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The electrical conductivities of the intrinsically conducting polymer systems now range from that typical of insulators ($<10^{-10}$ S/cm[$10^{-10}(\Omega^{-1}\text{-cm})^{-1}$]) to that typical of semiconductors such as silicon ($\sim 10^{-5}$ S/cm) to greater than 10^4 S/cm (nearly that of a good metal such as copper, 5×10^5 S/cm). The origin of the conductivity in these polymers is reviewed. Applications of these polymers, especially polyanilines, have begun to emerge. These include coatings and blends 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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ELECTRICALLY CONDUCTING POLYMERS: SCIENCE AND TECHNOLOGY

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Introduction

For the past 50 years, conventional insulating polymer systems have been increasingly used as substitutes for structural materials such as wood, ceramics, and metals because of their high strength, light weight, ease of chemical modification/customization, and processability at low temperatures. In 1977, the first intrinsic electrically conducting organic polymer, doped polyacetylene, was reported,[1] spurring interest in "conducting polymers." These polymers are completely different from conducting polymers which are merely a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder. Though initially these intrinsically conducting polymers were neither processable nor air stable, new generations of these materials now are processable into powders, films and fibers from a wide variety of solvents, and also are 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} $(\Omega^{-1}\text{-cm})^{-1}$]) to that typical of semiconductors such as silicon ($\sim 10^{-5}$ S/cm) to greater than 10^4 S/cm (nearly that of a good metal such as copper, 5×10^5 S/cm).[2,4]

The origin of the conductivity in these polymers is reviewed

Applications of these polymers, especially polyanilines, have begun to emerge. These include coatings and blends 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-* and *cis*-polyacetylene [$(CH)_x$], poly(1,6-heptadiyne), the leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB) forms of polyaniline (PAN), polypyrrole (PPy), polythiophene (PT), poly(*p*-phenylene) (PPP), poly(*p*-phenylene vinylene) (PPV), polypyridine (PPyr), and poly(*p*-pyridyl vinylene) (PPyV).

Electronic Structure and Insulator-to-Conductor Transition

The electronic ground states of each of these polymers is that of an insulator, with a forbidden energy gap between filled and empty energy levels. For undoped *trans*-$(CH)_x$ 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. Poly(1,6-heptadiyne)[11] and the pernigraniline oxidation state of PAN[12] and their derivatives also have two-fold degenerate ground states; that is, single and double bonds (benzenoid and quinoid rings for the pernigraniline base polymer) can be interchanged without affecting the ground state energy. The remaining polymers illustrated in Figure 1 and their derivatives have nondegenerate ground states; that is, interchange of single and double bonds leads to electronic structures of different energy.

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 utilized to induce an insulator-to-conductor transition in electronic polymers. The doping procedures differ from conventional ion implantation used for 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.[13,14]

The negative or positive charges initially added to the polymer chain upon doping do not simply begin to fill the rigid conduction band (Lowest Unoccupied Molecular Orbital or LUMO level) or valence band (Highest Occupied Molecular Orbital or HOMO level), immediately causing metallic behavior. 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, charges added to the backbone at low doping levels or upon photoexcitation are stored in charged soliton and polaron states.[5-7,15,16,17] For nondegenerate systems, the charges introduced at low doping levels or photoexcitation are stored as charged polarons or bipolarons (e.g., for PT, PPy, PPV, PPP, and LEB and EB forms of polyaniline).[18] Photoexcitation also leads to generation of neutral solitons in degenerate polymers[19,20] and neutral excitons in nondegenerate polymers (important for polymer-based light emitting devices).[21,22,23] At high doping levels of *trans*-polyacetylene, it is proposed that the soliton energy levels essentially overlap the filled

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valence and empty conduction bands leading to a conducting polymer.[24,25] For nondegenerate polymers, high doping results in polarons interacting to form a "polaron lattice" or electrically conducting partialy filled energy band.[26,27,28] Some models suggest equilibrium between polarons and bipolarons.[29]

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 protonic acid doping of emeraldine base and *p*-doping of leucoemeraldine base to form the conducting emeraldine salt. Both inorganic acids, such as HCl, and organic acids such as HCSA (camphor sulfonic acid), are effective,[30] with the organic sulfonic acids leading to solubility in a wide variety of organic solvents, such as chloroform and *m*-cresol.[31] The protonic acid may also be covalently bound to the polyaniline backbone, as has been achieved in the water soluble sulfonated polyanilines,[32] Figures 3a and 3b. Similar electronic behavior has been observed for protonic acid doped PAN as for the other nondegenerate ground state systems.[26,27,33] 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.[34]

Doped polyacetylene has been the prototype system since the initial report[1] of the achievement of a conductivity of $\sigma \sim 100$ S/cm upon doping with iodine and other acceptors. Subsequently, $(CH)_x$ was synthesized by alternate routes that yielded higher conductivities upon doping.[35,36,37] The room temperature dc conductivity (σ_{DC}) for doped films of some of these new materials has been reported[35] to be as high as $\sim 10^5$ S/cm, rivaling that of traditional metals ($\sigma_{DC} \sim 10^4 \sim 6 \times 10^5$ S/cm). Recent advances in the processing of other conducting polymer systems have led to improvements in their σ_{DC} to the range of $\sim 10^3 -$

10^4 S/cm. It is noted that the absolute value of the highest conductivities achieved remains controversial. With these improvements in σ_{DC}, many traditional signatures of an intrinsic metallic nature 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 in the millikelvin range.

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. Figure 4 presents representative values[38] of the room temperature conductivities reported for the most widely studies doped conducting polymers. Also indicated is the dopant utilized for each value shown. The conductivities of each of these systems increase by more than 10 orders of magnitude upon doping the pristine polymer. The conductivity of a polymer, for example HCSA doped polyaniline, can vary greatly both in magnitude and temperature dependence 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 ıor Electrical Conductivity

Much work has focused on the nature of the charge carriers in the highly doped metallic state. Even though there is a high density of conduction electrons at the Fermi level (chemical potential) for the highly doped 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] X-ray diffraction studies of these systems show that they are generally of modest crystallinity,

with regions of the material which are more ordered while other regions are more disordered. Also, the fibrillar nature of many of the conducting polymers may lead to localization by reducing the effective dimensionality of the electrons delocalized in a bundle of polymer chains. Figure 5 presents 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. It is noted that the chains in the disordered regions may be either relatively straight, tightly coiled, or intermediate in disorder.

In a perfect crystal with periodic potentials, electron wave functions form delocalized Bloch waves.[39] Impurities and lattice defects in disordered systems introduce backward scattering of these electron waves with resulting[40] "Anderson localization." The electronic structure of the system strongly depends on the degree of disorder. The energy fluctuation in the random potentials broadens the bandwidth and creates smooth "band tails." Due to these band tails, the original band gap between the conduction and the valence bands of a semiconductor may be closed. 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.[41] When the Fermi level 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 σ of Mott's model is described as $\sigma = \sigma_0 \exp[-(T_0/T)^{1/(d+1)}]$, where d is the dimensionality and, for three-dimensional systems, $T_0 = c l k_B N(E_F) L^3$ (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 through the isotropic three-dimensional sample.

Other external parameters such as magnetic field or pressure can affect the localization/delocalization transition and the localization lengths. This model has received much experimental attention for doped and ion implanted polymers.[2,4,42]

For an isolated one-dimensional metallic chain localization of charge carriers arises for even weak disorder because of quantum interference due to static back-scattering of electrons.[41] This contrasts 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[43,44] represents the doped polymer as relatively ordered regions (or "crystalline islands") interconnected through polymer chains traversing disordered regions, Figure 5. 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 readily 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 increases in the localization length increases the conductivity with increasing temperature. This model accounts for localized behavior at low temperature despite conductivities at room temperature in excess of the Mott minimum conductivity. Three-dimensional crystalline order facilitates delocalization. It has been shown that 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] within which electrons are treated as free particles in a gas with a single scattering time τ. Despite its simplified assumptions, the Drude model explains high and frequency independent conductivity of traditional metals from dc to the microwave ($\sim 10^{10}$ Hz) frequency range, and a real part of the dielectric constant (ε_r) which is negative below the screened plasma frequency ($\omega_p^2 = 4\pi n e^2/m^*\varepsilon_b$; n is the density of carriers, m* is the carrier effective mass, and ε_b is the background dielectric constant). Within the low frequency Drude limit ($\omega\tau \ll 1$), the Drude response can be deduced as $\varepsilon_r = - \omega_p^2\tau^2$ and $\varepsilon_i = \omega_p^2\tau/\omega$, where ε_i is the imaginary part of the dielectric constant.

Electrical Conductivity of Conducting Polymers

The temperature dependent conductivity [$\sigma(T)$] of heavily iodine doped $(CH)_x$ and hexafluorphosphate (PF_6) doped PPy down to mK range vary as a function of aging (disorder).[45] The highest σ_{dc} at room temperature reported in this study is $\sim 5 \times 10^4$ S/cm for I_3 doped T-$(CH)_x$ and $\sim 10^3$ 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, σ increases by $\sim 20\%$ 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 termperatures.

Hydrochloric acid as well as camphor sulfonic acid doped polyaniline prepared in chloroform often have[43] log σ proportional to $T^{-1/2}$ as expected for quasi-one-dimensional variable range hopping (VRH), $\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}]$, where $T_0=16/[k_B N(E_F)Lz]$. 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 ($T_0\sim 700$–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.

Microwave Frequency Dielectric Constant

The microwave frequency dielectric constant provides a measure of the charge delocalization in individual samples. The low temperature dielectric constant, ε_{mw}, for a series of emeraldine hydrochloride samples is proportional to the square of the crystalline coherence length, ξ^2, independent of the direction of orientation of the sample with regard to the microwave frequency electric field.[43] This demonstrates that the charge is delocalized three-dimensionally within the crystalline regions of these samples. Using a simple metallic box model, $\varepsilon = \varepsilon_\infty + (2^{9/2}/\pi^3)e^2N(E_F)L^2$, and taking for the low temperature localization length the x ray crystalline correlation length determined by x ray diffraction, $N(E_F)$ 1.23 state/(eV 2-rings) (0.088 state/eV-(C+N)) for PAN-HCl. This compares very favorably with the value obtained from magnetic susceptibility experiments.

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. [2,4,43,44] For example, PAN-CSA (*m*-cresol) has a metallic negative dielectric constant (-4 x 10^4) and features a maximum in microwave frequency conductivity at ~180 K. A similar large and negative value of ε_{mw} and temperature dependence of ε_{mw} were determined for heavily iodine doped stretched Tsukamoto polyacetylene (-1.5 x 10^6) and PF_6 doped polypyrrole (-1 x 10^5). Using the Drude model for low frequencies ($\omega\tau <$ 1), a plasma frequency of ω_p=0.015 eV (120 cm^{-1}) and a room temperature scattering time of ~ 1.2 x 10^{-11} sec were calculated for the PAN-CSA (*m*-cresol) system, though the exact values correlate with the sample preparation conditions. Similar values are obtained for heavily iodine doped stretched Tsukamoto polyacetylene and PF_6 doped polypyrrole. These values of ω_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 τ is two orders of magnitude larger than usual for an alkali, noble, or transition metal. The origin of the anomalously large scattering time was suggested[43] to be the ineffectiveness of forward scattering of conduction electrons in the metallic state and the need for backward scattering (i.e., the Fermi surfaces of metallic polyaniline, polyacetylene, and polypyrrole are "open" as expected for highly anisotropic materials, and backward scattering from k_F to $-k_F$ may be necessary for momentum relaxation).

Optical Dielectric Function

For the conducting forms of doped polyacetylene and other conducting polymers, there are zero, two, three, or one zero crossings of the real part of the dielectric function (ε_1) as the frequency is decreased.[2,4,44] For the least conducting materials, ε_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, ε_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 $\sigma_{dc} \sim 400$ S/cm, ε_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. Figure 6 illustrates this range of behaviors for three differently doped samples of polyaniline. For very highly conducting doped polyacetylene, ε_1 crosses zero at the all conduction electron plasma frequency and remains negative to the lowest measured optical frequencies.[46]

Electromagnetic Interference Shielding, Electromagnetic Radiation Absorption, and Joining of Plastics

With the rapid advances and broad implementation of computer and telecommunication technologies there is an increased interest in shielding of electromagnetic interference (EMI) (especially in the radio and microwave frequency ranges). The usual shielding techniques focus on the use of standard metals and their composites, which have disadvantages due to limited physical flexibility, heavy weight, corrosion, difficulty of tuning the shielding efficiency, and recycleability.

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 σ and ε through chemical processing.[47] Also, they are relatively lightweight compared to standard metals, flexible, and do not corrode as common metals. Among intrinsically conducting polymers, the microwave frequency conductivity (σ_{mw}) are dielectric constant (ε_{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, with the relative contribution of reflection and absorption of radiation being dependent on the polymer preparation methods and resulting structural order. Figure 7 illustrates how the total shielding efficiency (SE_T) of representative conductive polymers is calculated to vary with thickness. The shielding capabilities are in the range of utility for many commercial ($\sim$ 40 dB) and military ($\sim$ 80 - 100 dB) applications. Blends of conducting and non-conducting polymers may also be applicable for shielding needs. Examples of areas of potential application range from reduced emissions from cellular telephones to "drop cloths" for reduced radar cross-section.

The development of intrinsically conductive polymers, especially polyanilines, provides an opportunity for use of conductive polymers in welding (joining) of

thermoplastics and thermosets. Either a pure intrinsically conducting polymer film or a gasket prepared from a compression molded blend of the intrinsically conductive polymer and a powder of the thermoplastic or thermoset to be blended 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).[48] The resulting joint may be as strong as that of the pure compression molded thermoplastic or thermoset, as illustrated on the cover of this issue for a joint of two high density polyethylene (HDPE) bars using a gasket of HDPE and PAN doped with HCl. In this figure it is apparent that the HDPE bar under tension yields at a location other than the intrinsically conducting polymer formed joint. Dependent upon the chemical composition of the conducting polymer and the dopants used, the resulting joint may be permanent (i.e., the conducting polymer is rendered non-conducting during the joining process) or reversible (i.e., the conducting polymer remaining is sufficiently conducting to allow subsequent absorption of electromagnetic radiation to heat the joint hot enough for separation of the parts).

Polyaniline-based anticorrosion coatings

The corrosion of steel has long been an important problem, causing losses in excess of 100 billion dollars annually world wide. Various methods have been devised to combat corrosion, including chrome treatment of steel surfaces, pickling inhibitors, sacrificial zinc layers, etc. In practice, almost all methods of corrosion protection work in one of the following ways: (I) cathodic protection, i.e., charge (e⁻) is donated to the steel from a sacrificial material, (ii) anodic protection, i.e., charge is withdrawn from the steel, or (iii) the steel surface is sealed off from corrosive attacks by a surface layer of another material commonly a metal oxide.

Efforts are presently underway to develop methods of corrosion protection of steel that are more effective and also more environmentally friendly than the present techniques. Among the more frequently studied polymers used for corrosion protection of steel is

polyaniline and its derivatives. Although the initial work of DeBerry studied electrochemically deposited polyaniline, later studies concentrated on solution deposited doped polyaniline.[49] Polyaniline has been shown to have corrosion protecting capabilities both when doped[48] and neutral.[50] For example, the emeraldine base form of polyaniline has been used in studies of corrosion protecting undercoats on steel and iron samples. Using X-ray photoelectron spectroscopy, the anti-corrosion performance of various application methods of the emeraldine base layer was studied, as well as the mechanism for corrosion protection. Emeraldine base polyaniline undercoats were found to offer corrosion protection for both the cold rolled steel and iron samples. The degree of protection did vary depending on the thickness of the iron oxide layer at the polymer/metal interface as well as on the thickness of the top oxide layer. The best results were achieved when both the top and interfacial oxide layers were removed prior to the polymer deposition. 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.

Transparent Electrodes for Light Emitting Polymers

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,[51] or incorporating networks of conducting polymer fibers in the light emitting polymers.[52] 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.[53]

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.

Acknowledgment

Figure Captions

1. Repeat units of several electronic polymers.

2. Illustratior 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).

4. Overview of conductivity of conducting polymers at room temperature. (a) stretched $[CH(l_3)]_x$ (from Ref. 38a), (b) stretched $[CH(l_3)]_x$ (from Ref. 38b), (c) $[CH(l_3)]_x$ (from Ref. 38c), (d) $[CH(l_3)]_x$ (from Ref. 38d), (d') $[CH(l_3)]_x$ (from Ref. 38e), (e) stretched PAN-HCl (from 38f), (f) PAN-CSA from *m*-cresol (from Ref. 38g), (g) PAN-CSA from *m*-cresol (from Ref. 38h), (h) PAN derivative: poly(o-toluidine) POT-CSA fiber from *m*-cresol (from Ref. 38i), (i) POT-HCl (from Ref. 38j), (j) sulfonated PAN (from Ref. 38k), (k) stretched $PPy(PF_6)$ from (Ref. 38l), (l) $PPy(PF_6)$ (l') PPy(TsO) (from Ref. 38m, 38n), (m) iodine doped poly(dodecylthiophene) (from Ref. 38o), (n) $FeCl_4$ doped PT (from Ref. 38p), (o) $PPV(H_2SO_4)$ (from Ref. 38q), (p) $PPP(AsF_5)$ (from Ref. 38r), (q) $^{84}Kr^-$ implanted (polyphenylenebenzobisoxazole) (from Ref. 38s), (r) undoped *trans*-$(CH_x$ (from Ref. 38t), (s) undoped *cis*-$(CH)_x$ from (Ref. 38u), (t) undoped PAN (EB) (from Ref. 38v) (u) undoped PPy (from Ref. 38w), (v) undoped PT (from Ref. 38p (w) undoped PPV (from Ref. 38x), (x) undoped PPP (from Ref. 38y). The conductivity reported for the undoped polymers should be considered an upper limit due to the possibility of impurities.

5. 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 (of length 's').

6. Real part of room temperature dielectric repsonse versus frequency for (A) PAN-CSA (m-cresol), (B) PAN-CSA (chloroform/m-cresol), and (C) Pan-HCL ('intermediate cross linked'). From Ref. 2.

7.   Thickness dependence of total shielding efficiency (SET) of highly conducting polymers: (A) stretched heavily iodine doped Tsukamoto polyacetylene, (B) camphor sulfonic acid doped polyanline cast from m-cresol solvent, (C) PF_6 doped polypyrrole.

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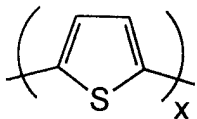[52] Y. Yang, E. Westerweele, C. Zhang, P. smith, and A.J. Heeger, *J. Appl. Phys.* **77** (1995) p. 694.

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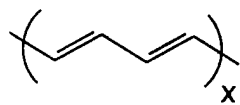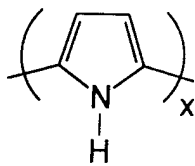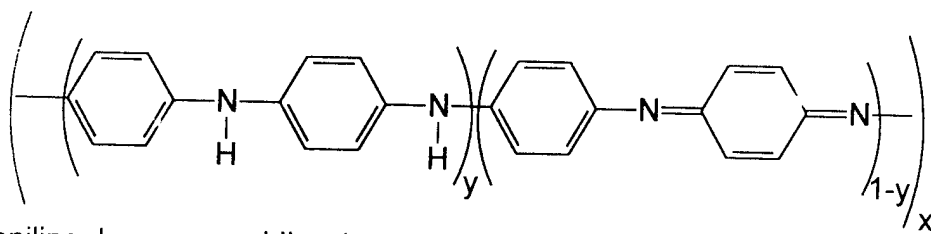
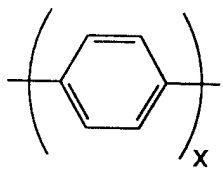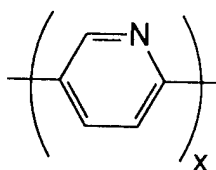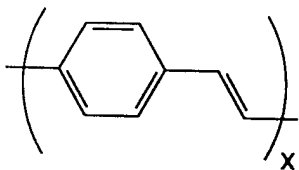trans-polyacetylene
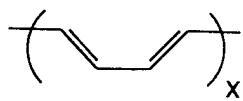
cis-polyacetylene

polythiophene

polypyrrole

polyaniline: leucoemeraldine (y=0), emeraldine (y=0.5), and pernigraniline (y=1)

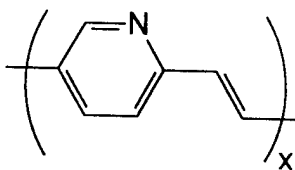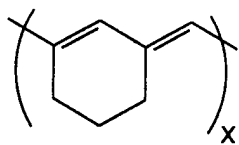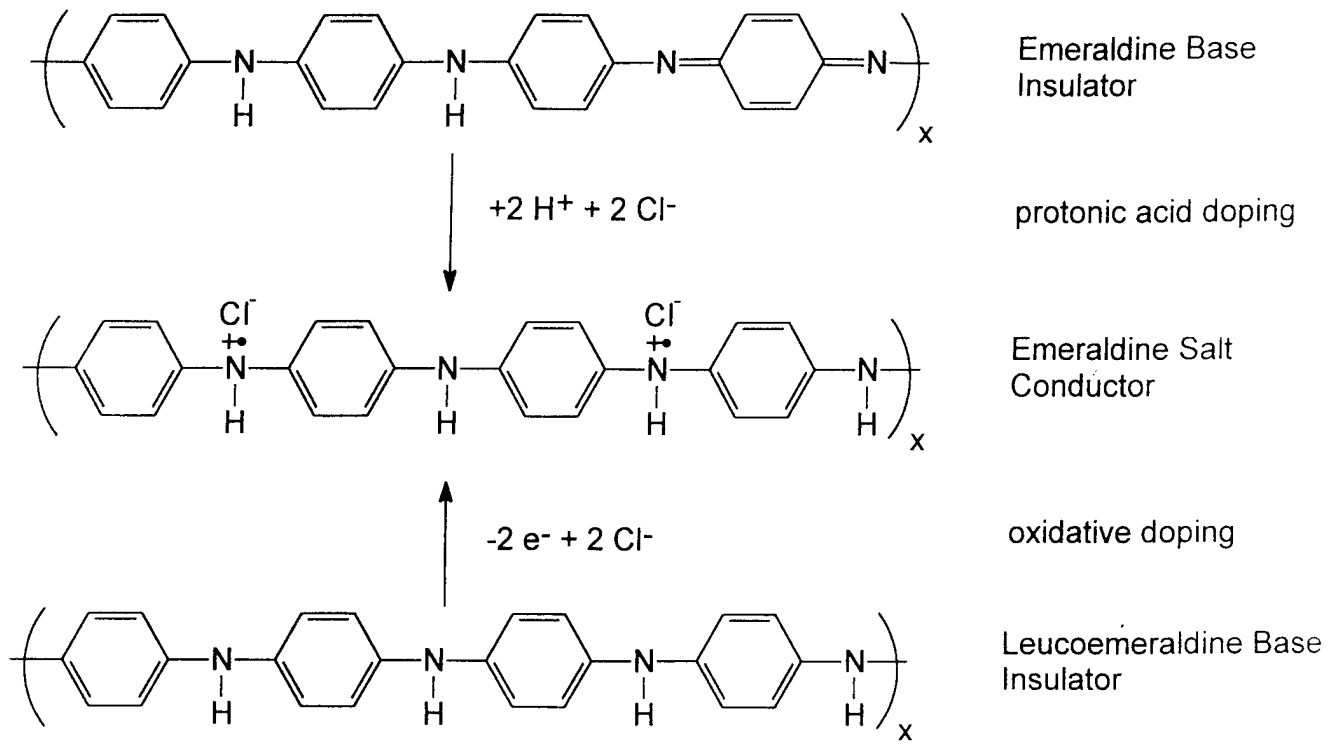poly(*para*-phenylene)
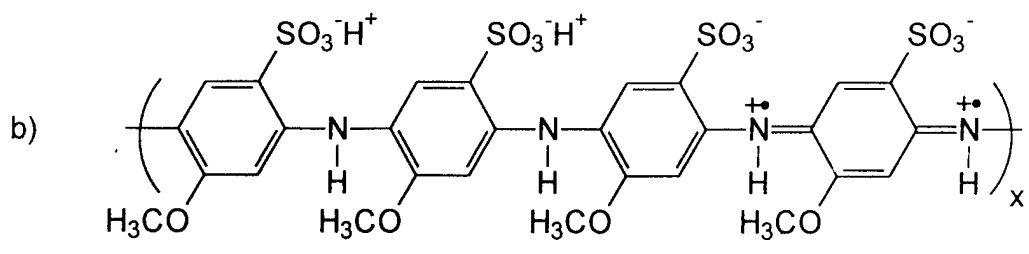
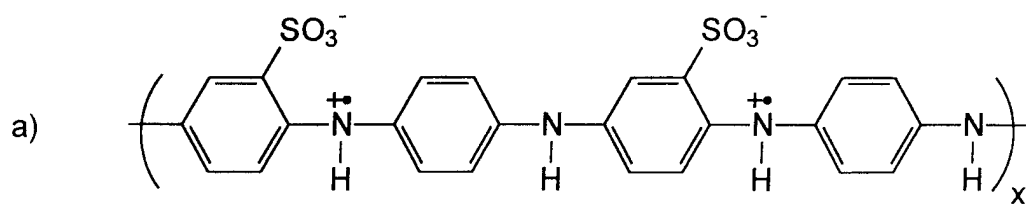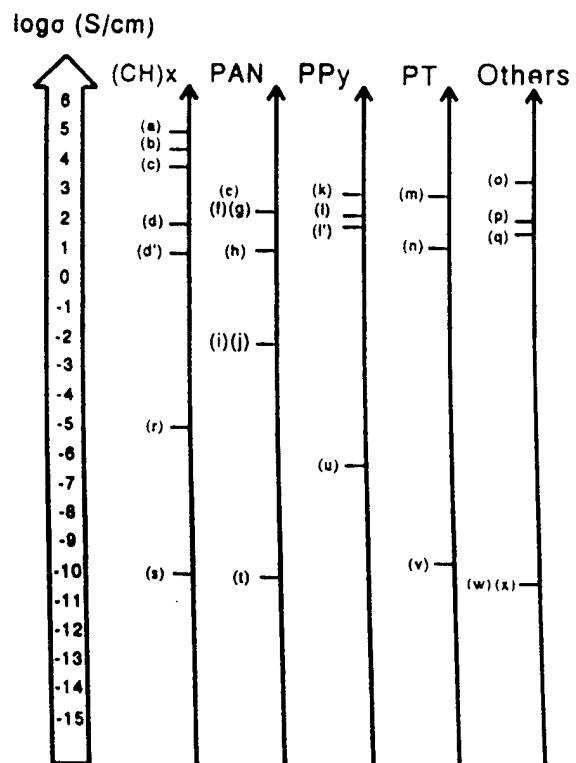poly(*para*-pyridine)
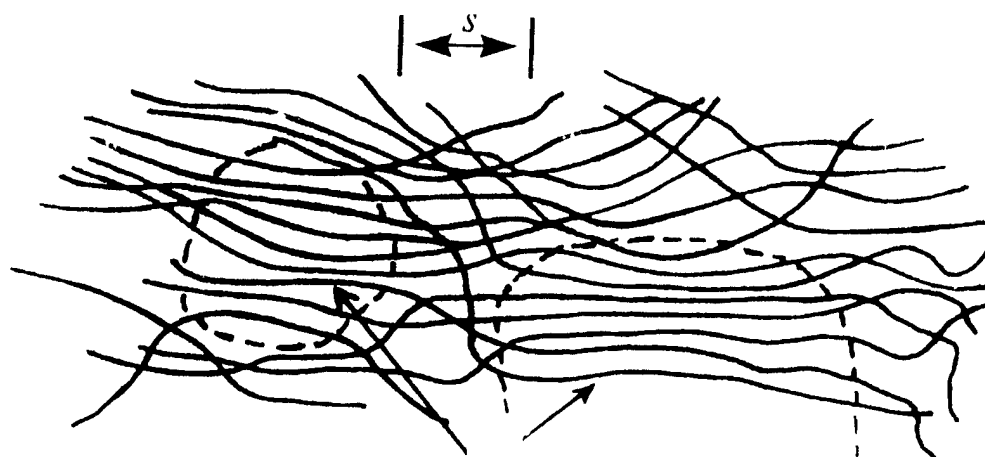
poly(*para*-phenylene vinylene)

poly(*para*-pyridiyl vinylene)
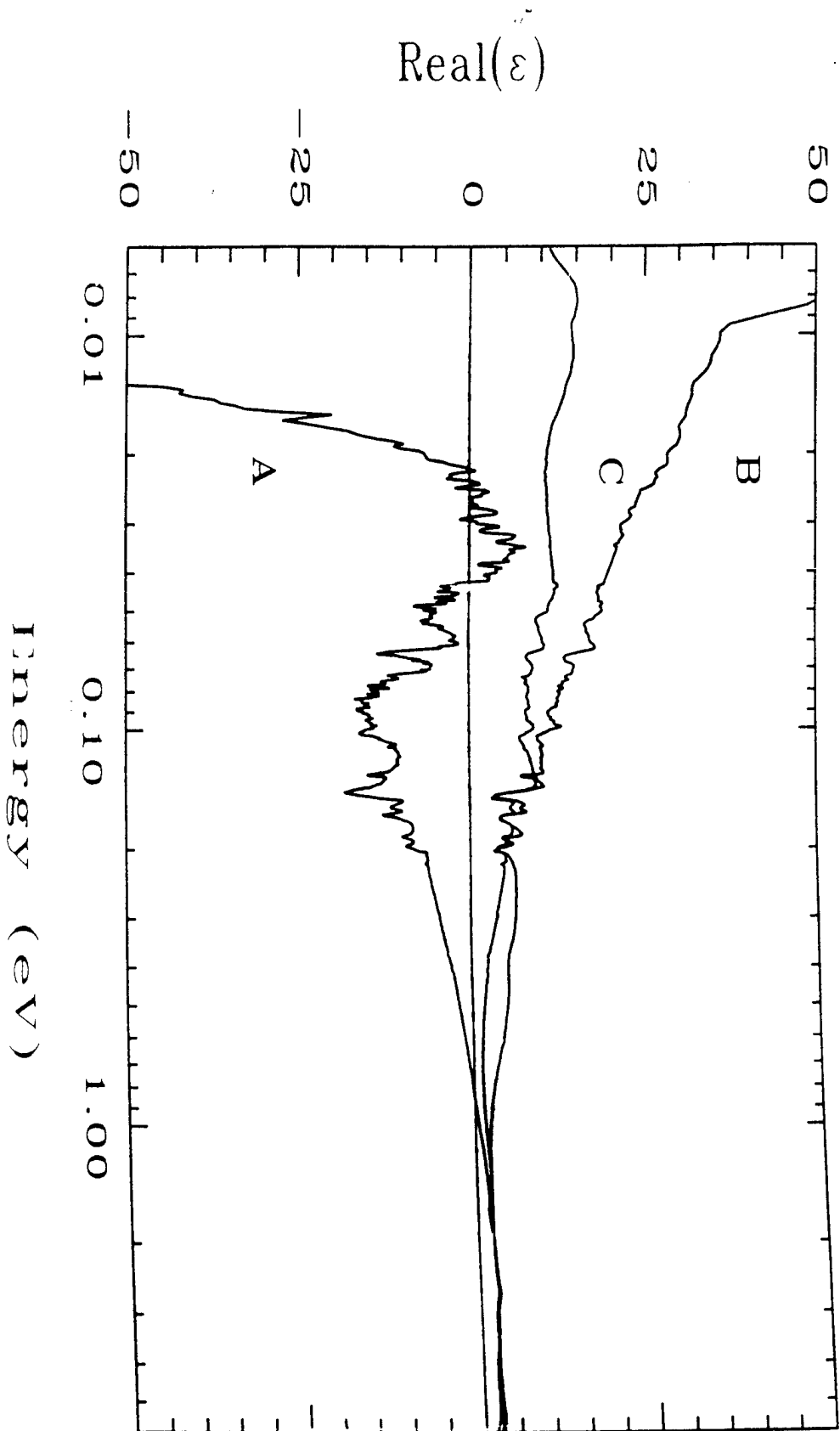
poly(1,6-heptadiyne)

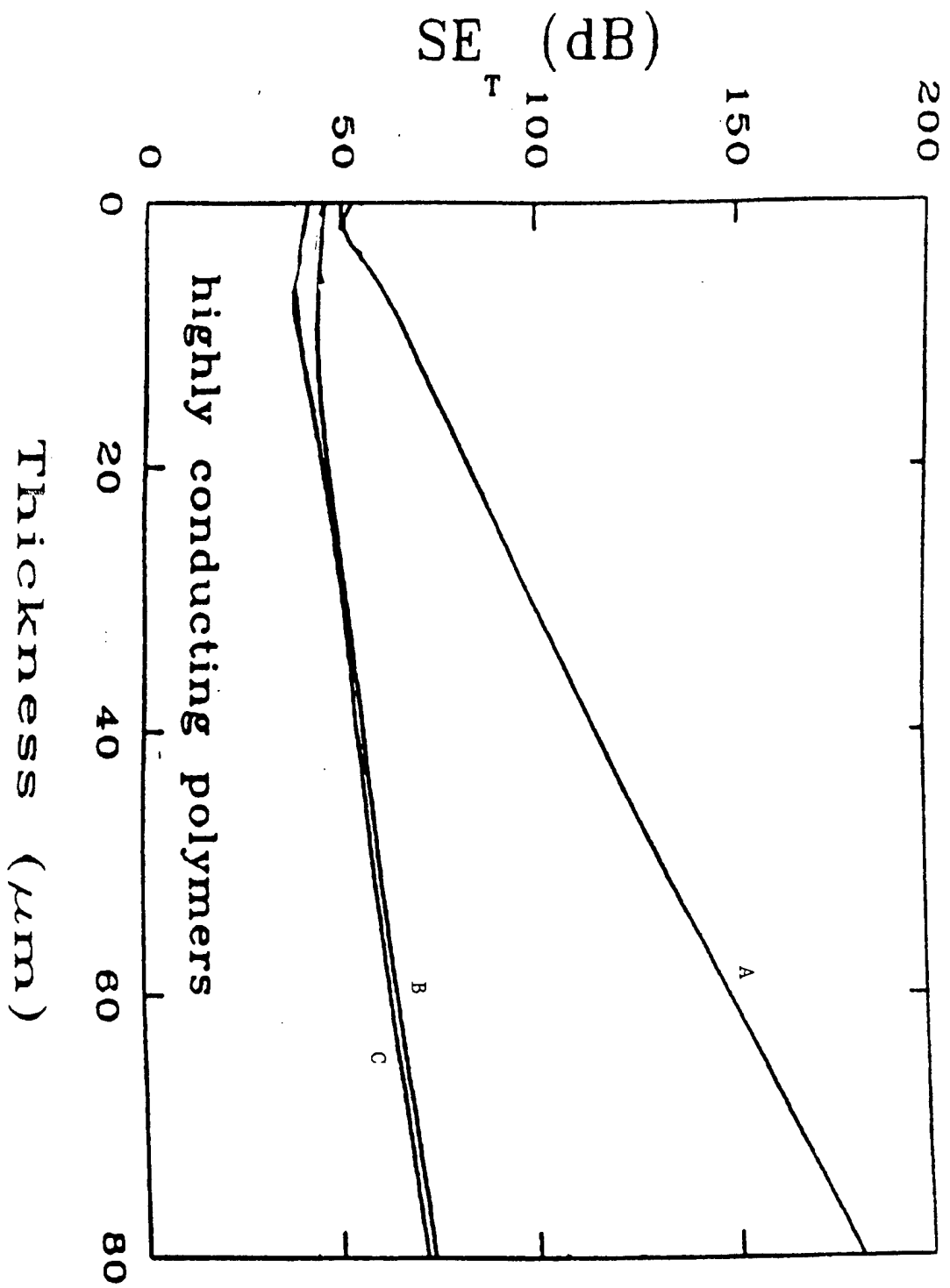Emeraldine Base
Insulator

+2 H+ + 2 Cl-   protonic acid doping

Emeraldine Salt
Conductor

-2 e- + 2 Cl-   oxidative doping

Leucoemeraldine Base
Insulator

Epstein, Fig. 2

a)

SO_3^- ‎ ‎ ‎ ‎ SO_3^-

b)

$SO_3^-H^+$ ‎ $SO_3^-H^+$ ‎ SO_3^- ‎ SO_3^-

H_3CO ‎ H_3CO ‎ H_3CO ‎ H_3CO

Epstein, Fig. 3

logσ (S/cm)

(CH)x	PAN	PPy	PT	Others

6
5 (a)
4 (b)
  (c)
3   (c)   (k)   (m)   (o)
2 (d)   (f)(g)   (l)   (p)
1 (d')   (h)   (l')   (n)   (q)
0
-1
-2   (i)(j)
-3
-4
-5 (r)
-6   (u)
-7
-8
-9
-10 (s)   (t)   (v)   (w)(x)
-11
-12
-13
-14
-15

Epstein, Fig. 4

Ordered Regions

SE$_T$ (dB)

Thickness (μm)

highly conducting polymers

Epstein, Fig. 7