Structural Basis for Semiconducting and Metallic Polymer/Dopant Systems

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I. Introduction

The performance, cost, and processibility advantages of organic polymers have led to the increasing displacement of conventional metals and inorganic materials in a variety of areas, from structural applications to applications in photoconductor, pyroelectric, and piezoelectric devices. However, until quite recently these application possibilities have been limited to those in which either high electrical conductivity was not desired or in which composite structures with conventional metals could be utilized. This situation is now changed with the discovery that polymers such as polyacetylene and related chain-bridged polymers,[1-5] polyphenylenes,[6-9] and poly(phenylene chalcogenides)[10,11] can be transformed into semiconducting and metallic conductors via the addition of either electron donor or electron acceptor dopants.

Electrical conductivities can be varied by as much as 18 orders of magnitude by varying dopant concentration, so that electronic property control is feasible over the whole range from insulator to semiconductor and then to metal. But, to put things in perspective, it must be remembered that this research area is embryonic. Extending the technology of conducting polymers to provide materials having a total properties profile that is optimal is a challenging task. This process involves the development of a deeper understanding of the physics and chemistry of polymer complexes.

Progress in understanding molecular charge-transfer complexes has critically depended upon the availability of large dimension single crystals. Such crystals made possible the evaluation of inherent anisotropic electronic properties and the sometimes subtle structural changes that determine these properties. The situation is completely different for conducting organic polymers that are formed by the addition of electron donors or acceptors to insulating polymers. The polycrystalline or amorphous nature of parent polymers and the disorder introduced during complex formation provide a barrier for determining critical aspects of their structures and properties. Hence, the conducting polymers are essentially a multicomponent black box, which can be experimentally examined in aggregate by electrical and spectroscopic methods or theoretically examined by use of highly idealized and simplified concepts of the box components.

A variety of organic polymers will be examined in order to better define the variation in molecular, crystallographic, and defect structures that are compatible with high conductivities. These materials fall in three families depending upon the backbone type: polyenes (polyacetylenes) and related chain-bridged polymers,[1-5] polyphenylenes,[6-9] and poly(phenylene chalcogenides).[10,11] Dopant species and polymer dopant interactions are important for the analysis, which is enormously complicated by irreversible chemical modification of polymer backbone that sometimes accompanies formation of conducting polymer complexes.

II. Molecular Structures of Undoped Polymers

Polymer chain structure, both as present in undoped polymer and as modified by the doping process, appears to be the key determinant for the electronic properties of the polymer/dopant systems. Polymer and dopant components can occupy comparable volumes in heavily doped materials. However, there is no evidence for any investigated system that electronic conductivity along dopant molecular arrays provides the major contribution to observed conductivities. More specifically, the signs of Hall coefficients[8,12] and the thermopower coefficients[1,8,11,13,14] and the polarity of junction devices[8,14] are consistent with hole conductivity for acceptor-doped polymers and electron conductivity for donor-doped polymers.

Polymers that form highly conducting complexes need not have a planar backbone or a continuous system of overlapping carbon π orbitals. Structural investigations and theoretical calculations for *cis*- and *trans*-polyacetylene are consistent with a planar backbone structure for these polymers.[15-17] In contrast, nonplanar backbones are indicated for other polymers which form conducting complexes, such as poly(*p*-phenylene),[8,18,19] poly(*p*-phenylene sulfide),[20] and poly(*m*-phenylene). From structural data for phenylene oligomers, an angle of about 23° is predicted between neighboring phenyls in poly(*p*-phenylene). Nevertheless, poly(*p*-phenylene) forms AsF_5 complexes having comparable conductivities to those for polyacetylene (about 500 and 1200 S/cm, respectively, for unoriented polymers).[1,8] A more extreme case is provided by poly(*p*-phenylene sulfide), which forms AsF_5 complexes having conductivities of about 1 S/cm.[10,11] Neighboring phenyl rings are inclined by alternately +45° and −45°

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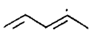
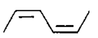
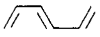
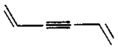
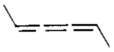
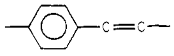
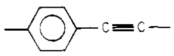
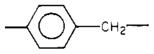
with respect to the planar zig-zag chain of the sulfurs.[20] Despite this backbone arrangement, the optical dichromism indicates that the lowest lying optical transition of poly(*p*-phenylene sulfide) is parallel to the polymer backbone.[21] The interaction of phenyl π orbitals with sulfur p orbitals is believed important for explaining the polarization results and for providing the delocalized electronic system necessary for high conductivities in the doped polymer. The oligomer calculations of Duke and Paton[22] and the polymer calculations of Bredas et al.[23] suggest the importance of this interaction for understanding the conducting complexes of poly(*p*-phenylene sulfide).

The introduction of methylene linkages (as an unbridged link in the polymer backbone) dramatically decreases observed conductivities for the doped poly-

TABLE I. Observed Conductivities (S/cm) for Unoriented, AsF_5-doped Polymers and Copolymers[1,5-11]

A	B	$(A)_x$	$(B)_x$	$(AB)_x$	$(AB_2)_x$
-HC=CH-	$-C_6H_4-$	1200	500	3	
$-C_6H_4-$	$-C_6H_4S-$	500	1	0.3	0.02
$-C_6H_4S-$	$-C_6H_4O-$	1	10^{-3}	10^{-4}	5×10^{-6}

TABLE II. Calculations Using the Ab Initio Quality Valence Effective Hamiltonian Method[23,26]

	ionization potential, eV[a]	width of highest occupied π band, eV	band gap, eV
polyacetylene			
all-trans 	4.7	6.5	1.4
cis, transoid 	4.8	6.4	1.5
trans, cisoid 	4.7	6.5	1.3
polydiacetylene			
acetylenic 	5.1	3.9	2.1
butatriene 	4.3	4.5	
poly(p-phenylene)			
coplanar phenyls	5.5	3.9	3.2
twisted (22° between phenyls)[b]	5.6	3.5	
perpendicular phenyls	6.9	0.2	
poly(m-phenylene)			
coplanar	6.1	0.7	4.5
twisted (28° between phenyls)[b]	6.2	0.2	
poly(p-phenylenevinylene) 	5.1	2.8	2.5
poly(p-phenylenexylylidene) 	5.6	2.5	3.4
polybenzyl 	6.5	0.6	

[a] The ionization potential has been corrected for lattice polarization energy by subtracting 1.9 eV from the calculated single chain value. The correction was chosen to provide good agreement between experimental and theoretical ionization potentials. [b] Rotation angles of 22° and 28° between phenyls in poly(p-phenylene) and poly(m-phenylene), respectively, are suggested by the geometry of model compounds.

mers. For example, the replacement of either every other chain chalcogen or all chalcogens with a methylene in poly(p-phenylene sulfide) or poly(p-phenylene oxide) reduces the electrical conductivity for the AsF_5 doped polymer from 1 and 10^{-3} S/cm, respectively, to less than 10^{-7} S/cm. This change in backbone structure is expected both to increase the ionization potential of the polymer and to interrupt electronic delocalization, so the conductivity results are not surprising. This is supported by theoretical calculations.[23]

Polymers having the most homogeneous chain structures appear to be the best candidates for obtaining complexes having the highest conductivities. As shown in Table I, regular copolymers are observed to dope to lower conductivities than do homopolymers containing any one of the constituent chain elements. Exceptions to the correlation might occur where doping causes chemical transformations or where copolymerization removes steric hindrances to planarity which are present in one of the homopolymers. Also, if one of the chain elements interrupts electronic connectivity in the polymer backbone, the copolymer complex might have a higher conductivity than the homopolymer having these linkages. Finally, this relationship does not appear to be generally valid for a statistical distribution of monomer units along the chain—as suggested by the higher conductivities (and correspondingly lower thermopower values) for the presumably random copolymers or block copolymers between pyrrole and N-methylpyrrole as compared with the same parameters for the methyl-substituted homopolymer.[2] Nevertheless, the correlation suggested by the data in Table I does provide some guidance for synthetic efforts directed at optimizing electrical conductivity for regular backbone structures.

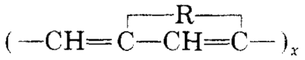
The apparent correlation between electrical conductivity and homogeneity of the backbone is not unreasonable, since chemical heterogeneity can yield carrier localization on the chain unit which provides the lowest potential for holes (or electrons in the case of donor doping). This is confirmed by ab initio quality quantum chemical calculations of Bredas et al.,[23] which demonstrate the link between the homogeneous character of the polymer backbone and the width of the highest occupied π band. The width of the π bands can be roughly related to the degree of delocalization of the π system along the polymer backbone and, to some extent, to the mobility of the carriers in these bands. As shown in Table II, the calculated band width of the highest occupied band for poly(p-phenylenevinylene) is about 2.8 eV, while for the constitutive homogeneous polymers, polyacetylene and poly(p-phenylene), the values are 6.5 and 3.5 eV, respectively. Poly(p-phenylenexylylidene), which consists of alternating para-substituted phenyl rings and acetylene groups, is predicted to have a higher ionization energy (5.6 eV) and slightly narrower band width (2.5 eV) than for poly(p-phenylenevinylene), in which these acetylene groups are replaced with vinylene groups (5.1-eV ionization potential and 2.8-eV band width). The latter compound is observed to form highly conducting derivatives,[9] but comparable results are not obtained for polymers having either p-phenyl groups separated by diacetylene groups or p-biphenyl groups separated by acetylene or diacetylene groups.[25]

The high ionization potential (6.2 eV) and narrow π bandwidth (0.2 eV) calculated for poly(m-phenylene) suggest that this polymer is an unlikely candidate for conducting complexes. Poly(m-phenylene), a fusible and soluble polymer, does form conducting complexes (10^{-3}–10^{-2} S/cm) upon doping with AsF_5. This unexpected result is believed due to dopant-induced chemical reaction (cross-linking), which could lead to a product polymer having a reduced ionization potential and an increased band width.[7,10] Cross-linking is suggested by the infusibility and insolubility of the polymer after doping with AsF_5 and subsequent compensation with dimethylamine. Furthermore, IR spectroscopy of the doped/compensated polymer suggests cross-linking at the ring position meta to the backbone bonds. Even when irreversible polymer reaction does not occur during the doping process, charge transfer can drastically modify the band structure of the polymer chain, as indicated by quantum chemical calculation[24] on lithium-doped polyacetylene. Consequently, caution is necessary in using a rigid band model to predict the behavior of doped polymers.

The calculations of Bredas et al.[26] have also been applied to the polydiacetylene system, $(=RC-C\equiv C-CR=)_x$, where R is a substituent group taken to be H in these computations. These polymers are obtained as large single crystals by the solid-state reaction of diacetylenes having rather bulky substituent groups.[27] The calculations predict an ionization potential of 5.1 eV and a π bandwidth of 3.9 eV, both of which are comparable to polyacetylene. (The calculated ionization potential is very close to recent experimental estimates.[28]) It might be expected, therefore, that similar acceptor doping results would be obtained for polydiacetylene and polyacetylene. This is not the case. Iodine doping experiments on a variety of polydiacetylenes (different R groups) conducted in our laboratories[29] and in other laboratories[30] show only relatively modest conductivities after I_2 doping ($\sigma \sim 10^{-6}$ S/cm). With more aggressive acceptor dopants, such as AsF_5,[29] there seems to be a rather clear tendency toward chemical interaction with the R groups. Similar results are obtained for film-forming (noncrystalline) polydiacetylenes.[29,31] Preliminary experiments with donor dopants have also been unsuccessful.[29]

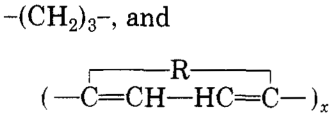
The contrasting behavior of substituted polydiacetylenes and polyacetylene is believed to result from the bulky side groups, which can interfere with the desired donor–acceptor interaction either chemically (as in the AsF_5 case for chemically reactive substituents) or structurally. In the latter case, the bulky substituent groups could prevent the desired geometrical arrangement for optimal charge transfer. In fact, substituted polyacetylenes may exhibit similar problems, as discussed below.

A variety of polymers having the polyene backbone $(-C{=}C-)_x$ have been investigated in the search for new conducting polymer complexes. These polymers can be divided into two categories: nonbridged and chain-bridged polyenes. In the latter category, the term polyene is used somewhat loosely to denote the above backbone and does not imply the absence of important interaction within ring structures involving this backbone. The first category comprises polymers whose backbone consists of units $-R_{1i}C{=}CR_{2i}-$. The simplest examples are polymers of the form $(-R_1C{=}CR_2-)_x$, such as polyacetylene, poly(phenylacetylene), and poly(dimethylacetylene). The second category differs in that two carbon atoms share a substituent which bridges the polyene backbone. The simplest examples are polymers of the form



$$(-\mathrm{CH}{=}\overbrace{\mathrm{C}-\mathrm{CH}{=}\mathrm{C}}^{\mathrm{R}}-)_x$$

where R is $-(CH_2)_3-$, and



$$(-\overbrace{\mathrm{C}{=}\mathrm{CH}-\mathrm{HC}{=}\mathrm{C}}^{\mathrm{R}}-)_x$$

where R is –NH– or S (poly(1,6-heptadiyne), polypyrrole, and polythiophene, respectively).[2-4,32] Highly conducting complexes have been obtained for each of these examples of chain-bridged polyenes. In contrast, the unsubstituted polyene (polyacetylene) is the only nonbridged polyene which is known[33] to form complexes having conductivities much greater than 10^{-2} S/cm. For example, poly(phenylacetylene) forms complexes with iodine.[34] However, the conductivity of these complexes is less than 10^{-4} S/cm and is largely ionic, not electronic, in nature.[34,35] Relatively low conductivities are also reported for iodine doped poly(methylacetylene) and poly(propargyl chloride) (about 10^{-3} S/cm).[36] Even for the chain-bridged polyacetylenes, there is evidence that substitution on the bridging element reduces obtainable conductivities. More specifically, the BF_4^- complex of polypyrrole provides a conductivity ($\sim 10^2$ S/cm), which is about 5 orders of magnitude higher than that for the corresponding complex of poly(*N*-methylpyrrole).[2]

The reason for the nearly 6 orders of magnitude difference in the observed conductivities of nonbridged, substituted polyenes and polyacetylene is not clearly established. The low observed conductivities for the former polyenes might reflect decreased π bandwidths, a nonplanar backbone geometry due to steric interactions, decreased interchain interactions, and/or the low molecular weights of investigated materials. Assuming that backbone geometry remains unchanged from polyacetylene, quantum chemical calculations on undoped poly(methylacetylene) and on poly(1,6-heptadiyne) predict a slightly decreased ionization potential compared with *trans*-polyacetylene.[23] This decrease is about 0.25 eV for poly(1,6-heptadiyne). Consequently, in the absence of changes in backbone planarity, changes in ionization potential do not provide a likely explanation for the low observed conductivity for substituted polymers such as poly(methylacetylene). The width of the highest occupied π band does significantly decrease as the result of lowering the symmetry within the unit cell, as compared with the case for polyacetylene, but not to a narrower width than for other polymers known to form conducting complexes.

Low mobility of hole carriers, rather than the absence of significant hole concentration, provides the likely explanation for the low electronic conductivity (less than 10^{-4} S/cm)[35] for iodine-doped samples of both crystalline *trans*-poly(phenylacetylene) and amorphous *cis*-poly(phenylacetylene). Although the degree of dopant ionization appears to be low at low dopant concentrations, Raman measurements (I_3^- and I_5^- observed, but not I_2) and the agreement between estimates of iodine mobility and the observed ionic conductivity suggest a high degree of dopant ionization for heavily doped poly(phenylacetylene) (about one iodine per monomer unit).[35] With an electronic conductivity component less than 10^{-5} S/cm and approximately all iodine present as I_3^-, the calculated effective hole mobility in poly(phenylacetylene) is less than about 10^{-7} $cm^2/(V\ s)$. This effective mobility (which includes the effect of interparticle and/or interphase resistances and the averaging of electrical anisotropy) is about 7 orders

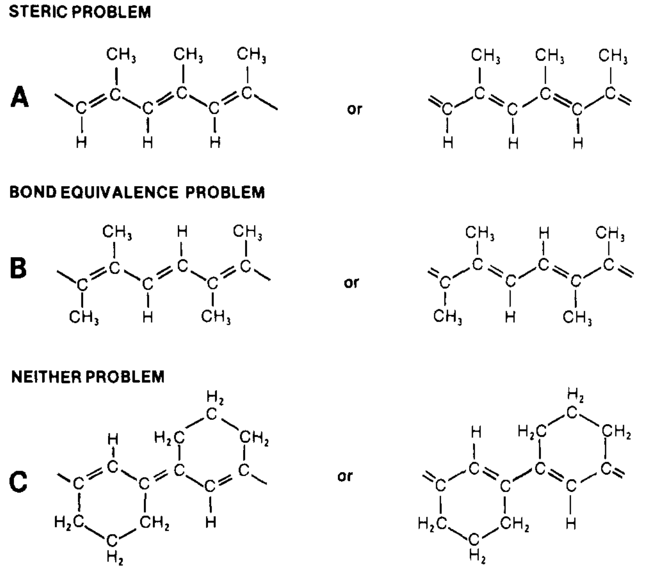


Figure 1. Factors effecting the electrical conductivity of charge-transfer complexes of substituted polyenes. For head-to-tail poly(methylacetylene), shown in (A), steric interaction between methyls precludes a planar backbone geometry. For head-to-head poly(methylacetylene), shown in (B), the alternation sequence shown on the right is not equivalent to the one shown on the left. Neither problem is encountered for poly(1,6-heptadiyne), shown in (C).

of magnitude lower than the effective mobility derived from Hall mobility measurements on AsF_5-doped poly(*p*-phenylene) and the lower limit estimate for iodine-doped polyacetylene.[8] Such a low mobility is typical for narrow bandwidth polymers and would be consistent with a grossly nonplanar poly(phenylacetylene) backbone. Nonplanarity is expected because of the bulky phenyl substituent groups. An additional feature might also be important here. While the maximum observed iodine doping level for poly(phenylacetylene) is comparable to that for iodine-doped polyacetylene ([I]/[C] is 0.15 and 0.3 for poly(phenylacetylene) and polyacetylene, respectively), the iodine can be completely removed from poly(phenylacetylene), by dynamic vacuum at room temperature,[35] but not from polyacetylene. This result suggests a much more weakly bound complex for the former polymer. The low effective mobility in poly(phenylacetylene) compared to that of polyacetylene could conceivably reflect in part a correspondingly low component of carrier mobility normal to the polymer chain.

The comparatively high conductivities for doped chain-bridged polyacetylenes (0.1–100 S/cm),[2–4,32] which can have approximately planar backbones, also suggest that steric factors are important for explaining the low observed conductivities of the nonbridged polyenes having bulky substituents. Structural localization of double bonds might also be relevant. For example, unfavorable steric factors, which preclude a near planar backbone geometry, are reduced in going from $[-(H_3C)C{=}C(CH_3)-]_x$ and $[-HC{=}C(CH_3)-]_x$ to the head-to-head all-trans methylacetylene polymer which can be represented by nonequivalent structures shown in Figure 1. However, the nonequivalent representations possible for the latter polymer mean that the double bond will be preferentially localized either between identically substituted carbon atoms or between differently substituted carbon atoms. In contrast with the case for poly(dimethylacetylene) or poly(methylacetylene), for which no highly conducting complexes are known, neither the problem of steric interactions nor the problem of nonequivalent structures need predominate for the chain-bridged polyene (C) shown in Figure 1, which forms highly conducting complexes.[4]

Note that it might be feasible to utilize finite chain effects (via suitable chain termination) to decrease the energy difference between electron localization on even or on odd bonds in polymers such as head-to-tail poly(methylacetylene). Chain termination can be chosen to favor a bond length sequence which is shifted by one bond length relative to that favored by the substituent pattern. For example, if substituents R_1 and R_2 favor a bonding sequence $-R_1C{=}CR_2{-}R_2C{=}CR_1-$, the head-to-head polymer chain can be terminated by reaction at R_2-substituted carbon atoms to form sp^3 carbons. It is also possible to favor the shifted bond-alternation sequence by interrupting backbone conjugation by occasional disubstitution or cross-linking (Diels–Alder or four-centered reaction between chains to form rings) at adjacent R_2 carbon atoms. The extent of conjugation length termination that is desirable to counterbalance the bond sequence favored by the substituent pattern should be determined by the degree of substituent stabilization for that sequence.

From the viewpoint of designing new conducting polymers, the optimal case for achieving a nonalternate structure upon doping would result from making all backbone carbon atoms equivalent. This ensures that both all backbone atoms and all backbone bonds can have identical electron densities in the absence of a Peierls distortion (Fermi surface instability). This design criteria for conducting doped polyacetylene compositions is unnecessarily severe, as is indicated by the violation for poly(1,6-heptadiyne). Furthermore, steric considerations of the optimal planar backbone geometry exclude virtually every substituent except hydrogen and, possibly, fluorine. A less severe design criteria, which is again neither necessary nor sufficient to ensure conducting derivatives, is to choose structures for which (in the absence of a Peierls distortion) the set of odd-numbered backbone carbon bonds (which need not all be equivalent) are equivalent to the set of even-numbered backbone carbon bonds. This ensures that there is no chemical preference in an infinite chain for bond localization at either even-numbered or odd-numbered bonds. The same considerations suggest the choice of monosubstituted acetylenes ($RC{\equiv}CH$) rather than disubstituted acetylenes ($RC{\equiv}CR$) for copolymerization with acetylene, since such disubstituted acetylenes would generally provide a structural difference between "average" odd and even bonds in the chain. Likewise, to the extent that comonomer to comonomer interactions are important (as in block copolymers), the same bond length guideline suggests choosing the reaction conditions for such monosubstituted acetylenes such that addition to the propagating chain end predominates at either the substituted carbon or at the unsubstituted carbon. Copolymers of acetylene and substituted acetylenes (or homopolymer mixtures) have been observed to dope to respectable conductivity levels.[36–38] However, the reported conductivities are lower than those obtained by doping unsubstituted polyacetylene, suggesting the possibility that the conductivity is principally due to lengths of unsubstituted polymer.

A final point is worthwhile discussing for polyenes for which the substituent pattern provides an energy difference between double bond location at odd or at even bonds. This point pertains to the formation of soliton defects, which have been used to explain a variety of electronic properties of nominally undoped and lightly doped unsubstituted polyacetylene. Soliton defects provide a boundary between chain segments having π-shifted alternation sequences (the single–double sequence shifted by one bond length). Monomer units in both chain segments have the same energy in the unsubstituted polyacetylene if interchain effects are neglected. This is not true for substituted trans polyenes such as head-to-head poly(methylacetylene). The energy for forming a soliton pair (soliton and antisoliton) will diverge as the separation within this pair increases. In contrast with the case for an unsubstituted trans polyacetylene chain or for poly(1,6-heptadiyne) with neglected interchain interactions, solitons are expected to occur as correlated pairs for high molecular weight chains. Even in the case of poly(1,6-heptadiyne), where the set of odd bonds is equivalent to the set of even bonds for the isolated chain, there is an important contrast with unsubstituted polyacetylene. Because neighboring carbon atoms are not equivalent in poly(1,6-heptadiyne) or in head-to-tail poly(methylacetylene), soliton and antisoliton defects would not generally have the same energies and should be distinguishable by different ESR spectra.

The dependence of electrical conductivity on the molecular weight of doped polymers is not well established. AsF_5 doping of phenylene oligomers provides a molecular weight increase via para coupling of adjacent chain ends, which precludes ready correlation of molecular weight and conductivity for the phenylene polymer/AsF_5 system.[7,8] The poly(p-phenylene) prepared by the Kovacic method contains 8 to 16 phenyls on the average,[39] corresponding to an average chain length of no more than 70 Å. End-group analysis indicates that the chain length can more than double upon AsF_5 doping, which provides a conductivity greater than 500 S/cm.[8] Low degrees of polymerization, or at least short conjugation lengths, are indicated for the poly(2,5-thienylene),[3,32] poly(m-phenylene),[40,41] poly(p-phenylenevinylene),[9] and polypyrrole[2] polymers, which form complexes having conductivity levels of 0.03, 10^{-3}, 3, and 10^2 S/cm, respectively. The possibility of cross-linking or chain extension caused by AsF_5 doping is not excluded for these polymers. As discussed earlier, infrared investigation indicates that cross-linking occurs for AsF_5-doped poly(m-phenylene). In addition, Wnek et al.[9,42] find HF evolution during the AsF_5 doping of poly(p-phenylenevinylene) and a conductivity independent of the degree of polymerization before doping, which is consistent with chain growth during doping. AsF_5 also induces a para-directed coupling of phenylene oligomers, but alkali metal dopants do not induce chain growth.[7] Conductivities obtained for polycrystalline compositions of potassium doped sexiphenyl, $H_5C_6(C_6H_4)_4C_6H_5$, are about 0.5 S/cm, as compared with about 30 S/cm for the polymer prepared by the Kovacic method.[7] Polyacetylene appears to provide quite long chain lengths, estimated to be between about 500 and 5000 Å.[43-46] However, because of conformational and/or chemical defects either in the undoped polymer or arising from the doping process, it is unlikely that the effective conjugation length is nearly so long.

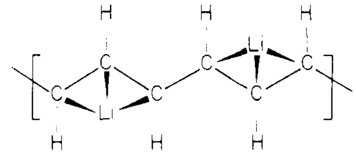


Figure 2. Model used for ab initio quantum chemistry calculations for lithium-doped *trans*-$(CH)_x$.

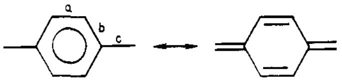
III. Molecular Structures in "Simple" Complexes

Certain polymer dopants appear to function simply as either electron acceptors or donors for the polymer chains. An example of this case is provided by alkali metal doping of polyacetylene and poly(p-phenylene).

Hartree–Fock ab initio calculations, using a Christoffersen minimal basis set, on undoped and on lithium doped *trans*-polyacetylene provide insight into the effect of polymer-dopant interactions on backbone geometry.[23] The investigated composition, $(C_6H_6Li_2)_x$, corresponds to approximately the maximum observed doping level for $(CH)_x$.[1] The model used in these single chain calculations is indicated in Figure 2. The asymmetric units along the chain, (C_3H_3Li), are related by a center of symmetry and the lithiums are equidistant from three adjacent carbon atoms. The length of nonadjacent bonds are set equal, as is believed to be the case for undoped polymer. The expected bond-alternate structure is derived for the undoped polymer, albeit with a smaller degree of bond length alternation ($\Delta r = 0.04$ Å) than is calculated by use of an extended basis set (0.10 Å).[47] With decreasing carbon–lithium separation the calculated charge transfer increases and the calculated degree of bond alternation decreases. The bond length difference in the backbone carbon–carbon bonds, normalized with respect to that calculated for the undoped polymer, decreases from 0.74 for 0.11 electron transfer to 0.53 for 0.20 electron transfer and vanishes for 0.31 electron transfer (about 0.1 electron per carbon). The conclusion of Brêdas et al.[23] that bond length alternation disappears at about 0.1 electron transferred per carbon is unaffected by removing the constraint that nonadjacent bonds have equal length. Since only single chain electrostatic energies are included in these calculations, the degree of charge transfer as a function of carbon–lithium separation is expected to be calculated less reliably (probably underestimated) than is the trend toward bond equalization with increasing charge transfer.

The results for lithium-doped $(CH)_x$ suggest that even modest charge transfer drastically alters chain geometry and, as a result, electronic structure. This casts doubt on the detailed use of rigid band structure models in the study of polymer-dopant interactions. The absence of bond alternation is consistent with the predictions of the soliton model for heavily doped $(CH)_x$.[48-50]

Crystallographic data on biphenyl[51] and biphenyl radical anions[52,53] can be used to estimate the molecular structure changes during doping of poly(p-phenylene) with alkali metals. These changes are in the direction provided by an increased admixture of the quinoidal resonance form:



The bonds parallel to the chain direction (bonds a and c) shorten and bonds inclined to this direction elongate in forming the biphenyl anion (1−). While bonds a and b are nearly equal in the neutral species (b−a = −0.008 Å), these bonds differ by about 0.05 Å in the anion. Bonds b and c in the neutral species, which differ by about the same amount as do adjacent bonds in polyacetylene (c−b = 0.10 Å), become nearly equal in the anion (c−b = 0.008 Å). The biphenyl anion is nonplanar in a sodium triglyme complex and in a rubidium tetraglyme complex and planar (or disordered) in a potassium tetraglyme complex. The rotation angles between phenyls in the former structures are 7.2° and 9.4°, compared with 10.2° for the neutral species (deuterated).[51-53] The alkali metal concentration in the biphenyl complexes (two phenyls per metal atom) nearly equals the highest observed sodium concentration in poly(*p*-phenylene), $(C_6H_4Na_{0.5})_x$.[6] Extrapolating the biphenyl results to poly(*p*-phenylene), we would expect the maximum bond length difference in this polymer to approximately halve upon doping.

Halogen-doped polyacetylene also provides conducting systems that can be viewed as "simple" charge-transfer complexes. Raman,[54-58] ultraviolet,[59] photoelectron,[54,60,61] and mass spectroscopies[62] demonstrate the existence of I_3^- and I_5^- species for iodine-doped polyacetylene, Br_3^- for bromine-doped polyacetylene, and Cl_3^- for chlorine-doped polyacetylene. For the lighter halogens, and apparently for iodine at high pressures,[63] side reaction (backbone halogenation) occurs, decreasing electrical conductivity of the complex via breakup of backbone conjugation. Except for this side reaction, the polymer–dopant interaction is the generation of hole carriers in the polymer chains via formation of the halide anions.

AsF_5-doped poly(*p*-phenylene) provides another important example of a "simple" acceptor-doped charge-transfer complex. Hall coefficient measurements at high dopant level are consistent with about one hole carrier per dopant molecule.[8] The only irreversible chemical modification that is observed on doping is an increase of molecular weight, via para coupling of polymer chain ends and the corresponding loss of hydrogen.[6-8] A chemical cycle is useful to demonstrate this point. AsF_5-doped poly(*p*-phenylene) evidences infrared and ultraviolet spectra that are quite different from those of the undoped polymer. However, compensation of the doped polymer with diethylamine, followed by water extraction of the reaction product, provides an amorphous polymer exhibiting the spectroscopic behavior of poly(*p*-phenylene). Annealing this polymer causes recrystallization to provide the characteristic X-ray diffraction pattern of the original crystalline polymer. As is true for AsF_5-doped polyacetylene and graphite,[64-66] infrared and Raman spectroscopy provides evidence for AsF_6^- as an intercalated species.[7,65] However, depending upon the doping conditions and the presence of impurities such as HF and AsF_3, other arsenic halide species are present in AsF_5-doped polyacetylene, poly(*p*-phenylene), and graphite.[1,6-8,64-68]

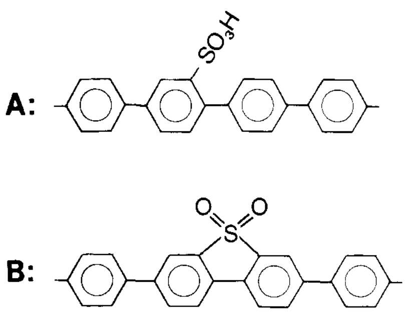


Figure 3. Chemical modification of poly(*p*-phenylene) induced by high temperature doping with SO_3.

Polymer chain conformation need not be retained during doping, as is evidenced by results obtained for electron-acceptor doping of *cis*-polyacetylene. Isomerization to the trans polymer is indicated by measurements of vibrational and UV–visible spectroscopies, nuclear magnetic second moments, ESR line widths, and/or heat capacities on samples doped with oxygen, halogens, and AsF_5.[56,59,69-71] Isomerization from *cis*- to *trans*-polyacetylene has also been recently reported for donor doping with either lithium or sodium.[71]

IV. Covalent Bond Formation during Doping

A second important class of conducting polymers are those that undergo irreversible chemical modification during doping. In some cases this chemical modification provides a more extended conjugated structure, with corresponding reduction in ionization potential and increase in π band widths. In other cases this reaction interrupts conjugation and, correspondingly, limits conductivity of the complexes.

The doping of polyphenylene with SO_3 from oleum provides an example where side reactions can occur to decrease the obtainable conductivity. IR spectra of the polymers after doping and prolonged washing to remove the dopant suggest that there are three competing reactions. In the first case a conductive charge transfer complex is formed ($\sigma \simeq 1$ S/cm). This complex will involve charge transfer between a polymeric cationic species and a dopant anion. In the second case the SO_3 reacts directly with the polymer backbone to form a sulfonic acid group (A in Figure 3). This type of reaction has been previously observed[72] upon treatment of the polymer with sulfuric acid. The attachment of sulfonic acid groups leads to a soluble, nonconductive material. The third type of chemical modification (B) results after the addition of a second SO_3 to an attached sulfonic acid group, followed by reaction with the neighboring phenyl and liberation of H_2SO_4. Permanent modification of the polymer has occurred in the latter two cases. Since such chemical modification leads to a loss of conductivity, reaction conditions should be chosen to promote the formation of the simple charge-transfer complex and impede the side reactions. Preliminary results indicate that use of rigorously dry SO_3 at lower temperature (≤ 0 °C) favors the formation of the charge-transfer complex.

Another system of interest is poly(*p*-phenylene sulfide) doped with AsF_5.[10,11,21] Elemental analysis of heavily doped, compensated, and extracted material indicates the loss of up to two hydrogen atoms per ring.

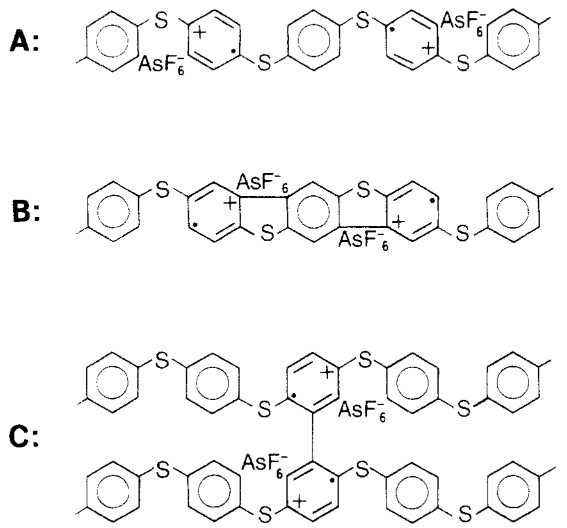


Figure 4. Reactions induced by the AsF_5 doping of poly(*p*-phenylene sulfide). The formation of a simple charge-transfer complex (A) is favored by low doping temperatures and low dopant concentrations. At high dopant levels, formation of dibenzothiophene linkages (B) predominates over interchain crosslinking (C).

In this case three possibilities are suggested (A, B, and C in Figure 4). The first possibility (A) corresponds to formation of a conductive charge-transfer complex with AsF_6^- as the anion, since the presence of this ionic species is clearly evident in the IR spectra of the doped polymer.[10,11,21] Also, AsF_3 evolution is observed in parallel with AsF_5 uptake by the polymer. The remaining two possibilities represent intrachain bridging to form thiophene rings (B) and interchain bridging (cross-linking) (C). Both of the latter reactions can account for the loss of hydrogen. The new materials (bridged and cross-linked) are shown as charge-transfer complexes since there is evidence that these altered polymers are highly conducting. Again the formation of A is slightly favored over B and C by conducting the doping process at lower temperature (−78 to −10 °C), but the dominant factor in the formation of B or C appears to be dopant concentration. High dopant concentration (>0.5 mol of AsF_6^- per monomer unit) favors the production of B and C.

Formation of B is apparently favored over that of C. Evidence of this is provided by our investigations on doped poly(dibenzothiophene sulfide), which incorporates every other sulfur atom in poly(phenylene sulfide) into a thiophene ring.[10] Treatment of this polymer with AsF_5 produces a conducting material, but even more interesting is the observation that the IR spectra of heavily doped, compensated, and extracted poly(*p*-phenylene sulfide) and poly(dibenzothiophene sulfide) are quite similar. The growth in the absorption band for out-of-plane vibrations of isolated hydrogen in both materials suggests that the end product in both cases is largely poly(benzothiophene), i.e., a polymer in which all sulfurs are contained in thiophene rings.

Quantum chemical calculations of ab initio quality[23] predict that polybenzothiophene has an ionization potential that is about 0.75 eV lower than that for PPS, as well as a slightly wider highest occupied band. Both trends favor higher conductivities upon doping, as is experimentally observed.

V. Molecular Assembly

Little experimental data are available to unravel the relationship between electrical properties and supramolecular organization. The enormous complexity of polymer structures poses the key problem. For example, the presence of folded, coiled, or extended chains, segregated or nonsegregated chain ends, intercrystallite tie molecules, and amorphous regions can affect microscopic electronic connectivity and the whole host of electronic properties. Macroscopic dc conductivity measurements can be affected by such features, as well as by features which can occur from micro- to millimeter scales, such as spherulitic or fiberlike morphologies.

All presently investigated polymers that can be doped to high conductivity levels are, unfortunately, grossly inhomogeneous. Crystalline and amorphous regions of the undoped polymers can have different ionization potentials, different electron affinities, different trap and scattering center characteristics and concentrations, and different dopant diffusion coefficients. Likewise, the equilibrium dopant concentration and the dopant concentration at which the semiconductor–metal transition occurs can reasonably be expected to depend upon differing states of order in different regions of the polymer. The inhomogeneity of the parent polymer will be replicated to a greater or lesser extent in the doped polymers, so measured properties will be influenced by a composite structure. For example, the often observed nonmetallic temperature dependence of bulk dc conductivity for highly conducting doped polymers might commonly reflect the dominance of interphase and interparticle resistivities.

An increasing conductivity for the doped polymer with increasing perfection of the precursor polymer is generally expected. However, it is not true that three-dimensional crystallinity is a necessary prerequisite for obtaining highly conducting ($\sigma > 10^{-2}$ S/cm) complexes. High-angle X-ray diffraction measurements indicate no significant long-range three-dimensional order for AsF_5-doped poly(*p*-phenylene sulfide),[10,11,21] despite the high conductivity observed (1 S/cm). Major conductivity differences are observed upon AsF_5 doping of poly(*p*-phenylene) prepared with different synthesis methods, but no obvious correlation is observed between the conductivity and the crystallinity of the precursor, undoped polymer. Comparable conductivity values are obtained for the AsF_5 doping of either amorphous or crystalline poly(*p*-phenylene sulfide). Likewise, high conductivity values (0.1 S/cm) are reported upon iodine doping of amorphous poly(1,6-heptadiyne).[4]

Deitz and co-workers[73] have reported that the electrical conductivity of iodine-doped polyacetylene strongly depends upon the method of polymer preparation. They observed about a 6 order of magnitude difference in electrical conductivity for polymerized acetylene samples having comparable dopant levels, $(CHI_{0.15-0.25})_x$. All crystalline samples doped to high conductivities; all amorphous samples provided poorly conducting doped materials. Taken alone, these results might be interpreted as implying that crystallinity in the precursor polymer is a necessary prerequisite for obtaining highly conducting doped compositions. However, as seen above for poly(*p*-phenylene sulfide) and poly(1,6-heptadiyne) systems, this is not a general result for other conducting polymers. Moreover, differences in the chemical structure of the polyacetylene chains (cross-linking, oxygen impurity, etc.) cannot be excluded as important determinants for the widely different conductivities of samples prepared using various synthesis methods. Perhaps the correlation with degree of order is secondary in the sense that inhomogeneities in chemical structure provide the low degree of order for the undoped polymers. It is also conceivable that amorphous polyacetylene is sufficiently labile, relative to the crystalline polymer, that the doping process causes side reactions which interrupt conjugation. Relevant to this point, the results of Gibson et al.[4] suggest that iodine dopant adds to the double bonds in the amorphous, chain-bridged polyacetylene, poly(1,6-heptadiyne). Such reactions of the iodine charge-transfer complex provide a likely explanation for the limiting conductivity observed during room temperature doping and for the instability of conductivity for doped poly(1,6-heptadiyne). In support of the view that some polymers do not form highly conducting complexes unless they are crystalline, a recent investigation by Sanechika et al.[74] is interesting. These authors obtained a conductivity of about 4×10^{-2} S/cm by doping crystalline poly(1,1′-ferrocenylene) with TCNQ (7,7,8,8-tetracyanoquinodimethane). This conductivity is about 10^3 higher than was previously obtained by doping the corresponding amorphous polymer with TCNQ.[74,75]

The term amorphous as applied to conjugated backbone polymers such as polyacetylene and poly(*p*-phenylene) does not imply that the "average" nearest-neighbor packing arrangement differs substantially from that in the crystalline polymers. Rather than reviewing "amorphous" rigid-rod polymers of these types as like a "bowl of cooked spaghetti", it is better to view them on a local scale as like a "full box of uncooked spaghetti". Viewed in this way, it is easy to understand how important interchain interactions can be maintained in an "amorphous" rigid-rod polymer. Such interactions can be crucial both for stabilizing metallic states and providing continuous conduction paths.

Although the doping process will replicate to some extent structural features of the parent polymer, the importance of these features in precursor and doped polymers is a distinguishable issue. For example, even though a doped complex does not have long-range three-dimensional order (perhaps because of disordered and statistically distributed dopant arrays), this does not imply that a random coil structure is an adequate precursor for obtaining highly conducting forms of this complex. Also, depending upon the temperature of doping, polymer flexibility, and whether or not plasticization occurs, recrystallization during doping is a possibility. It is possible, for example, that recrystallization might occur as a consequence of plasticization during the doping of poly(*p*-phenylene sulfide), followed by the introduction of massive disorder at higher dopant levels. However, even well-crystallized poly(*p*-phenylene sulfide) normally has a relatively low degree of crystallinity (60–65%) compared with that which can be readily obtained for polymers such as polyacetylene and polyethylene. Hence, it is reasonable to presume that doped "amorphous" regions and doped crystalline regions become conducting.

Parallel rod-like chains in polymer domains will largely remain parallel upon doping because of the unfavorable kinetics and thermodynamics for changing the relative orientation of chains. Evidence for the stability of such arrays is provided by experiments on polymers synthesized in channel complexes and on partially polymerized diacetylenes,[76,77] wherein over 50% of the total occupied crystal volume (nonpolymeric material) can be solvent extracted without eliminating the parallel orientation of polymer chains in the residual material. This maintenance of parallel chain orientation is indicated by anisotropy measurements on doped samples of previously oriented polyacetylene[1] and on doped single crystals of phenylene oligomers.[8]

If the parent polymer has a chain-folded lamellar morphology, kinetic arguments suggest that this morphology will be retained after doping at low temperatures, even though three-dimensional crystallinity need not be retained within the lamellae. Chain folding could be important for limiting the effective delocalization length of undoped and doped polymers. Also, dopant-induced chemical attack is most likely to occur at the fold surface, where such attack is both kinetically and thermodynamically more favorable than in the intracrystalline regions of the polymer. In the absence of dopant-induced chain scission, chain folding would provide lateral linkages between parallel chain segments that behave like cross-links in interfering with insertion of large dimension dopants between chains. It is most reasonable that rigid-rod molecules such as poly(*p*-phenylene) and polyacetylene should generally have an extended chain morphology, while the folded chain possibility becomes less unlikely for more flexible polymers. This contention is in agreement with the absence of strong small angle scattering normal to the orientation direction in drawn polyacetylene[78] and the expected morphology[79] if polymerization occurs by successive polymerization and crystallization of monomer units. However, this point is still unresolved since Lieser et al.[80] (based on their interpretation of electron diffraction results) report a folded chain morphology for polyacetylene. Low-angle X-ray diffraction measurements on highly oriented poly(*p*-phenylene sulfide) indicate density fluctuations with about a 90-Å separation in the chain direction.[81] This result, obtained for mechanically drawn melt-molded films, suggests that there is at least one example of a chain-folded polymer that becomes highly conducting upon doping.

Despite the high crystallinity obtainable for polyacetylene synthesized by the Shirakawa method, detailed X-ray diffraction analysis by Asaishi et al.[78] suggests that the degree of intracrystallite disorder is much higher than for highly crystalline, flexible polymers such as polyethylene. Also, these polymer samples (with which most of the polyacetylene doping experiments have been done) exhibit extremely high surface areas (about 60 m^2/g), large void volumes, and 200-Å diameter polycrystalline threads.[1,78,80] Consequently, dopant diffusion into such polyacetylene is greatly enhanced compared to that expected for a large dimension single crystal of polyacetylene. As polymeric materials are made more homogeneous and better ordered, this problem of uniform dopant penetration into the entire crystal volume will become more serious. Relatively sharp boundary layers between doped and undoped regions are observed even for the AsF_5 doping of amorphous poly(*p*-phenylene sulfide) films, which do not have the easy diffusion paths afforded by the large void volume in polyacetylene.

The covalent bonding between monomer units in polymer chains considerably restricts energetically feasible periodic packing arrangements in polymeric charge-transfer complexes, as compared with those for molecular charge-transfer complexes. The restriction is most severe for two-dimensional polymers such as graphite and transition-metal disulfides, for which the dopants must form layers between the polymer sheets. The same restriction pertains to linear polymers for which the dominant determinant for crystal packing in the doped polymers is strong interchain hydrogen bonding to form sheets of polymer chains. For rigid-rod, unsubstituted polymers having parallel chains (such as poly(*p*-phenylene) and polyacetylene) and dopants having dimensions comparable to or larger than the chain cross section, the dopant molecules are expected to pack in linear arrays in the chain-axis direction or as two-dimensional arrays parallel to the chain-axis direction.

Nonaggregated dopants, which are more uniformly dispersed throughout the polymer (analogous to the case of nondegenerately doped semiconductors such as silicon), are reasonable only at very low dopant concentrations (where mixing entropy dominates) or for systems in which a statistical distribution of dopant species results in neither high polymer strain energies nor a large volume fraction of molecular-dimension voids. One such type of system possibly arises for single-phase polymers containing dopants (such as Li^+) that have dimensions small compared to the polymer chain cross section (so that a variety of interstitial sites that have low strain energy are available) and for which small ion dimensions provide highly unfavorable electrostatic interactions for ion aggregates. Another type of system results for polymers in which the relative orientation of neighboring chains is highly statistical even on a local level (such as in largely random coil, amorphous polymers). A high degree of three-dimensional cross-linking of parallel, rigid-rod polymers will eventually geometrically limit dopant levels and dopant aggregate dimensions for dopants having dimensions large compared with the local separation of cross-linked chains. Decreased electron affinities and increased ionization potentials with decreasing average conjugation length can likewise limit dopant levels. Lefrant et al.[69] report that oxygen-reacted polyacetylene, which has a substantially reduced conjugation length, dopes less completely than does the parent polymer exposed to the same doping conditions.

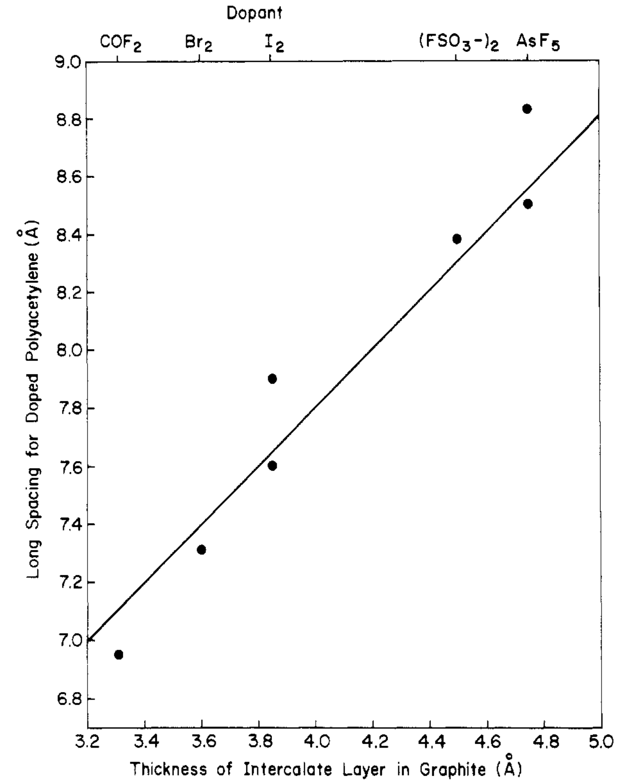


Figure 5. The long interplanar spacing for acceptor doped polyacetylene[15,64] as a function of the effective thickness of a dopant layer in graphite. The iodine/graphite result is derived from measurements for bromine/graphite.

Dopant insertion on alternate close-packed planes of polymer chains appears to be favored for heavily acceptor-doped polyacetylene. A new, long-spacing X-ray diffraction peak arises for these polymer/dopant systems.[15,64] This spacing can be interpreted as the distance between two layers of dopant molecules (or two dopant-rich planes) separated by a close-packed plane of polyacetylene chains. Evidence for this result is provided in Figure 5. The long-spacing diffraction peak is shown to increase linearly with the effective van der Waals thickness of the dopant layer (or dopant-rich layer), as measured by the amount the intersheet distance in stage one graphite would expand for the same dopant. In the case of iodine and COF_2, for which the graphite result is unobtained, the thickness parameter was calculated by scaling the observed graphite parameter for bromine according to the relative van der Waals radii of the largest atoms in the dopant molecules. The NMR second moment measurements during iodine doping by Mihaly et al. and the measurements of bulk dimensional changes during iodine doping by Francois et al. are consistent with this model.[82] Complexes in which the dopant molecules pack in linear arrays in channels within the polymer host have recently been observed for both donor dopants (tetragonal phases for Na^+, K^+, Cs^+, and Rb^+) and acceptor dopants (AsF_6^-) in polyacetylene.[81] In addition, a high stage structure is suggested by recent results for polyacetylene lightly doped with iodine. Columns of anions (I_3^- and I_5^-) partially displace the polyacetylene chains on every fourth close-packed layer of these chains.[81]

A model for the packing arrangement of the polyacetylene/iodine complex at high dopant level is shown in Figure 6. The I_3^- dopant species are present in a close-packed plane of anions, which separate close-packed planes of polyacetylene chains. As shown by the chain-axis projection in Figure 6, the donor polymer molecules within the polymer planes are packed analogously to donor molecules in segregated stack, molecular conductor complexes. Hence, it is reasonable to expect that the interchain band width in polyacetylene would be comparable with that in the stack direction of conducting molecular charge-transfer salts. This comparison implies considerable interchain interaction, even though the interchain band width would

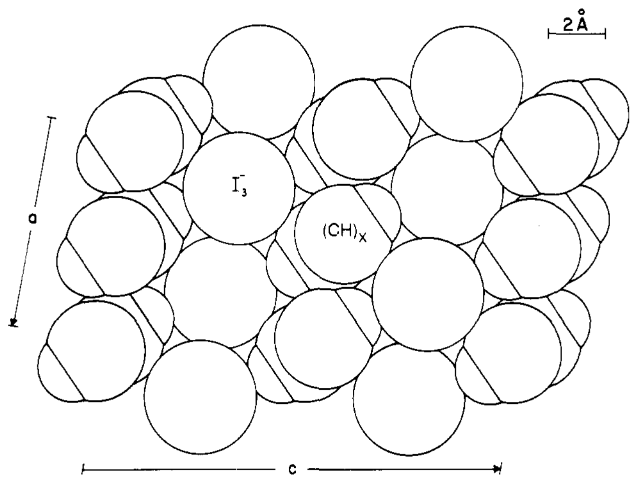


Figure 6. A structural model for iodine-intercalated polyacetylene. The small, medium, and large radii represent the van der Waals dimensions of hydrogen, carbon, and iodine, respectively, in this chain-axis projection. I_3^- ions parallel to the chain axis direction (*b*) form (001) layers which separate close packed planes of polyacetylene chains. While details of the crystal packing are unknown, this model does provide a close packed structure which generates a long X-ray diffraction spacing identical with that observed.

be quite small compared to the intrachain band width (i.e., 0.1 eV vs. 10 eV).[83] Consequently, it would not be surprising if two high conductivity directions exist—in the chain direction and in a direction defined by molecular overlap between polymer chains. The conductivity component normal to the chain-axis direction might explain the low anisotropies observed for doped poly(*p*-phenylene)[7] and poly(*p*-phenylene sulfide) systems.[10,11,21] Without such a conductivity component it is difficult to understand why such high conductivities are observed for unoriented samples in which chain ends and structural defects interrupt chain-direction electronic connectivity.

The line width of the emergent long spacing can be used to calculate a coarse lower limit on the dimension of a sequence of dopant-containing and undoped planes, measured normal to the dopant plane. For various doped samples of cis-rich and trans-rich polyacetylene, having iodine dopant levels between $(CHI_{0.06})_x$ and $(CHI_{0.23})_x$, the line width at half-height is in the range between 1.6 and 2.4° ($\Delta 2\theta$ for Cu Kα radiation). According to the Scherrer equation,[84] the corresponding dimensions of the sequence of dopant-rich planes have a lower bound of between 33 and 50 Å, or between about four and six layers of intercalated dopant. For the FSO_3^--doped polymer the same type of analysis provides a lower limit estimate of two to three layers of dopant-rich planes. Since higher order reflections were not resolved in any of these spectra and, consequently, no correction could be made for broadening of the second kind (paracrystalline distortions), the actual dimensions might be considerably higher.

There is evidence that at low dopant concentrations intercalation can occur inhomogeneously, so as to produce coexistent regions of undoped polymer and stage 1 intercalate, possibly with partial occupation of the dopant layer with polyacetylene chains. This is illustrated in Figure 7 for $[CH(FSO_3)_{0.036}]_x$, where the X-ray diffraction patterns of undoped and doped cis-rich polymers are compared. The new long spacing, corresponding to stage 1 intercalation, arises at 8.4 Å, but no significant changes occur in the relative intensities and positions of diffraction lines present in the undoped polymer.

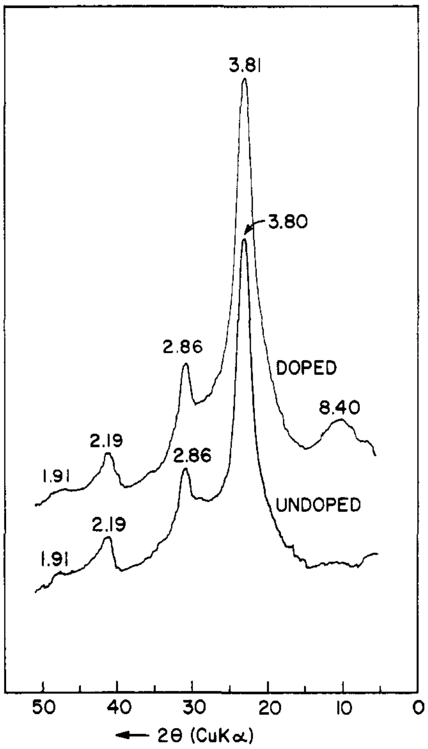


Figure 7. Comparison of the X-ray diffraction results for unoriented polyacetylene before and after doping with $(FSO_3)_2$. At the low dopant level considered here, $[CH(FSO_3)_{0.036}]_x$, the only significant change is the emergence of a new spacing at 8.4 Å in the doped polymer. The interplanar spacings (Å) are indicated on these microspectrophotometer scans of film data.

There has been considerable controversy about whether or not lightly doped polyacetylene consists of a dispersion of metallic doped domains in a nonmetallic matrix. Tomkiewitz and co-workers[85] have argued, based on susceptibility measurements, that the AsF_5 doping of polyacetylene is so inhomogeneous that formation of metallic domains result for an overall composition of $y = 0.003$ (ratio of arsenic fluoride species to backbone carbon). This is substantially below the critical concentration claimed for the semiconductor-to-metal transition, $y = 0.01–0.02$, from conductivity measurements and above 0.02 from susceptibility measurements.[49] Mortensen et al.[86] also interpret the observed exponential dependence of resistance on inverse field in terms of the metallic domain model, which has previously been used to explain the exponential -$T^{-1/2}$ temperature dependence of conductivity.[85] Using either the ratio of exponential coefficients for the temperature and field dependence of conductivity or the crossover field between the ohmic and nonohmic behavior, Mortensen et al.[86] calculate a separation of about 60 Å between metallic domains for a sample doped to $y = 0.005$. The authors interpret the apparent semiconductor–metal transition at a few percent doping level as due to the percolation of metallic domains. This percolation model is not physically unreasonable, despite the fact that doping proceeds from the outside to the inside of polymer fibers. Metallic particles separated by insulating regions could conceivably result from either (1) a thermodynamic driving force for phase separation of lightly doped polymer into heavily doped and largely undoped polymer or (2) disordered interparticle regions that remain insulating until high overall dopant concentration. If such phase separation occurs in doped polyacetylene, then this polymer displays quite different behavior than does intercalated graphite. For graphite it appears that high stage compositions are generally thermodynamically stable with respect to phase separation to provide lower stage compositions and undoped graphite.[87]

Epstein et al.[88] have argued that while dopant distribution may be nonuniform in doped polyacetylene, dopant segregation into metallic domains does not occur at low dopant concentrations (y less than about 1%). This conclusion is based on magnetic susceptibility[89] and optical measurements[90] on arsenic pentafluoride doped $(CH)_x$ and on electric field, frequency, and temperature dependent conductivity studies and magnetic susceptibility studies[88,91,92] on iodine-doped $(CH)_x$. The Pauli susceptibility, which was reported previously for lightly doped polymer and used as evidence for metallic particles,[85] was near zero for $y < 0.01$.[89] It now appears that metallic domains can form in lightly doped polyacetylene as a consequence of diffusion-limited dopant penetration, but such domains do not arise as inherent structural features in lightly doped polyacetylene. However, further work is required to clearly resolve the controversy associated with this point.

VI. *Future Directions and Problem Areas*

Progress in developing a detailed understanding of conducting polymers depends upon the discovery of methods for synthesizing these materials as large-dimension single crystals. Large-dimension single crystals with high structural perfection are available for only one type of organic linear polymer—the polydiacetylenes.[27] The method used to synthesize the diacetylenes, matrix-controlled solid-state polymerization, provides the most promising route to single crystals of conducting polymers.

Some progress has been made by use of solid-state reactions to produce conducting polymers. For example, Shacklette et al.[7] have reported that gas-phase doping of single crystals of phenylene oligomers ($C_6H_5(C_6H_4)_nC_6H_5$, where $n = 2$ to 4) results simultaneously in both polymerization to poly(p-phenylene) and formation of a highly conducting complex between the poly(p-phenylene) and the arsenic halide. This reaction is matrix controlled to the extent that the reaction product is chain oriented. However, as is true for the conductor obtained directly by gas-phase doping of poly(p-phenylene), the reaction product is not well ordered. Irradiation-induced polymerization of cyclohexadiene in a thiourea complex, followed by solvent extraction of the thiourea and solid-state bromination and dehydrobromination of the poly(cyclohexadiene), also provides chain-oriented poly(p-phenylene).[93-95] As for poly(p-phenylene) made by oxidative coupling of benzene,[96] AsF_5 doping substantially decreases order of this material.

Because of the decrease in order which typically accompanies dopant intercalation, the ideal matrix-controlled reaction would involve a single-phase polymerization of a single crystal adduct between monomer and the dopant species (or a precursor to the dopant species). This reaction could be induced by thermal annealing, irradiation, or a diffusing gas, but should not necessitate large changes in crystal dimensions due to the incorporation of reactants or the evolution of reaction products. In all known cases where such dimensional changes occur, massive introduction of phase imperfections result. An alternate synthetic route to large dimension single crystals of conducting polymers would involve polymerization of a monomer nearly simultaneously with cocrystallization with the dopant species—analogous to the "successive crystallization and polymerization" processes investigated by Wunderlich and co-workers[97] for nonconducting polymers. Finally, the use of anisotropic substrate crystals offers attractive possibilities for the synthesis of three-dimensionally oriented conducting complexes. These substrates can function as templates either for the cocrystallization of polymer and dopant or for both monomer polymerization and dopant cocrystallization. Both solid-state polymerization and reaction on anisotropic substrates have been used to obtain crystals (or oriented crystal aggregates) of the metallic and superconducting polymer $(SN)_x$, albeit crystals containing gross structural defects.[98-102]

Independent of progress made in synthesizing single crystals, the important future applications of conducting polymers are likely to utilize these materials in their least expensive form—probably as polycrystalline or as "amorphous" films and fibers. The absence of convenient processability is a problem area for most of the polymers that are doped to form conducting derivatives. Polymers such as polyacetylene,[103] poly(1,6-heptadiyne),[4] and doped polypyrrole can be obtained as films by sedimentation of microfibrils formed during polymerization or by reaction of the monomer on a substrate[2,104,105] (electrode in the case of doped polypyrrole). These polymers are neither melt nor solution processable. Poly(p-phenylene) of reasonably high molecular weight is also both infusible and insoluble. Processability is obtained only because of the extremely high thermal stability of poly(p-phenylene), over 500 °C under vacuum, which permits fabrication using sintering techniques that are analogous to those used in powder metallurgy.[106] Poly(p-phenylene sulfide) is presently the only reported melt or solution processable polymer which can be doped at low temperatures to form complexes having conductivities greater than 1 S/cm.[10,11]

Environmental stability and embrittlement caused by doping are problem areas for most of the conducting polymers. Little has been reported about either aspect. Doped polypyrrole (which has been modified by air exposure[2]) appears to be the most environmentally stable conducting polymer (excluding those polymers known to have graphitic structures). This stability may result from the low ionization energy of polypyrrole and the resulting environmental stability of the polymer cation.[107] Modulus increases lateral to the chain direction are an expected consequence of replacing van der Waals bonds in the precursor polymer with electrostatic interactions in the charge-transfer complexes. However, at least for oxygen-doped polyacetylene, dopant-induced cross-linking provides a reasonable explanation for dopant-induced embrittlement. Little has been said about property contributions from intercrystallite (interdomain) regions in conducting polymers because little is known in this area. However, it would be quite surprising if many properties, including mechanicals and conductivity, were not profoundly affected by the microstructures present in the parent polymers and structural changes in boundary regions during doping.

The future for the conducting polymers areas will clearly have many surprises, both in fundamental property discoveries and in applications development. Many application areas have been proposed, such as in low current circuitry, electromagnetic and electrostatic shielding, batteries,[108,109] stabilized electrodes,[110] semiconductor devices,[14,111] solar cells,[111–113] etc. Which of these materialize is a matter of speculation, but will likely involve further evolution of materials to meet use requirements. Many interesting properties remain to be discovered. For example, low-temperature superconductivity was recently reported[114,115] in molecular charge-transfer complexes involving some of the same acceptors used in conducting polymer complexes. The broad conduction bands compared with those in molecular charge-transfer complexes, the structural anisotropy afforded by linear polymers, and the likely existence of novel electronic defect structures, such as solitons, promises a diversity of interesting properties.

VII. References

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