponding to the acceptor in the doped polymer, that is, the I_3^-, are not in the gap but quite deep below the top of the polymer valence band.

The conducting polymer chains, like organic molecules in general, adopt a different geometry in the ionized state than in the neutral state. This is a consequence of the fact that polymer lattices are much more readily distorted than, say, the stiffer three-dimensional silicon lattice. Thus, on doping the polymer, electronic energy levels associated with the geometry modifications are removed from the top of the valence band and the bottom of the conduction band and brought into the gap. This process widens the original gap between the conduction and valence bands but does not lead to holes in the valence band. Thus, it is clear that such holes are not the source of charge carriers. In fact, the source of the charge carriers is believed to be related to the charge transfer–induced geometric modifications of the polymer chains, which lead to the formation of radical cations (polarons) and dications (bipolarons) (*35–37*).

If, for example, the polypyrrole chain is oxidized by removal of an electron, the lattice distorts locally around the resulting positive charge which appears on the polymer chain, forming a polaron. This lattice distortion (shown in Fig. 7) involves switching of the positions of the carbon-carbon double and single bonds and requires elastic energy since the resulting structure is of higher energy. However, calculations (*38*) have shown that this is more than compensated for by the lower ionization energy of the distorted form of the chain. If a second electron is now removed from the same chain, calculations show that it is energetically favorable to remove it from the polaron to create a bipolaron (see Fig. 7) rather than a second polaron. Although doubly charged, the bipolaron is spinless and can be considered analogous to a Cooper pair in the Bardeen-Cooper-Schrieffer theory of superconductivity, which consists of a pair of electrons coupled together through a lattice vibration, that is, a phonon (*39*).

In the case of polypyrrole, these polarons and bipolarons extend over about four pyrrole rings and can become mobile (*38*). The presence of both these species has been detected in polypyrrole from ESR and optical experiments (*40*). Although bipolarons are stable relative to polarons, the latter can be seen at low and intermediate doping concentrations because the kinetics of their interconversion is slow (*41*). At low dopant concentrations, ESR measurements show that the number of spins increases with the conductivity, as would be expected if the charge carriers are polarons (*40*). However, at higher dopant concentrations, the ESR signal saturates and then decreases, consistent with the fact that polarons combine to form spinless bipolarons. No ESR signal is detected in the highly conducting state, indicating that mobile bipolarons are the charge carriers. This conductivity mechanism is very different from that typical of doped inorganic semiconductors or normal metals in that all the electronic bands are either completely filled or empty, a situation classically associated with the insulating state (*38*).

In the case of polymers such as trans-polyacetylene which have degenerate ground states (that is, two ground-state geometric structures of identical total energy), the bipolaron can dissociate into two isolated spinless charged species (Fig. 8), referred to as charged solitons. This charge separation does not cost energy and effectively lowers the Coulombic repulsion between the two charges. These charged solitons were, historically, the first postulated spinless carriers and were invoked to explain the spinless conductivity when it was first observed in trans-polyacetylene (*33, 42*). However, most conducting polymers have nondegenerate ground states; thus, the geometric distortion of the ground state produced on separating the bipolaron into two solitons requires energy. Because of this energy, the solitons are confined in pairs as bipolarons, and so the soliton should be viewed as a rather special case of the spinless carrier of importance for polymers with degenerate ground states. On the other hand, the polaron-bipolaron model is a very general model for conduction in all conjugated polymers with degenerate and nondegenerate ground states.

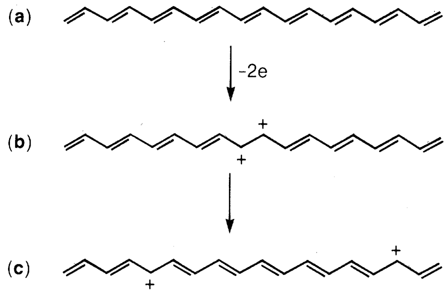


Fig. 8. Instability of bipolarons relative to charged solitons in trans-polyacetylene. (a) Removal of two electrons from polyacetylene to form (b) a bipolaron and dissociation of the bipolaron to form (c) two charged solitons.

Conclusions

We have presented a brief overview of some of the activity in conducting organic materials. Obviously, some important results have been omitted, and we recommend to the reader the more detailed reviews given in the references. We have emphasized some common features of the two main classes of organic conductors: the charge transfer which leads to the ionic nature of both the conducting polymers and the charge transfer salts, and the quasi–one-dimensional nature of these materials which results in physical properties not found in inorganic isotropic materials. In the case of the polymers, we have discussed the role of polarons, bipolarons, and solitons. It is important to appreciate that most of the exciting phenomena found in these materials have not resulted from theoretical predictions but from the difficult, empirical efforts of synthetic chemistry. For the future, this is still the only viable approach, considering the minimal level of understanding of the correlations between chemical or crystalline structure and specific solid-state properties. Certainly, new materials will determine the scientific or technological future of this field. Perhaps too much has already been said of the potential commercial application of these conductors (*13, 15, 43, 44*). We shall not indulge in further speculation along these lines, but point out that so far the technological impact of these materials has been minimal. Though the chances of finding organic superconductors with transition temperatures greater than their inorganic counterparts seem remote, the future for scientific and technological progress must be viewed optimistically in the light of the unanticipated discoveries in this field during the past 10 years.

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45. We thank J. L. Brédas for many helpful comments.