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Accounts

Alkylsulfonioarylene and Thioarylene Polymers Derived from Sulfonium Electrophiles

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Superacidification of sulfoxides and sulfinates effects the electrophilic substitution reaction of the resulting hydroxysulfonium ions onto aromatic rings with the elimination of H_2O at room temperature. The present account emphasizes the utility of the reaction for use as an elementary step in organic synthesis. The product, the alkyldiarylsulfonium ion, often quantitatively obtained, allows the synthesis of alkylsulfonio-bridged (λ^4-alkylsulfanyliumdiyl) aromatic polymers. High molecular-weight poly(alkylsulfonioarylene) salts with a wide range of structural dimensionalities from linear to network architectures have been made accessible by the regioselective condensation of aryl sulfoxides. The polymers 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, according to the dimensionality of the molecule. The synthetic chemistry of the alkylsulfonioarylene polymers as well as their possible applications in high molecular-weight poly(thioarylene) synthesis, photochemical recycling processes of an engineering plastic poly(thio-1,4-phenylene), and photo-resist technologies, are reviewed.

The studies of sulfonium ions have usually focused on trialkylsulfonium and dialkylarylsulfonium ions because they can participate in several synthetically valuable reactions.[1] Typically, they are susceptible to carbon-sulfur bond cleavage via nucleophilic displacements. Warming the sulfonium salt may cause elimination of a β-hydrogen to yield a mixture of a sulfide and an alkene.[2] Proton abstraction from the sulfonium ion by treatment with a strong base gives a sulfur ylide which can undergo molecular rearrangement to form a sulfide. The wide application of stable sulfonium ions is due primarily to their use in synthesis. The ever-increasing synthetic importance of derived sulfur ylides[3] is evident, especially in the preparation of epoxides and cyclopropanes. The importance of the photochemistry of aliphatic sulfonium salts, useful as photoacid generators, has been recognized because of the increasing requirements of ArF excimer laser lithography for nanoscale fabrication of semiconductor devices.[4] Photochemical decomposition is the initial stage of the acid-generator process of aliphatic sulfonium salts in lithography.

We have developed the chemical procedures to prepare a variety of alkyldiarylsulfonium salts and their corresponding polyelectrolytes, alkylsulfonioarylene ((λ^4-alkylsulfanyliumdiyl)arylene) polymers. If one varies the aryl group, a diverse range of molecular topologies can be realized, and these have been structurally characterized. 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 the fractal dimensionality of 1–2, and ladder-like pseudo two-dimensional thioniapolyacenes, to three-dimensional polymer networks (Fig. 1). The synthesis of this multidimensional series is based on both the high regioselectivity and the high-yielding conversion of the super acid-induced condensation of aryl sulfoxides. Continued interest in the synthesis of these mateials is driven by academic interests as well as potential industrial applications. For example, 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-phenylene), and functional materials for optoelectronic devices.

This account presents an overview of our work and of related investigations of other groups in designing functional materials based on alkylsulfonioarylene polymers and in demonstrating their utility in certain applications. This article will focus on our efforts in developing the aromatic electrophilic substitution of sulfonium ions for use as elementary reactions in organic synthesis and as a novel scaffold for the synthesis of

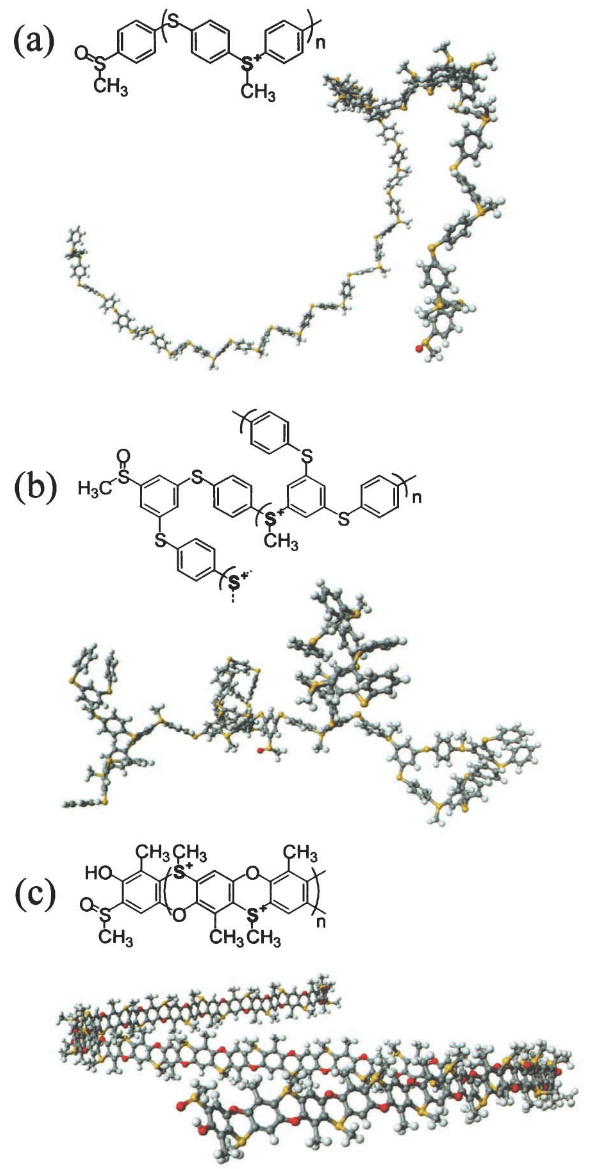
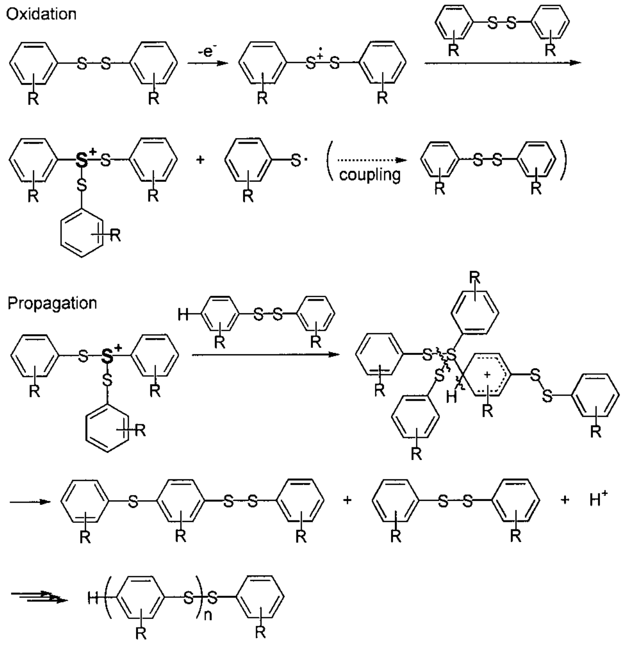


Fig. 1. Snapshots of methylsulfoniophenylene chains containing 45 benzene rings with (a) a linear, (b) a hyperbranched, and (c) a phenoxathiinium-type ladder-like structure during a molecular dynamics simulation at 300 K. The conformations are energy-minimized by repeated force-field minimization and annealing dynamics simulations. Carbon atoms are shown as grey; hydrogen, white; oxygen, red; and sulfur, yellow.

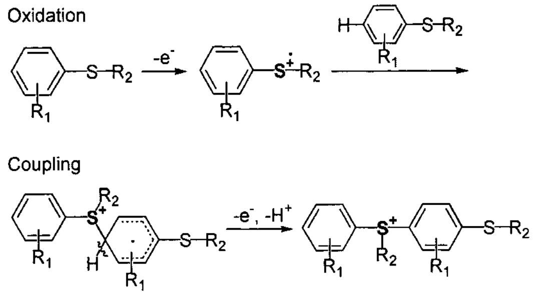
sulfur-containing polymers. In addition, more recent work in the design of new monomers that permits the convenient synthesis of ladder-like molecules will be discussed, as well as the opportunities they offer for materials applications. Finally, some research directions will be suggested for applications of these materials and for new monomer designs.

1. Synthesis and Properties of Linear Polymers

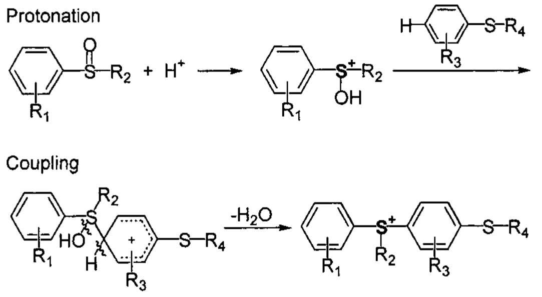
1.1 Sulfonium Ions as New Sulfur Electrophiles. Our interest in sulfur electrophiles originates from the finding in the late 1980's that diphenyl disulfide undergoes oxidative polymerization under strongly acidic conditions to produce oligo(thio-1,4-phenylene), containing one disulfide bond in the chain, with a weight-averaged molecular weight of 5×10^3.[5] 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. A linear thio-1,4-phenylene structure without any branching or cross-linking has been confirmed by spectroscopy. Further modification of the oligomer has been achieved by the thermolysis or the reductive cleavage of the disulfide bond as a functional group that is mainly located at the end of the chain.[6] 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 (Scheme 1). 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 may be concurrent with the elimination of H^+. A model compound of the active species, methylbis(methylsulfenyl)sulfonium hexachloroantimonate ($[CH_3S(SCH_3)_2][SbCl_6]$), has been isolated by the oxidation of dimethyl disulfide.[7] The reaction proceeds in nonpolar solvents such as CH_2Cl_2 and $(CHCl_2)_2$ in the presence of strong acids such as CF_3SO_3H and CF_3CO_2H to suppress the nucleophilic decomposition of the sulfonium ion. A variety of oxidants effect the oxidation of diaryl disulfides to the sulfonium ions. The earliest oxidation with Lewis acids[8] was then expanded successfully to oxidation with quinones,[9] anodic oxidation,[10] photo-oxidation,[11] and finally to the oxovanadium-catalyzed O_2-oxidation.[12] The O_2-oxidative polymerization of diphenyl disulfide with the oxovanadium catalyst has been described in a textbook[13] as a synthetic route to PPS having possible commercial utility. The reaction is also applicable to the synthesis of alkyl-substituted polymers. For example, bis(3,5-



Scheme 1.



Scheme 2.



Scheme 3.

dimethylphenyl) disulfide and bis(2,5-dimethylphenyl) disulfide yield poly(thio-2,6-dimethyl-1,4-phenylene) and poly(thio-2,5-dimethyl-1,4-phenylene), respectively. The higher molecular weights of these polymers are based on their higher solubility.

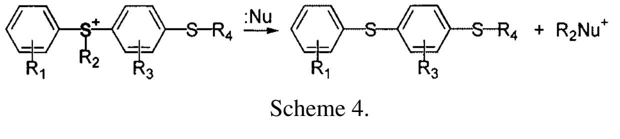
Sulfur nucleophiles are typically involved in aromatic sulfonation with $H_3SO_4^+$ or $H_2S_2O_7$, in halosulfonation with $ClSO_2OH$, and in sulfurization with SCl_2 and $AlCl_3$.[14] Poly(thioarylene)s have also been prepared by the sulfurization of a variety of aromatic compounds with SCl_2 or S_2Cl_2 coupled with the oxidation of concomitant disulfide bonds with quinones.[15] Phenylbis(phenylsulfenyl)sulfonium ion is a new addition to those conventional sulfur nucleophiles, which have prompted extensive studies because of their synthetic utility (vide infra).

Asymmetric alkyldiarylsulfonium ions are synthesized by the oxovanadium-catalyzed O_2-oxidative coupling of alkyl aryl sulfides (Scheme 2).[16] The cation radicals produced by the oxidation of alkyl aryl sulfides electrophilically attack the phenyl ring to produce the sulfonium ions. The oxidative coupling of alkyl aryl sulfides with O_2 is catalyzed by bis(acetylacetonato)oxovanadium(IV) ($VO(acac)_2$) in the presence of tetrabutylammonium perchlorate, CF_3SO_3H, and $(CF_3CO)_2O$ in CH_2Cl_2.[16] The coupling reaction is accompanied by quantitative O_2 uptake; for each mole of O_2 consumed, 2 moles of the product are obtained. A wide range of alkyl aryl sulfides are coupled to produce the corresponding sulfonium ions in almost 100% yield. However, cyclopropyl phenyl sulfide is not coupled because of the concomitant elimination of a labile methine proton. O_2-Oxidative coupling of diphenyl sulfide does not proceed because its oxidation potential (1.7 V vs Ag/AgCl) is higher than those of sulfides bearing electron-donating alkyl groups; the cyclic voltammogram of methyl phenyl sulfide exhibits an irreversible oxidation peak at a lower potential (1.5 V vs Ag/AgCl) in an electrolyte solution of CH_2Cl_2. The isolated coupled sulfonium ion (methyl[4-(methylthio)phenyl]phenylsulfonium perchlorate) is oxidized at potentials higher than 1.9 V (vs Ag/AgCl); incorporation of the electron-withdrawing alkylsulfonio groups results in a significant positive shift in the oxidation potential that retards the further oxidation of the sulfonium ions.[16] The oxidative coupling of an alkyl aryl sulfide is also achieved by the electrolytic oxidation of the sulfide in sulfolane in the presence of $LiClO_4$[17] and by chemical oxidation with $SbCl_5$.[18]

The sulfoxide bond is so polarized ($R_1R_2S{=}O \longleftrightarrow R_1R_2S^+{-}O^-$) 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).[19] On the other hand, the super acid-induced condensation of methyl phenyl sulfoxide with thioanisole yields the methyl[4-(methylthio)phenyl]phenylsulfonium ion which is isolated as a stable perchlorate salt (Scheme 3).[20] The protonated sulfoxide, the hydroxy(methyl)phenylsulfonium ion, electrophilically attacks the phenyl ring of thioanisole to yield the coupled sufonium ion with the elimination of H_2O. The reaction has been applied to the condensation of a variety of alkyl aryl sulfoxides and alkyl aryl sulfides (Scheme 3). Such condensation is influenced by the acidity of the reaction mixture.[20] The strongest Brønsted acid, CF_3SO_3H ($H_0 = -14.1$), is the most effective. The reaction is still almost quantitative in strong acids such as H_2SO_4 and CH_3SO_3H, but hardly proceeds at all in weaker acids such as CF_3CO_2H and CH_3CO_2H. Previous studies on the acid-base equilibrium for the protonation of methyl phenyl sulfoxide ($C_6H_5S(O)CH_3 + H^+ \rightleftarrows C_6H_5S^+(OH)CH_3$; $K_a = [C_6H_5S(O)CH_3][H^+]/[C_6H_5S^+(OH)CH_3]$) provided the reliable pK_a value of -2.27 ± 0.2.[21] Thus only strong acids with H_0 ($= pK_a - \log[C_6H_5S^+(OH)CH_3]/[C_6H_5S(O)CH_3]$) lower than -2.27 induce the condensation of methyl phenyl sulfoxide with thioanisole and that CF_3CO_2H ($H_0 = -2$) and CH_3CO_2H ($H_0 = 2$) are ineffective because they can not protonate the sulfoxide.[20]

The orientation and the reactivity of the phenyl ring in thioanisole toward the electrophile at various temperatures have been studied in $(CHCl_2)_2$ as the solvent.[22] At temperatures lower than 40 °C, the condensation of thioanisole with the hydroxy(methyl)phenylsulfonium ion is regioselective to give exclusively the methyl[4-(methylthio)phenyl]phenylsulfonium ion without the *ortho*-substituted product. Raising the reaction temperature gives rise to the *ortho* substitution to yield the methyl[2-(methylthio)phenyl]phenylsulfonium ion as the side product. However, the minor amount of the side product (only 1.3% of the total coupled product) even at 100 °C demonstrates the high regioselectivity of the condensation.[22]

Another important feature of alkyldiarylsulfonium ions is the nucleophilic dealkylation which proceeds quantitatively to produce the corresponding diaryl sulfides (Scheme 4). Typically, the methyl[4-(methylthio)phenyl]phenylsulfonium ion is demethylated with pyridine to produce 4-(methylthio)phenyl



Scheme 4.

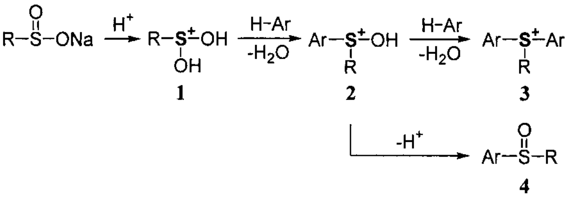
phenyl sulfide and an *N*-methylpyridinium salt.[20] The predominant asymmetric diaryl sulfide formation has been confirmed in the super acid-induced condensation of methyl phenyl sulfoxide with diphenyl ether, diphenyl sulfide, and naphthalene, followed by demethylation with pyridine.

The alkyldiarylsulfonium ions are stable and can even be isolated as single crystals (vide infra). The reaction of the alkyldiarylsulfonium ion with nucleophiles (:Nu) is regioselective to yield exclusively the dealkylated products, diaryl sulfides, without the formation of dearylated side products. Reasonable accounts for these properties have been provided by PM3 semiempirical MO calculations of the sulfonium ions.[20,23] The LUMO level of the methyldiphenylsulfonium ion (-5.40 eV) is the highest among the values calculated for sulfonium cations (-6.33 eV for the chlorodiphenylsulfonium ion, -6.73 eV for the (trifluoromethyl)diphenylsulfonium ion, and -6.86 eV for the (methylsulfenyl)diphenylsulfonium ion), and is even higher than that of trityl ion (-6.3 eV) which is well-known to be isolated as a stable salt.[20] On the other hand, the two-center energies equivalent to the bond strength reveal that the methyl C–S$^+$ bond (-14.8 eV) susceptible to nucleophilic cleavage (Scheme 4) is weaker than the phenyl C–S$^+$ bond (-15.9 eV).[20]

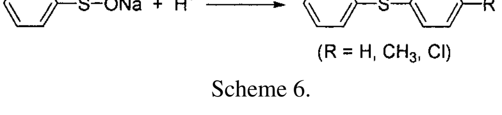
Tetraethylammonium bromide, iodide, and chloride also effect the nucleophilic dealkylation of alkyldiarylsulfonium ions to yield diaryl sulfides through an S_N2 mechanism.[22] Kinetic analysis on the demethylation of methyl[4-(methylthio)phenyl]phenylsulfonium triflate to methyl 4-(phenylthio)phenyl sulfide has been performed using halide ions as nucleophiles.[22] Methyl[4-(methylthio)phenyl]phenylsulfonium triflate and methyl 4-(phenylthio)phenyl sulfide show UV absorption bands at $\lambda_{\mathrm{max}} = 294$ nm ($\varepsilon_{\mathrm{max}} = 1.90 \times 10^4$ cm^{-1} M^{-1}) and $\lambda_{\mathrm{max}} = 273$ nm ($\varepsilon_{\mathrm{max}} = 1.78 \times 10^4$ cm^{-1} M^{-1}), respectively, in CH_3CN. A series of UV spectra recorded during the demethylation of the methyl[4-(methylthio)phenyl]phenylsulfonium ion show an isosbestic point at 282 nm which indicates the quantitative conversion of the sulfonium ion to the sulfide. The demethylation obeys a pseudo first-order rate law. The typical rate constant ($k = 42$ M^{-1} s^{-1}) has been evaluated for the demethylation of methyl[4-(methylthio)phenyl]phenylsulfonium triflate with tetraethylammonium bromide in CH_3CN at 25 °C.[22] The rate constants reflect the usual order of halide nucleophilicity ($I^- > Br^- > Cl^-$). The rate constant is also influenced by the counter ion of the sulfonium ($SbCl_6^- > CF_3SO_3^- = ClO_4^-$), and the alkyl group (the methyl[4-(methylthio)phenyl]phenylsulfonium ion > the phenylpropyl[4-(propylthio)phenyl]sulfonium ion). The activation energy (E_a) and the frequency factor (A) have been determined by Arrhenius plots.[22] The values of E_a and A for the demethylation of methyl[4-(methylthio)phenyl]phenylsulfonium triflate with tetraethylammonium bromide are $E_a = 94$ kJ mol^{-1} and $A = 9.5 \times 10^{15}$ M s^{-1}, and those for phenylpropyl[4-(propylthio)phenyl]sulfonium triflate are $E_a = 92$ kJ mol^{-1} and $A = 8.7 \times 10^{14}$ M s^{-1}. It is clear that the dealkylation rate constant is dominated by the frequency factor that decreases with bulky leaving groups due to the steric effect. The kinetics of the dealkylation also depend on the permittivity of the solvents. The largest rate constant has been observed in CH_2Cl_2 with low permittivity ($\varepsilon = 10$), which reflects the typical solvent effect in the nucleophilic reaction through the solvation of ionic species. Nucleophilic dearylation of triarylsulfonium ions has not been achieved because of their higher stability and lower reactivity due to the resonance effect.[22]

Sulfoxides are generally prepared by controlled oxidation of sulfides. The choice of oxidant and the reaction conditions are critical to avoid further oxidation to the sulfone. On a small scale, the preferred reagents are (i) sodium metaperiodate in aqueous CH_3OH at 0 °C, (ii) *m*-chloroperbenzoic acid in CH_2Cl_2 or $CH_3CO_2C_2H_5$, the latter being more useful since it can be used at lower temperatures (-40 °C), and (iii) *t*-butyl hypochlorite in CH_3OH. The asymmetric oxidation of an alkyl aryl sulfide with a chiral oxidant such as a peroxotitanium complex (a Sharpless reagent) can provide a route to chiral sulfoxides. Sulfoxides may also be obtained by hydrolysis of halosulfonium salts; this route has been applied to prepare ^{18}O-labelled sulfoxides. Most sulfonium salts are synthesized via sulfides or sulfoxides. The typical conventional methods are the reaction of aryl Grignard reagents with diphenyl sulfoxide,[24] the copper-catalyzed arylation of aryl sulfides with diaryliodonium hexafluorophosphate,[25] and the reaction of aryl sulfides with methyl triflate.[26] Sulfinic acids are convenient starting materials for the synthesis of sulfones, sulfinic esters, sulfinamides, and their derivatives. The electrophilic reaction of sulfinic acids through protonation of the sulfinyl group has also been reported.[27] The super acid-induced condensation of aromatic compounds with sulfinate salts such as sodium methanesulfinate and sodium benzenesulfinate[28] has been established as a convenient one-pot synthesis of sulfoxides and sulfonium salts (Scheme 5).[27]

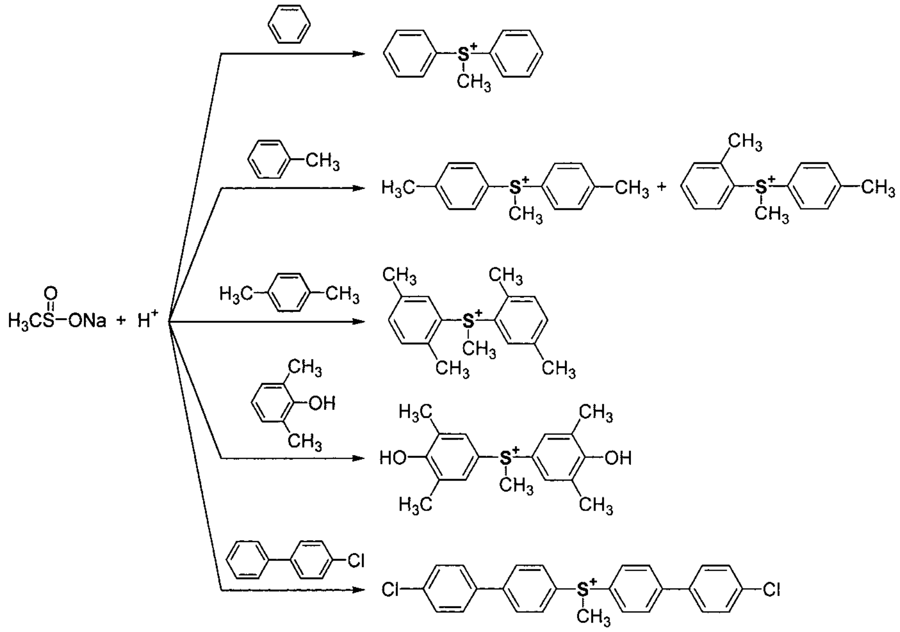
The reaction of sulfinates with aromatic compounds in 1:2 mol ratio has been performed in CF_3SO_3H. The sodium sulfinates, almost insoluble in CF_3SO_3H, are gradually dissolved as the reaction proceeds. The usual workup after the reaction gives the corresponding sulfonium salts **3** or sulfoxides **4** (Scheme 5).[27] Sulfoxides are the predominant products in > 98% yield when sodium benzenesulfinate is reacted with benzene, toluene, or chlorobenzene (Scheme 6). The reaction of sodium methanesulfinate and chlorobenzene gives 4-chlorophenyl methyl sulfoxide in 73% yield. Butyl phenyl sulfoxide is obtained in 36% yield from sodium 1-butanesulfinate and benzene. On the other hand, the reaction of sodium methanesulfinate with benzene gives methyldiphenylsulfonium tri-



Scheme 5.



Scheme 6.



Scheme 7.

flate in 92% yield. The corresponding sulfonium ions are obtained almost quantitatively from toluene, *p*-xylene, and 2,6-dimethylphenol by condensation with sodium methanesulfinate (Scheme 7). The condensation of sulfinates and aromatic compounds presumably proceeds through the electrophilic reaction of a sulfonium ion **1** in Scheme 5 as the active species produced by the protonation of the oxygen atom of the sulfinic acid in CF_3SO_3H. The sulfonium ion **1** has a lower LUMO level (−6.56 eV) than those of conventional sulfurizing agents such as SCl_2 (−2.60 eV), S_2Cl_2 (−3.24 eV), CH_3SCl (−1.32 eV), and C_6H_5SCl (−1.55 eV), which means that it can act as a powerful electrophile to attack a variety of aromatic compounds to yield the arylated sulfonium ion **2**. The selectivity of the overall reaction (sulfonium **3** vs sulfoxide **4**) may depend on the relative reactivity of the sulfonium ion **2** with the additional aromatic compounds. The electrophilic reaction of the sulfonium ion **2** is suppressed with aromatic compounds bearing electron-withdrawing groups such as chlorobenzene (Brown's substituent constant $\sigma_p{}^+ = 0.11$), which leads to the predominant formation of the sulfoxide **4** through the deprotonation of the sulfonium ion **2**.[27] On the other hand, the formation of the diarylsulfonium ion **3** is favored with aromatic compounds bearing electron-donating groups with lower $\sigma_p{}^+$.[27]

The reactivity of sulfonium compounds as electrophilic reagents and as electron acceptors is related to the atomic arrangement around the sulfur atom. A number of crystal structures of interesting sulfonium salts have been reported, such as those of dihalosulfonium salts[29] and an aurated sulfonium salt.[30] However, little attention has been given to a systemized study of the crystal structure of aromatic sulfonium salts. In attempts to obtain typical parameters for bond lengths and angles and torsional angles of aromatic sulfonium compounds, typical alkyldiarylsulfonium salts, methyldiphenylsulfonium hexafluoroantimonate and 1,4-bis(methylphenylsulfonio)benzene bis(hexafluorophosphate), have been subjected to X-ray crystallographic analysis.[31] The sulfur atom in the methyldiphenylsulfonium ion (Fig. 2(a)) covalently bonded with the three carbon atoms extends 0.747 Å above the $C_\alpha C_\beta C_\gamma$ plane. The arrangement of the four atoms represents a typical trigonal pyramidal structure. The bond lengths of the sulfur atom and the phenyl carbons are indicative of the oxidation state of the sulfur atom. Indeed, the S–C_β and S–C_γ bond lengths (1.78 Å) are slightly longer than the C–S bond length of diaryl sulfides

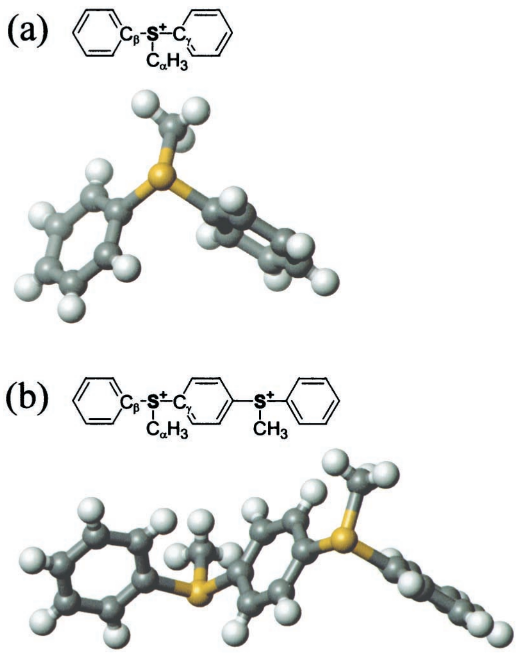


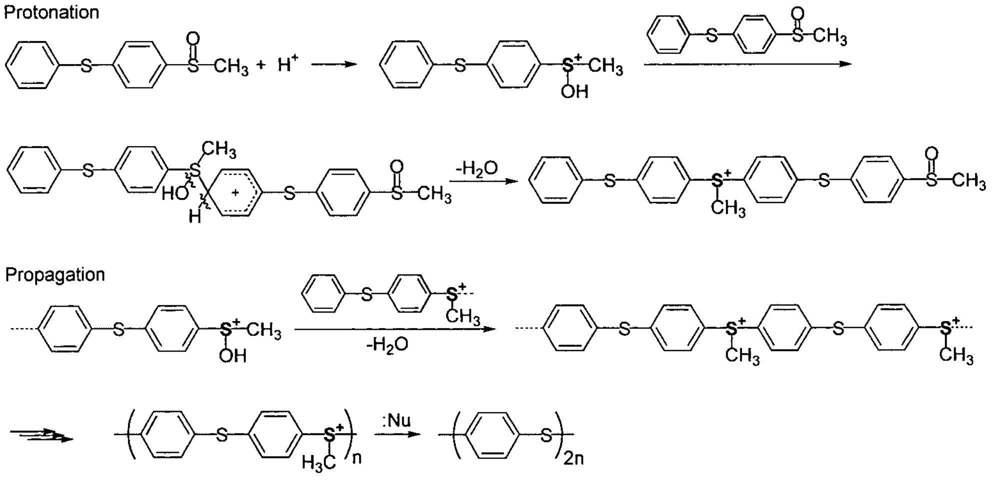
Fig. 2. Structures of the cations of methyldiphenylsulfonium hexafluoroantimonate (a) and 1,4-bis(methylphenylsulfonio)benzene bis(hexafluorophosphate) (b) determined by X-ray crystallography.

such as bis(4-methylphenyl) sulfide (1.75 Å) and bis(4-bromophenyl) sulfide (1.75 Å)[30] due to the decrease in the electron density of the 3p lone pair which resonate with the π electrons of the benzene ring. The enhanced p-character of the C–S bond and the s-character of the sulfur atom of the sulfonium ion compared to those of sulfides are also revealed by the significant decrease in the C–S–C bond angle upon the conversion of sulfide into sulfonium (the methyldiphenylsulfonium ion, 103.6(3)°; bis(4-methylphenyl) sulfide, 109°; bis(4-bromophenyl) sulfide, 109°; diphenyl sulfide, 113°).[2] The S–C_α bond length (1.804(8) Å) is comparable with the value of typical alkylsulfonium compounds.[32] The 1,4-bis(methylphenylsulfonio)benzene ion (Fig. 2(b)) occupies a C_2 crystallographic site symmetry. The sulfur atom, surrounded by the three carbon atoms, extends 0.755 Å above the $C_\alpha C_\beta C_\gamma$ plane; this represents a trigonal pyramidal arrangement. The S–C_β and S–C_γ bond lengths are longer than the C–S bond length of diaryl sulfides.[2] The S–C_α bond length (1.76(2) Å) is typical of alkylsulfonium compounds.[32] The almost spherical hexafluorophosphate anion is located near the sulfonium groups. The positions of the three carbon atoms around the sulfur atom show that the unshared electrons on the sulfur atom, unlike those of nitrogen in quaternary ammonium salts, hold their configuration to accomplish the tetrahedral arrangement. Comparison of the two crystal structures in Fig. 2 reveals a good coincidence of the bond lengths and the angles in the sulfonium ions. Typically, the S^+–C(phenyl) bond lengths in the methyldiphenylsulfonium ion (1.78 Å) are almost equal to those in the 1,4-bis(methylphenylsulfonio)benzene ion (S–C_β, 1.77; S–C_γ, 1.81 Å). Moreover, the (phenyl)C–S^+–C(phenyl) bond angles in the two ions (103.6(3)° and 103.8(6)°) are almost identical and the torsions of the best least-squares planes of the adjacent phenyl rings (83.12° and 92.48°) are comparable. By analogy, one could estimate that alkylsulfonio-1,4-phenylene polymers (vide infra) would also have similar structural features. As the most typical parameter to characterize the polymeric structure, one can estimate the spacing, or the distance between the repeating units, along the alkylsulfonio-1,4-phenylene chain from the atomic distance between the two sulfur atoms in the 1,4-bis(methylphenylsulfonio)benzene ion (6.26 Å); this parameter has been used to determine the crystal structure of the polymer.[31]

1.2 Synthesis and Properties of Linear Alkylsulfonioarylene Polymers. Although the polycondensation of sodium sulfide with *p*-dichlorobenzene has already been established as the synthetic process for an engineering plastic PPS, finding a new synthetic route to PPS is still a focus of extensive studies. In addition to the classical synthetic method of thioarylene polymers by the Friedel–Crafts reaction of sulfur with aromatic compounds and the nucleophilic substitution reaction of aryl halides with thiolates,[33] several useful methods have recently been found. These include the aforementioned oxidative polymerization of diaryl disulfides,[5,8–12] the thermolysis of diaryl disulfides in the presence of aryl iodides,[34] the condensation of diaryl disulfides with aryl bromides in the presence of KI,[35] and the ring-opening polymerization of cyclic aryl sulfides.[36] However, the high crystallinity as well as the thermal stability and the low solvent solubility of thioarylene polymers have often raised barriers to their synthesis and characterization.

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 (Scheme 8).[20,23] PPS has been exclusively obtained by the subsequent nucleophilic dealkylation of the prepolymer by taking advantage of the high-yielding conversion of alkylsulfonio groups to thioether bonds.

The polymerization of methyl 4-(phenylthio)phenyl sulfoxide has been performed in CF_3SO_3H in the presence of P_2O_5 as the dehydrating agent.[20] Pouring the highly viscous mixture after the reaction into H_2O affords the polymer quantitatively as a white precipitate that is soluble in common solvents such as CH_3CN, acetone, DMSO, HCO_2H, and H_2SO_4. Solution viscosity (η) of the polymer in CH_3CN/H_2O (1 : 1 = v/v) has been determined to be 1.5–2.5 in the presence of 50 mM CF_3SO_3Na. The viscosity values reveal typical behaviors of a polyelectrolyte. Refluxing the solution of the prepolymer in



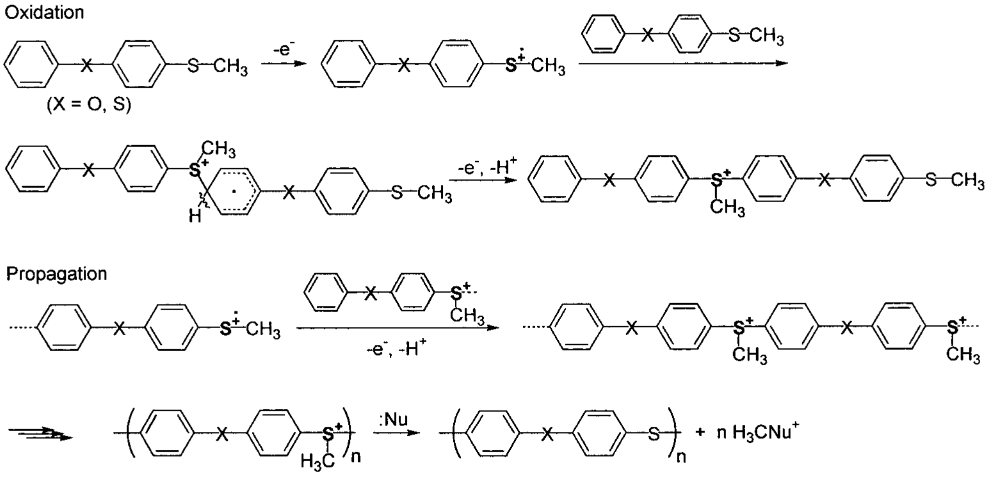
Scheme 8.

pyridine gives rise to the nucleophilic dealkylation of the alkylsulfonio groups to afford PPS as a white precipitate. The degree of polymerization of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) has been deduced from the molecular weight of the obtained PPS which has been determined to be M_w = 2.4 × 10^5 (M_w/M_n = 5.6) by high temperature GPC using 1-chloronaphthalene at 200 °C as an eluent and polystyrene as a standard. Thermal transition temperatures of the obtained PPS has been determined by DSC measurements to be T_g (the glass transition temperature) = 96 °C, T_c (the temperature for exothermic crystallization) = 156 °C, and T_m (melting point) = 260 °C. The temperature for 10% weight loss ($T_{d10\%}$) has been determined to be 535 °C in thermogravimetry. The polymer melts at lower temperatures than the lower molecular-weight Ryton V-1 (commercially available PPS, M_w (determined by the same GPC instrument) = 2.2 × 10^4, T_m = 280 °C) which is in accordance with the predictions[37] that the T_m of PPS could decrease in a very high molecular-weight region. The limiting viscosity number $[\eta]$ of the HCO_2H solution of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) in the presence of CF_3SO_3Na has been related to the viscosity average molecular weight M_v deduced from the M_w of PPS by the Mark–Houwink–Sakurada equation $[\eta] = KM_v^{\alpha}$ ($K = 7.46 \times 10^{-7}$, $\alpha = 1.30$).[38]

Taking advantage of the synthetic process of PPS at room temperature (i.e., under the T_g of PPS), we have obtained an amorphous, transparent PPS film. Dipping the transparent cast film of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) in the CH_2Cl_2 solution of tetraethylammonium bromide or chloride for > 20 h affords a PPS film retaining its transparency without defects. The lack of any X-ray diffraction peak supports the amorphous state of the product which, however, undergoes rapid relaxation upon heating (i.e., annealing) to the thermodynamically more stable crystalline state.[22]

Methyl 4-(phenylthio)phenyl sulfide undergoes oxidative polymerization with $SbCl_5$ in CH_2Cl_2 to yield poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hexachloroantimonate) (Scheme 9).[18] Similarly, oxidative polymerization of methyl 4-(phenoxy)phenyl sulfide yields poly(methylsulfonio-1,4-phenyleneoxy-1,4-phenylene hexachloroantimonate). Nucleophilic dealkylation of the polymer gives poly(oxy-1,4-phenylenethio-1,4-phenylene). The resulting polymer (M_w = 2.4 × 10^4) is insoluble in any solvent at room temperature, but swells in hot $CHCl_3$ and dissolves in hot DMSO. The thermal transition temperatures have been determined to be T_g = 83 °C, T_c = 136 °C, T_m = 177 °C, and $T_{d10\%}$ = 515 °C.[18] Oxidation of methyl 4-(phenylthio)phenyl sulfide with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in sulfolane in the presence of CF_3CO_2H, followed by precipitation of the product from aqueous $HClO_4$, effects the high-yielding conversion to poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene perchlorate).[17] Demethylation with pyridine gives PPS with a molecular weight of M_w = 9.5 × 10^3. Electrolysis of the solutions of the monomers in sulfolane at 1.7 V vs Ag/AgCl in the presence of $LiClO_4$ as the supporting electrolyte also effects the oxidative polymerization to provide the corresponding polymers.[17]

Attempts to employ abundant O_2 as an oxidant for the oxidative polymerization of the thioanisole derivatives have also been made.[39] Thioanisole is quantitatively oxidized with O_2 to yield methyl phenyl sulfoxide in the presence of a catalytic amount of $Ce(NH_4)_2(NO_3)_6$ (CAN) at high pressures.[40] In the presence of CH_3SO_3H, the CAN-catalyzed oxidation of thioanisole with O_2 at an ambient pressure, followed by demethylation with pyridine, yields 22% of methyl 4-(phenylthio)phenyl sulfide and 78% of methyl 4-(phenylthio)phenyl sulfoxide. The predominant formation of the coupled products indicates that CAN acts as a catalyst for the oxidation of thioanisole with O_2 and that the resulting methyl phenyl sulfoxide undergoes acid-induced condensation with thioanisole to yield the coupled sulfonium ions. The polymerization of methyl 4-(phenylthio)phenyl sulfide has been carried out in CH_3SO_3H under O_2 in the presence of P_2O_5 as a dehydrating agent and a small amount of CAN as the catalyst. The reaction is accompanied by quantitative O_2 uptake to provide poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene perchlorate) by pouring the mixture after the reaction into aqueous $HClO_4$. The polymerization is considered to follow a mechanism in which CAN-catalyzed O_2-oxidation of the monomer would first yield methyl 4-(phenylthio)phenyl sulfoxide which then couples by the electrophilic reaction of the hydroxy(methyl)[4-(phenyl-



Scheme 9.

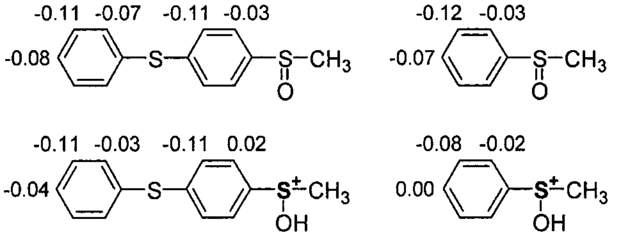


Fig. 3. Carbon net charges of sulfoxides and their protonated sulfonium ions obtained by PM3 MO calculations.

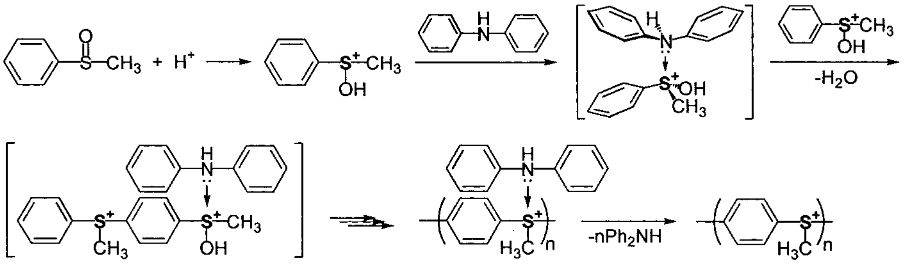
thio)phenyl]sulfonium ion (Scheme 8), rather than a mechanism of coupling through the cation radical of the monomer as the electrophile (Scheme 9). Demethylation of the product with pyridine provides PPS with a molecular weight of $M_w = 2.0 \times 10^5$ and thermal transition temperatures of $T_g = 93$ °C, $T_c = 158$ °C, and $T_m = 260$ °C.[39]

Methyl phenyl sulfoxide does not undergo polycondensation in CF_3SO_3H, because the protonation of the sulfoxide lowers the electron density of the phenyl carbons. Such lack of reactivity has been supported by PM3 semi-empirical MO calculation.[31] The carbon net charges of the hydroxy(methyl)phenylsulfonium ion are less negative and thus less susceptible to the reaction with electrophiles than those of the parent compound (Fig. 3). It is clear from the calculated net charges that the phenylsulfenyl (and phenoxy) group bound to the 4-position of the hydroxy(methyl)sulfoniobenzene ion serve as an electron-rich spacer to render the terminal phenyl ring less cationic and more susceptible to the electrophilic reaction, which permits the coupling of methylsulfoniophenylene chains (i.e., the propagation step) in Schemes 8 and 9.

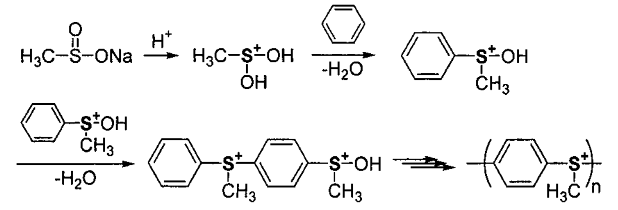
Electron-donating molecules have CT interactions with the sulfonium ion.[31] Among the various compounds bearing a lone pair of electrons such as amines and ethers, diphenylamine has been selected as an effective donor because it does not form a salt with CF_3SO_3H. The CT interaction with external donors could compensate for the inductive effect of the sulfonio group and could raise the electron density of the phenyl ring in the sulfonium ions to promote the condensation of the hydroxy(methyl)phenylsulfonium ion. The polymerization of methyl phenyl sulfoxide has been carried out in CF_3SO_3H in the presence of an equimolar amount of diphenylamine (Scheme 10).[31] Treatment of the resulting viscous dark brown solution with diethyl ether quantitatively gives poly(methylsulfonio-1,4-phenylene triflate) as a white powder.

Müllen et al.[41] have reported that the super acid-induced polycondensation of methyl 4-(phenylamino)phenyl sulfoxide with CF_3SO_3H yields poly(methylsulfonio-1,4-phenyleneimino-1,4-phenylene triflate) (vide infra). The diphenylamine unit is not incorporated into the product obtained from methyl phenyl sulfoxide and diphenylamine.[31] The product, poly(methylsulfonio-1,4-phenylene triflate), has been successfully converted to PPS by the demethylation strategy using pyridine. The molecular weight of the resulting PPS has been determined to be $M_w = 3.6 \times 10^3$ ($M_w/M_n = 2.4$). The rather low molecular weight of the product might reflect the electric field effect from the multi-positive charge accumulated on the polyelectrolyte which could retard the electrophilic attack of the sulfonium ion at the terminal phenyl ring. The product melts at 278 °C.[31]

The polymerization of methyl phenyl sulfoxide in CF_3SO_3H is quite sensitive to the basicity of the amine.[31] The reaction is quantitative with diphenylamine ($pK_b = 34.2$) and with 3-chlorophenyl(phenyl)amine ($pK_b = 31.5$) because of their appropriate basicity[42] to interact with the sulfonium ion. Weaker bases such as phenothiazine ($pK_b = 31.1$) do not form a CT complex, and stronger bases such as *N*,*N*′-diphenyl-1,4-phenylenediamine ($pK_b = 35.1$), di-*p*-tolylamine ($pK_b = 35.7$), and aniline ($pK_b = 41.9$) would rather form stable triflate salts. The polymerization of methyl phenyl sulfoxide requires 60–100 mol% amounts of diphenylamine to proceed quantitatively. The addition of more amounts of the amine decreases the acidity of the solution to give the polymer in lower yields. The CT complex formation between the amine and the sulfonium ion has been confirmed using methyldiphenylsulfonium triflate ($[(C_6H_5)_2(CH_3)S][CF_3SO_3]$) as a non-polymerizable model compound.[31] The CT transition band has been observed near 400 nm in CH_2Cl_2 as a shoulder of a large π–π^* band of diphenylamine in the UV-vis. spectrum. The 1 : 1 CT complex formation according to $[(C_6H_5)_2(CH_3)S]^+ + (C_6H_5)_2NH \rightleftarrows [(C_6H_5)_2(CH_3)S{\cdot}HN(C_6H_5)_2]^+$ and the equilibrium constant K ($= [(C_6H_5)_2(CH_3)S{\cdot}HN(C_6H_5)_2{}^+]/[(C_6H_5)_2(CH_3)S^+][(C_6H_5)_2NH] = 0.41\ M^{-1}$) has been determined from the Benesi–Hildebrand plots.[43] The formation constant of the methyldiphenylsulfonium/3-chlorophenyl(phenyl)amine complex is comparable ($K = 0.48\ M^{-1}$).[31] The CT complex formation has also been confirmed by the upfield shift of the sulfoniomethyl protons in ^1H NMR upon the addition of diphenylamine and further upfield shift at reduced temperatures where donor-acceptor association would be favored. The concomitant downfield shift has been observed for the imine proton in diphenylamine. The mechanism of polymerization involving the CT complex has been proposed (Scheme 10).[31] It is likely that the CT complex reacts with the sulfonium ion rather than itself,



Scheme 10.



Scheme 11.

since there is no vacant site in the CT complex to react with the external phenyl ring. Reasonable support has been provided by the stoichiometry of the reaction in which only 60–100 mol% of diphenylamine is sufficient for the quantitative conversion of methyl phenyl sulfoxide.[31]

The reaction of a methanesulfinate ion with benzene in CF_3SO_3H can be exploited for the synthesis of poly(methylsulfonio-1,4-phenylene triflate).[44] Whereas a mixture of the sulfinate ion and benzene in 1:2 mol ratio yields methyldiphenylsulfonium triflate as the major product (Scheme 7),[27] the equimolar solution provides the polymer in 42% yield, in addition to the methyldiphenylsulfonium salt as a side product. The active species in the polymerization is the dihydroxy(methyl)sulfonium ion that reacts with benzene to form a hydroxy(methyl)phenylsulfonium ion, followed by a successive condensation to yield the polymer (Scheme 11).[44] The origin of the regioselectivity for the coupling of the hydroxy(methyl)phenylsulfonium ion remains unsettled. The phenyl ring in the dimethylphenylsulfonium ion is nitrated preferentially at the *meta* position to the sulfonio group.[45] On the other hand, under strongly acidic conditions to enhance the 3d–2p interaction in the methylsulfoniophenylene moiety (vide infra), the orientation and reactivity of the phenyl ring in the dimethylphenylsulfonium ion may be governed by the resonance effect of the sulfonio group (i.e., the delocalization of the lone pair on the sulfur atom into the phenyl ring though a p-π/d-π resonance) rather than the electron-withdrawing inductive effect.[44]

The polymer has been isolated as a white powder which is soluble in H_2O, DMSO, CF_3CO_2H, and H_2SO_4, and slowly undergoes demethylation in H_2O and DMSO due to the nucleophilic attack of the solvent.[44] The polymer is stable up to 135 °C in the solid state and at 110 °C for 12 h in CF_3SO_3H. The nucleophilic demethylation of the product with pyridine allows the quantitative conversion to yield PPS with a molecular weight of $M_w = 2.7 \times 10^3$ ($M_w/M_n = 1.4$) and a melting point of $T_m = 278$ °C.[44] The sulfur bonds in the polymers have been characterized by XPS. The methylsulfoniophenylene polymer typically shows the sulfur 2p core-level signals at 165.7 (S2p3/2) and 167.0 eV (S2p1/2) due to the sulfonium moieties; such signals obviously differ from those of PPS at 162.5 and 164.1 eV due to the thioether bonds.[44] Both signals are observed for the methylsulfoniophenylenethiophenylene chain containing alternative sulfonio and thioether bonds.

A number of aromatic molecules have been examined as the monomer with the methanesulfinate ion. The polymerization of *p*-xylene with an equimolar amount of sodium methanesulfinate in CF_3SO_3H yields poly(methylsulfonio-2,5-dimethyl-1,4-phenylene triflate) in 43% yield which is soluble in acetone and CH_3CN but not in H_2O. The polymerization does not proceed with more sterically crowded durene. A higher molecular-weight polymer has been obtained from diphenyl ether with a HOMO level of −9.27 eV which is higher than that of benzene (−9.55 eV).[44] Diphenyl sulfide (−9.31 eV), however, reacted to give a lower molecular-weight polymer, due probably to the unraveled side reactions such as the transmethylation between the methylsulfonio bond and the thioether bond.

1.3 Crystal Structure of the Methylsulfoniophenylene Polymer. PPS is known to be partly crystalline; it shows relatively strong X-ray powder diffraction peaks superimposed on an amorphous halo. These peaks have allowed the crystal structure determination.[46] On the other hand, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene hexafluorophosphate) is amorphous and shows no X-ray diffraction peak.[31] The increase in the spacing along the polymer chain (i.e., the size of the repeating unit) from that of PPS seems to prevent the polymer from forming good microcrystals.

The methylsulfonio-1,4-phenylene chain with a smaller repeating unit is expected to be crystalline. Because the triflate salt is hygroscopic, the powder diffraction data has been collected with the hexafluorophosphate salt.[31] The high crystallinity of poly(methylsulfonio-1,4-phenylene hexafluorophosphate) has been demonstrated by the sharp reflections without even the amorphous halo. The sole unit cell has been induced by the following considerations. Orthorhombic unit cells are the most frequently observed for a number of structurally related aromatic polymers such as PPS,[46] poly(oxy-1,4-phenylene),[47] and poly(carbonyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylene),[48] whereas an exception has also been found in the typical tetragonal unit cell of poly(oxy-2,6-diphenyl-1,4-phenylene).[49] Most of the recorded reflections could be satisfactorily indexed by assuming an orthorhombic unit cell of dimensions a = 10.875 Å, b = 10.449 Å, and c = 18.629 Å.[31] The lengths of the a and b axes are close to those determined for the sulfonium salts in Fig. 2. The observed interplanar spacing d coincides with the calculated value. A crystallographic density of 1.67 g/cm^3 has been calculated for eight monomeric units per cell, which correlates acceptably with the typical crystal density of the sulfonium salts in Fig. 2, considering that the polymer is highly crystalline. All other possible unit cell dimensions allowing the indexing of the reflection peaks have been excluded on the basis of the density considerations. In view of the arrangement of the 1,4-bis(methylphenylsulfonio)benzene ion in the unit cell, the polymer chain is likely to be arranged along the long c axis. The systematic absence of the reflections hk0 with h+k odd, 0kl with k odd, and h0l with l odd corresponds to the space group *Pbcn* (# 60). Fig. 4(a) shows the structure of the polymer chain determined with the aid of the typical bond parameters of the sulfonium salts in Fig. 2.[31] Fig. 4(b) shows the possible arrangement of the polymer chain in the unit cell projected along the a axis.[31] Two molecular chains pass through the unit cell: one through the center, the other through the corner. In view of the symmetry of the space group, the centers of gravity of the phenylene groups labeled **A** and **C** are placed in the unit cell at the special positions 0, 0, 0; 0, 0, 1/2; 1/2, 1/2, 0; and 1/2, 1/2, 1/2, which are the centers of symmetry. Those labeled **B** and **D** are placed at the special positions 0, −y, 3/4; 0, y, 1/4; 1/2, 1/2 + y, 1/4; and 1/2, 1/2 − y, 3/4. This arrangement implies

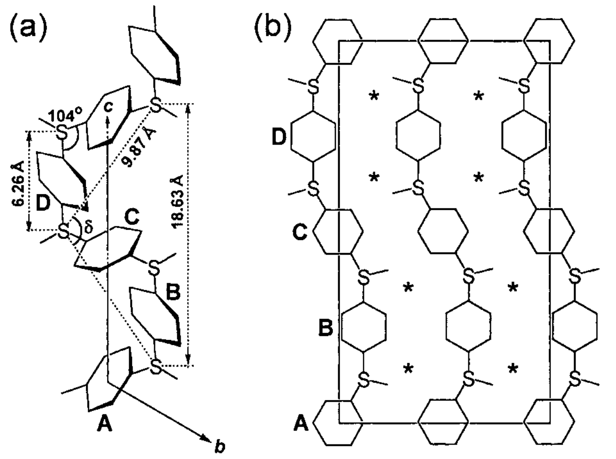
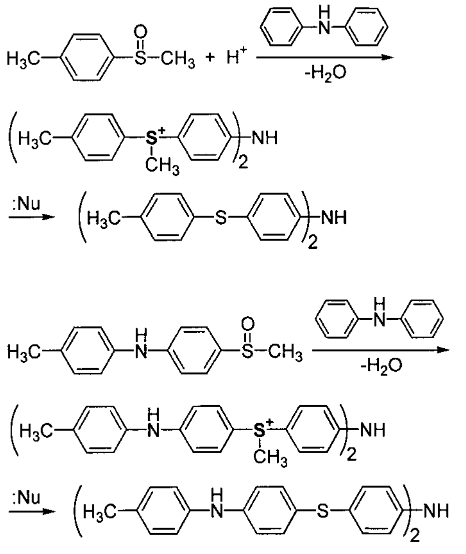


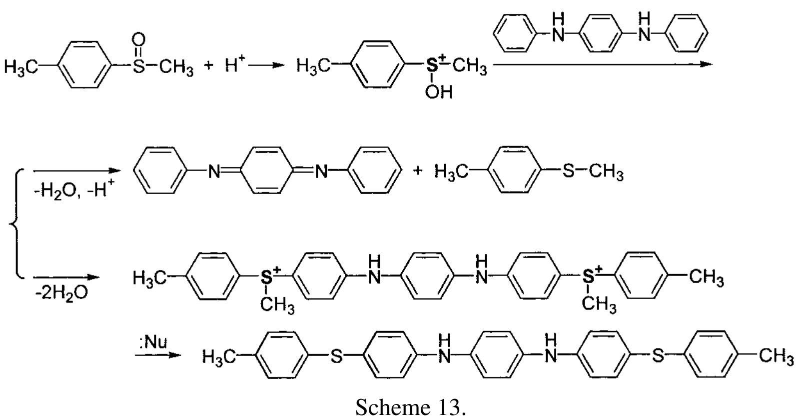
Fig. 4. (a) Estimated conformation of a polymer chain in the crystal of poly(methylsulfonio-1,4-phenylene hexafluorophosphate). Bond lengths and angles are from those in 1,4-bis(methylphenylsulfonio)benzene bis(hexafluorophosphate) (Fig. 2). (b) Arrangement of the polymer chain in the unit cell projected along the *a* axis. Positions for hexafluorophosphate ions are shown as asterisks.

that four monomeric units are involved in the period of the *c* axis, which is compatible with the estimated bond length and angles in Fig. 4(a). The hexafluorophosphate ions occupy the eight general equivalent positions in the unit cell (Fig. 4(b)).[31] The angle of δ in Fig. 4(a) is determined to be 141°, which characterizes the polymer structure. The crystal structure of the polymer has a repeat distance different from that of the chemical structure and consists of four benzene nuclei and four sulfonio linkages, yielding a repeat distance of 18.6 Å along the *c* axis. Reflection intensity calculations to determine the rotation angle of the phenylene groups around the S–S axis have been unsuccessful, due probably to the significant disorder of the hexafluorophosphate ions in the crystal. The crystal structure implies that the atomic arrangement around the sulfur atoms in the methylsulfonio-1,4-phenylene chain is similar to that of the sulfonium salts in Fig. 2, and that the polymer has a vacant site to allow the CT interaction with diphenylamine, as shown in Scheme 10.[31]

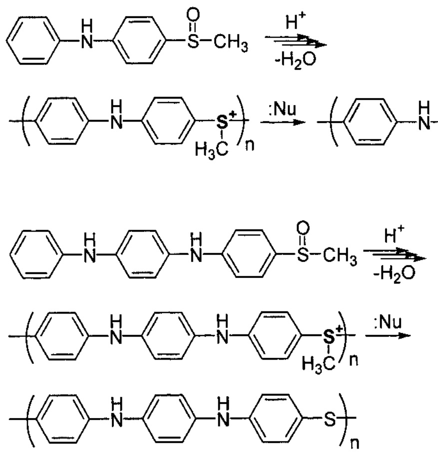


Scheme 12.

1.4 Polyaniline-PPS Hybrids. A hybrid of polyaniline and PPS, poly(thio-1,4-phenyleneimino-1,4-phenylene), has been prepared by Müllen et al.[41] with a view to obtain a polyaminyl radical as an organic analogue of poly(sulfur nitride) that shows metallic conductivity.[50] The synthetic concept consists of the super acid-induced condensation of alkyl aryl sulfoxides and diarylamines. The model compound, bis[4-(4-tolylthio)phenyl]amine, has been prepared in a high yield by the condensation of 4-(methylsulfinyl)toluene and diphenylamine in CF_3SO_3H, followed by the demethylation of the resulting sulfonium salt by treatment with refluxing pyridine (Scheme 12).[41] The next higher model compound, bis{4-[4-(4-tolylamino)phenylthio]phenyl}amine, has also been prepared quantitatively from methyl 4-(4-tolylamino)phenyl sulfoxide and diphenylamine.[51] On the other hand, the condensation of 4-(methylsulfinyl)toluene and *N,N′*-diphenyl-1,4-phenylenediamine competes with the oxidation of the amine by the hydroxy(methyl)-4-tolylsulfonium ion (i.e., the protonated sulfoxide) to produce a quinonoidal diimine and 4-(methyl)thioanisole (Scheme 13).[52] In CH_3SO_3H, the condensation of the sulfoxide and the amine dominates over the oxidation of the amine, whereas the oxidation of the amine prevails in stronger acids such as $HClO_4$ and CF_3SO_3H.[52] The effect of acidity is thus not straightforward and has to be considered in the case of the polymerization of monomers containing a 1,4-phenylenebisimino moiety (vide infra).



Scheme 13.



Scheme 14.

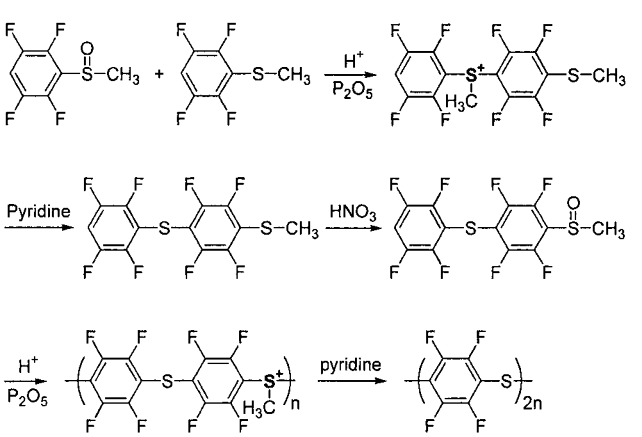
The polymerization of methyl 4-(phenylamino)phenyl sulfoxide in CF_3SO_3H yields poly(methylsulfonio-1,4-phenyleneimino-1,4-phenylene triflate) (Scheme 14) which is soluble in DMSO, DMF, and NMP.[41] Demethylation of the polymer by treatment with refluxing pyridine affords poly(thio-1,4-phenyleneimino-1,4-phenylene) with the leucoemeraldine base form which is soluble in THF, DMF, NMP, and DMSO.[41] The molecular weight of the product has been determined to be $M_w = 3.9 \times 10^5$ ($M_w/M_n = 2.6$) by GPC using THF as an eluent and polystyrene as a standard.[51] Only a diffuse peak at $2\theta = 20°$ in X-ray diffraction measurements and the lack of both premelt crystallization exotherm and melting endotherm in DSC measurements establish that the polymer is in an amorphous state ($T_g = 145$ °C), which is not influenced even by annealing treatments above T_g.[51] Flexible, optically clear, and colorless free-standing film with a modulus of elasticity of 1.3 GPa and a maximum extension of 110% has been obtained by casting the THF solution of the polymer, which undergoes oxidative degradation upon irradiation with light under air.[41] The polymer film attached at a surface of an electrode shows a broad redox response in the range of 0.6–1.2 V vs $Ag/AgNO_3$ in cyclic voltammetry recorded in an electrolyte solution of CH_3CN.[51] While the pristine polymer is insulating ($\sigma < 10^{-9}$ S/cm), the polymer doped with $FeCl_3$ showed electric conductivity of $\sigma = 1.4$ S/cm.[41]

On the other hand, treating methyl 4-[4-(phenylamino)phenylamino]phenyl sulfoxide with CH_3SO_3H for 24 h at room temperature affords poly(methylsulfonio-1,4-phenyleneimino-1,4-phenyleneimino-1,4-phenylene methanesulfonate) (Scheme 14) that is soluble in DMSO, DMF, and NMP.[52] Demethylation has been performed in refluxing pyridine to yield poly(thio-1,4-phenyleneimino-1,4-phenyleneimino-1,4-phenylene) ($M_w = 1.4 \times 10^5$, $M_w/M_n = 2.0$) that is soluble in THF, DMF, NMP, and DMSO.[52] Polymerization of methyl 4-[4-(phenylamino)phenylamino]phenyl sulfoxide in a stronger acid such as $HClO_4$ and CF_3SO_3H results in much lower molecular weights, due to the concomitant decomposition of the monomer by the oxidation of the 1,4-phenylenebisimino moiety with the protonated sulfoxide group (vide supra).[52]

The UV irradiation of a solution of bis[4-(4-tolylthio)phenyl]amine in toluene produced an aminyl radical with $g = 2.00374$, $a_{H0} = 0.338$ mT, $a_{Hm} = 0.133$ mT, and $a_N = 0.802$ mT.[41] Irradiation of bis{4-[4-(4-tolylamino)phenylthio]phenyl}amine in the presence of dibenzoyl peroxide yields a diradical with $g = 2.00374$ and a zero-field splitting of 1.76 mT at 135 K in toluene glass.[41] The corresponding triradical from bis{4-[4-(4-tolylamino)phenylthio]phenyl}amine or the polyradical from poly(thio-1,4-phenyleneimino-1,4-phenylene) has so far not been obtained due to the low stability of the aminyl radicals.[52]

1.5 Alkylsulfonioarylene Polyelectrolytes. Polyelectrolyte coatings on electrode surfaces have been widely used to attract and bind ionic complexes bearing charges opposite to that of the polyelectrolyte.[53] However, the number of useful polycations that are presently available is limited. The most extensively used polycation films are those of protonated or quaternized poly(4-vinylpyridine),[54] protonated poly(L-lysine),[55] a perfluorinated polymer with pendant ammonium groups,[56] a block copolymer of styrene and (diethylaminomethyl)styrene,[57] polyviologen,[58] poly(2-vinylpyrazine),[59] a poly[1-methyl-3-(pyrrol-1-ylmethyl)pyridinium] salt,[60] a polymer obtained by the electrochemical polymerization of *N*,*N*-dimethylaniline,[61] and γ-irradiated poly(diallyldimethylammonium chloride).[62] These N-cation polymers are used because of their wide potential windows, insolubility in electrolyte solutions, and permselectivity. The use of S-cation polymers as electrode-coating materials has been impeded by their high solubility in H_2O. Indeed, even an aromatic polyelectrolyte such as the methylsulfonio-1,4-phenylene polymer is soluble in H_2O.[44] On the other hand, a polymer with a lower content of sulfonio groups is insoluble but does swell in H_2O and anion-exchanges with a ferricyanide ion.[63] Poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) is electro-inactive between -0.6 and $+1.2$ V vs Ag/AgCl and can be used as an electrolyte in this potential window and in a wide range of pH between 1 and 13.[63] The cast film of the polymer adhering to an electrode surface has been employed to bind a ferricyanide ion to the electrode surface from electrolyte solutions. Ion selectivity of the polymer has been evaluated using the incorporated ferricyanide ion as a redox probe.[57] The complex incorporated by the polyelectrolyte shows significant shifts in formal potential to less positive values, due to the binding of ferricyanide by the polycation coating being stronger than that of ferrocyanide. The apparent formal potential for the incorporated ferricyanide/ferrocyanide redox couple (E^f_{app}) changes as the concentration of a supporting electrolyte is varied.[63] An ideal anion permselectivity[64] has been observed in aqueous solutions of CH_3SO_3Na ($E^f_{app}/\log[CH_3SO_3^-] = -59$ mV). The incorporation and binding of the ferricyanide ion into the polymer is essentially due to the electrostatic interaction.[63]

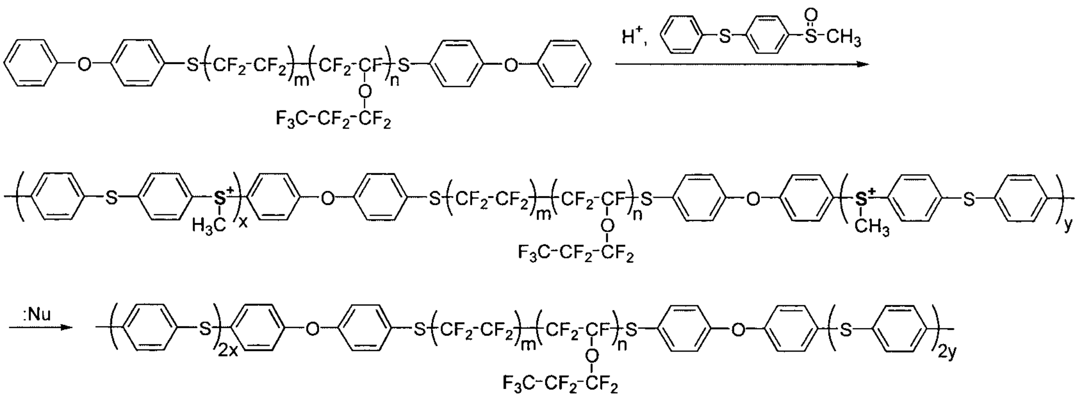
1.6 New Derivatives of Alkylsulfonioarylene and Thioarylene Polymers. Fluorinated polymers such as poly(tetrafluoroethylene) exhibit remarkable properties including thermal and chemical stability, low refractive index, low frictional resistance, low wettability, and toughness.[65] In contrast to the polymers containing perfluoroalkyl groups, those containing perfluorophenylene groups are quite rare because of the limited synthetic methods. Perfluorophenylene groups are also expected to contribute to increasing the crystallinity and hence the thermal stability and mechanical strength of the polymers. The typical perfluorophenylene-containing polymers are polyketones,[66] polysulfides,[67] and poly(disilane)s.[68] Perfluorinated oligo(thio-1,4-phenylene) shows photocatalytic activities for the reduction of H_2O and olefins through the formation of polymeric radical salts.[69] The synthetic methods reported for the perfluorinated PPS are based on nucleophilic aromatic substitution (i.e., the polycondensation of hexafluorobenzene with sodium sulfide or the self-polycondensation of pentafluorobenzenethiolate salts) at high temperatures above 200 °C.[70] Because the fluorine substituents significantly enhance the reactivity of the monomers, the resulting polymers usually contain branched and/or cross-linked structures. On the other hand, a synthetic route to the linear perfluorinated PPS, poly(thio-2,3,5,6-tetrafluoro-1,4-phenylene), has successfully been devised using the polycondensation of a corresponding alkyl aryl sulfoxide followed by the nucleophilic dealkylation strategies.[71] The monomer, 4-(2,3,5,6-tetrafluorophenylthio)-2,3,5,6-tetrafluorophenyl methyl sulfoxide, is prepared by the condensation of tetrafluorothioanisole and 2,3,5,6-tetrafluorophenyl methyl sulfoxide in CF_3SO_3H, followed firstly by the demethylation of the resulting methyl[4-(methylthio)-2,3,5,6-tetrafluorophenyl]-2,3,5,6-tetrafluorophenylsulfonium ion with pyridine, and secondly by the oxidation of the coupled product, 4-(2,3,5,6-tetrafluorophenylthio)-2,3,5,6-tetrafluorophenyl methyl sulfide, with HNO_3 (Scheme 15).[71] The addition of an excess amount of P_2O_5 as a dehydrating agent effects the quantitative condensation of the sulfoxide, because the four fluorine substituents may render the phenyl ring less susceptible to the electrophilic coupling reaction. The polymerization of 4-(2,3,5,6-tetrafluorophenylthio)-2,3,5,6-tetrafluorophenyl methyl sulfoxide proceeds efficiently in CF_3SO_3H in the presence of P_2O_5 to produce poly(methylsulfonio-2,3,5,6-tetrafluoro-1,4-phenylenethio-2,3,5,6-tetrafluoro-1,4-phenylene triflate) as a white powder in 100% yield (Scheme 15) that is insoluble in most organic solvents and only slightly soluble in DMF and H_2SO_4.[71] Demethylation of the polymer with pyridine affords poly(thio-2,3,5,6-tetrafluoro-1,4-phenylene) which is partly soluble in 1-chloronaphthalene at 210 °C. The molecular weight of the soluble part has been determined to be $M_w = 3.8 \times 10^3$ ($M_w/M_n = 1.8$) by high temperature GPC using 1-chloronaphthalene at 210 °C as an eluent and polystyrene as a standard. The polymer is crystalline and shows a high T_m at 373 °C with a heat of fusion (ΔH) of 68 J/g. The T_m is much higher than that of the unfluorinated PPS (T_m = 282 °C) because the perfluorination contributes to the lower entropy of fusion (ΔS), and is even higher than that of the structurally undefined fluorinated PPS (T_m = 322 °C).[72] The stability against thermal degradation is lowered by the perfluorination, due to the weakening of the (phenyl)C–S–C(phenyl) bond. The surface energies of melt-pressed samples placed on glass slides have been determined from contact angle measurements with H_2O, CH_2I_2, ethylene glycol, and HCHO. The surface tension of the perfluorinated PPS (41 mN/m) is comparable to those of other aromatic polymers (poly(ethylene terephthalate) = 44 mN/m, polystyrene = 41 mN/m) but higher than that of poly(tetrafluoroethylene) (22 mN/m) and only slightly lower than that of the unfluorinated PPS (43 mN/m).[71]



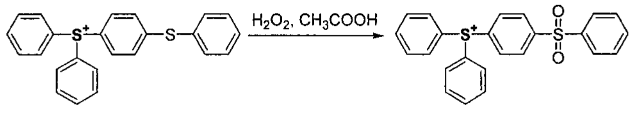
Scheme 15.

The super acid-induced condensation of methyl (4-phenylthio)phenyl sulfoxide has also been exploited for the synthesis of copolymers containing perfluoroalkane blocks.[73] While the addition of perfluoroalkane compounds to PPS is expected to improve the toughness and sliding properties, PPS alloys usually confront many problems because of the high T_m and crystallinity. Moreover, the copolymerization with perfluoroalkanes has been impeded by the high reaction temperatures required for the conventional synthesis of PPS based on the nucleophilic aromatic substitution of thiolates, which results in the decomposition of the perfluoroalkane moieties accompanied with the elimination of HF due to the nucleophilicity of the thioether bonds in the polymer. The synthesis of the block copolymer (Scheme 16) hinges on the use of a perfluoroalkane chain bearing phenyl rings at the both ends that is prepared from α,ω-diiodopoly[tetrafluoroethylene-*co*-perfluoro(propyl vinyl ether)] ($M_w = 6 \times 10^3$) and 4-phenoxybenzenethiol.[73] The copolymerization with methyl (4-phenylthio)phenyl sulfoxide has been carried out in a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane and CF_3SO_3H to yield poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate)-*block*-{poly[tetrafluoroethylene-co-perfluoro(propyl vinyl ether)]}-*block*-poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) after removal of the homopolymer, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate), and the unreacted perfluoroalkane segment.[73] Nucleophilic demethylation of the product with pyridine yields poly(thio-1,4-phenylene)-*block*-{poly[tetrafluoroethylene-*co*-perfluoro(propyl vinyl ether)]}-*block*-poly(thio-1,4-phenylene) as a pale yellow powder (Scheme 16). The immiscibility of PPS and the perfluoroalkane segment gives rise to a microphase separation in the copolymer which shows a three-dimensional stitch with a diameter of 2 nm in a SEM analysis after an O_2 plasma etching treatment.[73] The thermal transition temperatures are thus almost identical with those of PPS.

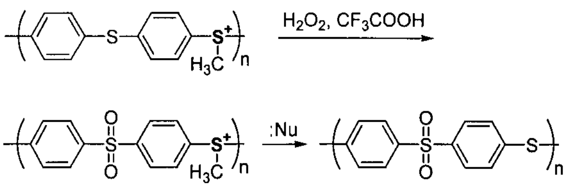
The high solubility of the methylsulfonio-1,4-phenylenethio-1,4-phenylene chain in polar solvents allows a variety of chemical modifications by polymer reactions. A convenient synthesis of poly(thioether sulfone) has been established by the oxidation of the polymer with H_2O_2, followed by nucleophilic demethylation with pyridine.[74] Poly(sulfonylarylene)s are typical amorphous polymers with high T_g, thermal and chemical resistance, high modulus of rigidity, and stable electrical properties such as dielectric relaxation and dielectric loss over a wide range of temperatures below T_g.[75] The polymers



Scheme 16.



Scheme 17.

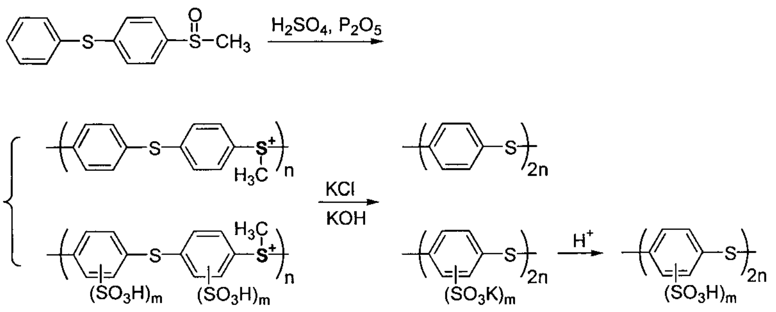


Scheme 18.

consist of phenyl rings linked with sulfonyl bonds or alternatively with other groups such as ether, thioether, and alkylidene bonds. Poly(ether sulfone) and polysulfone are the typical commercially available polymers. The conventional synthesis of poly(sulfonyl-1,4-phenylenethio-1,4-phenylene) (i.e., a poly(thioether sulfone)) by the nucleophilic aromatic substitution reaction of bis(4-chlorophenyl) sulfone and sodium sulfide in NMP at high temperatures usually yields a polymer with structural defects and a large amount of the contaminated salt. On the other hand, the high-yielding conversion of a diphenyl[4-(phenylthio)phenyl]sulfonium ion to a diphenyl[4-(phenylsulfonyl)phenyl]sulfonium ion by oxidation with H_2O_2 in the presence of CH_3CO_2H (Scheme 17) can be exploited for the synthesis of poly(thioether sulfone).[74]

Oxidation of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) with H_2O_2 in $CHCl_3$ at 60 °C in the presence of CF_3CO_2H allows the selective conversion of the thioether bonds to the sulfonyl bonds while the methylsulfonio bonds remain intact, yielding a polymer with alternating sulfonyl and methylsulfonio bonds (Scheme 18).[74] The nucleophilic demethylation of the polymer by treatment with an aqueous solution of NaCl provides poly(sulfonyl-1,4-phenylenethio-1,4-phenylene) as a white powder (Scheme 18). No molecular-weight degradation occurs during the overall synthetic process.[74] A high molecular-weight polymer ($M_w = 1.9 \times 10^5$) shows T_g at 215 °C and $T_{d10\%}$ at 495 °C.[74]

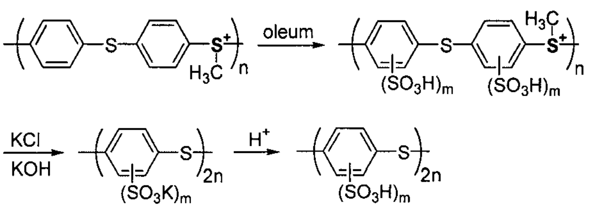
Sulfonated PPS has successfully been obtained by the sulfonation of a soluble methylsulfonio-1,4-phenylenethio-1,4-phenylene chain, followed by treatment with a nucleophile. So far, much efforts have been made to sulfonate thermostable aromatic polymers such as poly(1,4-phenylene),[76] poly(carbonyl-1,4-phenyleneoxy-1,4-phenyleneoxy-1,4-phenylene),[77] poly(oxy-1,4-phenylene),[78] and other engineering plastics[79] with a view to obtain polyelectrolytes that can operate at high temperatures for fuel cell applications. Although these polymers can be sulfonated with a sulfonation degree of 1.0 per repeating unit by heating at 75 °C in concentrated H_2SO_4,[80] a higher degree of sulfonation is difficult to achieve because of their low solubility and concomitant side reactions during the sulfonation, such as the inter-chain cross-linking.[81] Proton conductive polymers would be useful not only as separators in batteries, fuel cells, electronic displays, and chemical sensors, but also as materials for hydrogen storage.[82] Perfluoro sulfonate ionomer (Nafion) membranes have been used for this purpose due to their efficient proton conductive properties, permselectivity, and long term thermal and chemical stability.[83] The conductivity of Nafion reaches 10^2 S cm^{-1} in the fully hydrated protonic form, but plummets at temperatures above the boiling point of H_2O because of the loss of H_2O and the concomitant thermal decomposition.[84] Direct sulfonation of PPS with SO_3 usually results in a low degree of sulfonation (i.e., lower than 0.5 sulfonic acid group per phenylene unit) and the formation of undesirable ladder-like or cross-linked structures.[85] On the other hand, the sulfonated PPS can easily be obtained by the polycondensation of methyl 4-(phenylthio)phenyl sulfoxide in H_2SO_4, followed by the demethylation of the resulting sulfonated methylsulfonio-1,4-phenylenethio-1,4-phenylene chain by treating with a nucleophile such as an amine, pyridine, and aqueous KCl (Scheme 19).[86] The degree of sulfonation per phenylene unit (m) increases with a prolonged reaction time at high reaction temperatures (100 °C for 10 h) and reaches $m = 0.05$; the process is, however, accompanied by a decrease in the molecular weight ($M_w = 3.6 \times 10^3$) because the chain propagation competes with the sulfonation at the terminal phenyl ring.[86] An important structural aspect has been derived from the thermal property of the products with a low degree of sulfonation ($m < 0.09$); these products are considered to be random copolymers with a crystalline component of thiophenylene units and an amorphous component of noncrystallizable sulfonated thiophenylene units.[86] The systematic drop of T_m, caused by the interruption of the



Scheme 19.

crystal growth along the chain direction by the sulfonated units, obeys the Flory equation[87] ($1/T_m = 1/T_m{}^0 - R \ln(X_A)/\Delta H_f$, where $T_m{}^0$ and ΔH_f refer to totally crystalline homopolymer A and are the melting point and the heat of fusion per mole of repeating units, respectively, X_A is the mole fraction of A in the copolymer, and R is the gas constant), which implies that the polymers are randomly sulfonated without cross-linking through sulfonyl bonds and that the sulfonated units are non-crystallizable and reside in the amorphous region in the copolymer.[86] The parameters for the thermal transition of virtual, ideal, and totally crystalline PPS has been evaluated to be $T_m{}^0 = 313$ °C and $\Delta H_f = 21$ J/g. Such values are comparable with those of real PPS ($T_m{}^0 = 315$ °C[88] and $\Delta H_f = 80$ J/g[89]) if one takes into account the overestimation of the crystallinity. The acid-induced polycondensation of methyl 4-(phenylthio)phenyl sulfoxide in the presence of SO_3, a strong sulfonating agent for aromatic molecules, yields a polymer with a higher degree of sulfonation. The H_2SO_4–P_2O_5 system has been adopted since P_2O_5 dehydrates H_2SO_4 to produce SO_3, and the by-product H_3PO_4 can also effect the acid-induced polycondensation of the sulfoxide. The polymerization of the sulfoxide in the presence of P_2O_5 in H_2SO_4 (P_2O_5/sulfoxide = 2) at 100 °C yields highly sulfonated methylsulfonio-1,4-phenylenethio-1,4-phenylene chain with $m = 0.5$. An even higher degree of sulfonation ($m = 1.2$) has been accomplished at elevated reaction temperatures above 120 °C. Treatment of the polymer with aqueous KCl and KOH at 100 °C yields the poly[thio-(sulfonato-1,4-phenylene)] salt ($m = 1.2$) that is soluble in H_2O (Scheme 19).

In commercial oleum (10%-SO_3/H_2SO_4), an even stronger sulfonating agent, the sulfonation of the sulfoxide is favored over the polymerization, whereas the methylsulfonio-1,4-phenylenethio-1,4-phenylene chain is sulfonated efficiently (Scheme 20);[81] the sulfonation of the chain predominates over the cross-linking that is suppressed by the electron-withdrawing methylsulfonio groups. The sulfonated PPS obtained after the treatment with a nucleophile is a pale brown powder, and is soluble in H_2O, DMF, and DMSO.[86] The degree of sulfonation increases at elevated temperatures during the sulfonation; the value reaches $m = 1.4$ at 80 °C and $m = 2.0$ at 120 °C. Undesirable cross-linking with sulfonyl bonds occurs at temperatures higher than 140 °C due to the dehydration of the sulfonic acid group.[86]



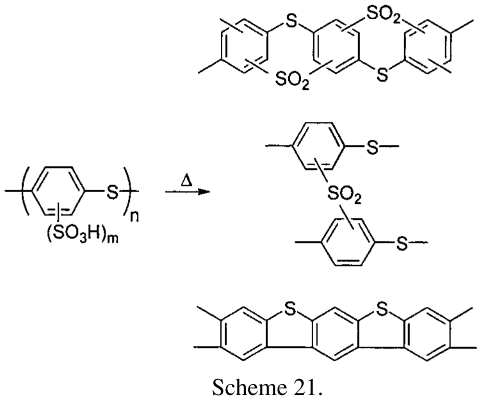
Scheme 20.

The poly[thio-(sulfonato-1,4-phenylene)] salt is protonated using a cationic exchange resin (cross-linked poly(styrenesulfonic acid)) to the acid form, poly[thio-(sulfo-1,4-phenylene)] (Scheme 20). The highly sulfonated product ($m = 2.0$) is amorphous; a transparent film has been obtained by casting the aqueous solution. The thermal decomposition of the film is initiated at 265 °C, a temperature higher than that of Nafion by 75 °C. The proton conductivity (σ) of the film has been measured by the complex impedance method at a controlled relative humidity (RH). The conductivity at RH = 30% has been evaluated to be $\sigma =$ ca. 10^{-5} S cm^{-1}. The value increases exponentially with RH due to the enhanced hydrogen bond formation between the sulfonic acid groups, as proposed in the case of Nafion.[90] The conductivity reaches $\sigma = 2.0 \times 10^{-2}$ S cm^{-1} at RH = 94%, a value that corresponds to 10.3 H_2O per sulfonic acid group.[86] The content of H_2O is even higher than that of Nafion with an equivalent weight (EW) of 1200 that contains ca. 5.0 H_2O per sulfonic acid group. The high proton conductivity and good H_2O affinity of the sulfonated PPS have been ascribed to the lower equivalent weight (134EW). The activation energy of $E_a = 17$ kJ/mol for the polymer with $m = 2.0$ has been derived from the Arrhenius-type dependence of the conductivity which is comparable with that of Nafion ($E_a = 19$ kJ/mol with 14.3% H_2O).[91] The polymer becomes the most proton conductive at 80 °C ($\sigma = 4.5 \times 10^{-2}$ S cm^{-1}) and retains a conductivity value on the order of 10^{-2} S cm^{-1} even at higher temperatures up to 180 °C.[86]

Since the proton conduction is based on the migration of oxonium ions ($(H_2O)_nH^+$) through the hydrophilic clusters of sulfonate aggregates, the conductivity gradually decreases at high temperatures with the loss of H_2O and the destruction of the clusters.[92] Attempts have been made to replace volatile H_2O with polymers such as poly(oxyethylene),[93] poly(iminoethylene),[94] and poly(vinyl alcohol)[95] as the matrix for the sulfonic acid groups in Nafion and poly(styrenesulfonic acid). Poly[thio-(sulfo-1,4-phenylene)] ($m = 0.85$, $T_g = 115$ °C, 210EW) is miscible with poly(oxyethylene) ($M_w = 6 \times 10^2$, $T_g = -41$ °C) to form a flexible and transparent composite film.[96] The homogeneous composite shows a single glass transition at $T_g = 20$ °C with the composition of poly[thio-(sulfo-1,4-phenylene)]/poly(oxyethylene) = 1/1 (w/w) and at 5.0 °C with 1/2 (w/w). Due to the dissociation of the sulfonic acid groups within the poly(oxyethylene) matrix, the composite film shows a moderate proton conductivity even under anhydrous conditions. A conductivity of $\sigma = 1.2 \times 10^{-5}$ S cm^{-1} at 30 °C has been obtained for a composite with the composition of 1/2 (w/w), which increases with temperatures up to 1.3×10^{-3} S cm^{-1} at 130 °C without degradation for 100 h.[96] The conductivity at the high temperature is even 2–3 orders of magnitude higher than that of a heterogeneous Nafion/poly(oxyethylene) composite.[96]

Poly[thio-(sulfo-1,4-phenylene)] has been employed as a thermostable dopant for polyaniline.[97] With acid dopants such as HCl and H_2SO_4, an electric conductivity (σ) of polyaniline on the order of 10^1 S cm^{-1} has been achieved[98] but the loss of the dopant by evaporation and/or diffusion reduces the conductivity during long-term use. Nonvolatile polymeric acid dopants such as poly(styrenesulfonic acids),[99] Nafion,[100] poly(ethylenesulfonic acid),[101] and poly(acrylic acid)[102] have been employed to improve the conductive properties of polyaniline, but they are not effective for use at high temperatures. On the other hand, the electrolytic oxidative polymerization of aniline in an aqueous solution of poly[thio-(sulfo-1,4-phenylene)] yields an electroactive composite that does not decompose up to 200 °C under N_2;[97] the enhanced heat resistance reflect the stability of the thio-1,4-phenylene chain against thermal degradation. The poly[thio-(sulfo-1,4-phenylene)]/polyaniline salt with a doping level of $[SO_3H]/[\text{aniline unit}] = 0.50$ shows $\sigma = 1.5$ S cm^{-1} at 30 °C and retains the conductivity at 150 °C for 24 h, whereas the conductivity of the poly(styrenesulfonic acid)/polyaniline composite is one order of magnitude lower ($\sigma = 3.4 \times 10^{-1}$ S cm^{-1} with the same doping level) and rapidly decreases at high temperatures.[97]

Most of the strongly acidic cation-exchange resins available are based on sulfonated cross-linked polystyrene; such resins are chemically stable but easily decompose at temperatures above 150 °C.[103] A cation-exchange polymer with a higher thermal stability has been obtained by the thermal cross-linking of poly[thio-(sulfo-1,4-phenylene)] at the expense of some of the sulfonate groups.[104] Heating the polymer ($m = 0.6$) at 300 °C in air effects the dehydration condensation of the sulfonate group and the phenyl ring to yield the cross-linked product which is insoluble in H_2O (Scheme 21).[104] The product contains intramolecular (**1**) and/or intermolecular (**2**) sulfonyl bonds to cross-link the phenyl rings, in addition to the poly(benzothiophene)-type carbon-carbon bonds (**3**) observed for SO_3-doped PPS (Scheme 21).[105] Thermal stability is improved upon cross-linking ($T_{d10\%} = 420$ °C), accompanied by the decrease in ion-exchange capacity from 3.7 to 1.2 meq/g.[104]



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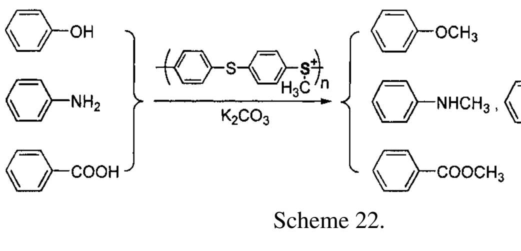
Scheme 21.

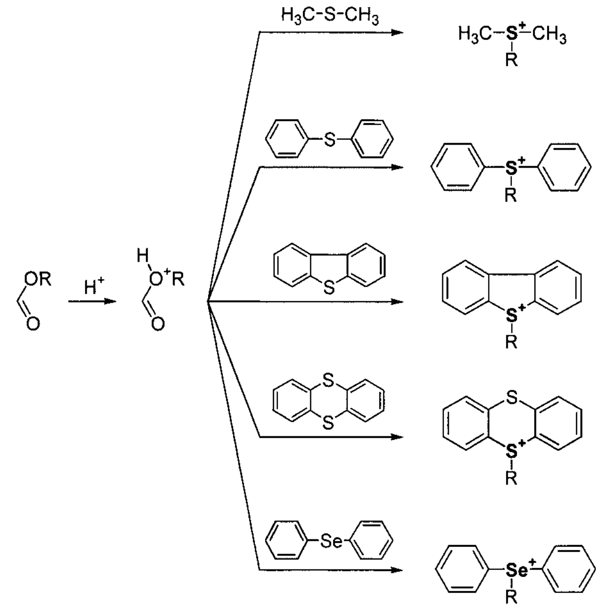
2. Transalkylation Reactions

2.1 Polymeric Methylating Agents. While kinetic studies on methyl group transfers from aryldimethylsulfonium ions have provided an important clue to the nature of various nucleophiles such as the *N*-methylbenzohydroxamate ion,[106] little attention has been paid to their synthetic utility. The methylsulfonio-1,4-phenylenethio-1,4-phenylene ion is an excellent methylating agent for nucleophiles such as phenol, aniline, and benzoic acid (Scheme 22).[107] The polymeric reagent is favored over conventional aryldimethylsulfonium ions because the sulfide bond-enriched polymer after the reaction becomes insoluble and precipitates from solutions; such use provides a simple and convenient methylation process without the need of purification of the products. The transmethylation from the polymer proceeds in CH_3CN at room temperature with high conversions ($> 99\%$).[107]

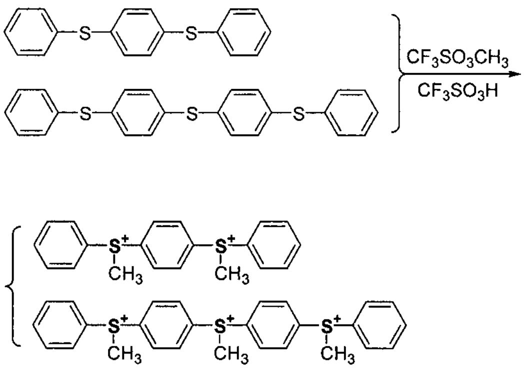
2.2 Alkylation of Sulfides. A number of alkylating and arylating reagents for sulfides to yield sulfonium ions have been reported, such as alkyl iodides,[108] diaryliodonium salts,[109] trialkyloxonium salts,[110] and alcohols or esters with excess strong acids.[111] Transmethylation from methyl triflate proceeds efficiently, whereas phenyl triflate does not phenylate sulfides.[26,112] The direct arylation of diaryl sulfides to triarylsulfonium ions is quite rare. On the other hand, a high-yielding synthetic process has been established that gives a variety of sulfonium salts bearing alkyl and/or aryl groups by the acid-induced condensation of sulfides and esters (Scheme 23).[113] Dimethyl sulfide reacts with methyl formate in CF_3SO_3H at room temperature to yield the trimethylsulfonium salt in 93% yield.[113] A strong acid ($H_0 < -7.0$) is required for the quantitative formation of the product. Diphenyl sulfide is methylated with methyl formate to produce a methyldiphenylsulfonium triflate in 85% yield. Dibenzothiophene and thianthrene are also methylated to the corresponding sulfonium salts under similar conditions. Selenonium salts are obtained from selenides. The alkyl groups transferring from the esters appear to have less essential effect on the reactivity; the reaction of diphenyl sulfide and ethyl formate or butyl formate gives ethyldiphenylsulfonium triflate in 80% yield or *n*-butyldiphenylsulfonium triflate in 82% yield, respectively. Interestingly, the *n*-butyl group does not undergo rearrangement during the transfer from esters to sulfides, in contrast to the classical reactions of sulfides with *n*-butyl halides which produce *s*-butylat-



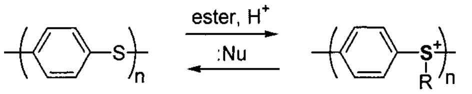
Scheme 22.



Scheme 23.



Scheme 24.



Scheme 25.

ed by-products.[113] The active alkylating species would be the alkyloxonium ion produced by the superacidification of the esters (Scheme 23). The formation of the related oxonium ion RO^+H_2 has been proposed in $HClO_4$–alcohol mixtures in which alkyl sulfides are readily converted to trialkylsulfonium perchlorates without the rearrangement of the alkyl group.[114] Formate esters are more reactive as alkylating reagents than acetates, which may reflect the lability of the oxonium ion produced by the protonations of the esters. The oxonium ion derived from the formate would be a better leaving group due to the lack of a hyperconjugative interaction with the methyl group; such interaction contributes to the stabilization of the oxonium ion from the acetate. While the reaction of diphenyl sulfide with phenyl acetate in CF_3SO_3H gives bis(4-acetylphenyl) sulfide as a major product, addition of P_2O_5 effects the transphenylation from the acetatete (and from the formate) to yield the triphenylsulfonium salt in moderate yields (ca. 40%).

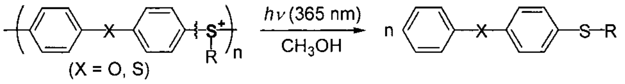
Attempts to alkylate the thioether bonds in PPS have also been made in order to endow the polymer with solubility in common solvents at room temperature. The alkylation with alkyl halides in the presence of $AgBF_4$ results only in low-yielding conversion, due to the low solubility of PPS.[115] The oxidation of PPS with strong oxidants such as SO_3, AsF_5, and $AlCl_3$ gives polymeric cations soluble in acids or aromatic hydrocarbon solvents;[116] such oxidation is, however, irreversible and is accompanied by undesirable sulfonation, cross-linking and/or decomposition of the chain to degrade the polymer. On the other hand, the transalkylation from esters under superacidic conditions proceeds well with thio-1,4-phenylene chains to yield the corresponding alkylsulfonio-1,4-phenylene chains (Scheme 24).[117] The methylation of diphenyl sulfide with methyl triflate in CF_3SO_3H is almost quantitative to give methyldiphenylsulfonium triflate in 99% yield. This allows control of the degree of methylation with the feed amount of the ester. The reaction of 1,4-bis(phenylthio)benzene with an equimolar amount of methyl triflate gives methylphenyl[4-(phenylthio)phenyl]sulfonium triflate in 74% yield, whereas the bismethylated product, 1,4-bis(methylphenylsulfonio)benzene bis(triflate), is obtained in 98% yield by the methylation with double the molar quantity of methyl triflate.[117] Bis[4-(phenylthio)phenyl] sulfide is similarly methylated to methylbis[4-(methylphenylsulfonio)phenyl]sulfonium tris(triflate) with thrice the molar quantity of the ester.[117]

The methylation of PPS ($M_w = 1.9 \times 10^4$, $M_w/M_n = 2.8$) has been carried out using methyl triflate in CF_3SO_3H at 110 °C (Scheme 25).[117] The polymer gradually dissolves in CF_3SO_3H during the reaction to give a homogeneous red solution. The fully methylated polymer, poly(methylsulfonio-1,4-phenylene triflate), has been obtained in 100% yield by precipitation from diethyl ether. The higher conversions accomplished with triflates than those with formates and acetates reflect the reactivity of the oxonium ions; those from triflates are more susceptible to the S_N2 reaction with sulfides due to the inductive effect of a CF_3SO_2 group. The conversions with ethyl esters are lower than those with methyl esters, because ethyl groups in the oxonium ions are more inert in the S_N2 reaction due to steric effects.[117] The ethyldiphenylsulfonium ion is less stable at high temperatures than the methyldiphenylsulfonium ion because the former with β-hydrogen atoms undergoes Hofmann elimination to give sulfides and alkenes; such reactivity may also be reflected in the lower conversions in the ethylation of PPS.[117] Butylated PPS has not been obtained due to the lack of the reactivity in butyl esters such as butyl formate.

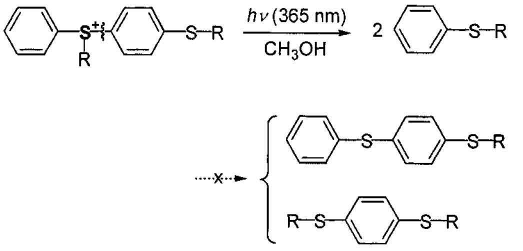
The fully methylated PPS is soluble in polar organic solvents at room temperature. The polymer is also soluble in H_2SO_4 and HCO_2H, but not in CH_3CO_2H. The methylated PPS reverts to PPS by treatment with refluxing pyridine for a sufficiently long time (ca. 10 h) without molecular-weight degradation; this indicates that a regeneration or recycling process of PPS is available.[117]

3. Photochemical Recycling Process

The irradiation by ultraviolet light at the π–π^* transition band of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) results in depolymerization to yield the corre-



Scheme 26.



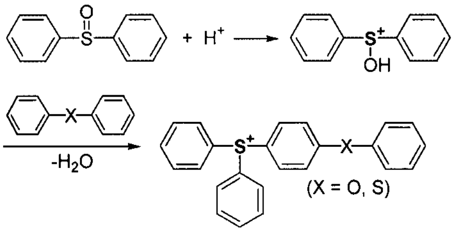
Scheme 27.

sponding monomer, methyl 4-(phenylthio)phenyl sulfide, accompanied by proton generation (Scheme 26).[118] Combination of the depolymerization with the aforementioned methylation of PPS (Scheme 25) provides a photochemical recycling process for PPS through the methylsulfoniophenylene chain to the monomer (Schemes 8 and 9).

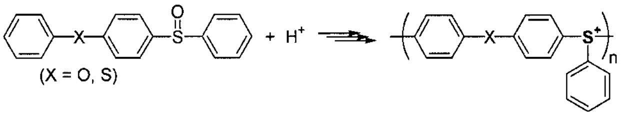
The high-yielding conversion to the monomer through the depolymerization is based on the regioselective bond cleavage of the sulfonium ions.[119] Irradiation of the solution of methyl[4-(methylthio)phenyl]phenylsulfonium triflate (λ_{max} = 294 nm) in CH_3OH or CH_3CN with 365 nm ultraviolet light effects the decomposition of the sulfonium ion to yield exclusively thioanisole without the formation of 4-(methylthio)phenyl phenyl sulfide or 1,4-bis(methylthio)benzene as side products. The reaction reveals a highly selective cleavage of the S^+-C(phenyl) bond adjacent to the electron-donating methylsulfenyl group (Scheme 27).[119] Irradiation with ultraviolet light at 250 nm results in a lower selectivity due to the concomitant decomposition of thioanisole.[119] Photolysis of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) (λ_{max} = 317 nm) in CH_3OH or CH_3CN yields methyl 4-(phenylthio)phenyl sulfide with less than 5% yields of side products such as diphenyl sulfide and bis[4-(methylthio)phenyl] sulfide.[119] The polymer is decomposed more rapidly ($<$ 80 s) than the methyl[4-(methylthio)phenyl]phenylsulfonium ion ($<$ 14 min) upon irradiation with 365 nm light, due to the red-shifted absorption relative to that of the monomeric sulfonium ion and thus to the larger molar extinction coefficient at 365 nm.[118]

The quantum yields for the photolysis of the sulfonium ions depend on the alkyl or aryl group bound to the sulfur atom. The [4-(phenoxy)phenyl]diphenylsulfonium ion, prepared by the super acid-induced condensation of diphenyl sulfoxide and diphenyl ether in the presence of P_2O_5 (Scheme 28), is decomposed with a higher quantum yield (Φ = 0.58 at 313 nm) in CH_3OH than the methyl[4-(methythio)phenyl]phenylsulfonium ion (0.18) due to the larger molar extinction coefficient of triarylsulfonium moieties, in principle, at the photo-irradiation wavelength.[119]

Poly(phenylsulfonio-1,4-phenylenethio-1,4-phenylene triflate), prepared similarly from phenyl 4-(phenylthio)phenyl sulfoxide (Scheme 29), is accordingly converted to the corresponding mononer with a higher quantum yield (Φ = 0.88 at 334 nm) than poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) (0.49).[119] The quantum yields for the photolysis of the sulfonium ions are reflected in their efficiency as photo-acid generators.[119]



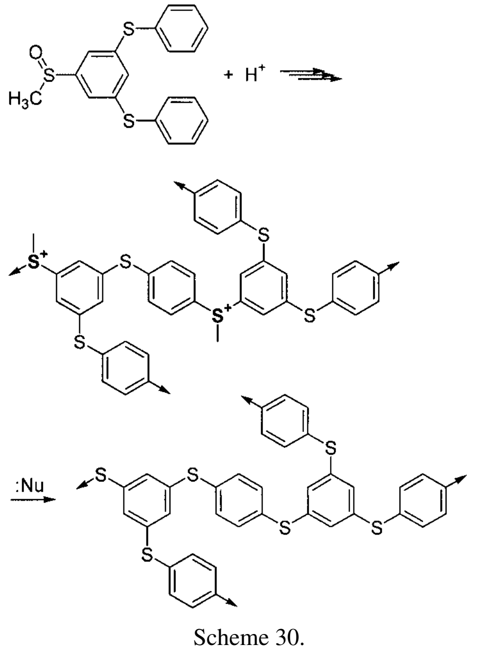
Scheme 28.



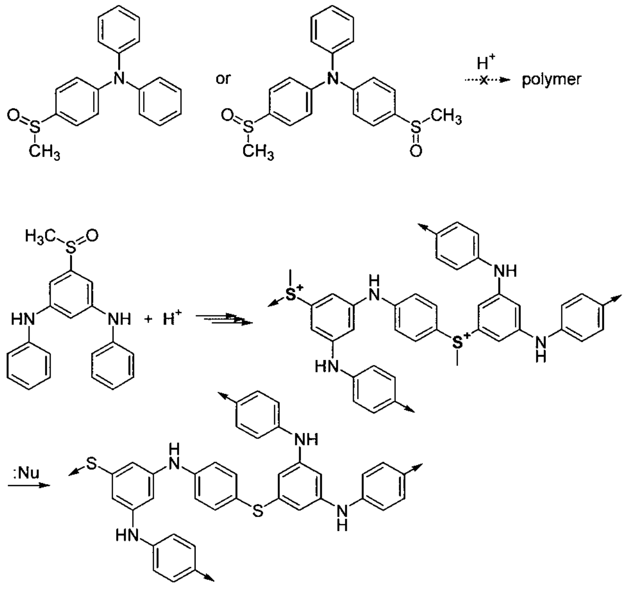
Scheme 29.

4. Hyperbranched Polymers

Hyperbranched polymers, generally synthesized through self-condensation of AB_x-type ($x > 1$) monomers, exhibit low tendency to organize, which is reflected in their low solution viscosity and melt viscosity, high solubility in organic solvents, and intrinsic amorphous states. The first AB_2-type alkyl aryl sulfoxide monomer to be polycondensed in strong acids, methyl 3,5-bis(phenylthio)phenyl sulfoxide (Scheme 30), was designed by Jikei and Kakimoto.[120] The corresponding hyperbranched sulfonium salt has been successfully obtained as a red powder that is soluble in polar solvents such as sulfolane, nitromethane, and acetone. Treatment of the product with refluxing pyridine effects the high-yielding conversion to the hyperbranched PPS with a molecular weight of M_w = 2.6 × 10^4



Scheme 30.



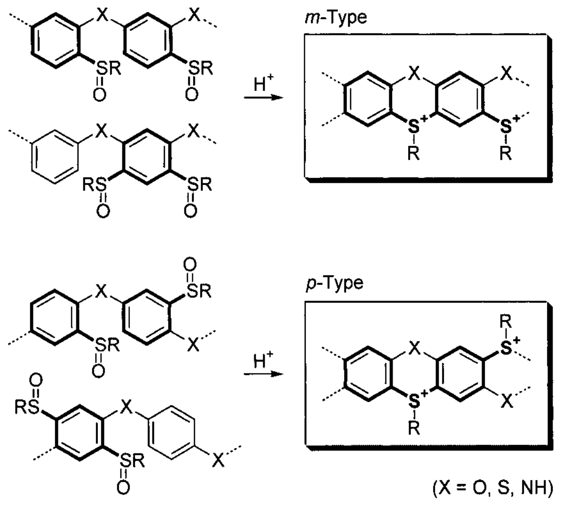
Scheme 31.

(M_w/M_n = 1.5) as an amorphous white powder (T_g = 124 °C). In sharp contrast to the linear PPS which is insoluble in any solvent at room temperature and only soluble in NMP and 1-chloronaphthalene at high temperatures, the hyperbranched PPS is highly soluble in $CHCl_3$ and DMF even at room temperature.[120]

A hyperbranched polymer based on the polyaniline-PPS hybrid structure has been synthesized by Müllen et al.[52] Attempts to polymerize AB_2-type monomers bearing a triphenylamine unit, *N*-[4-(methylsulfinyl)phenyl]diphenylamine and *N*-phenylbis[4-(methylsulfinyl)phenyl]amine, have met with failure (Scheme 31).[52] Reasoning that the polymerization of these monomers might be disfavored because of the concomitant oxidation of the triphenylamine unit by the protonated sulfoxide group in strong acids (Scheme 13), they have selected methyl 3,5-bis(phenylamino)phenyl sulfoxide having two diphenylamine units as the monomer.[52] A hyperbranched polymer has preliminarily been obtained by polycondensation in CF_3SO_3H in the presence of P_2O_5, but the structure of the product has not been defined due to the unexpected low solubility of the product in common organic solvents, both in the polyelectrolyte state and in the neutral state after demethylation with boiling pyridine (Scheme 31).

5. Heteropolyacenes and Related Materials

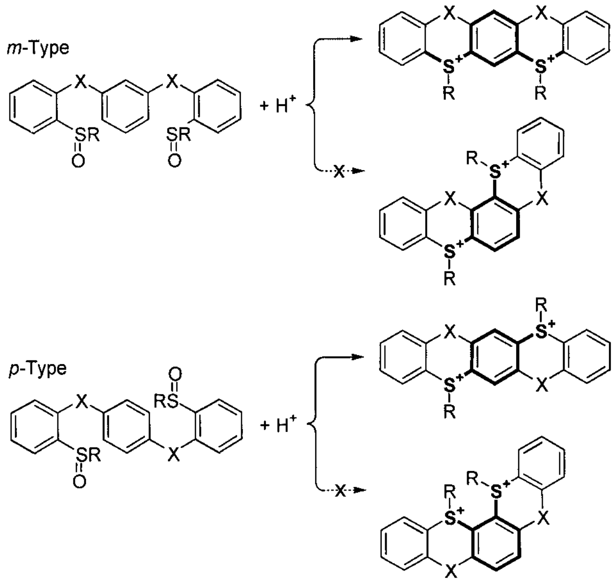
5.1 Synthetic Route of Heteropolyacenes. The interest in rigid-rod ladder-like (ribbon) polymers,[121] especially in the π-conjugated acene series,[122] has persisted over several decades due to their potential application as materials with thermal, mechanical, and chemical stability,[123] optical nonlinearity,[124] and electric conductivity upon oxidative or reductive doping.[125] The classical methods available for the synthesis of the ladder-like polymers are (1) a concerted route with repetitive cycloadditions[126] which typically involve a regiospecific Diels–Alder cyclization,[127] and (2) a multi-step route in which the single-stranded precursor can undergo polymer-analogous cyclization reactions.[128] Recent attention has also been paid to find effective polymer-analogous reactions of pendant functional groups to provide π-conjugated ladder-like polymers, such as the Schiff-base formation between alternating amine and ketone moieties[129] and electrophilic cyclization utilizing 4-alkoxyphenylethynyl groups.[130]



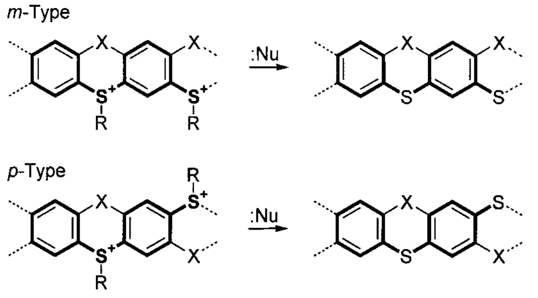
Scheme 32.

Novel synthetic approaches to preparing heteropolyacenes (Scheme 32) containing alkylsulfonio linkages have been reported, and the synthetic utility of aryl sulfoxides as the precursor for heterocyclic compounds has been demonstrated.[131] The synthetic concept of the heteropolyacene consists of a polymer-analogous super acid-induced condensation of aryl sulfoxides, as outlined in Scheme 32, 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 32) has been accomplished by the use of the corresponding prepolymer as the key intermediate bearing methylsulfinyl groups at suitable positions. This method is based on the highly regioselective condensation of the aryl sulfoxide during the six-membered ring formation. Trimer model reactions exclusively provide heteropolyacene model compounds containing 1,2,4,5-benzenetetrayl groups without undesirable isomeric side products containing 1,2,3,4-benzenetetrayl groups due to the steric effect (Scheme 33), which allows the synthesis of linear heteropolyacenes. 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 (vide infra),[131] and the susceptibility to nucleophiles allowing the conversion of alkylsulfonio groups to thioether bonds (Scheme 34).

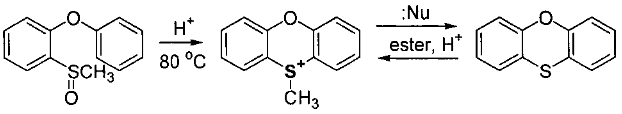
5.2 Phenoxathiinium-Type Heteropolyacenes. With a view to obtain a heteropolyacene containing phenoxathiinium-type repeating units, a model reaction has been carried out (Scheme 35).[131] Upon the exposure of 2-(methylsulfinyl)phenyl phenyl ether to CF_3SO_3H, a methylsulfonio linkage is formed that forces the two benzene units into planarity. The ring-closing reaction does not proceed at room temperature and requires heating at 80 °C. The product, 5-methylphenox-



Scheme 33.



Scheme 34.



Scheme 35.

athiinium triflate, has quantitatively been obtained in 97% yield. The product from intermolecular condensations is not detected when the reaction is carried out under dilution conditions. An alternative synthetic route to the 5-methylphenoxathiinium ion has been provided by the superacid-induced transmethylation (vide supra) using methyl formate and phenoxathiin (Scheme 35). Conversely, the treatment of the 5-methylphenoxathiinium ion with nucleophilic reagents such as pyridine results in the conversion of the methylsulfonio linkage to a thioether bond, yielding phenoxathiin quantitatively (Scheme 35).[131]

The 5-methylphenoxathiinium salt has been subjected to X-ray crystallographic analysis (Fig. 5(a)).[131] The sulfur atom covalently bonded with the three carbon atoms extends 0.829 Å above the $C_{\alpha}C_{\beta}C_{\gamma}$ plane. The arrangement of the four atoms represents a typical trigonal-pyramidal structure. The S–C_{α} bond length (1.813 Å) is comparable with the value of typical alkylsulfonium compounds.[32] The S–C_{β} and S–C_{γ} bond lengths (1.77 Å) are slightly longer than the C–S bond length of phenoxathiin[132] (1.75 Å), due to the decrease in the electron density of the 3*p* lone pair which resonate with the π electrons of the benzene ring. The cation is separated by the triflate anion which is arranged in the proximity of the cations and occupies a σ crystallographic site symmetry.

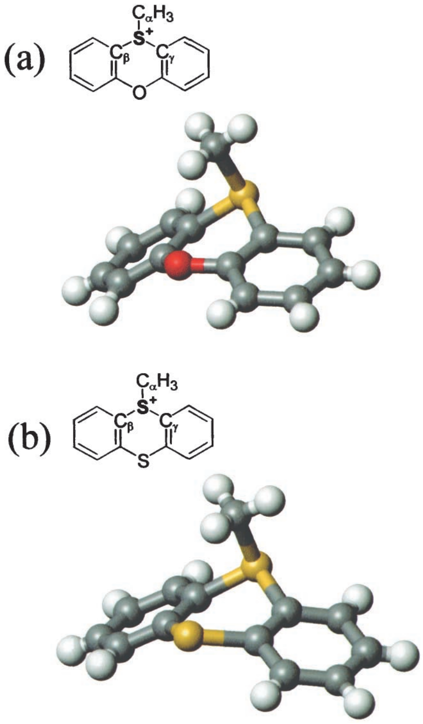
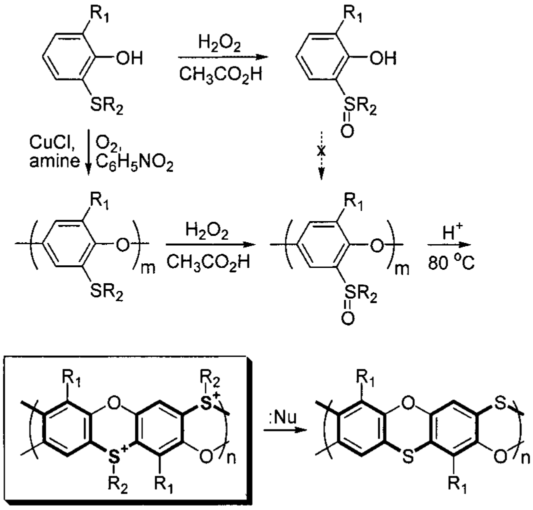


Fig. 5. Structures of the cations of 5-methylphenoxathiinium triflate (a) and 5-methylthianthrenium triflate (b) determined by X-ray crystallography.

In ^{1}H NMR, a deshielding effect of 0.68 ppm is observed for the CH_3S^+-atoms in the 5-methylphenoxathiinium ion relative to the $CH_3S(O)$-atoms in the precursor 2-(methylsulfinyl)phenyl phenyl ether.[131] This effect can be rationalized by considering an enhanced electron-withdrawing (inductive) effect of the sulfur atom upon the conversion of the sulfoxide into the sulfonium ion. Interestingly, the CH_3S^+-resonance of the 5-methylphenoxathiinium ion in ^{13}C NMR appears at a higher magnetic field (δ = 36.8 ppm) than the $CH_3S(O)$-resonance of 2-(methylsulfinyl)phenyl phenyl ether (δ = 42.3 ppm). The shortening of the (phenyl)C–S bond upon the conversion of the 5-methylphenoxathiinium ion to phenoxathiin is reflected in the bathochromic shift of the *B* band near 300 nm in the absorption spectra; the shift can be ascribed to the enhanced auxochromic effect of the thioether bond relative to that of the methylsulfonio group.

2-Methyl-6-(methylsulfinyl)phenol does not undergo oxidative polymerization with a copper catalyst and O_2 (Scheme 36). Reasoning that the oxidation of phenols bearing an electron-withdrawing sulfoxide group might be disfavored because of the high oxidation potential and/or the undesired coordination of sulfoxide to the copper catalyst, we have selected 2-methyl-6-(methylthio)phenol as the monomer. Poly(oxy-2-methyl-6-methylthio-1,4-phenylene) with a molecular weight of $M_w = 3.5 \times 10^4$ ($M_w/M_n = 3.5$) has been obtained from 2-



Scheme 36.

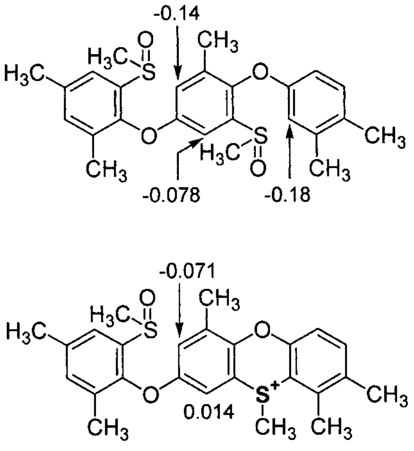


Fig. 6. Carbon net charges of oxyphenylene trimer models for the oxy-2-methyl-6-methylthio-1,4-phenylene chain before and during the course of ladderization obtained by PM3 MO calculations.

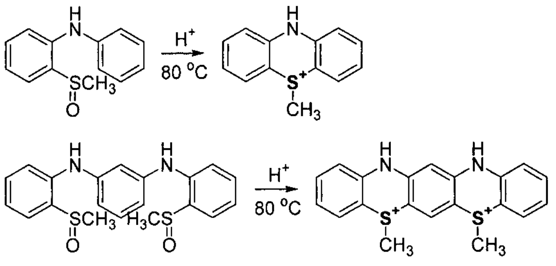
methyl-6-(methylthio)phenol with a Cu-tmeda catalyst (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) under O_2, using nitrobenzene as a solvent.[131] Oxidative polymerization of the monomer in CH_3OH gives the lower molecular-weight product ($M_w = 4.0 \times 10^3$, $M_w/M_n = 2.0$) due to the precipitation of the oligomer during the reaction; the product has also been employed to give the heteropolyacene with a higher solubility in organic solvents by taking advantage of the low molecular weight. The oxidative polymerization of 2-(methylthio)phenol with the copper catalyst and O_2 gives the corresponding polymer with lower yields and molecular weights;[131] the product involves oxy-1,2-phenylene units and branched structures in addition to the oxy-1,4-phenylene units. Such defects are undesirable for the subsequent ring closing reaction.

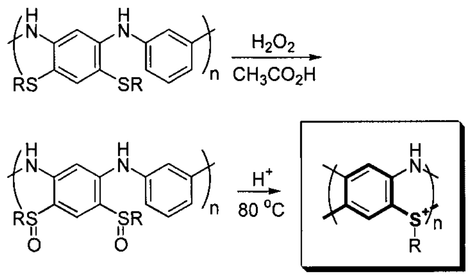
The synthesis of the defect-free heteropolyacene requires the quantitative conversion of both the oxidation of the oxy-2-methyl-6-methylthio-1,4-phenylene chain and the ring-closing of the resulting oxy-2-methyl-6-methylsulfinyl-1,4-phenylene chain (Scheme 36). A variety of oxidants have been examined to oxidize the pendant methylsulfenyl groups in the prepolymer. The oxidation of the oxy-2-methyl-6-methylthio-1,4-phenylene chain with an equimolar amount of H_2O_2 in CH_3CO_2H at room temperature using CH_2Cl_2 as a solvent effects the high-yielding conversion of methylsulfenyl to methylsulfinyl groups without the formation of the undesired methylsulfonyl groups and molecular-weight degradation.[131] Further oxidation to methylsulfonyl groups tends to occur in the presence of excess H_2O_2 or at elevated temperatures. Other oxidants, such as nitric acid and iodosylbenzene, result in lower-yielding conversion to the sulfoxide. The exposure of the oxy-2-methyl-6-methylsulfinyl-1,4-phenylene chain to CF_3SO_3H at 80 °C under dilution conditions induces the polymer-analogous ring-closing reaction of the pendant methylsulfinyl groups to afford the heteropolyacene with phenoxathiinium-type repeating units (Scheme 36); it is soluble in acidic media such as CF_3SO_3H and fairly soluble in organic solvents such as DMSO.[131] The product is obtained as a black powder whose defect-free structure has been confirmed by CP/MAS and ^1H NMR. In the CP/MAS spectra, the $\mathit{C}H_3S^+$-resonance of the heteropolyacene ($\delta = 29.1$ ppm) appears at a higher magnetic field than the $\mathit{C}H_3S(O)$-resonance of the prepolymer, poly(oxy-2-methyl-6-methylsulfinyl-1,4-phenylene) ($\delta = 42.4$ ppm), consistent with the spectral change upon the conversion of 2-(methylsulfinyl)phenyl phenyl ether to the 5-methylphenoxathiinium ion.[131] In addition, there is no remaining $C\mathit{H}_3S(O)$- resonance in the ^1H NMR spectra of the heteropolyacene. The IR and NMR spectra indicate that intermolecular methylsulfonio linkages are unlikely in the product; at much higher concentrations (> 10 mol/L), an insoluble and undefinable polymer network results from the intermolecular condensation of the prepolymer.[131] One could also suppose that the ring-closing reaction does not necessarily occur selectively in the *para* position to the oxo functions. However, spectroscopic results shows no indication of ortho-coupling. The experimental behavior is supported by the PM3 semiempirical MO calculation of the model compounds; the net charges on the carbon atoms indicate that those at positions *ortho* to the methylsulfinyl and methylsulfonio groups are more cationic and less susceptible to the electrophilic substitution reaction than the carbon atoms at positions *para* to these groups (Fig. 6).[131] The regioselectivity in ladderization is also explained by a steric effect. Cyclization at an ortho-position to the methylsulfonio group gives a rather unstable structure in which hydrogen atoms of two methylsulfonio groups can collide with each other.

PPS and PPO are known to show two complementary types of solid-state properties. While PPS is a partly (ca. 65%) crystalline material, PPO is mainly amorphous (T_g = 205–220 °C, T_m = 267 °C)[133] and is completely miscible with polystyrene. Their linear hybrid, poly(oxy-1,4-phenylenethio-1,4-phenylene), is a crystalline polymer,[18,35] and the melting point of the annealed, sufficiently high molecular-weight polymer (T_m = 191 °C)[35] is ca. 90 °C lower than that of PPS because of an increase in ΔS_m associated with the T_m due to the lower molecular symmetry. Indeed, C–O bonds (1.36 Å) are significantly shorter than C–S bonds (1.74 Å), and C–O–C angles (124°) are larger than C–S–C angles (110°).[46] The ladder-like hybrid of PPS and PPO (i.e., the heteropolyacene with phenoxathiin-type building blocks) displays interesting thermal properties, including a very high $T_{d10\%}$ due to the double stranded, rigid, and planar structure. Indeed, it has been reported[134] that, among poly(pyromellitimide)s containing a variety of aromatic groups in the diamine component, the highest stability in thermogravimetry is achieved with a polymer containing the phenoxathiin group; all polyimides based on the same diamines and the anhydrides of biphenyltetracarboxylic acids or oxybis(benzenedicarboxylic acid)s show the same trend,[134] which is quite natural since the phenyl rings are linked with two bonds ensuring the high thermal stability of the diamine component.

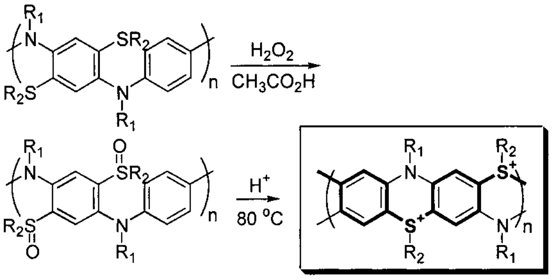
The high-yielding conversion of the 5-methylphenoxathiinium ion to phenoxathiin by treatment with pyridine (Scheme 35) has prompted the examination of the demethylation of the phenoxathiinium-type heteropolyacene (Scheme 36).[131] The efficacy of this reaction for use in polymers has been demonstrated by the successful conversion of the alkylsulfonioarylene polymers to the corresponding thioarylene polymers (vide supra). Treatment of the phenoxathiinium-type heteropolyacene with refluxing pyridine for a sufficiently long time to ensure the completion of the reaction yields the demethylated product as a pale brown powder (Scheme 36).[131] The absence of the $\mathit{C}H_3S^+$-resonance in CP/MAS and of the IR signals due to triflate anions establish the structure of the phenoxathiin-type heteropolyacene. A comparison of the $T_{d10\%}$ of the linear analogues, such as PPS, PPO, and poly(oxy-1,4-phenylenethio-1,4-phenylene) with that of the phenoxathiin-type heteropolyacene reveals significant enhancement of the stability against thermolysis by the ladder-like framework; the heteropolyacene shows the onset of decomposition near 450 °C, followed by only a slight weight loss, and the thermal stability ($T_{d10\%}$ = 555 °C) is even higher than that of the linear hybrid.[131] The phenoxathiinium-type heteropolyacene and the phenoxathiin-type heteropolyacene both show no X-ray diffraction peak, revealing that they are amorphous. The DSC analysis shows no thermal transition before the decomposition, indicating the lack of glass transition in the temperature range of interest due to the rigid structures.[131]

5.2 Phenothiazinium-Type Heteropolyacenes. It has been reported that the reductive ring closure of 1,1′-diphenyl-2-nitrothioether provides phenothiazine.[135] The reaction has been applied to the synthesis of triphenodithiazine (12*H*,14*H*-5,7-dithia-12,14-diazapentacene).[136] However, the corresponding ladder-like polymers or oligomers may not be obtained by this method because of the inherent low conversion. On the other hand, it has been demonstrated that phenothaizine ring systems, the 10*H*-5-methylphenothiazinium ion and the triphenodithiazinium (12*H*,14*H*-5,7-dimethyl-5,7-dithionia-12,14-diazapentacene) ion, are quantitatively obtained by the super acid-induced intramolecular condensations of [2-(methylsulfinyl)phenyl](phenyl)amine and *N*,*N*′-bis[2-(methylsulfinyl)phenyl]-1,3-phenylenediamine, respectively (Scheme 37).[137] This reaction provides the synthetic route to the corresponding defect-free phenothiazinium-type heteropolyacene. The reaction does not take place at room temperature and requires heating at 80 °C.[137] The ring-closed products, 10*H*-5-methylphenothiazinium triflate and 12*H*,14*H*-5,7-dimethyl-5,7-dithionia-12,14-diazapentacene bis(triflate), have been obtained in > 95% yields.[137]


Scheme 37.


Scheme 38.

A *m*-type heteropolyacene (Scheme 32) containing benzenetetrayl units linked with imino and methylsulfonio bonds has been prepared from poly(imino-4,6-bis(methylsulfinyl)-1,3-phenyleneimino-1,3-phenylene) by the super acid-induced intramolecular condensation of the pendant methylsulfinyl groups (Scheme 38).[137] The oxidative polymerization of aniline, the most convenient method to obtain polyaniline, is not applicable to 2-(methylsulfinyl)aniline due to the high oxidation potential. The oxidative polymerization of 2-(methylthio)aniline has met with failure; it gives only unidentified products, probably due to side reactions between the aminyl radical and the methylthio group. Attempts to polymerize halogenated anilines bearing methylsulfinyl substituents have also met with failure. Reasoning that the Pd-catalyzed polymerization might be disfavored because of the steric effect and/or the electron-withdrawing nature of the sulfoxide group, we have adopted a synthetic route involving the three steps similar to those in the synthesis of the oxy-2-methyl-6-(methylsulfinyl)-1,4-phenylene chain (vide supra).[137] The prepolymer, poly(imino-4,6-bis(methylthio)-1,3-phenyleneimino-1,3-phenylene) with a molecular weight of $M_w = 1.2 \times 10^4$ ($M_w/M_n = 2.0$), has been synthesized by the Pd-catalyzed arylamination of 1,3-dibromo-4,6-di(methylthio)benzene with 1,3-phenyenediamine.[137] The sterically hindered phosphine compound 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) serves as a good ligand for the polymerization. The oxidation of the polymer with H_2O_2 in CH_3CO_2H using CH_2Cl_2 as a solvent effects the high-yielding conversion of methylsulfenyl to methylsulfinyl groups.[137] The exposure of the resulting imino-4,6-bis(methylsulfinyl)-1,3-phenyleneimino-1,3-phenylene chain to CF_3SO_3H at 80 °C for 20 h induces the ring-closing reaction to afford the phenothiazinium-type heteropolyacene (Scheme 38).[137] Interestingly, the polymer with a planar π-conjugated structure does not have any bulky substituent and yet dissolves in polar organic solvents such as DMSO and DMF as well as in HCO_2H, H_2SO_4, and CF_3SO_3H due to the ionic methylsulfonio groups. The DSC analysis shows no thermal transition before the decomposition which initiates at

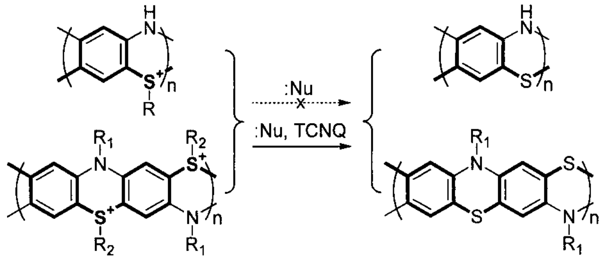


Scheme 39.

temperatures above 165 °C, indicating the lack of glass transition due to the rigid structure.

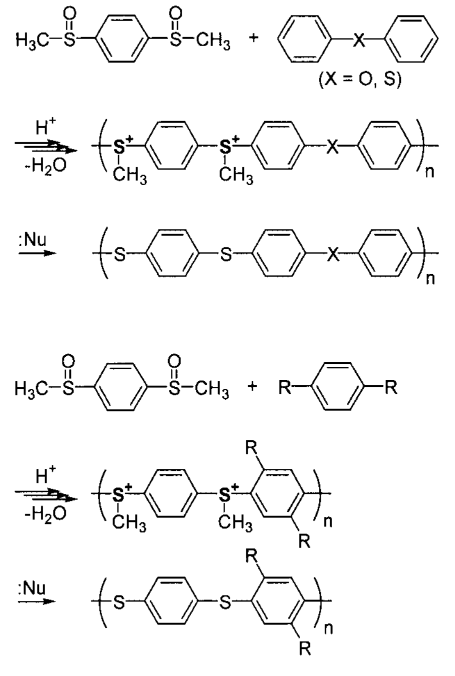
The *p*-type isomer (Scheme 32) has similarly been prepared from poly(*N*-ethylimino-2,5-bis(methylsulfinyl)-1,4-phenylene-*N*-ethylimino-1,4-phenylene) (Scheme 39).[138] The corresponding prepolymer, poly(*N*-ethylimino-2,5-bis(methylthio)-1,4-phenylene-*N*-ethylimino-1,4-phenylene) with a molecular weight of $M_w = 7.4 \times 10^3$ ($M_w/M_n = 3.7$), has been successfully prepared by the Pd-catalyzed arylamination of 1,4-dibromo-2,5-bis(methylthio)benzene with *N*,*N*′-diethyl-1,4-phenylenediamine using (+)-(*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine as a phosphine ligand.[138] The oxidation of the prepolymer with H_2O_2, followed by the ring-closing reaction, affords the *p*-type heteropolyacene (Scheme 39) as a black powder that is soluble in acidic media such as CF_3SO_3H and in polar organic solvents such as DMSO.[138]

Unlike the common alkyldiarylsulfonium ions, the alkylsulfonio groups in the phenothiazinium-type heteropolyacenes are unreactive to nucleophiles; the dealkylation reaction does not take place by treatment with pyridine or tetraalkylammonium halides, or even with stronger nucleophiles such as triethylamine and aqueous NaOH (Scheme 40). The lack of reactivity against nucleophiles can be ascribed to the stabilization of the sulfonium ion by the aforementioned donor-acceptor interaction (Scheme 10) with the imino groups in the polymer. The demethylation is accomplished by the treatment with nucleophiles in the presence of TCNQ as an external acceptor which interferes with the intramolecular CT interaction (Scheme 40).[138] The products, the phenothiazine-type heteropolyacenes without residual TCNQ, have been obtained in high yields. The intramolecular CT interaction in the phenothiazinium ion is reflected in the chemical shift of the methylsulfonio protons in ^{1}H NMR which appear at a much higher magnetic field ($\delta = 2.95$ ppm) than those of the phenoxathiinium ion ($\delta = 3.49$ ppm)[131] and the thianthrenium ion ($\delta = 3.50$ ppm)[139] due to the decrease in the effect of deshielding of methyl groups by the sulfonium ion through electron donation from the adjacent imino group.

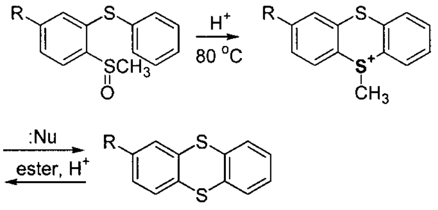


Scheme 40.

5.3 Thianthrenium-Type Polyheteroaenes. The thianthrene ring system deserves much attention as a redox active center[140] and a spin coupler[141] due to the stability of the cation radical which can even be isolated for independent experiments.[142] The unique reactivity of the cation radical is represented by its addition to a variety of alkenes to provide bisthianthrenium adducts.[143] The product can then be recycled to thianthrene by reaction with nucleophilic dealkylating reagents such as pyridine (vide supra). A heteropolyacene bearing thianthrenium-type repeating units could serve as a multielectron redox center applicable to alkene sensors[143] and high spin polymers.[144] The synthesis of the thianthrenium-type heteropolyacene hinges on the use of 1,4-bis(methylsulfinyl)benzene as a bifunctional monomer which has been found to condense with a wide variety of aromatic molecules. The protonation of a methylsulfinyl group is not impeded by the methylsulfonio group at the *para* position of the benzene ring, and hence the polymerization with an equimolar amount of diphenyl sulfide in CF_3SO_3H yields poly[methylsulfonio-1,4-phenylene(methylsulfonio)-1,4-phenylenethio-1,4-phenylene bis(triflate)] (Scheme 41). The high molecular weight of the product determined after conversion to PPS by the treatment with pyridine ($M_w = 1.4 \times 10^5$, $M_w/M_n = 3.3$) corroborates the high reactivity of the bifunctional monomer (Scheme 41). Poly(oxy-1,4-phenylenethio-1,4-phenylenethio-1,4-phenylene) with a molecular weight of $M_w = 2.6 \times 10^4$ ($M_w/M_n = 3.5$) has been obtained by polymerization with diphenyl ether, followed by treatment with refluxing pyridine (Scheme 41), whose melting point ($T_m = 188$ °C) is ca. 90 °C lower than that of PPS and comparable or even lower than that of poly(oxy-1,4-phenylenethio-1,4-phenylene)[35] as a result of an increased ΔS_m due



Scheme 41.



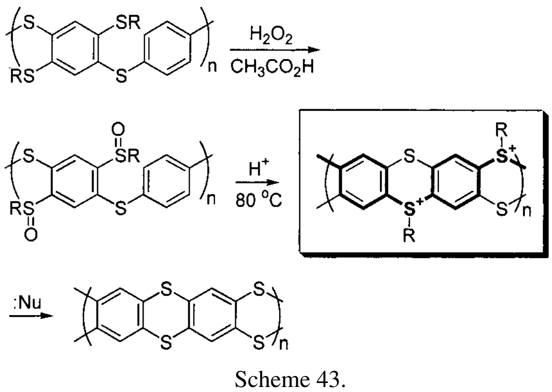
Scheme 42.

to the lower symmetry. Aromatic molecules that react with a strong acid, such as diphenylamine and pyridine, are not applicable as the monomer. Polymerization does not proceed with benzene, naphthalene, or biphenyl either because they induce a significant decrease in the electron density upon the formation of the arylsulfonio bond, which depresses the subsequent propagation reactions. On the other hand, 1,4-bis(methylthio)benzene bearing two electron-donating methylsulfenyl groups is susceptible to polycondensation with 1,4-bis(methylsulfinyl)benzene. This reaction produces poly[methylsulfonio-1,4-phenylene(methylsulfonio)-2,5-bis(methylthio)-1,4-phenylene bis(triflate)] on which the synthesis of the thianthrenium-type heteropolyacene hinges (Scheme 41). Demethylation of the polymer by the treatment with refluxing pyridine affords poly[thio-2,5-bis(methylthio)-1,4-phenylenethio-1,4-phenylene] with a molecular weight of $M_w = 4.1 \times 10^3$ ($M_w/M_n = 1.7$).[139]

A model reaction for the synthesis of thianthrene ring systems has been carried out (Scheme 42). Upon exposure of 4-methyl-2-(methylsulfinyl)phenyl phenyl sulfide to CF_3SO_3H at 80 °C, a methylsulfonio linkage is formed that forces the two benzene rings into planarity. The product, 3,5-dimethylthianthrenium triflate, has been obtained in 90% yield. An alternative synthetic route to a thianthrenium salt has been provided by the super acid-induced transmethylation to thianthrene using methyl formate, which yields 5-methylthianthrenium triflate (Scheme 42). Conversely, the treatment of the 5-methylthianthrenium ion with nucleophilic reagents such as pyridine results in the conversion of the methylsulfonio linkage to a thioether bond.[139]

5-Methylthianthrenium triflate has been subjected to X-ray crystallographic analysis (Fig. 5(b)). The torsion angle of the best least-squares plane of the adjacent benzene rings in the 5-methylthianthrenium ion (41.06°) is smaller than that in the methyldiphenylsulfonium ion (83.12°), demonstrating the planarity of the 5-methylthianthrenium ion. Interestingly, the interplanar angle of the 5-methylthianthrenium ion is intermediate between those of thianthrene (50.65°) and its cation radical (6°).[145] In ^1H NMR, a deshielding effect of 0.95 ppm is observed for the methylsulfonio protons in the 3,5-dimethylthianthrenium ion ($\delta = 3.64$ ppm) relative to the methylsulfinyl protons in the precursor, 4-methyl-2-(methylsulfinyl)phenyl phenyl sulfide ($\delta = 2.69$ ppm), due to the enhanced electron-withdrawing (inductive) effect of the sulfur atom upon the conversion of the sulfoxide into the sulfonium ion.[139]

The oxidation of poly[thio-2,5-bis(methylthio)-1,4-phenylenethio-1,4-phenylene] with an equimolar amount of H_2O_2 in CH_3CO_2H at room temperature using CH_2Cl_2 as a solvent effects the high-yielding conversion of the methylthio groups to the methylsulfinyl groups without the formation of the undesired methylsulfonyl groups (Scheme 43). GPC analysis of the product reveals that no molecular-weight degradation occurs during the oxidation. Further oxidation to the methylsulfonyl groups tends to occur in the presence of excess H_2O_2 or at elevated temperatures. The exposure of poly[thio-2,5-bis(methylsulfinyl)-1,4-phenylenethio-1,4-phenylene] to CF_3SO_3H at 80 °C under dilution conditions induces the polymer-analogous ring-closing reaction of the pendant methylsulfinyl groups to afford the thianthrenium-type heteropolyacene as a brown powder which is soluble in organic solvents such as CH_3CN (Scheme 43). The methylsulfonio resonance of the product ($\delta = 3.16$ ppm) appears at a lower magnetic field than the methylsulfinyl resonance of the prepolymer, consistent with the spectral change upon the conversion of 4-methyl-2-(methylsulfinyl)phenyl phenyl sulfide to the 3,5-dimethylthianthrenium ion. Based on the high-yielding conversion of the 5-methylthianthrenium ion to thianthrene by the treatment with pyridine, the thianthrenium-type heteropolyacene has been demethylated by treatment with refluxing pyridine for a sufficiently long time to ensure the completion of the reaction. The product, a thianthrene-type heteropolyacene, is obtained as a pale brown powder insoluble in any solvents (Scheme 43).[139]

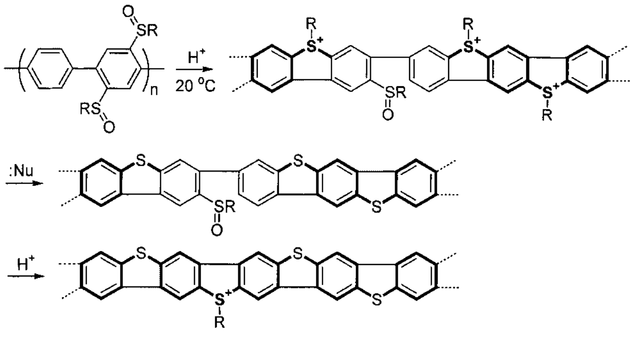


Scheme 43.

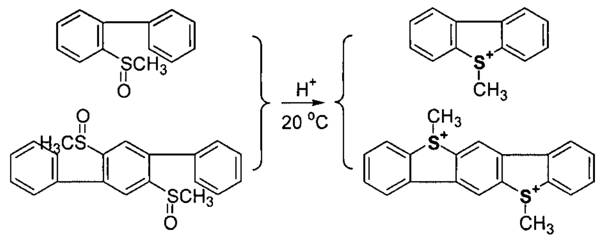
5.4 Benzothiophenium-Type Heteropolyacenes. An alkylsulfonio-bridged 1,4-phenylene ladder-like oligomer (i.e., the benzothiophenium-type heteropolyacene) with a ribbon-like structure has been prepared.[146] The corresponding prepolymer, the alkylsulfinyl-substituted oligo(1,4-phenylene), has been obtained by Suzuki aryl–aryl coupling[147] between 1,4-bis(alkylsulfinyl)-2,5-dibromobenzene and bis(2,3-dimethylbutane-2,3-diyl) 1,4-phenylenebisboronate. The polycondensation of an equimolar mixture of 1,4-dibromo-2,5-bis(methylsulfinyl)benzene and the boronate has been carried out with a Pd(0) catalyst in refluxing 1,2-dimethoxyethane and aqueous $NaHCO_3$ for 20 h to produce oligo[2,5-bis(methylsulfinyl)-1,4-phenylene-1,4-phenylene] as an off-white powder with the degree of oligomerization of $n = 6$ determined by TOF mass spectroscopy (Scheme 44).[146] The product is soluble in $CHCl_3$, diethyl ether, NMP, HCO_2H, and H_2SO_4.

A ring-closing reaction to yield the benzothiophenium ion has been confirmed using model compounds (Scheme 45). The superacidification of 1-(methylsulfinyl)biphenyl and 1,4-diphenyl-2,5-bis(methylsulfinyl)benzene produces the corresponding benzothiophenium ions, respectively, in high yields.[146]

An intramolecular ring-closing reaction of the prepolymer



Scheme 44.



Scheme 45.

has been carried out in three steps as follows. In the first step, the exposure of the prepolymer to CF_3SO_3H at room temperature under dilution conditions to avoid the intermolecular cross-linking reaction yields the partially ring-closed product bearing both methylsulfonio and methylsulfinyl groups with a conversion of only 77%, due to the strong electron-withdrawing effect of the methylsulfonio group bound to the phenyl ring that retards the further condensation of the sulfoxide (Scheme 44). In the second step, the partially ring-closed polymer is reacted with nucleophiles to yield the demethylated product as a yellow powder bearing methylsulfinyl groups and thioether bonds instead of methylsulfonio groups. The ring-closing reaction in CF_3SO_3H is completed in the third step due to the electron-donating effect of the neighboring phenylsulfenyl groups. The ladder-like oligomer bearing both benzothiophene-type repeating units and benzothiophenium-type repeating units has been obtained as a brown powder which is soluble in HCO_2H, H_2SO_4, and CF_3SO_3H but insoluble in CH_3OH, CH_3CN, and $CHCl_3$.[146]

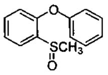
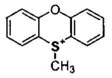
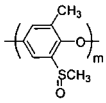
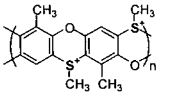
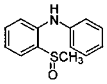
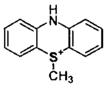
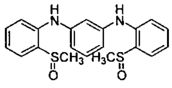
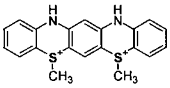
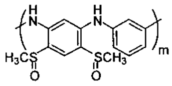
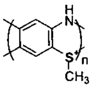
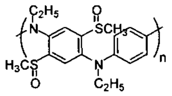
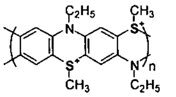
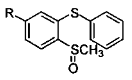
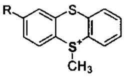
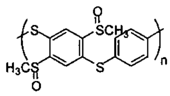
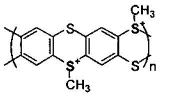
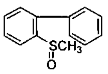
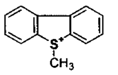
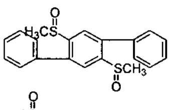
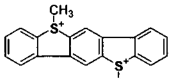
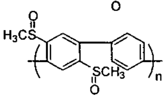
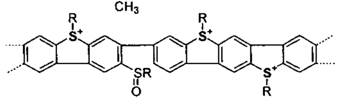
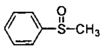
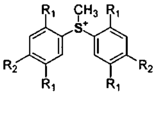
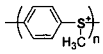
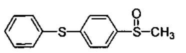
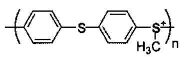
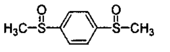
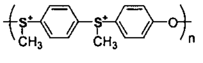
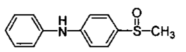
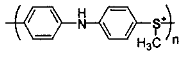
6. 3d-2p Resonance in Conformationally Constrained Arylsulfonium Salts

6.1 Resonance Effects in Arylsulfonium Ions. An important issue in the chemistry of π-conjugated ladder-like polymers is to resolve the problem of their inherent low solubility, which renders their structure elucidation and practical application very difficult. The problem of improving the solubility has frequently been addressed by derivatizing ladder-like structures with suitable side groups to destabilize the interchain interaction. Indeed, rigid skeletons generally require flexible alkyl substituents to improve their solubility and processability, sacrificing the crystallinity and intermolecular interactions.[148] The synthesis of a new definable and characterizable π-conjugated ladder-like backbone is thus an important subject of study. On the other hand, polyelectrolytes could be considered as a candidate for a highly soluble ladder-like framework even without such side groups. The first ladder-like polymer electrolyte, to our knowledge, is a polycarbenium ion with thioxanthylium-type repeating units reported by Müllen et al.,[128] which has been claimed to be isoelectronically related to poly[*n*]acenes. However, the characterization of the polymer has been impeded by insufficient solubility in common solvents.[128]

The principal findings in the chemistry of heteropolyacenes include the facts that the conversion of poly(oxy-2-methyl-6-methylsulfinyl-1,4-phenylene) to the phenoxathiinium-type 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[3] (R_2S^+-$^-CR'_2$ $\longleftrightarrow$ $R_2S{=}CR'_2$) 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.[1] 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,[149] 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.[1,150] 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.[151] 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.[152] 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 phenoxathiinium-type heteropolyacene and the 5-methylphenoxathiinium ion under neutral and superacidic conditions reveal that the delocalization of the positive charge on the sulfur atom could also occur into the benzene ring under strongly acidic conditions and that it could be enhanced with the ladder-like framework. The resonance effects in arylsulfonium ions are reminiscent of the formation of a novel heteroaromatic system upon the protonation of vinylene trithiocarbonate with FSO_3H–SbF_5 in SO_2 at the thiocarbonyl sulfur,[153] and the extension of the π-conjugation length via the vacant p-orbital of a boron atom.[154]

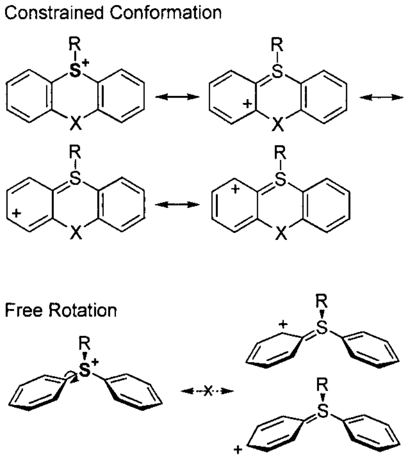
6.2 Resonance Effects in Heteropolyacenes. The ^1H NMR spectra reveal that the CH_3S^+-atoms in the phenoxathiinium-type heteropolyacene are deshielded by only 0.11 ppm compared to the $CH_3S(O)$-atoms in the prepolymer, poly(oxy-2-methyl-6-methylsulfinyl-1,4-phenylene); the magnitude of the deshielding is much smaller than that of the model com-

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts of Methyl Groups Bound to Sulfur Atoms$^{a)}$

Sulfoxides (precursors)	^{1}H	^{13}C	Ref.	Sulfonium ions	Abbr.	^{1}H	^{13}C	Ref.
	2.81$^{b)}$	42.3$^{b)}$	131		**1** **1/H**$^+$	3.49$^{c)}$ 2.99$^{e)}$	36.8$^{d)}$ 36.0$^{e)}$	131 131
	2.78$^{b)}$	42.2 42.4$^{f)}$	131 131		**2**	2.89$^{d,g)}$	29.1$^{f)}$	131
	2.75	40.9	137		**3**	2.95$^{d)}$	33.7$^{d)}$	137
	2.93	38.7	137		**4**	3.02 3.05$^{d)}$	35.0 35.1$^{d)}$	137 137
	2.92	41.0	137		**5**	3.14$^{d)}$		137
	2.55		138		**6**	2.89		138
 (R = CH_3)	2.69	44.0	139	 (R = H) (R = CH_3)	 **7**	3.50$^{c)}$ 3.53$^{c)}$	25.5$^{c)}$ 23.7$^{c)}$	139 139
	2.74$^{b)}$		139		**8**	3.16$^{h)}$		139
	2.27	41.5	146		**9**	3.66$^{c)}$	34.4$^{c)}$	146
	2.40	41.5	146		**10**	4.50$^{c)}$	35.7$^{c)}$	146
	2.62		146		**11**	3.15–3.32$^{i)}$		146
	2.72	43.8	20	 (R$_1$ = R$_2$ = H) (R$_1$ = H, R$_2$ = CH_3) (R$_1$ = CH_3, R$_2$ = H)	**12**	3.83$^{d)}$ 4.01$^{c)}$ 3.63 3.57	26.9$^{d)}$ 28.9$^{c)}$ 28.9 27.5	27 27 27 27
					**13**	3.85$^{j)}$	28.9$^{j)}$	31
	2.67	46.0	20		**14**	3.79$^{d)}$ 3.78$^{k)}$ 3.60$^{h)}$	28.1$^{l)}$ 28.9$^{k)}$ 29.0$^{h)}$	17 23 38
	2.70	43.9	139		**15**	3.76$^{i)}$		139
	2.70$^{d)}$	43.5$^{d)}$	51		**16**	3.70$^{d)}$	24.0$^{d)}$	51

a) δ in ppm. Excepts where noted, solvent = $CDCl_3$. b) In CD_2Cl_2. c) In acetone-d_6. d) In DMSO-d_6. e) In CF_3SO_3H. Standard (external) = TMS/$CDCl_3$. f) CP/MAS. g) Low molecular-weight part. h) In CD_3CN. i) In CF_3SO_3D. j) In D_2O. k) In DCO_2D. l) In $HCO_2H/CDCl_3$.

pound 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 (Table 1). 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



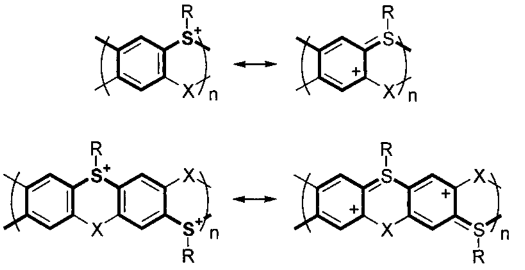
Scheme 46.

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. It follows that the decrease in the deshielding effect for the CH_3S^+-atoms in the case of the ladder-like polymer can not be ascribed to the electron-donating effect of the methyl group on the benzene ring in the phenoxathiinium-type heteropolyacene. These results can be rationalized only by considering a significant carbenium ion contribution to the resonance structure of the phenoxathiinium-type heteropolyacene (Scheme 46), 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. Such a deshielding effect for the phenyl protons is reminiscent of the downfield shift of ring fluorine resonances in the ^{19}F NMR spectrum of (pentafluorophenyl)dihalosulfonium ions under strongly acidic conditions due to the accommodation of the positive charge by the pentafluorophenyl ring through p-π/d-π interactions.[149]

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 (Fig. 5(a))[131] and methyldiphenylsulfonium hexafluoroantimonate (Fig. 2(a)),[31] the control of the 5-methylphenoxathiinium ion without the oxo linkage between the two benzene rings. Obviously, 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[31] (83.12°). In addition, while a comparison of crystal structures of phenoxathiin[132] and diaryl sulfides[30] ((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. Moreover, the smaller C–S–C bond angles in the methyldiphenylsulfonium ion[31] (103.6°) than those in diaryl sulfides[30] (C–S–C angle: bis(4-methylphenyl) sulfide, 109°; bis(4-bromophenyl) sulfide, 109°; diphenyl sulfide, 113°), which has been ascribed to the enhanced p-character of the C–S bond and the s-character of the sulfonium center,[2] does not hold for the annulated compounds (C–S–C angle: the 5-methylphenoxathiinium ion, 98.3°; phenoxathiin, 98°). These characteristics could be an indication that, with the planarized benzene rings in the 5-methylphenoxathiinium ion, the π-electron density is partly accommodated by the methylsulfonio group.

It has been hypothesized that the charge delocalization should be pronounced when the resulting carbenium ions are stabilized in strongly acidic media (Scheme 46). Müllen et al. have reported that CF_3SO_3H acts as a key dehydrating agent to allow the formation of a carbenium-containing π framework.[128] The ^1H NMR spectrum of the 5-methylphenoxathiinium ion dissolved in CF_3SO_3H reveals a decrease in the deshielding effect with a magnitude of 0.5 ppm for the CH_3S^+-atoms relative to those under neutral conditions, consistent with extensive charge delocalization into the aromatic rings. Additional evidence supporting this interpretation has been provided by the optical absorption spectra. In the absence of acid, the conversion of phenoxathiin to the 5-methylphenoxathiinium ion does not lead to the bathochromical shift of the absorption band, which indicates that the methylsulfonio linkage, as well as the sulfide linkage, act as conjugation barriers. On the other hand, the CF_3SO_3H solution of the 5-methylphenoxathiinium ion is deep blue and shows new absorption bands near λ_{max} = 513 and 578 nm due to the resonance structure (Scheme 46). No cation radical is detected in the ESR spectrum of the blue solution. The formation of the protonated carbonium and oxonium species is unlikely, due to the positive charge on the sulfur atom of the 5-methylphenoxathiinium ion. The absorption band in the visible region is not attributable to the intramolecular CT transition because there is no indication of intermolecular donor-acceptor interactions[31] between the methyldiphenylsulfonium ion and diphenyl ether in CF_3SO_3H even at very high concentrations. It seems reasonable to suppose that the 5-methylphenoxathiinium ion has a more planar conformation in strongly acidic media than in the crystal state due to the enhanced carbenium ion contribution to the resonance form (Scheme 46). Neutralization of the CF_3SO_3H solution of the 5-methylphenoxathiinium ion reinstates the ^1H NMR and optical absorption spectra identical to those obtained with the neutral solution of the pristine 5-methylphenoxathiinium ion, ensuring the reversibility of the changes upon the superacidification of the 5-methylphenoxathiinium ion.

Rigid planar conjugated systems are characterized by a distinct bathochromical shift of the longest wavelength absorption with the increasing number of fused aromatic subunits.[155] Furthermore, they generally show very sharp absorption edges due to their rigid character.[128] The significant red shifts of the absorption band upon the formation of the phenoxathiinium-type heteropolyacene 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, which is close to the absorption band of the 5-methylphenoxathiinium ion under acidic conditions. The featureless absorption edge tailing to ca. 940 nm indicates that the contribution of the delocalized state to the resonance form of the phenox-



Scheme 47.

athiinium-type heteropolyacene (Scheme 47) 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.[129]

It must be noted that the electron delocalization through the ladder-like polymer backbone, rather than the mere planarization of the benzene rings, is responsible for the spectral changes upon the ladderization. A comparison of the absorption spectrum with that of a two-unit model derived from 1,4-bis[(2-methylsulfinyl)phenoxy]benzene by the ring-closing reaction, which shows λ_{max} at 298 nm without significant tailing edge in neutral media, reveals that the molecular length, rather than the tetrasubstituted benzene units, mainly affects the tailing of the absorption edge of the phenoxathiinium-type heteropolyacene under neutral conditions. Added support has also 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 of $\sigma = 2 \times 10^{-5}$ S cm^{-1}, the phenoxathiin-type heteropolyacene is an insulator ($\sigma < 10^{-11}$ S cm^{-1}). The lack of emission bands in the phenoxathiinium-type heteropolyacene and in the 5-methylphenoxathiinium ion indicates that the sulfur atoms play a role in the exciton quenching. A comparison of the spectroscopic properties of the sulfonium ions under acidic and neutral conditions provides additional insights into the π-electron delocalization through the sulfonium group. In the first place, the lack of noticeable changes upon superacidification in the ^{1}H NMR and the optical absorption spectra of the methyldiphenylsulfonium ion (Scheme 46) and those of the methylsulfonio-1,4-phenylene ion with unconstrained phenylene ring conformations demonstrates, conversely, the efficacy of affecting planarity by the oxo linkages in the 5-methylphenoxathiinium ion (Scheme 46) and the phenoxathiinium-type heteropolyacene (Scheme 47) for the charge delocalization. In the second place, the lack of a noticeable difference between the spectroscopic properties of the phenoxathiinium-type heteropolyacene in CF_3SO_3H and those in neutral media indicates that the ladder-like framework also seems to play a role in the stabilization of the carbenium resonance forms (Scheme 47). In the final place, while the phenoxathiinium-type heteropolyacene is black, poly(methylsulfonio-1,4-phenylene triflate) is a white powder and colorless in both neutral and superacidic media.

The 5-methylthianthrenium ion (Fig. 5(b)) shows structural and spectroscopic properties similar to those of the 5-methylphenoxathiinium ion (i.e., the small magnitude of the deshielding effect (0.84 ppm) for the CH_3S^+-atoms compared to the $CH_3S(O)$-atoms in the precursor and the short S–C_β and S–C_γ distances (1.77–1.78 Å)).[139] A smaller deshielding effect of only 0.42 ppm observed for the CH_3S^+-atoms in the thianthrenium-type heteropolyacene relative to the $CH_3S(O)$-atoms in the prepolymer (Table 1) can be rationalized by considering an enhanced carbenium ion contribution to the resonance structure (Scheme 47), the charge delocalization into the benzene ring causing a decrease in the deshielding effect for the CH_3S^+-atoms.

The 10*H*-5-methylphenothiazinium ion and the 12*H*,14*H*-5,7-dimethyl-5,7-dithionia-12,14-diazapentacene ion show even smaller magnitudes of the deshielding effect (Table 1) for the CH_3S^+-atoms relative to the $CH_3S(O)$-atoms in the corresponding precursors, because of the intramolecular charge transfer effect from the lone pair of the nitrogen atom to the vacant 3d orbital of the adjacent sulfur atom.[31] The 10*H*-5-methylphenothiazinium ion has an absorption maximum at 349 nm which is bathochromically shifted from that of phenothiazine (λ_{max} = 317 nm).[137] Further bathochromical shifts are observed in the 12*H*,14*H*-5,7-dimethyl-5,7-dithionia-12,14-diazapentacene ion (λ_{max} = 426 nm) and the phenothiazinium-type heteropolyacene (λ_{max} = 440 nm).[137] The optical band gap estimated from the onset wavelength (520 nm) is E_g = 2.4 eV. The phenothiazinium-type heteropolyacene is fluorescent. The photoluminescent spectrum from a DMSO solution shows an emission maximum at 584 nm when excited at 340 nm.[137] A flexible film has been obtained by casting from the solution; this film shows an electric conductivity of $\sigma = 8 \times 10^{-6}$ S cm^{-1} without doping.[137] The bathochromic shift of the absorption maximum has also been observed upon the formation of the benzothiophenium units (Scheme 45).[146] The small torsion angles of the phenylene rings due to the bridging with the methylsulfonio group results in the expansion of the π conjugation. The effect is more remarkable in the benzothiophenium-type heteropolyacene (Scheme 44).[146] However, attempts to establish the π-electron delocalization into the sulfonio moiety in these polymers have failed due to the following reasons. In the first place, the extensive π-conjugation in the benzothiophenium-type heteropolyacene containing thioether bonds and methylsulfonio linkages (Scheme 44) has been ascribed rather to the forcing into planarity of the benzene rings than to the *p*-π/d-π interaction between the methylsulfonio linkages and the benzene ring. Secondly, the optical band gap estimated from the tailing edge of the absorption spectrum of the phenothiazinium-type heteropolyacene indicates that the π-electron conjugation does not extend throughout the polymer chain; the localized intramolecular donor-acceptor interaction between the imino and methylsulfonio moieties has also been considered to play a role in the visible absorption.[31,137] Taking into account the lack of such donor-acceptor interaction between oxo and methylsulfonio linkages, one can ascribe the smaller band gap in the phenoxathiinium-type heteropolyacene only to the π-electron delocalization through the polymer backbone.

Fig. 7 shows the relationship between the chemical shifts of

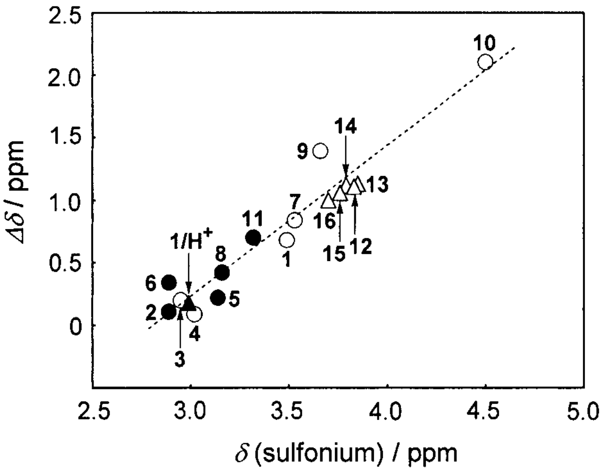


Fig. 7. Plots of the chemical shifts of the CH_3S^+-atoms in arylsulfonium ions (the heteropolyacenes (●), the ring-closed model dimers and trimers (○) and the linear alkylsulfonioarylene chains (△) in the neutral media, and the 5-methylphenoxathiinium ion in CF_3SO_3H (▲)) in ^1H NMR versus the magnitude of the deshielding effect relative to the $CH_3S(O)$-resonances of the corresponding sulfoxides as the precursors. Abbreviations are as in Table 1.

the CH_3S^+-resonances of the aromatic sulfonium ions in ^1H NMR and the magnitudes of the deshielding compared to the $CH_3S(O)$-resonances of the corresponding sulfoxides as the precursors. The almost linear relationship reveals the lack of great differences between the chemical shifts of the $CH_3S(O)$-resonances of the sulfoxides, thus allowing for the comparison of the extent of the deshielding effect for the CH_3S^+-groups in the sulfonium ions. It is clear that the CH_3S^+-resonances in the heteropolyacenes (closed circles) appear in the highest magnetic-field region among those of the alkyldiarylsulfonium ions, demonstrating the advantage of the ladder-like framework for the resonance structure (Scheme 47). The CH_3S^+-resonance of the 5-methylphenoxathiinium ion in CF_3SO_3H is observed near those of the heteropolyacenes due to the enhanced resonance structure under acidic conditions. The significant shielding of the CH_3S^+-atoms in the phenothiazinium-type ions is ascribed to the intramolecular charge transfer interaction. The CH_3S^+-atoms in the six-membered ring-closed model dimers are slightly shielded due to the partially delocalized resonance state. The highly deshielded CH_3S^+-atoms in alkyldiarylsulfonium ions with unconstrained phenylene conformations reveal the lack of noticeable 3d–2p resonance effects.

7. Other Architectures and Future Perspectives

Long alkyl chains attached to the hydrophilic alkylsulfonioarylene chain as the side group can affect the structural dimensionality of the main chain, which has been observed as characteristic thermal behaviors. A typical example has been provided by a liquid crystalline mesophase that is found during the heating of a comb-like polymer, poly(octadecylsulfonio-1,4-phenyleneoxy-1,4-phenylene triflate).[156] The polymer shows two distinct endotherms at T_1 = 43 °C (ΔH = 14 J/g) and T_2 = 60 °C (ΔH = 10 J/g).[156] The first endotherm at T_1 has been attributed to the thermal transition from the crystalline to the mesophase, based on the octadecyl chains. The second endotherm at T_2 is due to the isotropic melting behavior of the polymer. Since the two transitions are reversible and can be detected during the heating and the cooling repeatedly, the comb-like polymer is expected to serve as a thermotropic liquid crystalline material.

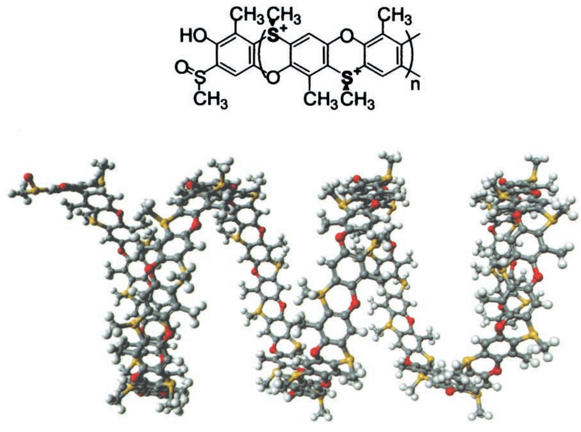


Fig. 8. Estimated helical conformation of the phenoxathiinium-type heteropolyacene with stereoregular methylsulfonio groups.

Polymers with stereoregular methylsulfonio groups could provide higher dimensional structures, such as the possible helical conformation of the phenoxathiinium-type heteropolyacene (Fig. 8). Because the super acid-induced intramolecular condensation of aryl sulfoxides with optical chirality has been found to afford optically active heteropolyacenes, one could expect that the helical heteropolyacene is obtained from a prepolymer with stereoregular alkylsulfinyl groups.

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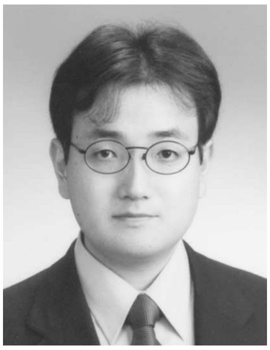

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