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In 1977, the first intrinsic electronically conducting organic polymer, doped polyacetylene, was reported, spurring interest in "conducting polymers." These polymers are a different class of materials than conducting polymers, which are merely a physical mixture of a non-conductive polymer with a conductive material such as metal or carbon powder. Initially these intrinsically conducting polymers were neither processable nor air stable. However, later generations of these polymers were processable into powders, films, and fibers to form electrically conducive blends. Applications of these polymers, especially polyanilines, have begun to emerge. These include blends and coatings for electrostatic dissipation and electromagnetic interference (EMI) shielding, electromagnetic radiation absorbers for welding (joining) of plastics, conductive layers for light-emitting polymer devices, and anticorrosion coatings for iron and steel.

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POLYMERS ARE METALS TOO!

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Introduction

In 1977, the first intrinsic electrically conducting organic polymer, doped polyacetylene, was reported,[1] spurring interest in "conducting polymers." These polymers are a different class of materials than conducting polymers, which are merely a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder. Initially these intrinsically conducting polymers were neither processable nor air stable. However, later generations of these polymers were processable into powders, films and fibers from a wide variety of solvents, and also air stable.[2,3] Some forms of these intrinsically conducting polymers can be blended into traditional polymers to form electrically conductive blends. The electrical conductivities of the intrinsically conducting polymer systems now range from that typical of insulators ($<10^{-10}$S/cm [10^{-10} (W^{-1}-cm)$^{-1}$]) to that typical of semiconductors such as silicon ($\sim10^{-5}$ S/cm) to greater than 10^4 S/cm (nearly that of a good metal such as copper, 5 x 10^5 S/cm).[2-4] Applications of these polymers, especially polyanilines, have begun to emerge. These include blends and coatings for electrostatic dissipation and electromagnetic interference (EMI) shielding, electromagnetic radiation absorbers for welding (joining) of plastics, conductive layers for light emitting polymer devices, and anticorrosion coatings for iron and steel.

The common electronic feature of pristine (undoped) conducting polymers is the π-conjugated system which is formed by the overlap of carbon p_z orbitals and alternating carbon-carbon bond lengths.[5,6,7] (In some systems, notably polyaniline, nitrogen p_z orbitals and C_6 rings also are part of the conjugation path.[8,9]) Figure 1 shows the chemical repeat units of the pristine forms of several families of conducting and semiconducting polymers, i.e., *trans*-polyacetylene [*t*-$(CH)_x$], the leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB) forms of polyaniline (PAN), polypyrrole (PPy), polythiophene (PT), poly(*p*-phenylene) (PPP), and poly(*p*-phenylene vinylene) (PPV).

The electronic ground states of each of these polymers is that of an insulator, with a forbidden energy gap between filled (analagous to Hightest Occupied Molecular Orbitals or HOMOs) and empty energy levels (analagous to Lowest Unoccupied Molecular Orbitals or LUMOs). For undoped *t*-$(CH)_x$ the energy gap arises from the pattern of alternating single (long) and double (short) bonds [5,6,7], with an additional contribution due to electron-electron Coulomb repulsion.[10] Interchange of short and long bonds results in an equivalent (degenerate) ground state. The pernigraniline oxidation state of PAN[11] and its derivatives also has a two-fold degenerate ground state; that is, single and double bonds (benzenoid and quinoid rings) can be interchanged without affecting the ground state energy. The remaining polymers illustrated in Figure 1 have nondegenerate ground states; that is, interchange of single and double bonds leads to electronic structures of different energy.

Increase in Conductivity with Doping

The conductivities of the pristine electronic polymers are transformed from insulating to conducting through the process of doping, with the conductivity increasing as the doping level increases[2-7] Both *n*-type (electron donating, e.g., Na, K, Li, Ca, tetrabutylammonium) and *p*-type (electron accepting, e.g., PF_6, BF_4, Cl, AsF_6) dopants have been used to induce an insulator-to-conductor transition in electronic polymers. The doping differ from conventional ion implantation of three-dimensional semiconductors, typically being carried out by exposing the polymer films or powders to vapors or solutions of the dopant, or electrochemically. (In some circumstances, the polymer and dopant are dissolved in the same solvent before forming the film or powder.) Unlike substitutional doping as occurs for conventional semiconductors, in electronic polymers the dopant atomic or molecular ions are positioned interstitially between chains, and donate charges to or accept charges from the polymer backbone. The polymer backbone and dopant ions form new three-dimensional structures. There is a rich variety in these structures, with differing structures occurring for different dopant levels and variations in the processing routes, and a wide range of degrees of local order.[12,13]

The strong coupling between electrons and phonons (vibrations) causes distortions of the bond lengths in the vicinity of the doped charges.[7] For the degenerate ground state polymers, the charges added to the backbone at low doping levels are stored in charged soliton and polaron states for degenerate polymers,[5-7,14,15,16] and as charged polarons or bipolarons for nondegenerate systems.[17] For nondegenerate polymers, high doping results in polarons interacting to form a "polaron lattice" or electrically conducting partialy filled energy band.[18,19,20] Some models suggest equilibrium between polarons and bipolarons.[21] At high doping levels of *trans*-polyacetylene, it is proposed that the soliton energy levels essentially overlap the filled valence and empty conduction bands leading to a conducting polymer.[22,23]

In contrast to the *n*- and *p*-type doping processes applied to polyacetylene, polypyrrole, polythiophene, leucoemeraldine base, etc., for the polyaniline emeraldine base (EB) form, the conductivity varies with proton (H^+ ion) doping level (protonic acid doping). In the protonation process, there is no addition or removal of electrons to form the conducting state.[26] Figure 2 schematically demonstrates the equivalence of *p*-doping of leucoemeraldine base and protonic acid doping of emeraldine base to form the conducting emeraldine salt. Both organic acids such as HCSA (camphor sulfonic acid), and inorganic acids, such as HCl, are effective,[24] with the organic sulfonic acids leading to solubility in a wide variety of organic solvents, such as chloroform and *m*-cresol.[25] The protonic acid may also be covalently bound to the polyaniline backbone, as has been achieved in the water soluble sulfonated polyanilines,[26] Figures 3a and 3b. Similar electronic behavior has been observed for protonic acid doped PAN as for the other nondegenerate ground state systems.[26,27] That is, polarons are important at low doping levels, and, for doping into the highly conducting state, a polaron lattice (partially filled energy band) forms. Polaron pairs, or bipolarons are formed in less ordered regions of doped polymers.[28]

Doped polyacetylene has been the prototype system since the initial report[1] of the achievement of a conductivity of s~100 S/cm upon doping with iodine and other acceptors. Subsequently, $(CH)_x$ was synthesized by alternate routes that yielded higher conductivities upon doping.[29,30,31] reportedly[36]as high as $\sim10^5$ S/cm, rivaling that of traditional metals such as copper (s_{DC}~ 6 ¥ 10^5 S/cm). Recent advances in the processing of other conducting polymer systems have led to improvements in their s_{DC} to the range of $\sim10^3$ - 10^4 S/cm. The absolute value of the highest conductivities achieved remains controversial. Many traditional signatures of an intrinsic metallic nature now have become apparent, including negative dielectric constants, a Drude metallic response, temperature independent Pauli susceptibility, and a linear dependence of thermoelectric power on temperature. However, the conductivities of even new highly conducting polymers, though comparable to traditional metals at room temperature, generally decrease as the temperature is lowered. Some of the most highly conducting samples remain highly conducting though even at millikelvin.

Since there is still a great diversity in the properties of materials synthesized by even the same synthetic routes, correlated structural transport, magnetic, and optical studies of the same materials are important. The conductivities increase by more than 10 orders of magnitude upon doping the pristine polymers. The conductivity of a polymer, for example HCSA doped polyaniline, can vary greatly both in magnitude (in this case, nearly four orders of magnitude) and temperature dependence (both increasing and decreasing conductivity with decreasing temperature) as a result of processing in different solvents. The effect of solvent and solvent vapors on the structural order and subsequent electrical conductivity of intrinsically conducting polymers, especially polyanilines, is termed[30] "secondary doping."

Models for Electrical Conductivity

Much work has focused on the nature of the charge carriers in the highly doped metallic state. The carriers may be spatially localized so they cannot participate in transport except through hopping.[2-4]The prime source of localization which has been studied is structural disorder in the polymers.[13] Figure 4 is a schematic view of the inhomogeneous disorder in these doped polymers, with individual polymer chains passing through both ordered regions (typically 3 - 10 nm accross) and disordered regions. The percent 'crystallinity' may vary from near zero to 50 or 60% for polypyrroles and polyanilines, respectively, to greater then 80% for polyacetylenes. The chains in the disordered regions may be either relatively straight, tightly coiled, or intermediate in disorder.

In a perfect crystal electron wave functions form delocalized Bloch waves.[32] Impurities and lattice defects in disordered systems introduce backward scattering of these electron waves with resulting[33] "Anderson localization." The ramifications, including a finite density of states $N(E_F)$ produced at the Fermi level E_F between mobility edges, were discussed by Sir Neville Mott.[34] When the Fermi level or chemical potential lies in the localized region, the conductivity at zero temperature is zero even for a system with a finite density of states. The Mott variable range hopping (VRH) model is applicable to systems with strong disorder such that the disorder energy is much greater than the band width. The general form of the temperature dependent conductivity s of Mott's model is described as $s = s_0 \exp[-(T_0/T)^{1/(d+1)}]$, where d is the dimensionality and, for three-dimensional systems, $T_0 = clk_B N(E_F) L^3$ (c is the proportionality constant, k_B the Boltzman constant, and L the localization length). If the Fermi level is at an energy such that the electronic states are extended, then finite conductivity at zero temperature is expected. This model assumes that the substantial disorder is homogeneous throughout the isotropic three-dimensional sample. This model has received much experimental attention for doped and ion implanted polymers.[2-4,35]

For isolated one-dimensional metallic chains localization of charge carriers arises for even weak disorder because of quantum interference due to static back-scattering of electrons,[41] contrasting to the strong disorder required for localization in three-dimensional systems. The localization effects in the inhomogeneously disordered (partially crystalline) conducting polymers are proposed to originate from one-dimensional localization in the disordered regions. The inhomogenous disorder model[36,37] represents the doped polymer as relatively ordered regions (or "crystalline islands") interconnected through polymer chains traversing disordered regions, Figure 4. The individual polymer chains often are longer then the island and inter-island length scales. Within this model, conduction electrons are three-dimensionally delocalized in the “crystalline” ordered regions (though the effects of paracrystalline disorder may limit delocalization within these regions). In order to transit between ordered regions, the conduction electrons must diffuse along electronically isolated chains through the disordered regions where the electrons easily become localized. The localization length of these electrons depends the details of the disorder (e.g., electrons traveling along tightly coiled chains are expected to have much shorted localization lengths then electrons traveling along expanded coil or relatively straight chains). Phonon-induced enlargement of the localization length increases the conductivity with higher temperature. Three-dimensional crystalline order facilitates delocalization. Nematic-like order can also increase delocalization, though less effectively. If the localization length for some conduction electrons exceeds the separation between the ordered regions then the total delocalization will be substantially enhanced.

For conventional metals, many of the electrical transport properties can be described by the Drude model[39] with a single scattering time t. Despite its simplified assumptions, the model explains high and frequency independent conductivity of traditional metals from dc to the microwave (~10^{10} Hz) frequency range, and a real part of the dielectric constant (e_r) which is negative below the screened plasma frequency ($w_p^2 = 4pne^2/m^*e_b$; n is the density of carriers, m* is the carrier effective mass, and e_b is the background dielectric constant). In the low frequency Drude limit (wt << 1), the Drude response can be deduced as $e_r = - wp^2t^2$ and $e_i = wp^2t/w$, where e_i is the imaginary part of the dielectric constant.

Electrical Conductivity of Conducting Polymers

The temperature dependent conductivity [s(T)] of heavily iodine doped $(CH)_x$ and hexafluorphosphate (PF_6) doped PPy down to mK range vary as a function of aging (disorder).[38] The highest s_{dc} at room temperature reported in this study is ~5 ¥ 10^4 S/cm for I_3 doped T-$(CH)_x$ and ~ 10^3 S/cm for the highest conducting PPy(PF_6). For both of these materials, the conductivity decreases with decreasing temperature to a minimum at T_m ~ 10 K. Below T_m, s increases by ~20% and then is constant to 1 mK. Some highly conducting preparations of PAN-CSA show similar behavior. Samples of the same chemical composition but prepared from different solvents may have different local order, thus very differnt conductivities. Less highly conducting samples of doped polyacetylene, doped polyanline, and doped polypyrrole become insulating at low temperatures.

Hydrochloric acid as well as camphor sulfonic acid doped polyaniline prepared in chloroform often have[44] log s proportional to $T^{-1/2}$ as expected for quasi-one-dimensional variable range hopping (VRH), $s = s_0 \exp[-(T_0/T)^{1/2}]$, where $T_0=16/[k_BN(E_F)Lz]$. Here L is the one-dimensional localization length and z the number of nearest neighbor chains. Generally, the higher conductivity samples have a weaker temperature dependence at low temperatures (T_0~700–1000 K for T<80 K), and lower conductivity samples a stronger temperature dependence (T_0~4000 K). The smaller T_0 for the more highly conducting samples has been associated with weaker localization due to improved intrachain and interchain order.

The microwave frequency dielectric constant provides a measure of the charge delocalization in individual samples. The low temperature dielectric constant, e_{mw}, for a series of emeraldine hydrochloride samples is proportional to the square of the crystalline coherence length, x^2, independent of the direction of orientation of the sample with regard to the microwave frequency electric field,[44] demonstrating that the charge is delocalized three-dimensionally within the crystalline regions of these samples. The low temperature localization length and the crystalline correlation length determined by x ray diffraction are in agreement, as is the density of states.

The sign, magnitude, and temperature dependence of the 6.5 ¥ 10^9 Hz dielectric constant for very highly conducting T-$[CH(I_3)_y]_x$, PPy-PF_6, and *m*-cresol prepared PAN-CSA are quite striking.[2,4,36,37] Each of these systems has a large (10^4 - 10^6) and negative value of e_{mw}. Using the Drude model for low frequencies (wt < 1), plasma frequencies of w_p=0.01 - 0.02 eV (~200 cm^{-1}) and room temperature scattering times of ~ 10^{-11} sec were calculated. The exact values correlate with the sample preparation conditions. The w_p are much smaller than one expects from the usual Drude model, suggesting that only a small fraction of the conduction band electrons participate in this low frequency plasma response. Similarly, the value of t is two orders of magnitude larger than usual for an alkali, noble, or transition metal, perhaps associated with the time for electrons to transit the disordered regions.

For the conducting forms of doped conjugated polymers, there are zero, two, three, or one zero crossings of the real part of the dielectric function (e_1) as the frequency is decreased.[2,44,45]For the least conducting materials, e_1 remains positive for the entire optical frequency range (50–50,000 cm^{-1}), reaching values of several hundred at microwave frequencies. For higher conductivity materials, e_1 crosses zero between 1 and 3 eV (the all-conduction-electron plasma response) and then becomes positive again below 1000 cm^{-1}, reaching values in excess of 10^4 at microwave frequencies. For the most metallic samples, two behaviors have been reported dependent upon the system. For doped PAN and PPy with s_{dc} ~ 400 S/cm, e_1 demonstrates the previous two zero crossings, and a third zero crossing occurs to negative values at a “delocalized conduction electron plasma frequency” of several hundred wavenumbers. For very highly conducting doped polyacetylene, e_1 crosses zero at the all conduction electron plasma frequency and remains negative to the lowest measured optical frequencies.[39]

Applications

Intrinsically conducting polymers are promising materials for shielding electromagnetic (EM) radiation and reducing or eliminating EMI because of their relatively high conductivity and dielectric constant and ease of control of their s and e through chemical processing.[40] Also, they are relatively lightweight compared to standard metals, flexible, and do not corrode as do common metals. Among intrinsically conducting polymers, the microwave frequency conductivity (s_{mw}) are dielectric constant (e_{mw}) of polyaniline particularly are controllable through chemical processing (e.g., stretch ratio, molecular weight, doping level, counter ion, solvent, etc.). The total shielding efficiency of conducting polymers increases as the thickness of the polymer film increases. The shielding capabilities are in the range of utility for many commercial (~ 40 dB) and military (~ 80 - 100 dB) applications.

The development of intrinsically conductive polymers, especially polyanilines, provides an opportunity for use of conductive polymers in welding (joining) of thermoplastics and thermosets. Intrinsically conducting polymer film or blend of the intrinsically conductive polymer and the thermoplastic or thermoset to be joined is placed at the interface between two plastic pieces to be joined. Exposure to microwave frequency radiate results in heating of the joint and subsequent fusing (welding).[41] The resulting joint may be as strong as that of the pure compression molded thermoplastic or thermoset.

The corrosion of steel has long been an important problem. Polyaniline has been shown to have corrosion protecting capabilities both when doped[42] and neutral.[43] The mechanism for corrosion protection was found to be anodic, i.e., the polyaniline film withdraws charge from the metal, pacifying its surfaces against corrosion. Large values (up to ~1.5 cm) of throwing power were obtained for emeraldine base protected cold rolled steel.

There is a need for low voltage, reliable operation of light emitting polymer devices. One approach to improving the operation of these devices is to overcoat the transparent conducting indium tin oxide electrode with a layer of nearly transparent conducting polymer, especially polyaniline,[44] or incorporating networks of conducting polymer fibers in the light emitting polymers.[45] Use of layers of the semiconducting emeraldine base to sandwich some light emitting polymer layers has resulted in a symmetrically configured alternating current light emitting (SCALE) polymer device that operates in both dc and ac modes.[46]

Summary

Intrinsically conducting polymers are a broad class of (often) processable materials based upon doped π conjugated polymers. Their conductivities vary from that of insultators through to that of semiconductors and even good metals. A wide variety of electronic phenomena are observed. Because of the broad choice of materials and properties, this class of polymer is potentially of use in a large number of technologies.

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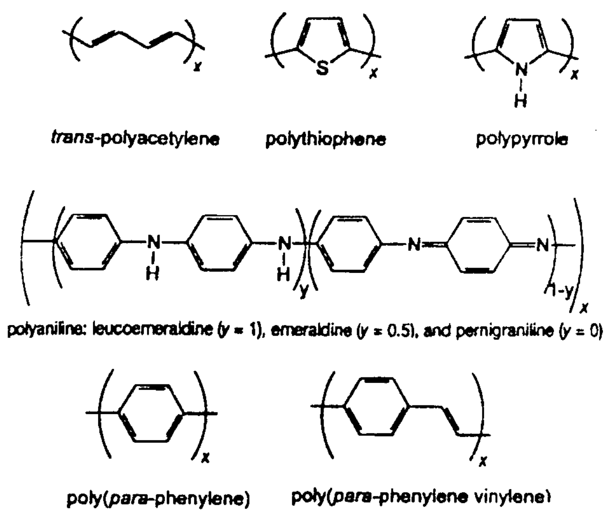
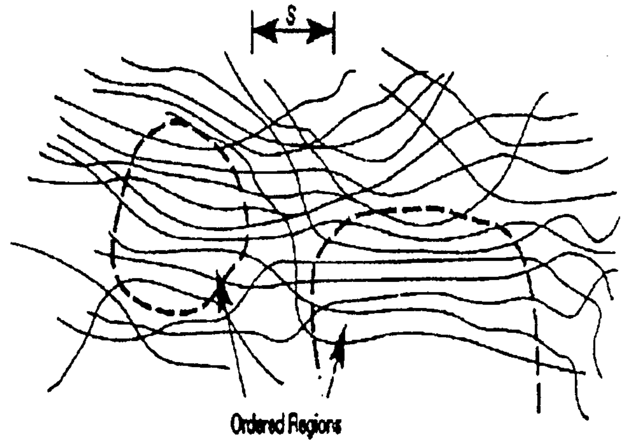
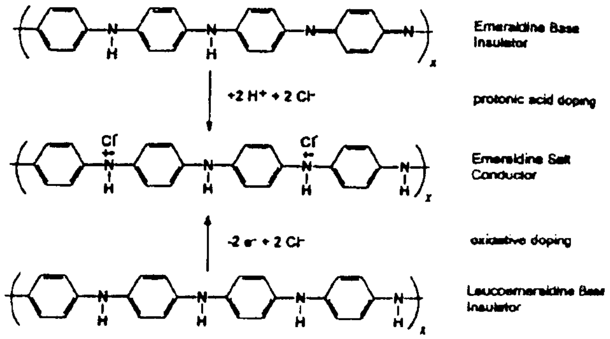


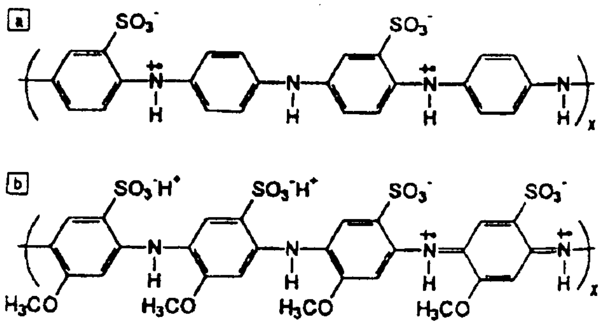
1. Repeat units of several electronic polymers.



4. Schematic view of the inhomogeneous disorder in these doped polymers, with individual polymer chains passing through both ordered regions (typically 3 - 10 nm across) and disordered regions (of length 's').



2. Illustration of the oxidative doping (p-doping) of leucoemeraldine base and protonic acid doping of emeraldine base, leading to the same final product, emeraldine salt.



3. Schematic illustrations of (a) 50% sulfonated and (b) 100% sulfonated polyanilines (self-doped forms).