Electrically Conducting Polymers
A New Class of Electronic Materials

W.R. Salaneck, Linköping

(Department of Physics, IFM, Linköping University)

A polymer molecule is a large molecule which consists of a long, often linear, chain of smaller simple chemical units. The term *polymer* is also often used to refer to one of the common polymeric materials called "plastics" which are known for their wide range of (mostly) mechanical properties, and at the same time, for their lack of electrical properties, *i.e.*, as electrical insulators. Not all polymeric materials exhibit plastic behaviour, however, so the terminology is misleading. There are two relatively distinct areas of polymeric materials: *biological*, such as proteins; and essentially *non-biological* (often man made). Within this broad definition of the materials of polymer science, there can be counted no less than seven Nobel prizes in polymer chemistry, and five in polymer structure, in the last half century.

Despite the well known insulating nature of most organic polymeric materials, references to (slightly) electrically semiconducting and conducting polymer materials can be found in the literature over the last several decades. A series of discoveries through the 1970's, however, led to the generation of a new area of research within condensed matter physics and chemistry, namely that of electrically conducting organic polymers. Although many individual original contributions have been important, the doping of free-standing films of polyacetylene using AsF_5 or I_2 molecules to an electrical conductivity of about 10^3 $(\Omega cm)^{-1}$, by Heeger, MacDiarmid and Shirakawa in 1977, appears to represent the "discovery" of modern-day conducting polymers as a new class of electronic materials (see discussion in Yu L., 1988).

Background

Here we use the term polymer to mean a polymeric material composed of long, linear macromolecules based upon carbon, and the words polymer molecule when referring to an individual molecule. Although there are important exceptions, conventional polymers can be considered as consisting of flexible long-chain polymer molecules which interact with each other relatively weakly, principally through van der Waals or electrostatic dipole interactions. The individual polymer molecules, simplified for discussion purposes, can be considered as consisting of a backbone of carbon atoms, singly bonded to one another via σ-bonds. If the carbon atoms in the backbone are saturated (with as many single bonds as each carbon atom can possibly support, *i.e.*, four), then each carbon atom in the backbone is bonded to two side-groups. In the simplest case, the side-groups consist of hydrogen atoms, and the polymer is known as polyethylene or common household "plastic wrap". The chemical structure (geometry) of polyethylene is illustrated at the top of Fig. 1. There are no extended π-states delocalized along the carbon backbone of polyethylene. The σ-band structure of polyethylene results in an electronic band gap (optical absorption edge) of about 8.5 eV, which is one of the major reasons that polyethylene is an insulator. Some common hydrocarbon-based side-groups, however, which may be added in place of one hydrogen atom on each carbon atom, may contain *localized* π-electrons, *e.g.*, as in phenyl, carbonyl or nitrile groups. These polymers still do not have *delocalized* π-states along the backbone.

On the other hand, polymers which contain π-electronic states highly delocalized along the polymer backbone, and are said to be *conjugated*, may be doped (see below) to high electrical conductivity. The conjugated molecular chains have relatively small electronic band gaps, with optical absorption thresholds of about 1.5 to 3 eV, depending upon the polymer material. It is the delocalized electronic states of microscopically one-dimensional polymer chains that give rise to the variety of interesting and unusual physical and chemical properties of electrically conducting polymers. Many features stem from the fact that these polymer materials in particular, and organic molecules in general, can be considered mechanically "soft", as compared, for example, with a fairly rigid inorganic crystal lattice. As one consequence, the electronic structure of these conjugated-backbone polymers is strongly related to the molecular geometry of the backbone which is dependent upon the ionic state of the molecule.

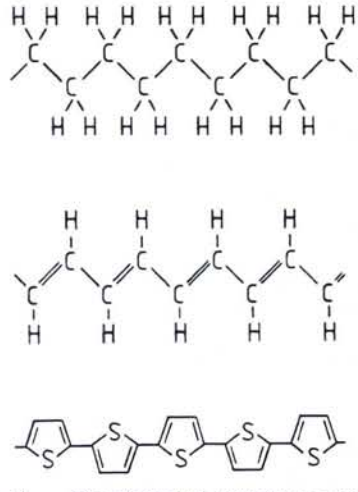

Fig. 1 — The chemical structures of three polymers are shown. Top: polyethylene; middle: trans-polyacetylene; and bottom: polythiophene.

Conducting polymers must be doped in order to promote high electrical conductivity. Values of 1 through almost 10^6 $(\Omega cm)^{-1}$ are achieved, depending upon the particular polymer-dopant system. Electronically, the process is not a real doping process in the spirit of conventional semiconductors. In conducting polymers, it involves the addition of electrons or holes to the polymer chains, through charge exchange with the dopant species, as in the formation of a charge transfer complex, or a salt. Experimentally, this doping is typically done either by exposure of the polymer material in thin-film form to molecular dopant molecules in the gas phase, in solution, or through electrochemical means. The mechanical softness of the intrinsic polymer chains allows for easy diffusion of the dopant molecules into the bulk of the material, even at room temperature.

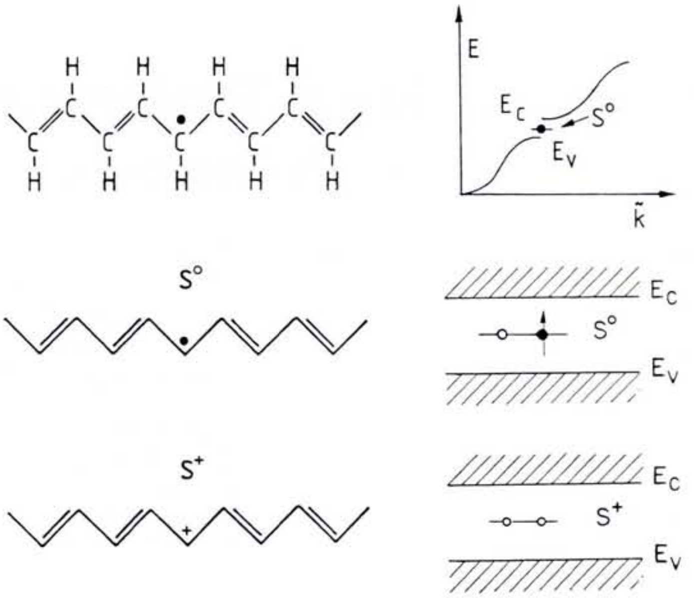

Fig. 2 — An approximation to a neutral soliton in the least bound π-band of polyacetylene is shown at the top. Note the bond alternation pattern on either side of the unpaired spin (•). The corresponding energy band diagram is at the middle right. The presence of S^o results in two new optical transitions, which are degenerate when S^o lies near the middle of the energy gap (E_c-E_v). At the bottom is shown the case of a positively charged soliton, S^+.

Doping leads to a charge-induced change in the local chemical (geometric) structure of the polymer backbone, which, in turn, leads to a local change in the electronic structure of the doped polymer. Among other things, new self-localized energy states, commonly called defects, arise within the otherwise forbidden energy gap; states which directly determine the optical, magnetic and temperature-dependent electrical-transport properties, including the ultimate high conductivities, of conducting polymers. These defects are really the lowest energy charge-carrying eigenstates of the coupled electron-lattice system, and only incidentally resemble bond-alternation defects. In other less well known cases, however, the magnitude of the forbidden energy gap itself in conducting polymers can be directly affected by electronic structural changes associated with, for example, thermally induced changes in the geometry of the conjugated polymer backbone, in this case leading to large changes in the optical properties of the material and a corresponding degradation of the electrical-transport properties.

Charge-Induced States

Today, at least the basic ideas surrounding these self-localised charge-induced eigenstates (illustrated as geometrical defects) are fairly well understood, as summarized in the book by L. Yu (1988), and recently for the Congress of the Condensed Matter Division of the European Physical Society (Salaneck and Lundström, 1989). Polyacetylene, or $(CH)_x$, is geometrically the simplest of the conjugated backbone polymers. The chemical structural formula of *trans*-$(CH)_x$ is shown in the middle of Fig. 1. The individual polymer molecule consists of a planar zigzag array of sp^2-hybridized carbon atoms, with alternating single (−) and double (=) bonds. The system is dimerized, since the double bonds are slightly shorter than the single bonds. The strictly alternating single/double-bond structure corresponds to delocalized π-states along the polymer backbone. A simple representation of the π-electronic structure, as a sinusoidal π-valence band and a π^*-conduction band, is illustrated in Fig. 2, top. As in an intrinsic inorganic semiconductor, the Fermi level, E_F, falls in the centre of the energy gap, E_g. In undoped $(CH)_x$, E_g is about 1.7 eV, and the electrical conductivity $\sigma < 10^{-8}$ $(\Omega cm)^{-1}$, governed mostly by intrinsic defects. Since an interchange of the carbon single- and double-bonds produces the identical geometry, with the same electronic structure, and the same total ground state energy, $(CH)_x$ is termed an *equivalent* (or *degenerate*) *ground state* system.

If the carbon single- and double-bonds are interchanged in only a portion of the $(CH)_x$ chain, two bond-alternation defects are created. (We shall continue to refer to these charge-induced self-localized states as defects, because of the obvious geometrical manifestations, as well as the common usage of the terminology.) One such defect is illustrated in the middle of Fig. 2. Note the short-hand notation of the chemical structure. Each defect corresponds to an unpaired electron, or free radical, represented by the dot (•) in Fig. 2. Such defects, also known as solitons, after the mathematics which describes their behaviour, are spread out smoothly over about 15 to 20 C-atoms, but are represented by a single vertex for simplicity in the figure. A localized energy state associated with this soliton (S^o) appears near the centre of the energy gap (E_g) in Fig. 2, middle. Since no electronic charge was added to (or subtracted from) the polymer chain in generating this pair of what appear to be bond-alternation defects, these new free-radical states within the semiconductor energy gap are neutral. The S^o, which is the lowest energy elementary excitation of the coupled electron-lattice system, carries a spin of one-half, yet has no net charge ($q = 0$, $s = 1/2$).

When polyacetylene is doped, extra electrons or holes are placed upon the polymer chains. The excess charges induce charged self-localized geometrical (soliton) states, which are the lowest energy charge-carrying states of the ionic system. Since single/double-bond interchange occurs upon generation of a bond-alternation defect, these defects are created in pairs. For example, through acceptor doping of polyacetylene, when two electrons are removed from the valence band, the system relaxes to a more stable geometrical state, corresponding to two geometrical defects, each of which is equivalent to an ionized S^o, or rather a S^+, as illustrated in Fig. 2, bottom. Since an electron was removed from an S^o, the S^+ corresponds to $q = e^+$ and $s = 0$. The system is similar for donor doping, with S^- defects being the lowest energy charge-carrying states, corresponding to $q = e^-$, $s = 0$. Although a number of subtle features have not been included in the above simplified discussion, the basic ideas of the unusual charge-spin relationships can be seen. Doping-induced soliton states near the centre of the energy gap E_g lead to a new optical absorption band near 1/2 E_g, as can be seen from the energy level diagram in Fig. 2, bottom, as well as increased electrical conductivity without the generation of spins, in sharp contrast to the case of doping of conventional inorganic semiconductors. In addition, an electron-hole pair created by the absorption of a photon with energy $h\nu > E_g$, decays, within a time characteristic of an optical phonon frequency, to a

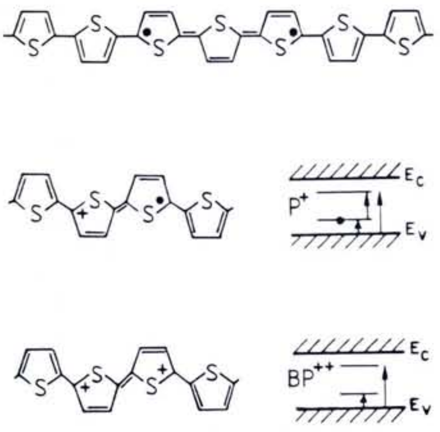

Fig. 3 — At the top, two nearby bond-alternation defects are illustrated. Note the bonding pattern on either side of the unpaired spins (●). In the lower two panels are shown the cases of a singly ionized pair (P^+) and a doubly ionized pair (BP^{++}), with the corresponding energy level diagrams at the right. The additional optical transitions are indicated.

charged soliton-antisoliton pair, $S^+\underline{S}^-$. The term anti (and the bar in the symbol $\underline{S}$) refers to the phase of the bond-alternation defects. Since there is a phase change of π when crossing one of the S-particles in Fig. 2, at the second S (an anti-S, or $\underline{S}$), somewhere else on the chain, the phase changes back by -π. Because of the associated geometrical distortion in the bond length distribution, as illustrated in the middle of Fig. 2, the optically-excited solitons have relatively long life times, which can be 10's of microseconds even at liquid nitrogen temperatures.

Essentially all conducting polymers other than *trans*-$(CH)_x$ have a more complex geometry. One common example is that of polythiophene, shown in Fig. 1, bottom. The alternating carbon single- and double-bond sequence, which is planar and similar to *cis*-$(CH)_x$, can be seen, with the exception that the sulphur atoms bridge pairs of carbon atoms in the thiophene rings. In the figure, it is understood that a carbon atom is situated at each vertex where four lines meet, and a CH-group is located where only three lines meet. Following a discussion similar to that for polyacetylene above, a pair of free radicals can be generated by interchanging the carbon single- and double-bonds over a section of the polymer chain, as illustrated in Fig. 3, top. In the thiophene ring, however, the single/double-bond interchange leads to a different geometrical state, which is of higher total energy than that of normal thiophene, hence the name, *non-equivalent ground state system*. The interchanging of the carbon single/double-bonds in each thiophene ring, as the two unpaired spins are drawn apart, increases the number of single- and double-bonds exchanged, which increases the total energy of the system. This leads to the equivalent of a distance-dependent restoring force, like a spring, and a pair of defects have an attractive interaction. In terms of solitons, two S's interact to form a bonding and an antibonding pair of electronic states within the energy gap of the polymer, E_g. If the pair of new states is singly ionized, it is called a polaron (P^+ acceptor for doping, as in Fig. 3, middle), and when doubly ionized it is called a bipolaron (BP^{++} for acceptor for doping, as in Fig. 3, bottom). Polarons lead to three new optical absorption bands for photons with energy $h\nu$ less than E_g, while bipolarons lead to two new absorption bands for $h\nu < E_g$, as indicated in Fig. 3, right.

In non-degenerate ground state polymers, at the very lowest doping levels, the excess charges may be accepted in either polaron or bipolaron states, depending upon the identity of the polymer. At very high doping levels, however, non-degenerate ground state polymer systems (possibly all conducting polymers) may become polaronic, with a half-filled polaron band responsible for the electronic and magnetic properties. The so-called polaron lattice is expected to be unstable in strictly one-dimension. The existence of the polaron lattice then requires a degree of higher dimensionality, either from polymer chain-chain interactions themselves, or more likely from Coulombic interactions with and through the dopant ionic species in the doped system. Defects in non-degenerate ground state systems also can be generated optically, as in the case of polyacetylene. The non-degenerate ground state polymer materials have not yet been prepared with the same degree of order among the polymer chains, however, as the best *trans*-$(CH)_x$, which is probably why the best electrical conductivities are only $10^3 - 10^4$ $(\Omega cm)^{-1}$.

Temperature-Induced States

An additional type of defect exists in the poly(3-alkylthiophene)'s, or P3AT's, where an alkyl-group, C_nH_{2n+1}, is attached to the thiophene rings. The chemical (geometrical) structure of one particular P3AT, poly(3-hexylthiophene) or P3HT, *i.e.* $n = 6$, is shown in Fig. 4, top. The P3AT's in general change colour with changes in temperature, *i.e.*, exhibit a *thermochromic* effect (Inganäs *et al.*). The aliphatic groups, or alkyl side-chains, contain no π-states. For a given geometry of the polymer backbone, the aliphatic alkyl-groups have no direct effect on the π-system.

In one popular current model, as yet uncharacterized temperature-dependent (possibly liquid-crystal-like) molecular interactions possibly among the aliphatic side-chains themselves, force the thiophene-ring backbone to distort from the geometry of unsubstituted polythiophene, leading to a colour change. At a given temperature, there is a balance between, on the one hand, these possible side-chain interactions which tend to twist the thiophene rings out of the planar geometry, and on the other hand, the π-electron delocalization effects, which favour the planar (maximum π-delocalization) geometry. Despite the uncertainty in the *cause* of the effect, the *nature* of the geometrical consequences has been characterized.

A very gentle spiral in the geometry will not affect the π-system to any noticable degree. On the other hand, a twist through a torsion angle (θ in Fig. 4, top left) of θ = π/2, will completely break the π-conjugation. Values of 0 < θ < π/2 lead to intermediate degrees of "breaking" of the conjugation. The number of coplanar thiophene rings, η, in between twists determines an approximation to a conjugation length, which is an order parameter character-

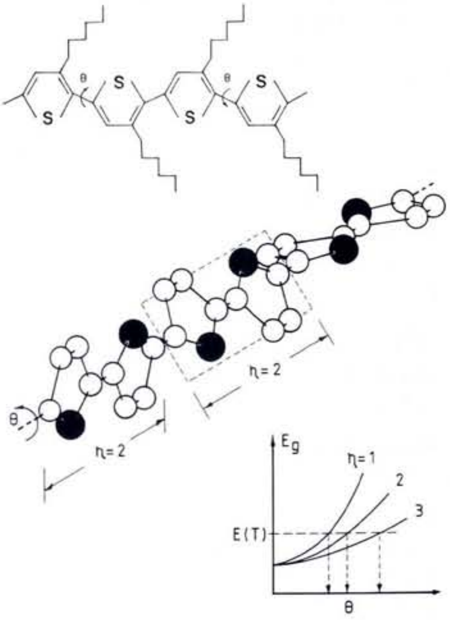

Fig. 4 — At the top is shown the chemical structure of poly(3-hexylthiophene). In the middle is illustrated a dimer model, of pairs of coplanar thiophene rings twisted through an angle θ = 45°. The black balls represent the sulfur atoms. At the lower-right is shown a schematic diagram of the change in the optical band gap, E_g, as a function of the torsion angle, θ, for the twisting of η coplanar thiophenes rings.

istic of the thermochromism. The geometry for the special case of $\eta = 2$ and $\theta = \pi/4$ is illustrated in Fig. 4, middle, while the magnitude of E_g (η, θ) is sketched in the lower right. Note that although there are only discrete values of θ and η allowed for a given shift in E_g, the net colour-change effect, or thermochromism, corresponds to an average over a range of values of η and θ at a given temperature. These defects in the conjugation are proposed to lead to *lower* electrical conductivities, but to a potentially useful optical (thermochromic) effect.

Status

In terms of applications, the future seems to be arriving for these new electronic materials. There are several areas, in different stages of development, which could be mentioned:

- Doped highly-aligned polyacetylene exhibits a room temperature electrical conductivity approaching that of single-crystal copper (Naarmann, FRG).
- The non-linear optical properties of polyacetylene seem quite promising for optical communications. One of the third harmonic generation coefficients is among the largest observed, while the material will tolerate high laser intensity (Heeger *et al.*, USA).
- A field-effect transistor based upon polyacetylene exhibits promising characteristics for switching light in integrated electro-optics, as well as a novel device for studying fundamental properties of conducting polymers (Burroughes *et al.*, UK).
- Rechargable batteries involving a lithium anode and a polyaniline cathode (MacDiarmid *et al.*, USA) are being produced in Japan, at the rate of hundreds of thousands per year, for use in electronics, such as back-up batteries for personal computers and solar-powered calculators. These batteries do not contain any heavy metals, such as mercury or cadmium, which can be important from an environmental point of view.
- Aligned polyacetylene, grown with the help of a liquid crystal matrix technique, exhibits mechanical properties approaching those of Kevlar (Shirakawa *et al.*, Japan).
- Chemically modified polythiophenes and their polymer-blends can be "blown" into continuous thin-films, and otherwise processed by many conventional polymer processing techniques (Österholm *et al.*, Finland).
- Industry is certainly moving and EPS is responding with a Europhysics Industrial Workshop (EIW-6, see page 150) which is already generating much interest.

Future

As for the future, chemical modifications of conducting polymers are already leading to new materials which are more stable in the atmosphere, and often exhibit even higher electrical conductivities than their less stable counterparts. The newest conducting polymer materials often exhibit additional useful properties, such as processability, flexibility, and higher mechanical strength, sometimes approaching the properties of conventional (insulating) polymers. Polymer blends and composites with conventional polymers are being produced today which combine the best features of each type of polymer. Although applications of conducting polymers are just now starting to appear in the market place, as research continues, new and unanticipated applications will certainly appear for these materials of the future.

FURTHER READING

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