CONDUCTING POLYMERS

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Contents

Summary

Conducting polymers (CPs) were first produced in the 1960s and they are the most recent generation of polymers. CPs have both electrical and optical properties similar to those of metals and inorganic semiconductors, but they also exhibit the attractive properties associated with conventional polymers, such as ease of synthesis and flexibility in processing. This primer presents an introduction to the physical and electrochemical properties and covers main applications of CPs in many fields. The first part is focused on the charge transport mechanism of CPs. Synthesis strategies applied to CPs are reviewed in the second part. The following sections are focused on the ion transport kinetics during redox processes of CPs and the advantages of use functionalized monomer in order to obtain CPs with desirable properties. Finally some applications of CPs are reviewed.

1. Introduction

Conducting polymers were “practically” predicted in 1962 by John Pople and S.H. Walmsley before their experimental discovery. In this classical paper Pople and Walmsley introduced the concept of “solitons” in polyacetylene (PA). The authors suggested that such a defect could be mobile and, if charged, could be responsible of high electrical conductivity. In a series of papers in 1963, D.E. Weiss and coworkers reported high conductivity in iodine oxidized polypyrrole. In the first part of this series the authors described a chemical examination of polypyrrole and they suggested that it may be regarded as a three-dimensional network of pyrrole rings interconnected by direct carbon to carbon linkages. In the second part the authors suggested that the molecular iodine is present as a charge-transfer complex. In the latter paper (part III) they described further experiments that show the influence of charge-transfer complexes of polypyrrole on its electronic properties. These papers also describe the effect of iodine doping on conductivity, the conductivity type (n or p), and electron spin resonance studies on polypyrrole. In 1968 the properties of organic semiconductors, especially the polyanilines, were reviewed by R. De Surville.

A key discovery in the development of CPs was the finding in 1973 by Walatka *et al.* that the inorganic polymer polysulfur nitride (PSN) is a metal. The metallic character of PSN, is an intrinsic property of the material, related to 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. Most other polymeric materials correspond to closed-shell systems, where all the electrons are paired, and such an electronic configuration leads to dielectric polymers.

In 1977 Gill *et al.* observed that the room-temperature conductivity of PSN, can be enhanced by an order of magnitude following exposure to bromine and similar oxidizing agents. 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 Br_3^- in the case of exposure to bromine). Another major breakthrough in the area of CPs happened in 1977 when McDiarmid *et al.* applied to PA, an intrinsically insulating organic polymer, the same redox chemistry used by D.E. Weiss *et al.* and Gill *et al*. They discovered that the conductivity of PA can be increased by exposing it to oxidizing or reducing agent. In 2000 the Nobel Prize in chemistry was awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, recognizing their breakthrough discovery of high conductivity in PA. This process is often referred to as "doping" by analogy with the doping of inorganic semiconductors, but this term is not correct because in this case a net redox reaction happens inside the polymeric material and the insulating neutral polymer is converted into an ionic complex consisting of a polymeric cation (chemical reaction 1), or anion (chemical reaction 2), and a counterion. 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. The doping reactions are usually summarized as:

$$\mathrm{CP}_{\text{Neutral chains}} + n(\mathrm{A}^-)_{\text{aq}} + m\mathrm{S} \rightarrow [\mathrm{CP}^{+n}\mathrm{A}_n^-\mathrm{S}_m] + n\mathrm{e} \qquad [1]$$

$$\mathrm{CP}_{\text{Neutral chains}} + n(\mathrm{C}^-)_{\text{aq}} + n\mathrm{e} + m\mathrm{S} \rightarrow [\mathrm{CP}^{-n}\mathrm{C}_n^-\mathrm{S}_m] \qquad [2]$$

where the different symbols mean: aqueous (aq), anion (A^-) cation(C^+), electron (e), solvent (S) and “m” and “n” are stoichiometric coefficients. In 1979 Diaz *et al*. manufactured free-standing PPy films with excellent electrical and mechanical properties using an electrochemical method, proving that the electrochemical synthesis is more suitable than the chemical synthesis when thin films and specific oxidation states of polymer are needed.

In summary, CPs have in common a significant overlap of delocalized π-electrons along the polymer chain (Figure 1), but this is itself insufficient for electrical conductivity, for which redox perturbation of the polymer chain is necessary. For example, the oxidation of the polymer produces a more conducting material, an electron-deficient polycationic chain where the charge compensation is achieved by the uptake of anions from the surrounding medium (Figure 1b). CPs are therefore ionomeric in their conductive forms. In practical applications the most widely used polymers are of the PA, polypyrrole (PPy), polythiophene (PT) and polyaniline (PANI) types, on grounds of stability and ease of preparation.

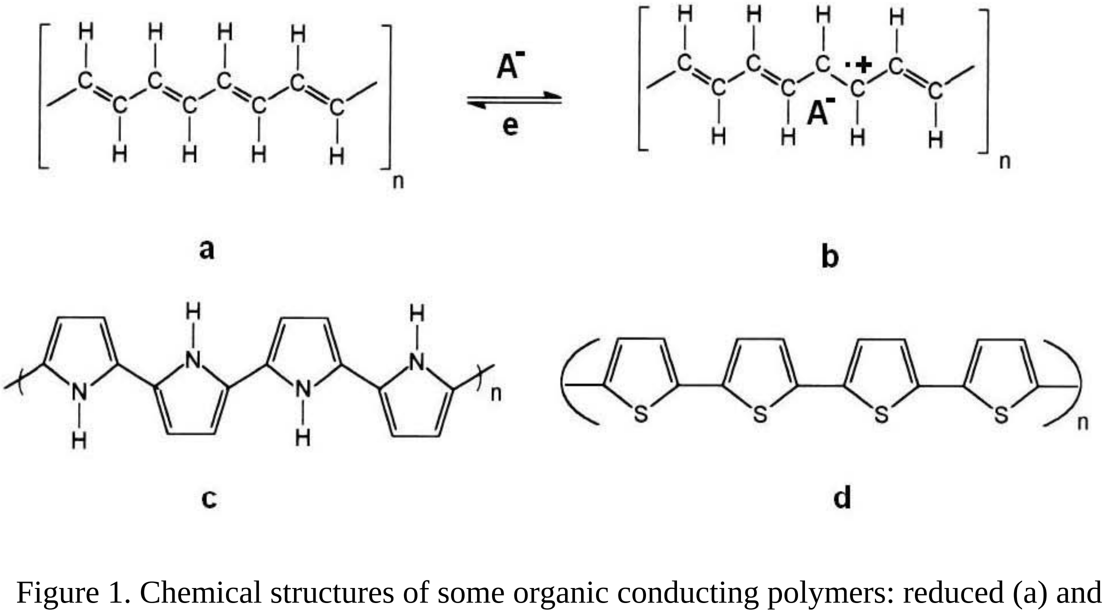

Figure 1. Chemical structures of some organic conducting polymers: reduced (a) and oxidized (b) polyacetylene, polypyrrole (c) and polythiophene (d).

Unfortunately, due to the large amount of work carried out in this field, a review of this type cannot be comprehensive. Hence, for this primer, recent developments and examples of the state-of-the art were selected. Wherever possible, we direct the reader to the primary literature where significantly more examples and details await the interested reader.

2. Nature of the Charges Appearing on the Polymer Chains upon Doping

An extraordinarily large range of conductivity can be obtained upon doping of CPs, the conductivity increases as the doping level rises. Both n and p type dopants, as well as protonic acid doping, have been used to induce an insulator–metal transition in CPs. Charges introduced into the polymers and oligomers through doping are stored in different states called solitons, polarons, and bipolarons. The nature of the charge carriers is dependent on material and doping level.

When a charge moves through a dielectric crystal, it will be permanently surrounded by a region of lattice polarization. Moving through the crystal, the charge carries the lattice distortion with it. The moving charge together with the accompanying self-consistent polarization field can be treated as a quasiparticle called a “polaron” with its own particular characteristics, such as effective mass, total momentum, energy, etc. In an organic polymer chain, it is energetically possible 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 of the HOMO and downward shift of the LUMO. In this way is possible the formation of what condensed-matter physicists call a polaron. In chemical terminology, the polaron is just a radical ion (charge carriers with a net spin associated with a lattice distortion and the presence of localized electronic states in the gap).The ability of a charge to significantly deform the lattice around it is the manifestation of a strong electron-phonon coupling. In the absence of chemical and physical defects, the charge transport mechanism in both CPs and molecular single crystals results from a delicate interplay between electronic and electron-vibration (phonon) interactions. According to the seminal Su–Schrieffer–Heeger (SSH) model, addition of extra charges to the polymer chains is expected to lead to the formation of polarons, the appearance of localized electronic levels inside the otherwise forbidden bandgap, and the emergence of new optical transitions.

Now, it is important consider what happen 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 this case we have two polarons)? In the former case, a bipolaron is formed. Bipolaron is defined as a pair of like charges (such as dication) associated with a strong local lattice distortion. The bipolaron can be thought which as analogous to the Cooper pair in the BCS theory of superconductivity, 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.

Doped PT, polyparaphenylene (PPP), and PPy can display conductivity which does not seem to be associated with unpaired electrons but rather with spinless charge carriers. Electron spin resonance (ESR) experiments indicated that charge carriers in conducting organic polymers are different from those in inorganic semiconductors. At low doping, the ESR signal grows and it is according to the fact that polarons with spin 1/2 are formed. At intermediate doping, the ESR signal saturates and then decreases, which is consistent with polarons recombination to form spinless bipolarons. At high doping level no ESR signal is observed although the system is highly conducting, indicating that the charge carriers in that regime are spinless.

Trans-PA is unique so far among CPs because it has a degenerate ground state, i.e., two “geometric” structures corresponding exactly to the same total energy. An interesting property of pristine PA is that it shows a strong EPR signal, indicating the formation of neutral radicals during its synthesis. Possibly, chains with uneven numbers of carbon atoms are apparently formed. During the initial phases of doping this EPR signal disappears. Unlike chemists, solid-state physicists like to view the above spin or charge-carrying segments of PA as perturbations or, as they call them, “excitations” in very long or infinite PA chains. It has been suggested 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. The latter is a consequence of the existence of a degenerate ground state in trans-PA. 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. 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. 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.

The charge transport in PANI was initially described as quasi-one-dimensional conductor with three-dimensional “metallic” states. The significant charge-interchain-transfer rate inside the crystalline region was supposed to result in the “metallic” bundles. Between the bundles are the amorphous (less-ordered) regions in which charge hopping dominates the macroscopic conductivity. The latter model was not consistent with the new experimental data. By means of low and high field ESR measurements, it was proved that the conducting properties of PANI and poly[N-methyl(aniline)] (PNMA) are predominantly caused by a three-dimensional charge hopping between different polymeric chains rather than by individual one-dimensional conducting chains. However, the intrinsic properties of the charge carriers in PANI are still under debate.

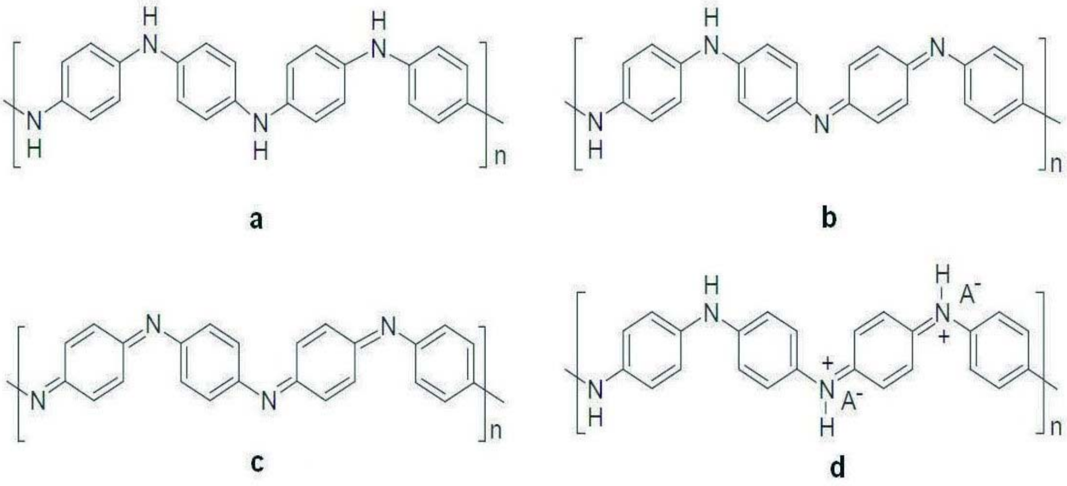

Figure 2. Oxidation states of polyaniline: leucoemeraldine (a), emeraldine base (b), pernigraniline (c) and emeraldine salt (d).

Both polarons and bipolarons are considered to contribute to the conduction of polymers like PPy, PPP, and PT. This is clearly distinctive to PANI and its derivatives, which become insulating and spinless at high oxidation states. Polaron pairs are supposed to be responsible for these decreases. The double charged polaron pairs are supposed not to be conducting, because the hopping probability of two charges in a single chain simultaneously is too small. PANI and its derivatives are different from other CPs like PPy in that the nitrogen atoms participate in conjugation and they do not have the bipolaronic spinless conducting state (Figure 2). In summary, formation of polaron pairs causes the localization of polarons, and this may be responsible for the disappearance of spin and decrease in conductance at high doping levels in PANI and PNMA.

3. Mechanism of Charge Transport in CPs

Understanding the basic charge transport mechanisms of CPs is not only of fundamental academic interest. It has great technical relevance because more professional knowledge may help to increase transport efficiency with the consequences of increased device speed, reduced power loss and avoidance of excessive heating in such promising fields as pixel-resolved full color organic light emitting diode (OLED) displays, organic field effect transistor (OFET) integrated circuits, artificial muscles or photovoltaic cells.

At present a theoretical prediction of mobility of charge carriers for a given molecule in a given crystal structure is not possible. Therefore, first of all, reliable experimental data are required to find out, how large the transport parameters are, and under which conditions which kind of transport model can be applied. The question of whether polarons or bipolarons are the more stable entities in CPs is still under debate.

The charge-transport properties of conjugated materials critically depend on the packing of the molecules or chains and the degree of order in the solid state, as well as on the density of impurities and structural defects. As a result, the measured mobility values can vary largely as a function of sample quality. From the perspective of a theoretical physicist, CPs are viewed as the limit of finite linear π-conjugated molecules. From a materials perspective, CPs are considerably more complex than theorists' idealizations. Typically, the polymers do not yield good crystals (polydicetylene is an exception) and they consist of mixed crystalline and amorphous regions. On the other hand, injection of charges into (disordered) conjugated polymers is believed to induce local distortions of the geometric structure.

Sirringhaus *et al*. have presented evidence that, at very high p-doping levels, the transport properties of PT become those of a metal. 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 valence band (VB) and the conduction band (CB), respectively. During p-type doping, this results in a new unfilled VB and the possibility of a conventional metallic-like conduction mechanism. This can only happen with PT due to its low bandgap value (2.0 eV) and the possibility to reach high dopant concentrations (theoretically estimated around or larger than one dopant per every other monomer unit). Such doping levels are not experimentally achieved with other CPs. Figure 3 shows the change of electric resistance of a PT film with the applied potential. It is clear that increasing the p-type doping (at higher potentials) a dramatic increase of conductivity (decrease of resistance) is observed.

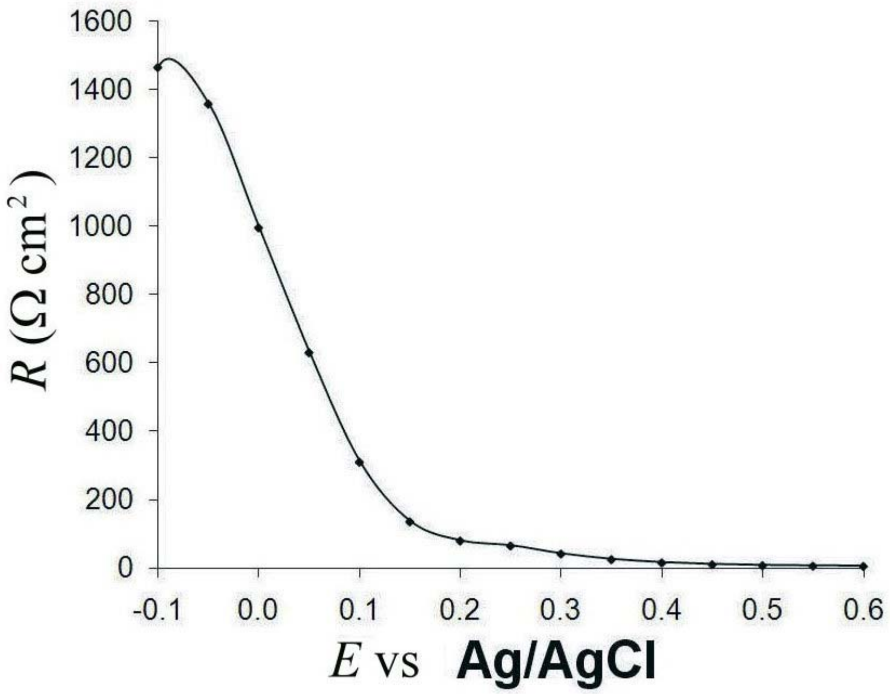

Figure 3. Variation of film resistance, perpendicular to the electrode, with the applied potential for the Pt(111) electrode coated with a polythiophene film (about 100 nm thick). Data measured using electrochemical impedance spectroscopy. The electrolyte was 0.1 M $NaClO_4$ in dry and argon saturated acetonitrile.

A synthetic method that allows the synthesis of highly conducting polymer with metallic behavior is called self-stabilized dispersion polymerization, as it was demonstrated for the case of PANI. In contrast to conventional homogeneous/dispersion polymerization using an aqueous medium containing aniline, acid and oxidant, this polymerization is carried out in a heterogeneous biphasic (organic and aqueous) mixture without the use of any stabilizers. It has been suggested that the anilinium hydrochloride monomer is like a surfactant, with a polar hydrophilic head and an organic hydrophobic tail. The monomers and growing polymer chains act as interfacial stabilizers, resulting in excellent dispersion of the organic phase inside the aqueous reaction medium. The organic phase tends to separate the aniline monomers and grown PANI chains from the reactive ends of the chain in the aqueous phase, thereby suppressing undesirable side reactions (such as ortho-coupling or Michael reductive additions). The PANI samples prepared with the above method showed room-temperature conductivities up to 1,000 S cm^{-1} and typical metallic behavior.

A second way for achieve high conductivities was demonstrated for the case of regioregular poly-3-hexylthiophene (RR-P3HT). Self-organization of the polymer chains leads to a lamellar structure with two-dimensional sheets built by strongly interacting conjugated segments; as a result, the material displays room temperature mobilities up to 0.1 $cm^2\ V^{-1}\ s^{-1}$. In 2001, Schön *et al*. demonstrated that the electrical properties of RR-P3HT can be modified over the largest range possible, from insulating to superconducting. The authors reported a distinct metal-insulator transition and metallic levels of conductivity in a polymer field-effect transistor. The active material was solution-cast regioregular poly(3-hexylthiophene), which forms relatively well ordered films owing to self-organization, and which yields a high charge carrier mobility (0.05–0.1 $cm^2\ V^{-1}\ s^{-1}$) at room temperature. At temperatures below 2.35K, with sheet carrier densities exceeding 2.5 x 10^{14} cm^{-2}, the PT film becomes superconducting. The authors suggest that the appearance of superconductivity seems to be closely related to the self-assembly properties of the polymer, where the introduction of additional disorder was found to suppress superconductivity. This may explain why superconductivity has not been observed in chemically doped conjugated polymers. In this case, the disorder introduced by the impurities probably destroys the superconducting phase.

One way to understand the properties of CPs and the relationship between them and the structure is the study the properties of oligomer series. In a seminal work Diaz *et al*. studied the electro-oxidation of various aromatic monomers and oligomers and particularly the relationships between the number of repeated units in the substrate molecule and the oxidation potential as well as the UV-vis absorption maximum of the oxidation product (soluble as well as deposited on the electrode). As is was predicted by theoretical calculations, it was observed that the oxidation potential shifts to less positive values with an increasing number of monomer units in the educt, whereas the absorption maximum shifts considerably to longer wavelengths. Banerjee *et al*. synthesized a well-defined series of poly-p-phenylene oligomers containing up to eight phenylene moieties with branched alkyl (i.e., 6-tetradecyl) groups as the end-capping substituents and solubilizing groups. The authors reported that the low-energy electronic transitions of the cation radical and all electronic and optoelectronic properties of poly-p-phenylenes, containing up to seven phenylene moieties, have a linear relationship with 1/n ratio (where n is number of phenylene moieties). For example, the authors reported the following quantitative relationship between the oxidation potentials and the number of phenylene rings in various polyphenylenes: Eox (V vs SCE) = 1.3 + 0.74/*n*. The slope from the equation for linear fit of the curve between Eox and 1/n is a quantitative measure of the effective conjugation. A linear extrapolation, of the latter relationship results in a value of 1.3 V vs SCE for the oxidation potential of an infinitely long poly-p-phenylene polymer. The lowering of the oxidation potentials with increasing number of phenylene units, in first approximation, could represent the rise of the HOMO levels as it is expected for all CPs.

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Biographical Sketch

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