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Conducting Polymers: A Review of Recent Work

The conductivities of all the currently reported conducting polymers are compared to those of the classical metals. The requirements for a technologically useful conducting polymer are considered and the degree to which existing conducting polymers meet these requirements is evaluated. The mechanism of doping is discussed together with the final state of the dopant and the polymer. The available structural data are described as well as the problems of structurally characterizing these systems. Some of the problems of inhomogeneous distribution of dopant species are also pointed out.

Historical survey

The discovery in 1973 by Walatka, Labes, and Perlstein [1] that polymeric $(SN)_x$ crystals were metallic, rather than semiconducting as previously believed, instigated a renewed wave of interest in conducting polymers. In 1975 [2], when $(SN)_x$ was shown to go superconducting below 0.3 K, chemists tried various synthetic routes to analogous compounds [3, 4]. Unfortunately, their efforts were not rewarded by success and $(SN)_x$ remained the only intrinsically metallic synthetic polymer. However, in 1977 it was shown that a variety of halogens, most notably bromine, could be incorporated into the $(SN)_x$ lattice, causing its room temperature conductivity to increase by an order of magnitude without destroying the superconducting transition [5-9]. Later in 1977, it was demonstrated that polyacetylene $(CH)_x$ films could be made to exhibit metallic and semiconducting properties by means of chemical modification (in this case leading to partial oxidation or reduction by reaction with electron acceptors and donors [10, 11]). Despite early optimism, derivatives of $(CH)_x$ prepared to date, *e.g.*, poly(phenylacetylene) [12] or poly(1,6-heptadiyne) [13], do not exhibit the high levels of conductivity of doped $(CH)_x$. Two new classes of conducting polymers were reported in 1979: the electrochemically prepared heterocyclic polypyrrole-BF_4 [14, 15] and the polyaromatic poly(p-phenylene) [16] chemically modified by reaction with AsF_5 or alkali metals. Most recently, this latter class of compounds has been extended to include materials derived from the partial oxidation of poly(p-phenylene vinylene) [17] and poly(p-phenylene sulfide) with AsF_5 [18, 19]. The conductivity in this latter system is rather unexpected in view of its grossly nonplanar chain structure. It has been reported that the conductivity of polythiophene [20] is enhanced by exposure to iodine but the reported conductivities ($\approx 10^{-4}\ \Omega^{-1}\ cm^{-1}$) are 10^5-10^9 lower than those of the polymers discussed above. The conductivities of the remainder of these materials compared to the classical metals are shown in Fig. 1. The structural formulae of most of the polymers mentioned are shown in Fig. 2. The polymer with the highest conductivity $(SNBr_{0.4})_x$ is two orders of magnitude less conducting than copper, while poly(p-phenylene sulfide) is six orders of magnitude less than copper. The relatively low conductivities of these polymers undoubtedly reflect the low mobilities characteristic of organic materials and particularly polymers lacking long-range order. However, the very high conductivity observed in the AsF_5 intercalate of graphite suggests that the potential conductivities in highly ordered organic systems may indeed approach that of copper [21, 22].

Application of conducting polymers

As indicated in the previous section, polymers can be made to exhibit semiconducting, metallic, or even superconducting properties not traditionally associated with these materials. This has encouraged the belief that polymers may eventually challenge the more classical materials in certain applications. For instance, conducting poly-

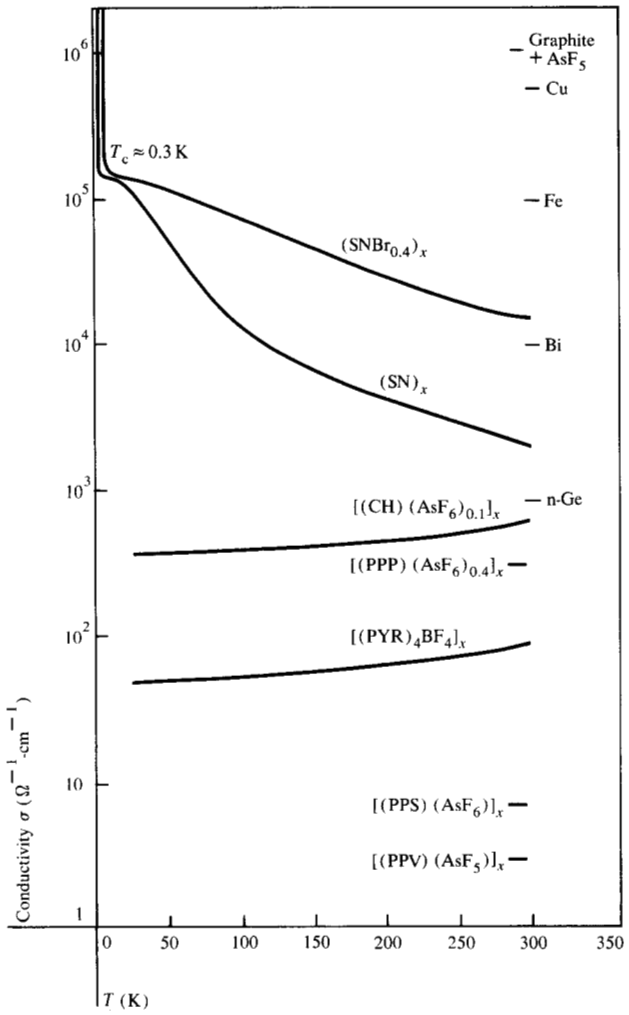

Figure 1 Conductivity *versus* temperature for various conducting polymers and classical conductors: PPP = poly(p-phenylene), PYR = pyrrole, PPS = poly(p-phenylene sulfide), PPV = poly(p-phenylene vinylene).

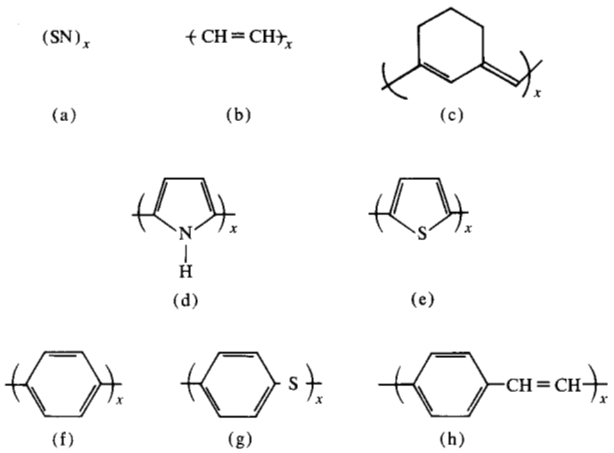

Figure 2 Structural formulae of various conducting polymers. (a) polythiazyl, (b) polyacetylene, (c) poly(1,6-heptadiyne), (d) polypyrrole, (e) polythiophene, (f) poly(p-phenylene) (g) poly(p-phenylene sulfide), and (h) poly(p-phenylene vinylene).

mers could function as antistatic coatings; $(SN)_x$ [23] and $(CH)_x$ [24, 25] can form Schottky barriers and act as solar cells; and undoped $(CH)_x$ has been used as the photoelectrode in a photochemical (photogalvanic) cell [26]. It has also been suggested that wires formed from AsF_5-doped graphite might replace copper in certain applications [21]. Exciting as these prospects may be, it is important to temper this excitement in view of the serious problems that must be solved before these materials can find widespread application in these technologies.

From the discussion of the magnitude of the conductivities of presently known conducting polymers (except perhaps AsF_5-treated graphite) it is obvious that they will not displace copper or the classical metals. In most applications, if they are to become practical materials rather than laboratory curiosities, their usefulness will most probably be found in a rather unique blend of electronic, mechanical, and processing characteristics. Indeed, conducting polymers are probably best considered not as competitors for the classical metals or semiconductors, but as opportunities for new applications allowed by the incorporation into conducting materials of such attractive polymer properties as melt and solution processibilities, low density, and plasticity or elasticity. Ideally, these polymers would also satisfy a variety of increasingly important ecological considerations such as low toxicity and non-energy-intensive synthesis and processing. Preparation from non-polluting aqueous media would, of course, be desirable. Advantage could also conceivably follow from the thermal conductivities and high absorption coefficients of these polymeric metals, which presumably scale with their electrical conductivities.

Though some of these properties, such as low density and high absorption coefficient, characterize all of the existing conducting polymers, some of the other desirable properties described here are not typical of either $(SN)_x$ or the chemically (as opposed to electrochemically) modified systems. In particular, neither $(SN)_x$ nor the chemically modified conducting polymers are stable in air (particularly the alkali-metal-reduced polymers) nor are they thermally stable much above room temperature. The majority of dopants used to impart conductivity to the polymers (*e.g.*, AsF_5, I_2, Br_2, etc.) are highly toxic. In addition, the chemical doping process universally appears to spoil the mechanical properties of these polymers, making them brittle where previously they were flexible. In

contrast to the chemically oxidized systems, electrochemically oxidized polypyrrole-BF_4, after initial air oxidation, is stable indefinitely in air and shows appreciable thermal stability, though its flexibility is not yet ideal [14, 15].

In addition to challenging the more classical materials in established technologies, these conducting polymers inherently offer additional opportunities. For example, it has been shown that polypyrrole [27] and $(CH)_x$ [28] can be repeatedly and rapidly electrochemically switched between the metallic and insulating states—a change which can be followed optically as well as electrically. Obviously, if full advantage is to be taken of these materials a significant amount of polymer engineering is necessary to improve their polymeric properties in the metallic or semiconducting state.

Mechanism of conductivity enhancement in polymers

Despite the inherent difficulties involved in the characterization of conducting polymers, the fact that charge transfer takes place between the polymer and dopant is generally accepted [11, 29]. This charge transfer gives rise to a delocalized polymeric ion and a counter ion derived from the dopant. Only in the cases of polyacetylene [11], poly(p-phenylene) [16], and poly(p-phenylene sulfide) [19] has it been possible to reduce the polymer. In all other cases the polymer is oxidized to produce a polymeric cation and the dopant is reduced to an anion.

Polypyrrole [14, 15] is quite similar in that there is a delocalized polypyrrole cation and a tetrafluoroborate anion. In this case, however, there is simultaneous electrochemical oxidation and polymerization of the pyrrole and the corresponding neutral polypyrrole may not be a precursor.

The structure of these conducting polymers is discussed later. For the case of the chemically modified polymers, the nature of the polymer-dopant reaction as determined by examination of the final states of the polymer and dopant is also described.

Structure of chemically conducting polymers

All the currently reported conducting polymers are totally insoluble, making characterization by conventional techniques very difficult. In addition, these conducting polymers are usually poorly crystalline. Only in the case of $(SN)_x$ has a complete x-ray structure been obtained [30]. As a result, most of the structural data have come from indirect techniques such as optical spectroscopy.

In the case of brominated $(SN)_x$ and of $(CH)_x$ doped with a variety of oxidants, it has been possible to show

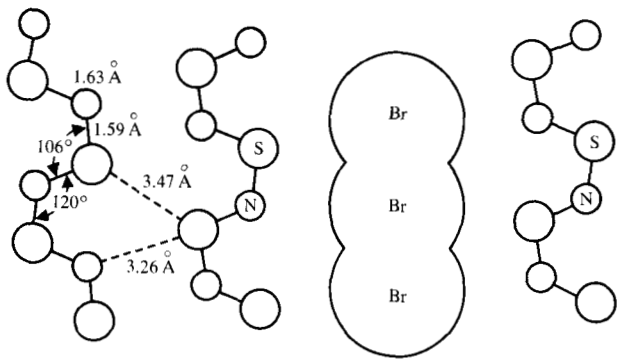

Figure 3 Structure of brominated $(SN)_x$ showing the orientation of Br_3^- ions relative to the $(SN)_x$ chains.

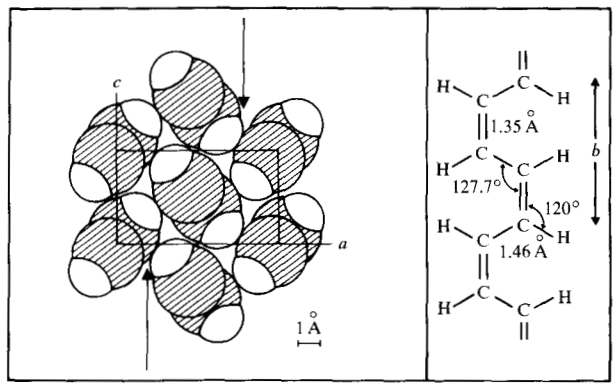

Figure 4 Crystal structure of *cis* $(CH)_x$. The arrows indicate how intercalation takes place between planes of $(CH)_x$ chains; crystal class: orthorhombic; space group: *Pnma*, where $a = 7.61$ Å, $b = 4.47$ Å, and $c = 4.39$ Å.

that the reduced form of the dopant intercalates between the polymeric cation chains of the oxidized polymer [9]. In brominated $(SN)_x$, infrared [31], Raman [32, 33], EXAFS (extended x-ray absorption fine structure) [34], x-ray [7, 33], and electron diffraction [7, 35] techniques show that Br_3^- and Br_2 are aligned along the chain axis (as shown in Fig. 3 for Br_3^-), giving rise to one-dimensional superlattices. For $(CH)_x$, the dopant anion enters the lattice so as to cause an expansion of the (100) plane spacing as shown in Fig. 4 [36, 37]. Table 1 gives the measured $d_{(100)}$ and $d_{(200)}$ interplanar spacings as well as the Van der Waals diameters D of the various intercalates as determined by

$$D(\text{Å}) = 2d_{(200)} - 3.80,$$

where 3.80 Å is the diameter of a $(CH)_x$ chain. (The unit

Table 1 Interplanar spacing of $(CH)_x$ films after intercalation, showing the Van der Waals diameter of the intercalated species as determined from the expansion of the lattice.

	$d_{(100)}$ (Å)	$d_{(200)}$ (Å)	D (Å)*
$(CH)_x$	—	3.80	
$(CHBr_{0.47})_x$	7.31	3.63	3.46
$(CHI_{0.2})_x$	7.96	3.93	4.06
$[CH(AsF_5)_{0.16}]_x$	8.83	4.39	4.98

*Van der Waals diameter of intercalant, D (Å) = $2d_{200}$ − 3.80.

Å used throughout this paper is equivalent to the SI metric value 0.1 nm.) There is no evidence of any ordering of the dopant anion along the $(CH)_x$ chain. The structures of all the other conducting polymers available to date are unknown. The crystal structure of poly(p-phenylene sulfide) [38] is known before doping but after doping this material also becomes very poorly crystalline. Some structural data are also available for poly(p-phenylene) itself before doping [39]. Polypyrrole-BF_4 is very poorly crystalline but electron-diffraction studies reveal several diffuse rings corresponding to the separation of flat chains of pyrrole rings, with the separation determined by the closest approach of their π systems [14, 15]. Kanazawa *et al.* [14] have shown that polypyrrole-BF_4 consists of pyrrole rings joined in the α positions with approximately four pyrrole rings for every BF_4 ion. At this time, the distribution of the tetrafluoroborate anions relative to the polypyrrole cation chains is unknown.

Nature of the dopant after reaction with the polymer

When charge transfer takes place between the polymers and the dopant, the dopant ends up as an anion in the case of acceptor dopants such as AsF_5 or the halogens, and as a cation in the case of donor dopants, which so far have only included the alkali metals [11, 16, 19].

For brominated $(SN)_x$, considerable agreement has been reached in the literature regarding the nature of the anions formed. A variety of techniques including infrared [31], Raman [32, 33], EXAFS [34], and electron diffraction [35] yield data that appear to be consistent with bromine existing in at least two forms, Br_2 and Br_3^-, though the presence of a third form, Br_5^-, cannot be excluded. Resonance Raman scattering of iodine-treated $(SN)_x$ has been interpreted as indicating the presence of I_5^- and I_3^- linked to distorted I_2 units [40]. In the case of ICl-doped $(SN)_x$, which has a conductivity approximately twice that of pristine $(SN)_x$, very little charge transfer appears to take place, in agreement with Raman [33] and electron diffraction results [35] showing that the ICl remains essentially unchanged. For $(CH)_x$, the situation seems fairly straightforward: Raman studies have shown that bromine forms Br_3^- [41-43] and that iodine forms I_3^- and probably I_5^- [42-44]. However, in the case of AsF_5 doping, two schools of thought have developed. MacDiarmid and his colleagues maintain [11, 45] on the basis of chemical analysis and ESCA data that the 5:1 fluorine to arsenic stoichiometry is maintained on doping, possibly by the formation of the $As_2F_{10}^{-2}$ species. Clarke *et al.* [37, 46] have presented infrared, Raman, and x-ray absorption-edge data in support of the following mechanism, identical to that proposed by Bartlett and his colleagues [47] for the reaction of AsF_5 with graphite:

$$2e + 3AsF_5 \rightarrow 2AsF_6^- + AsF_3.$$

Support for the presence of AsF_6^- in $(CH)_x$ doped with AsF_5 has also come from recent mass spectroscopic data [48, 49] and band structure calculations [50]. In the case of poly(p-phenylene) and poly(p-phenylene sulfide), we believe that a similar reaction with AsF_5 takes place. Again, AsF_6^- has been identified in infrared studies [18, 19]. Currently, no spectroscopic data have been presented for the poly(p-phenylene vinylene) or poly(1,6-heptadiyne)-AsF_5 systems.

Nature of the chemically oxidized polymers

Presently, there is only sufficient experimental data to describe the final state of two of the chemically modified conducting polymer systems described in this paper: $(SNBr_{0.4})_x$ and doped $(CH)_x$. In the $(SN)_x$ structure, the highest occupied orbital is a half-filled π^* level. In the simplest approximation, this level can be considered to be responsible for the high conductivity of pristine $(SN)_x$. A more general discussion of the electronic structure of conducting π-electron systems has been presented by Grant and Batra [51]. Oxidation of $(SN)_x$ should lead to removal of some of these π^* antibonding electrons, which in turn should lead to an increase in the S-N bond strength [29]. This increased strength is, in fact, manifested by an $\approx$20-cm^{-1} shift to higher frequency in the S-N stretching frequency on bromination [31].

The situation with $(CH)_x$ is somewhat different. Here, the highest occupied levels are bonding, so that oxidation would be expected to lead to a weakening of the C-C bond strength and a corresponding change in the Raman-active C-C bond stretching frequencies. Unfortunately, these expected changes in the Raman spectra of doped $(CH)_x$ are not observed and except for the effects of structural disordering accompanying intercalation of the dopant, the spectral features remain unchanged in position while decreasing in intensity as doping proceeds. Fortunately, the Fourier transform infrared spectrum of doped polyacetylene contains much more information [52, 53]. The most prominent peaks in the infrared spectrum of

AsF_5-doped polyacetylene are at 1385, 1295, and 832 cm^{-1}. These features may be assigned to Raman-active A_g modes made infrared-active by coupling of the electron oscillation along the chain with the skeletal stretching of the polymer backbone. Although all of the vibrational absorptions in $(CH)_x$ clearly arise from mixed modes, the band at 1385 cm^{-1} may be attributed primarily to the Raman-active *cis* and/or *trans* C—C and C=C stretching modes weakened by the electron transfer from the π system to the dopant and shifted considerably from the corresponding frequency in pristine $(CH)_x$ at $\approx$1550 cm^{-1}. It is interesting to note that the spectrum obtained on doping with AsF_5 is the same for both *cis* and *trans* $(CH)_x$. This suggests that after doping, the final configuration of the polymer is the same regardless of the configuration of the precursor. From these experiments, it is not possible to say whether this final configuration is *cis* or *trans*, but recent nmr experiments suggest that the *trans* configuration is the final form of the doped polymer [54].

Distribution of the dopant

Inducing conductivity in solid polymers by reaction with gaseous dopants at or below room temperature cannot be expected to result in a uniform distribution of dopant except at saturation. Indeed it was realized quite early that the bromine distribution in $(SN)_x$ was not uniform at concentrations below saturation. This problem limited the bulk of the studies of this material to the composition $(SNBr_{0.4})_x$ [9]. Other samples obtained either by removing bromine from the saturated compound or by limiting the bromine exposure led to inhomogeneous samples [8].

Similar problems exist in fibrous $(CH)_x$. Completely uniform distribution of dopant requires that diffusion of the dopant into the bulk of the polymer and into individual fibers be faster than the reaction of the dopant at the surfaces of the sample. Contrary to this, we have observed that the extent of dopant uptake depends on the thickness of the sample. For example, in the case of AsF_5 different percentage weight uptakes are observed under identical doping conditions, with thinner samples showing the greater extent of doping. A more dramatic effect of nonuniform doping is obtained by comparing the reflectivity of both sides of a $(CH)_x$ film grown on a glass substrate and briefly exposed to AsF_5 vapor. Figure 5, Curve A shows the reflectivity of such a film measured at the top surface, where the reflectivity looks metallic [55]. Curve B shows the corresponding data taken at the film-glass interface. The hump below 800 nm corresponds to the reflectivity of largely undoped $(CH)_x$. Above 800 nm this undoped material is transparent, allowing the incident light to penetrate further into the sample to reveal the metallic reflectivity of the underlying heavily doped region.

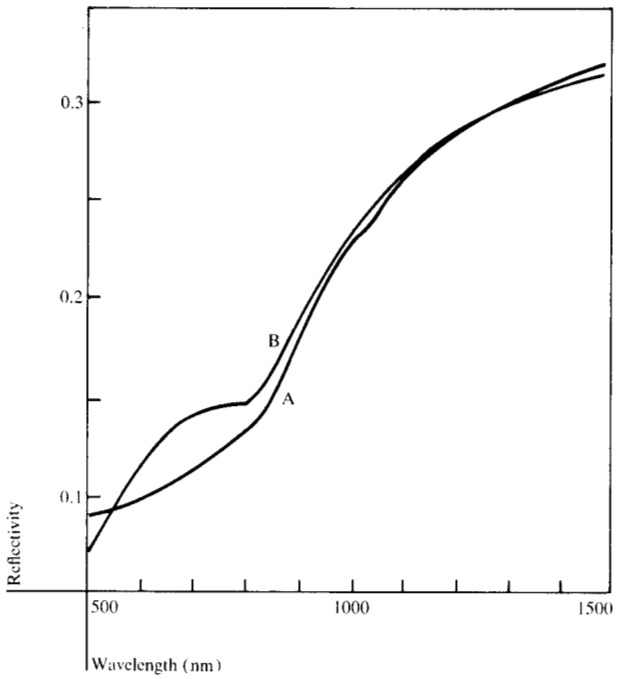

Figure 5 Optical reflectivity *versus* wavelength for an AsF_5-treated $(CH)_x$ film: Curve A, light reflected from upper surface; Curve B, light reflected from film-glass interface.

Prolonged doping to high levels presumably leads to a minimization of the problems of inhomogeneity.

Summary

Though none of the currently reported conducting polymers exhibit all of the properties desired for a technologically useful material, none of the problems seem to be insurmountable. The range of types of polymers that can be made to conduct continues to expand. As the complexity of the repeat unit increases, so does the opportunity for incorporating other appropriate physical properties by means of molecular engineering. The addition of electrochemically oxidized polypyrrole opens up new areas of investigation for conducting polymers, as does the observation of conductivity in grossly nonplanar poly(p-phenylene sulfide)-AsF_5. Much progress has been made in this field in the last five years; hopefully the near future will bring the understanding of the physics and chemistry of these systems necessary for their technological exploitation.

Acknowledgments

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