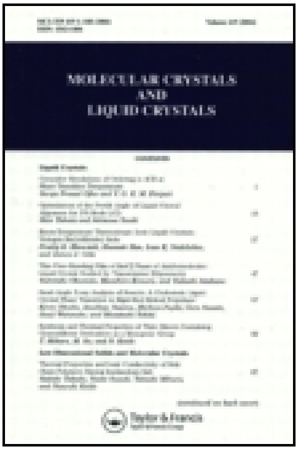

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Electrically conducting polyaromatic sulfides

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ELECTRICALLY CONDUCTING POLYAROMATIC SULFIDES

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Poly(p-phenylene sulfide), PPS, a melt and solution processible polymer, can be made highly conducting by doping with strong electron acceptors such as AsF_5. Virgin PPS is an insulator with a relatively high ionization potential compared to polyacetylene. This, coupled with its high melting and solubilization points, restricts possible dopants to those which are particularly aggressive and capable of reacting with PPS in the solid state. These aggressive dopants induce a variety of chemical changes in the polymer backbone upon doping. While fluorination and crosslinking occur to some extent, infrared spectra and independent chemical synthesis suggest that the predominant chemical change is <u>via</u> intrachain bridging (cyclization) of adjacent phenyl rings. In an attempt to find processible systems with lower ionization potentials and which are less prone to chemical modification, a variety of polyaromatic sulfides were prepared. The influence of polymer structure, morphology, and dopant-induced chemical modifications upon conductivity is discussed.

INTRODUCTION

Of the many, and rapidly growing number, of known polymers which can be made highly conducting (> 1 S cm^{-1}), only poly(p-phenylene sulfide), PPS, is processible by normal plastics technique. Typically, conductivities as high as 1 S/cm can be obtained with fibers, films or compacted powder pellets of PPS when treated with strong electron acceptors such as AsF_5.[1,2] Strong electron acceptors are dictated by the relatively high ionization potential of PPS (~ 6.3 EV)[3] relative to polyacetylene (4.7 eV).[3,4] Unfortunately, in addition to forming the desired charge transfer complexes, these aggresive dopants can induce a variety of complex reactions resulting in gross modification of the polymer backbone. Further, the high energy potential of these charge transfer complexes (ca + 1.5V vs. H_2/H^+) renders the conductive complex unstable to water vapor. However, environmental instability may limit but should not preclude technological applications of these conductive materials. An ultimate goal is to have conductive plastics which are processible and environmentally stable. Here, we examine some of the factors necessary to reach this goal.

RESULTS AND DISCUSSION

Conceptually, there are three important questions to answer when designing potential processible conductors:

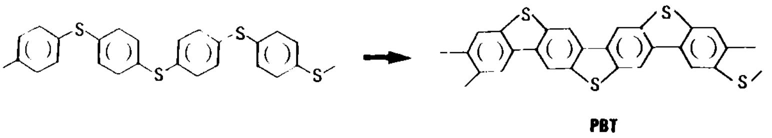
1. What structural features are important for polymer processibility?
2. What features are important for conductivity?
3. To what extent will these be mutually exclusive?

Polymer processibility is in part determined by the degree of chain flexibility, and the strength of intermolecular attractions. The entropy increase upon melting or solubilization of a polymer must provide a free energy term which exceeds the intermolecular enthalpy component. This entropy change is related to the energetically accessible configurations in the final state compared to those for the initial state, which is a function of polymer flexibility. Thus, comparing polymers having groups with similar cohesive energy densities, the incorporation of atoms or groups of atoms which increase rotational freedom within the polymer backbone generally serves to lower the melting point and increase the solubility of the polymer. The glass transition temperature tends to scale as a fraction of the melting temperture.

It is generally agreed that for a polymer to be electrically conducting a network of overlapping intra-or intermolecular orbitals is needed. This is clearly important for the creation of a large bandwidth and significant electron (or hole) mobility. Since most organic systems are closed shell systems (filled bands), one needs a mechanism for the creation of mobile electrons. This is generally accomplished by a "doping" process, (addition of an oxidizing or reducing agent) which gives rise to partially filled bands. Therefore, polymers which are easy to oxidize or reduce are desired. Both the conductivity and the stability of the polymer complex depend upon the proper marriage between the ionization potential or electron affinity of the polymer and energetics of charge transfer reaction of the dopant. If either the polymeric anion (cation) or the dopant-derived cation (anion) are easily oxidized (or reduced) by environmentally available species (O_2, H_2O, etc.), instability results.

One can see that the sulfur atom in PPS plays a unique role. In addition to introducing flexibility to the polymer backbone, the sulfur linkage provides for a continuous overlap of orbitals along the chain in PPS, even though the aromatic rings are essentially perpendicular to one another.[3,5] This polymer chain conformation, however, need not be retained as a result of the doping process.

Electrical conduction in PPS cannot be rationalized solely by these simple arguments. As mentioned earlier, strong electron acceptor doping of PPS appears to cause irreversible chemical modifications in the polymer. The virgin polymer, which analyzes for $(C_6H_{4.2}S_{1.0})_n$, is soluble in diphenyl ether at 220°C to greater than 10% by weight and shows a clear glass transition point (Tg 92°C) and melting point (Tm 280°C). However, after treatment with AsF_5 at room temperature to form the conductive complex ($\sigma \sim 3$ S/cm), and removal of the dopant species (inorganics), the resulting polymer is insoluble and infusible. It typically analyzes for $(C_6H_{2.68}S_{1.0}F_{0.3})_n$. Clearly the polymer has been fluorinated. More importantly, the resulting loss of hydrogen, as well as the loss of solubility and melting characteristics, suggests that the aryl rings on the polymer backbone have undergone further substitution, perhaps by aryl-aryl coupling. This is not unreasonable since it is well known that aromatics couple under oxidative conditions.[6,7,8] We have recently shown that AsF_5 induces the formation of dibenzothiophene linkages in PPS by adjoining adjacent aromatic rings.[9] (Eq. 1) In the limit



1

poly(benzothiophene), PBT would be formed. Closer inspection of PBT shows it consists of para-linked phenyl rings (poly p-phenylene) in which each aromatic ring is constrained to be coplanar by adjacent sulfur bridges. One could argue that this arrangement is ideal for conduction since it is well-known poly(p-phenylene) is a good conductor upon treatment with AsF_5 ($\sigma \approx 500$ S/cm).[10] This raises some serious questions about the role sulfur atoms play in the conduction mechanism in PPS. It might be that they just provide the necessary chain conformation and inductive activation for the bridging process to occur. Since the sulfur links between the rigid aromatic rings in PPS are the key to processibility, it is important to know if they are capable of supporting conduction along the polymer chain as well. Is doped PPS in the unbridged form a conductor? If so, how good is it?

In an attempt to answer these questions as well as to determine structural limitations to polymer conduction, we prepared a series of polymers structurally related to PPS, $(Ar\text{-}X)_n$, in which the nature of both the aromatic (Ar) and the link between them (X) was varied.[10]

Table 1 summarizes the results on doped polymer conductivity as a function of the nature of the link between aromatic rings. Here, and with all of the polymers reported in this work, the doping process with AsF_5 was conducted at -78°C, a temperature at which dopant induced chemical modification of the polymer backbone is greatly suppressed, unless otherwise noted. The conductivity obtained for PPS under these conditions is only 4×10^{-2} S/cm (entry 1) compared to 3 S/cm when doped at room temperature. Analysis of the material doped at -78°C indicates it has undergone only slight chemical modification.[9] When the sulfur link in PPS is replaced with oxygen, the conductivity of the resulting polymer/AsF_5 complex is at least two orders of magnitude lower. When this link is replaced by a methylene unit, one which does not have "p" orbitals to overlap with the π systems of the aromatics, only an insulating material is formed. The same result is obtained even if only every other sulfur atom in PPS is replaced with a methylene link (entry 3). This argues that "p" orbitals on the link are necessary for conduction in these polymers. In fact, when the methylene group in entry 3 is replaced by a carbonyl (entry 4), a conducting complex is formed upon doping, albeit one with a low conductivity. When this carbonyl functionality is replaced by a sulfone moiety (entry 5), again an insulating polymer is obtained. Here, the strong electron withdrawing nature of the sulfone group may cause localization of the positive charge on to the non-oxygenated sulfur atoms thereby greatly reducing electron mobility down the polymer chain. However, replacement of the sulfone groups with sulfoxide functionalities (entry 6) results in a polymer which exhibits conductivities similar to PPS. We have shown through infrared analyses that the sulfoxide functionality remains intact upon doping. These results show the important role the sulfur atoms play in supporting electronic conduction along the polymer chain in PPS.

Table 2 summarizes our results on the effect of the nature of the aromatic moiety on conductivity. As mentioned above, AsF_5 induces cyclization of adjacent aromatic rings giving rise to dibenzothiophene type structures along the polymer chain.[9] In fact, when the polymer which has every other sulfur atom in PPS incorporated into a thiophene ring [poly(thio-2,8-dibenzothiophenediyl), entry 1, Table 2] was prepared and doped, its conductivity was comparable to that of PPS. Further, its infrared spectrum after doping and removal of the inorganic doping agents strongly resembles that obtained from PPS. Thus, PPS and this material appear to be converted into essentialy the same composition after doping.[9]

When the linkage in PPS is changed from <u>para</u> to <u>meta</u> [poly(m-phenylene sulfide), PMPS, entry 2, Table 2] and the doping process is performed at temperatures greater than -25°C, a complex with a conductivity comparable to PPS is obtained. Infrared analysis shows that the original polymer has undergone extensive chemical modification. However, when PMPS was treated at -78°C with AsF_5, no chemical modification was noted and an insulating material was obtained. PMPS is a case where chemical modification of the polymer backbone is necessary for conduction to occur. This is reasonable since one cannot draw sensible resonance structures which delocalize charge along the polymer chain in PMPS. Based on steric and conformational arguments, we rationalize that the doping process induces bridging such that only every other sulfur atom in PMPS is incorporated into a thiophene ring. This polymer was prepared [poly(thio-3,7-dibenzothiophenediyl), entry 3, Table 2] and showed the surprisingly high conductivity of 18.5 S/cm upon AsF_5 doping.[12] This is at least an order of magnitude greater than that observed for PPS and is only about 20 times lower than for doped poly <u>p</u>-phenylene. In fact, the high conductivity could be rationalized on the basis that this polymer contains biphenyl units between sulfur links thus possessing more polyphenylene character. From the results in Table 2, it appears that in addition to continuous conjugation along the polymer chain, the incorporation of relatively large, co-planar sections of aromatic rings enhances the level of conductivity of the resulting polymer. Facilitation of electron transport between polymer chains via favorable stacking arrangements of aromatics might also be important.

As mentioned above, the conductivity of doped and unbridged PPS is unknown. An upper limit is probably 10^{-2} S/cm (entry 1, Table 1). In an attempt to get a lower limit on this value, we prepared a variety of methyl and fluoro substituted polyphenylenesulfides. These are listed in Table 3. The aim here was to prepare polymers which by virtue of substitution could not crosslink or bridge as a result of the doping process. Poly(2,5-dimethyl-1,4-phenylene sulfide) (entry 1, Table 3) upon doping is as conductive as PPS. Upon inspection of the polymer after doping, it was evident that adjacent phenyl rings bridged. Poly(2,6-dimethyl-1,4-phenylene sulfide),2,6-DMPPS, (entry 2, Table 3) which has the positions ortho to the sulfur atom blocked such that bridging of adjacent phenyl rings is precluded, showed a conductivity of only 2.3×10^{-5}. It would be tempting to assign this value as an upper limit for the conductivity in unmodified PPS. However, the steric requirements of the methyl groups must be considered. In fact, the tetramethyl derivative (entry 3, Table 3) was insulating on doping. Electron transport between chains, an important process for bulk conductivity in these systems, might be impaired by the steric requirements of the methyl substituents. Replacement of the methyl groups with fluorine, an atom whose steric requirements are nearly that of a hydrogen, gave a polymer with a bulk conductivity of 6.6×10^{-7}. This value is low, however, for probably two reasons; one, the doping levels achieved were only one-third those normally obtained with PPS; and two, the strong electron-withdrawing nature of the fluorine substituents may cause a considerable degree of charge localization on the sulfur atoms. These factors taken together seem to suggest that the conductivity obtained with 2,6-DMPPS represents at least a lower limit for the conductivity of unaltered PPS.

CONCLUSIONS

We have shown that the sulfur links between the aromatic rings in PPS support conduction along the polymer chains. Further, continuous orbital overlap along the polymer backbone, either in the virgin polymer, or as a result of chemical modification upon doping, is necessary for conduction in these systems. From the methyl and fluoro-substituted PPS derivatives, as well as from the low temperature doping experiments on PPS, we estimate the conductivity for doped and unaltered PPS to lie in the range of 10^{-4} - 10^{-2} S/cm.

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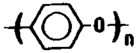
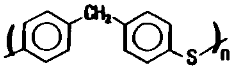
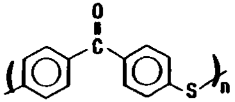
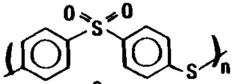
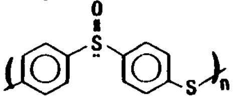
Table 1. Conductivity vs Nature Of The Link Between Aromatics

Entry	Polymer Structure	Thermal Characteristics(a)	Conductivity (S/cm) on doping with AsF_5 (b)
1		T_g 92°C, T_m 270°C	4×10^{-2}
2		T_g 85°C, T_m 238°C	1.4×10^{-4}
3		T_g 39°C, T_m 156°C	$<10^{-8}$
4		T_g 125°C, T_m 340°C	2.5×10^{-6}
5		T_g 179°C	$<10^{-8}$
6		T_g 131°C	7.5×10^{-3} (−78°C)^c 7×10^{-2} (+25°C)^d

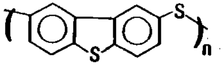
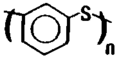
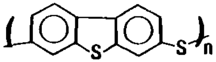
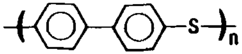
(a)Determined by differential scanning calorimetry (DSC) on the virgin polymer; T_g = glass transition temperature, T_m = melting temperature

(b)Powdered polymer was treated with AsF_5 gas at ca. 200 torr for 18 hr. at −78°C temperature (unless otherwise noted), excess AsF_5 and off-gases removed by dynamic vacuum, powders compacted into discs (10 mm. dia. x 1 mm. thick) and conductivities were measured at room temperature in a dry box by 4-point probe techniques. All polymers exhibited doping levels comparable to those obtained with PPS.

(c)Very slight chemical modification.

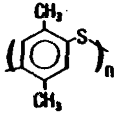
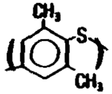
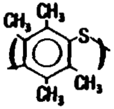
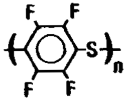
(d)Substantial chemical modification.

Table 2. Conductivity vs The Nature Of The Aromatic

Entry	Polymer Structure	Thermal Characteristics(a)	Conductivity (S/cm) on doping with AsF_5 (b)
1		T_g 182°C	4×10^{-1}
2		T_g 27°C, T_m 133°C	8×10^{-2} (-25°C)(c) $<10^{-8}$ (-78°C)
3		T_g 175°C, T_m 373°C	18.5
4		T_m 417°C	2.7×10^{-1}

(a)
Determined by differential scanning calorimetry on the virgin polymers.
(b)
See Table 1, footnote (b)
(c)
Doping at a temperature of -25°C or above causes substantial chemical modification in the polymer backbone.

Table 3. Methyl and Fluoro-Substituted PPS Derivatives

Entry	Polymer Structure	Thermal Characteristics(a)	Conductivity (S/cm) on doping with AsF_5 (b)
1		T_m 327°C	10^{-2}
2		T_g 123°C	2.3×10^{-5}
3		T_m 327°C	$<10^{-8}$
4		T_m 322°C	6.6×10^{-7} (c)

(a)
From DSC analysis; T_g = glass transition temperature, T_m = melting temperature
(b)
See Table 1, footnote (b)
(c)
Doped at room temperature but only a low doping level was obtained.