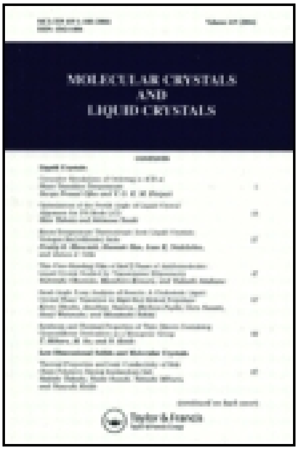

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Conducting complexes of conjugated polymers: A comparative study

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CONDUCTING COMPLEXES OF CONJUGATED POLYMERS: A COMPARATIVE STUDY

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There are now a number of different polymers which undergo dramatic conductivity increases on exposure to electron donors or acceptors. The discussion here will center on a comparison of the electrical and optical properties of the different systems, with special emphasis on polyphenylenes and polyphenylenesulfides. The very promising results provided by the Valence Effective Hamiltonian (VEH) technique for the valence band electronic structures of a wide range of undoped polymers will provide the framework for a comparison of the various conducting polymer systems.

I. INTRODUCTION

Conjugated polymers have for some time been of major interest to chemists and physicists alike. This interest has been enhanced greatly in recent years by the discoveries of a number of conjugated polymer systems[1-4] which could be "doped" to near metallic conductivities. The doping process involves exposure of the polymer to electron donors, such as the

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alkali metals, or electron acceptors, such as I_2 and AsF_5. Doping can also be accomplished electrochemically - a fact which has lead to rechargeable batteries based on conducting polymers.[5] Doping levels are generally quite high (typically 5-50 mole per cent) so that the phrase "doped polymers" can be a bit misleading if taken in the context of semiconductor physics. For doped inorganic semiconductors, the dopant is usually at very low concentrations and it represents a relatively minor perturbation on the band structure of the semiconductor and, therefore, on transport properties. This rigid band structure model is of limited applicability, even qualitatively, to doped conjugated polymers. For this reason, as well as the fact that many aspects of the electronic properties of these materials are not well-established, theoretical understanding of conducting polymers lags behind the rapid pace of experimental developments. This statement includes theory related to transport properties and theory related to predicting new con-conducting systems.

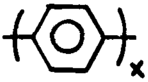
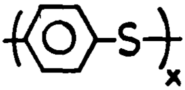
In this paper, we will briefly summarize the optical and electrical properties of phenylene-based conducting polymer systems: donor and acceptor doped poly(p-phenylene) and acceptor doped poly(p-phenylene sulfide). Comparisons will be made to the much studied polyacetylene system. Recent theoretical work[6] aimed at developing some predictive capability for acceptor doped systems will be discussed.

II. ELECTRICAL AND OPTICAL PROPERTIES

Several conducting polymer systems have been discovered recently including: poly(p-phenylene), PPP, announced by Ivory et al,[2] and poly(p-phenylene sulfide), PPS, announced simultaneously by Rabolt et al.[3] and Chance et al.[4] The PPS system is especially significant, since it represents the first conducting system containing a polymer which is processible by conventional polymer techniques.[7]

Table I summarizes maximum conductivities achieved for polyacetylene (PA), PPP, and PPS on doping with I_2 (a relatively weak electron acceptor), AsF_5 (a strong electron acceptor), and potassium (a strong electron donor). I_2 works only for PA, AsF_5 for all three, and potassium for PA and PPP. In each case the sign of the carriers, as measured by Hall effect, thermopower, etc.,[1-4,7-8] is consistent with transport in the polymer array, i.e., p-type for acceptor doping and n-type for donor doping.

Table I. Conductivities (S/cm) for doped polymers[a]

Polymer	$\sigma[I_2]$	$\sigma[AsF_5]$	$\sigma[K]$[b]
PA 	550 [0.13]	1200 [0.20]	50 [0.32]
PPP 	$<10^{-4}$	500 [0.40]	20 [0.50]
PPS 	$<10^{-4}$	3 [0.70][c]	$<10^{-4}$

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[a] Typical doping levels are given in brackets on the basis of probable dopant species (I_3^-, AsF_6^-, K^+) per monomeric unit as indicated in the first column.

[b] Results obtained by exposure of polymer to potassium naphthalide solution (THF).

[c] Doping at this level is accompanied by extensive chemical modification involving intramolecular crosslinking to form benzothiophene linkages.[7]

Important factors in determining whether or not a conducting system is formed on acceptor doping are: (1) the ionization potential of the polymer and (2) the extent to which charge can be delocalized along the chain. The former determines whether or not charge-transfer occurs with a given acceptor; the latter determines whether or not the charges (holes) induced in the chain will be mobile. Thus conjugated polymers are generally required since electron delocalization in these systems leads to low ionization potentials and large π-electron bandwidths.

Conjugation in π-electron systems is generally associated with planarity, which affords maximum π-electron overlap. Thus, at first glance, it is surprising that PPP and PPS form conducting complexes since both are nonplanar systems. Adjacent phenyl rings in PPP are rotated by ~23° with respect to one another. Adjacent phenyl rings in PPS are nearly perpendicular. In addition, the presence of aromatic moieties might be expected to lead to localization, since, for example, in the PPP case a loss of aromaticity is required in forming the mesomeric quinoid structure. We return to some of these questions in Section III. However, it is clear from Table I that PPP and PPS have higher ionization potentials than PA. The data also suggest that PPS has a lower electron affinity than either PPP or PA.

An important effect in the PPP and PPS systems is the potential for chemical modification on doping. Shacklette _et al_[9] have shown that oligomers of PPP (biphenyl, p-terphenyl, etc.) polymerize to form PPP on exposure to AsF_5, eventually forming a conducting PPP/AsF_5 complex with conductivity comparable to that obtained starting with the polymer. In the PPS case, exposure to high levels of AsF_5 or SbF_5 results in substantial intramolecular bridging to form dibenzothiophene linkages, as indicated by infrared spectroscopy and chemical analyses.[7] The limit of this bridging process is polybenzothiophene. The highest conductivity achieved in PPS without measurable chemical modification is ~0.01 S/cm.[7]

The optical properties of the polymers undergo dramatic changes on doping. Electronic absorptions intrinsic to the polymer decrease in intensity and are replaced by new transitions in the near-infrared region.[4,9-11] At high doping levels, the absorption due to the new transitions extends to very low energies, effectively masking the infrared vibrational transitions of the polymer. Spectroscopic results are summarized in Fig. 1 for PA,[10] PPP,[9] PPS,[4,7] and polypyrole.[11] Absorption bands intrinsic to these polymers are located at 1.8 eV, 3.5 eV, and 3.6 eV and 2.8 eV respectively. At low doping levels, new peaks appear in the near-infrared (around 1 eV) for PA, PPS, and polypyrole. For PPP, spectra at low doping levels have not, as yet, been obtained. The spectrum for PPP in Figure 1 was obtained after exposing a terphenyl film to AsF_5, which polymerizes the oligomers and forms PPP/AsF_5 complexes.[9] At high doping levels, the spectra for PA/AsF_5 show absorption throughout the infrared (as for PPP). For PPS, the spectra at high doping levels do not show nearly as much absorption in the infrared. This weaker infrared absorption is consistent with the lower conductivity for PPS/AsF_5.

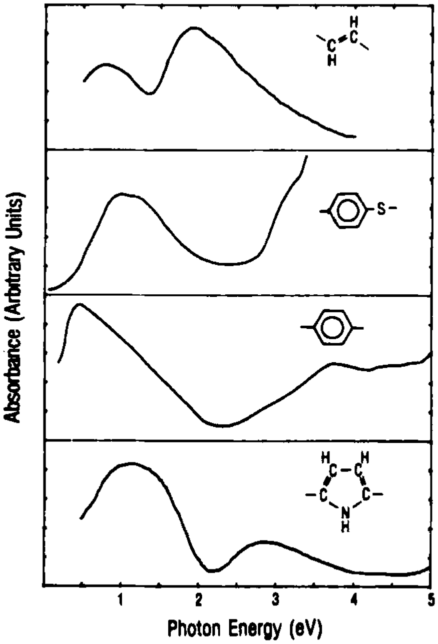

FIGURE 1 Absorption spectra for acceptor-doped polymers

For PA, a theoretical model based on solitons has been put forward to explain the dopant-induced near-infrared transition at 0.8 eV.[12] However, since the other polymers of FIGURE 1 lack the two degenerate ground states present in all-trans PA, they cannot support soliton states, and a systematic explanation of all the FIGURE 1 data with a soliton model is not possible. Brédas *et al*[13] have shown elsewhere that a polaron model offers an internally consistent, qualitative description of these data. In that model, the near-infrared absorbing species is a delocalized radical-cation (i.e., a hole or polaron) produced by loss of an electron to the acceptor. This model suggests that the extent of delocalization of the polaron in PPP is about three or four phenyl rings.

The extent of delocalization in the PPS systems is also apparently about 3 or 4 monomeric units, as judged from the "doping" of PPS "oligomers": $(C_6H_4)_3S_2$ ("trimer") or $(C_6H_4)_4S_3$ ("tetramer"). The near infrared transition energies, induced on exposure to AsF_5, of the trimer, tetramer, and polymer are 1.55, 1.24, and 1.21 eV respectively. Thus the tetramer and the polymer are nearly indistinguishable with regard to optical properties. However, the conductivity of the doped oligomers is less than 10^{-7} S/cm.

III. VEH CALCULATIONS

It has been demonstrated that good insight into the ground state properties of polymeric systems can be obtained by quantum chemical calculations.[14] However, the SCF (Self-Consistent-Field) ab initio Hartree-Fock techniques, which have proved very successful on small molecules, become almost prohibitively expensive when applied to polymers of interest. Cheaper semiempirical techniques could in principle be used, but are generally less reliable.

Recently, Nicolas and Durand[15] have developed an interesting approach based on the use of valence effective Hamiltonians (VEH). Applied to hydrocarbon molecules,[10] the VEH technique affords one-electron energy levels of ab initio double zeta quality at a cost comparable to semiempirical techniques such as Extended Huckel. The VEH model has recently been applied to polymer calculations.[7,16] It has been shown,[7] through calculations on polyacetylene and polydiacetlyene, that the polymer VEH method also provides ab initio double zeta quality results for band structure and density of states. Perhaps more important with regard to the conducting polymers area, the VEH technique provides reliable ionization potentials and bandwidths. The ionization potential determines whether a particular acceptor is capable of ionizing (or partially ionizing) the polymer. The bandwidth of the highest occupied band provides a measure of the extent of the delocalization in the system and can be roughly correlated with the mobilities of the charge carriers in that band. Thus bandwidths of the highest occupied band should show a qualitative correlation to conductivities achieved in similar polymers upon acceptor doping. Caution is needed on the latter point because of the demonstrated inadequacy of a rigid band model to explain the properties of highly conducting doped polymers.[17]

In this section we report, in summary form, VEH calculations for a wide range of hydrocarbon polymers in order to provide a systematic and theoretically consistent description of the valence electronic properties of systems of interest in the conducting polymers area. The complete methodology for obtaining molecular one-electron effective Hamiltonians from first principles has been developed in ref. 15 and has been extended for polymer systems in refs. 7 and 16. The main advantages of the VEH model are: (i) it is completely theoretical; (ii) it is not basis set dependent; and (iii) it gives ab initio quality results with negligible computer time, due to the evaluation of only one-electron integrals and the complete avoidance of SCF iterative cycles.

The VEH results for ionization potential (IP) bandwidth of the highest occupied band (BW), and π-electron bandgap (E_g) are summarized in Table II. Also included in the table are experimental estimates of IP and E_g where available and the maximum conductivities (σ) obtained on doping with I_2 (a relatively weak electron acceptor) and AsF_5 (a strong electron acceptor). Representative references for the experimental IP, E_g, and σ values are 1-5, 7-11, 18-27. The theoretical IP values have been scaled downward by 1.9 eV to correct approximately for polarization energy and possible shortcomings of the model.[7] Though the 1.9 eV correction is quite reasonable,[28] our IP results should be viewed as having been scaled to the experimental estimate for trans polyacetylene.[8,18]

The IP values are in good agreement with available experimental estimates. The IP for PPP and PPS are significantly larger than PA, thus explaining why I_2 works only for PA. The IP for polybenzothiophene, PBT, the product expected after intramolecular bridging of PPS, is seen to have a substantially lower IP than PPS. In fact, our theoretical estimate agrees with the experimental estimate from junction measurements on heavily doped (and therefore chemically altered) PPS. The BW values also show a satisfactory qualitative correlation to the conductivities achieved on AsF_5 doping.

Note that the BW value for PPS is fairly large, 1.2 eV, compared to the perpendicular PPP case, 0.2 eV. This result is a direct indication of the important role played by the sulfur atoms in providing a communication path for the π-systems of the perpendicularly oriented phenyl rings in PPS.

The E_g values obtained by the VEH technique are in surprisingly good agreement with experiment - especially when we consider the fact that no excited state information has been included in the parameterization because of the well-known poor performance of one-electron ab initio techniques regarding excited state energies. E_g values for nonplanar systems are not given because of the previously mentioned tendency for this method to give spuriously low σ* bands.[6]

The theoretical results for polydiacetylenes, $+(R)C-C\equiv C-C(R)+_x$, suggest these materials should also form highly conducting complexes, perhaps even with iodine. We have doped a number of PDA systems (different R groups) with I_2 and AsF_5, but have not found any case where a conductivity greater than 10^{-6} S/cm can be achieved. With AsF_5 doping, substantial chemical interaction with the R groups is indicated in some cases. The large R groups, necessary for the solid-state synthesis of PDA single crystals, may also impose steric restrictions which inhibit favorable polymer/dopant interaction.

TABLE II. Summary of VEH results for ionization potential (IP),[a] bandwidth of highest occupied band (BW), and bandgap (E_g). All energies in eV; conductivities in S/cm.[b]

Polymer	IP[c]	BW[d]	E_g[c]	$\sigma(AsF_5)$	$\sigma(I_2)$
Polyacetylene					
trans	4.7 [4.7]	6.5	1.4 [1.8]	1200	500
cis-transoid	4.8	6.4	1.5 [2.0]	-	-
trans-cisoid	4.7	6.5	1.3		
Polymethylacetylene	4.5	3.7	1.4	-	10^{-3}
Poly(1,6-heptadiyne)	4.4	2.5	1.4 [1.8]	0.1	0.1
Polydiacetylene					
acetylenic	5.1 [5.2]	3.9	2.1 [2.1]	0	0
butatrienic	4.3	4.5		-	-
Poly(p-phenylene)					
coplanar	5.5	3.9	3.2	-	-
twisted (22°)	5.6 [5.5]	3.5	- [3.5]	500	0
perpendicular	6.9	0.2	-	-	-
Poly(m-phenylene)					
coplanar	6.2	0.7	4.5	-	-
twisted (28°)	6.2	0.2	- [4.9]	0.001	0
Poly(p-phenylene vinylene)	5.1	2.8	2.5 [~3]	3	0
Poly(p-phenylene xylylidene)	5.6	2.5	3.4	-	-
Polybenzyl	6.5	0.6	-	0	0
Poly(p-phenylene sulfide)	6.3	1.2	-	0.01	0
Polybenzothiophene	5.5 [5.6]	1.3	3.1 [~3]	3	-

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[a] Theoretical IP after subtracting 1.9 eV to correct, approximately, for polarization energy.

[b] Zero conductivity in the table indicates $\sigma < 10^{-5}$ S/cm; dash indicates unknown.

[c] Experimental estimates for IP and E_g, where available, are given in brackets.

[d] BW values refer to the smallest possible unit cell taking into account screw axis symmetry.

IV. SUMMARY

Though PPP clearly has a higher ionization potential and a higher bandgap than PA, the profiles of their optical and electrical properties for the doped systems are very similar. They both would appear to form "simple complexes" on doping. This behavior is in contrast to the PPS system where chemical modification is seen to play an important role in achieving high conductivity on doping. Polymers which undergo chemical modification may be the most technologically significant of the conducting polymer systems, since processible polymers such as PPS can be used in that case. With this dopant-induced chemical modification, there need not be any conflict between the flexible backbone needed for processibility and the rigid backbone which is apparently required for high conductivity. Neither PPP nor PA is processible via conventional polymer techniques.

The general similarity of doped-PPP and doped-PA, particularly with regard to their electrical properties, is an observation which requires some emphasis, especially with regard to developing theoretical models for these highly conducting doped systems. Models, such as the soliton model, which can be applied to PA but cannot be generalized to PPP, must be viewed with caution, particularly when extended to describe high doping levels.

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