Polythiophenylene Synthesis through Multi-electron Transfer Process

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Summary: Superacidification of aromatic sulfoxides effects the electrophilic substitution reaction of the resulting hydroxysulfonium ions onto aromatic rings with the elimination of H_2O at room temperature. The product, the alkyldiarylsulfonium ion, allows the synthesis of alkylsulfonio-bridged (λ^4-alkylsulfanyliumdiyl) aromatic polymers. High molecular-weight poly(alkylsulfonioarylene) salts have been made accessible by the regioselective condensation of aryl sulfoxides. Polymers having a wide variety of structural dimensionalities such as linear, hyper-branched and ladder-type structures can be prepared by this method, which possess interesting properties such as good solubility in polar organic solvents and sometimes even in H_2O, susceptibility to nucleophiles to provide thioarylene derivatives, photo-degradability, and electric semiconductivity based on a 3d-2p interaction in aryl sulfonium ion.

Keywords: aryl sulfonium ion; polymer; polythiophenylene; superacidification of aromatic sulfoxides

Introduction

The synthetic process of a variety of alkyldiarylsulfonium salts and their corresponding polyelectrolytes, alkylsulfonioarylene ((λ^4-alkylsulfanyliumdiyl)arylene) polymers have been developed. The molecules span the range of dimensionalities from monomeric, zero-dimensional triorganylsulfonium salts through linear one-dimensional poly(alkylsulfonio-1,4-phenylene) derivatives, a hyperbranched polymer with fractal dimensionality of 1-2 and ladder-like pseudo two-dimensional thioniapolyacenes, to three-dimensional polymer networks. The synthesis of the multidimensional series is based on both the high regioselectivity and the high-yielding conversion of the super acid-induced condensation of aryl sulfoxides. The polymers can possess good solubility in polar organic solvents and sometimes even in H_2O, susceptibility to nucleophiles to undergo dealkylation to yield corresponding thioarylene derivatives, photo-degradability, and electric semiconductivity based on delocalized π-electrons through 3d-2p resonance. The polymers are thus useful as anion-exchange resins, precursors for high molecular-weight poly(thioarylene)s, polymeric proton generators in photo-resist technologies, key intermediates in photochemical recycling of an engineering plastic poly(thio-1,4-

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phenylene), and functional materials for optoelectronic devices. Here we focus on the synthesis and properties of a novel ladder-type polyelectrolyte, heteropolyacene.

Sulfonium Ions as New Sulfur Electrophiles

Our interest in sulfur electrophiles originates from the finding in the late 1980's that diphenyl disulfide undergoes oxidative polymerization under strongly acidic conditions to produce oligo(thio-1,4-phenylene), containing one disulfide bond in the chain, with a weight-averaged molecular weight of 5 x 10^3. The product is obtained as a white, highly pure powder, in contrast to the commercially available poly(thio-1,4-phenylene) (PPS) produced by the polycondensation of *p*-dichlorobenzene and sodium sulfide and contaminated with the eliminated salt. The active species of the polymerization is a phenylbis(phenylsulfenyl)sulfonium ion which electrophilically attacks the phenyl rings to substitute a hydrogen arom at the *para* position with the thioether bond. The electrophile attacks in the first step, giving rise to a positively charged intermediate (the arenium ion), and the leaving group (H^+) departs in the second step. The arenium ion (σ-complex) has not been isolated. Diphenyl disulfide is eliminated from the arenium ion to form the thioether bond, which is concurrent with the elimination of H^+. The oxidation of diphenyl disulfide with O_2 is catalyzed by an oxovanadium complex which reduces O_2 to H_2O with four electrons (Figure 1).[1-6]

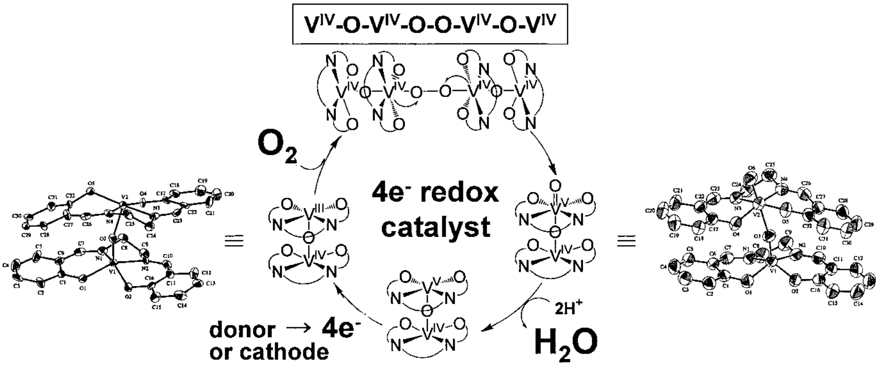


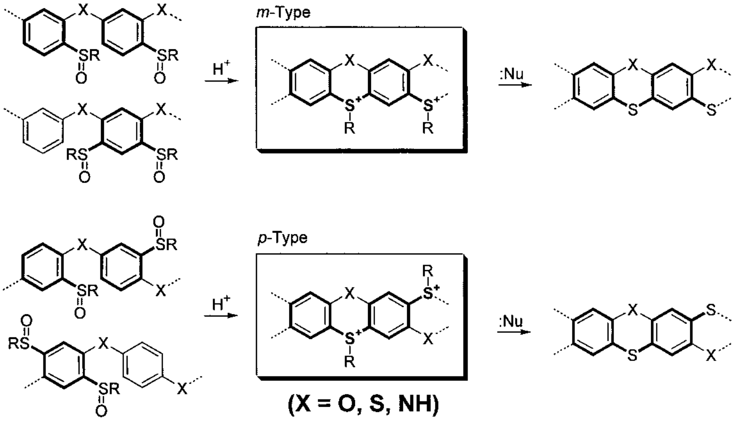
Fig. 1. Catalytic cycle of a μ-oxo divanadium complex in the four-electron reduction of O_2 to H_2O.

The multi-electron transfer process suppresses the formation of undesirable oxygenated by-products such as sulfoxides and sulfones because the partially reduced active oxygen species are not generated.

Sulfoxide bonds are so polarized ($R_1R_2S{=}O \leftrightarrow R_1R_2S^+{-}O^-$) that a number of electrophiles can attack at the negatively charged oxygen atom. The resulting activated sulfoxides are available for use as electrophiles (Swern reaction). A successful synthetic process of a high molecular-weight, structurally defined PPS has been devised using alkylsulfonioarylene polymers as precursors, taking advantage of their high solubility. The key prepolymer for PPS, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate), has been obtained by the super acid-induced polycondensation of methyl 4-(phenylthio)phenyl sulfoxide.[9-12] PPS has been exclusively obtained by the subsequent nucleophilic dealkylation of the prepolymer, taking advantage of the high-yielding conversion of alkylsulfonio groups to thioether bonds.

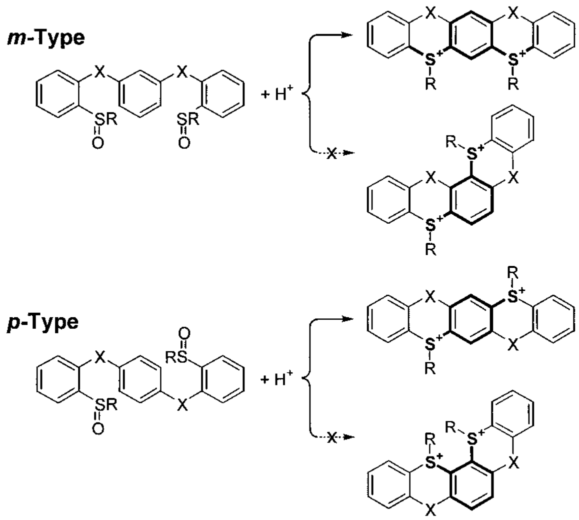
Synthesis and Properties of Heteropolyacenes

Novel synthetic approaches to preparing heteropolyacenes containing alkylsulfonio linkages have been developed. The synthetic concept of the heteropolyacene consists of a polymer-analogous super acid-induced condensation of aryl sulfoxides, as outlined in Scheme 1, which provides ladder-like polymers with benzenetetrayl repeating units linked with heteroatoms X and the alkylsulfonio groups. The ordered binding of X and the alkylsulfonio group (i.e., *m*- or *p*-type in Scheme 1) has been accomplished by the use of the corresponding prepolymer as the key intermediate bearing methylsulfinyl groups at suitable positions.



Scheme 1

This method is based on the highly regioselective condensation of the aryl sulfoxide during the six-membered ring formation, which suppresses the formation of isomeric by-products as shown in Scheme 2. The formation of defect-free heteropolyacenes is based both on the high-yielding conversions in the condensation of aryl sulfoxides and the high solubility of the resulting alkylsulfonioarylene polymers. Remarkable aspects of the heteropolyacene are the π-electron delocalization over the alkylsulfonio moiety, and the susceptibility to nucleophiles allowing the conversion of alkylsulfonio groups to thioether bonds (Scheme 1).



Scheme 2

Resonance Effects in Arylsulfonium Ions and Heteropolyacenes

The principal findings on heteropolyacenes include that the ring closure of the prepolymer bearing alkylsulfinyl groups to the corresponding heteropolyacene gives rise to a distinct bathochromical shift in the longest wavelength absorption and a drastic increase in the intrinsic electric conductivity. Thus, the issue for the heteropolyacenes has to do with whether the benzene rings could allow resonance through the cationic sulfonium site and thus develop π-conjugated ladder-like frameworks. The delocalization of the electron density into the low-lying vacant 3d orbitals of sulfur has been proposed in sulfur ylides ($R_2S^+\text{-}^-CR'_2 \leftrightarrow R_2S{=}CR'_2$) to rationalize the stabilization of the negative charge of the carbanion by the adjacent sulfur, though the preferred geometry of the carbon and sulfur atoms indicates that sulfur ylides do not contain appreciable C=S bond character. On the other hand, the p-π/d-π overlap and the charge delocalization in arylsulfonium moieties has been found in the (pentafluorophenyl)dihalosulfonium ion, which is indicated by the significant deshielding of the *ortho* and *para* ring fluorines in ^{19}F NMR. This is related to the proposed charge delocalization of the protonated aromatic thioketones into the aromatic ring through the mercaptocarbenium resonance forms. The charge delocalization has been demonstrated by the protonation-induced deshielding of the ring carbons and the shielding of the thiocarbonyl carbons in ^{13}C NMR, in contrast to the deshielding of the thiocarbonyl carbons in aliphatic thioketones due to the inductive effect. That the acidity of the *p*-(dimethylsulfonio)phenol ion ($pK_a = 7.30$) is higher than that of the *p*-(trimethylammonio)phenol ion ($pK_a = 8.35$) and that of the *m*-(dimethylsulfonio)phenol ion ($pK_a = 7.67$) is also indicative of the p-π/d-π interaction in the arylsulfonium moieties. Such an interaction contributes to the stabilization of the conjugate base through the quinonoid resonance form. In analogy to these observations, the NMR spectroscopic studies of the heteropolyacenes have been carried out[13] which reveal that the delocalization of the positive charge on the sulfur atom could also occur into the benzene ring and that it could be enhanced with the ladder-like framework.

The ^1H NMR spectra reveal that the CH_3S^+- atoms in the phenoxathiinium-type heteropolyacene[13] are deshielded by only 0.11 ppm compared to the $CH_3S(O)$- atoms in the prepolymer, poly(oxy-2-methyl-6-methylsulfinyl-1,4-phenylene); the magnitude of the deshielding is much smaller than that of the model compound of the repeating unit. In fact, a deshielding effect of 0.68 ppm is observed for the methyl protons in the 5-methylphenoxathiinium ion relative to those in 2-(methylsulfinyl)phenyl phenyl ether. In the methylsulfonio-1,4-phenylene ion (i.e., the corresponding polymer without the oxo linkage), the magnitude of the deshielding effect relative to the monomer, methyl phenyl sulfoxide, is even larger (1.1 ppm). On the other hand, a deshielding effect of *ca.* 0.9 ppm for the phenyl proton in the phenoxathiinium-type heteropolyacene relative to poly(oxy-2-methyl-6-methylsulfinyl-1,4-phenylene) is significantly larger than the deshielding effect of *ca.* 0.56 ppm for those in the 5-methylphenoxathiinium ion relative to 2-(methylsulfinyl)phenyl phenyl ether. These results can be rationalized by considering a significant carbenium ion contribution to the resonance structure of the phenoxathiinium-type heteropolyacene, the charge delocalization into the aromatic ring causing a decrease in the deshielding effect for the methyl protons and an increase in that for the phenyl protons.

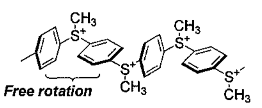
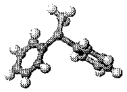
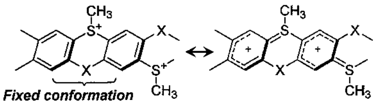
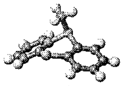
The model dimeric system provides further data for assessing the spectroscopic properties of the polymers. An important aspect is derived from the comparison of the crystal structures of 5-methylphenoxathiinium triflate and methyldiphenylsulfonium hexafluoroantimonate, the control of the 5-methylphenoxathiinium ion without the oxo linkage between the two benzene rings. The torsion angle of the best least-squares plane of the adjacent benzene units in the 5-methylphenoxathiinium ion (34.72°) is smaller than that in the methyldiphenylsulfonium ion

(83.12°). In addition, while a comparison of crystal structures of phenoxathiin and diaryl sulfides ((phenyl)C-S length: bis(4-methylphenyl) sulfide, 1.75 Å; bis(4-bromophenyl) sulfide, 1.75 Å) reveals that the oxo linkage seems to have no effect on the C-S bond lengths in sulfides, the S^+-C(phenyl) bond lengths in the 5-methylphenoxathiinium ion (1.77 Å) are shorter than those of the methyldiphenylsulfonium ion (1.78 Å), which is indicative of a slight increase in the S^+-C(phenyl) bond order. These characteristics are the indication that, with the planarized benzene rings in the 5-methylphenoxathiinium ion, the π-electron density can be accommodated by the methylsulfonio group.

Rigid planar conjugated systems are characterized by a distinct bathochromical shift of the longest wavelength absorption with the increasing number of fused aromatic subunits. Furthermore, they generally show very sharp absorption edges due to their rigid character. The significant red shifts of the absorption band upon the formation of the heteropolyacenes indicate that π electrons could delocalize through the polymer backbone. However, the absorption edge features are different from those expected for rigid π-conjugated polymers. The longest-wavelength band of the phenoxathiinium-type heteropolyacene is a broad shoulder near 600 nm. The featureless absorption edge tailing to *ca.* 940 nm indicates that the contribution of the delocalized state to the resonance form of the phenoxathiinium-type heteropolyacene is small and that π electrons can not delocalize throughout the backbone, due probably to the relative stability of the localized quinonoidal form. Nevertheless, the small optical band gap ($E_g = 1.3$ eV) estimated from the tailing edge is comparable to those of other π-conjugated ladder-like polymers.

Added support has been provided by the drastic change in the electronic properties upon the conversion of the phenoxathiinium-type heteropolyacene into the phenoxathiin-type heteropolyacene, a planarized analogue that is incapable of delocalization through the position occupied by the thioether bond; while the phenoxathiinium-type heteropolyacene is a semiconductor with an intrinsic electric conductivity (without dopants) of $\sigma = 2 \times 10^{-5}$ S cm^{-1}, the phenoxathiin-type heteropolyacene is an insulator ($\sigma < 10^{-11}$ S cm^{-1}). The advantage of the ladder-like framework for the 3d-2p resonance is evidenced by the less deshielded sulfoniomethyl protons, the shortened (phenyl)C-S^+ bond, and the intrinsic semiconductivity as summarized in Table 1. On the other hand, the highly deshielded CH_3S^+- atoms in alkyldiarylsulfonium ions with unconstrained phenylene conformations reveal the lack of noticeable 3d-2p resonance effects.

Table 1. Comparison of properties between linear methylsulfonio-arylene polymers and heteropolyacenes, proving π-electron delocali-zation over planarized arylsulfonium moieties.

	Structure	S^+-CH_3 (^1H NMR)	C-S^+ length (X-ray)	σ (Electric conductivity)
Linear Polymer		3.60~3.85 ppm	1.78~1.81 Å 	< 10^{-11} S/cm
Polyheteroacene		2.19~3.16 ppm	1.76~1.77 Å 	~10^{-5} S/cm

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