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Synthetic Routes to Polyheteroacenes: Characterization of a Heterocyclic Ladder Polymer Containing Phenoxathiinium-type Building Blocks

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ABSTRACT: The synthetic routes to ladder polymers that consist of benzenetetrayl subunits with oxo and methylsulfonio linkages are described. As the key intermediate, poly(phenylene oxide)s having pendant methylsulfenyl groups are prepared by copper-catalyzed oxidative polymerization of the corresponding phenols with O_2. The oxidation of the polymer with an equimolar amount of H_2O_2 in the presence of acetic acid effects the high-yielding conversion of methylsulfenyl to methylsulfinyl groups without the formation of the undesired methylsulfonyl groups. The superacidified condensation of the resulting polymer (Swern reaction of aryl sulfoxides) under dilution conditions induces the polymer-analogous intramolecular electrophilic ring-closing reaction of the hydroxymethylphenylsulfonium cation onto the adjacent benzene ring to yield the required ladder polymer, which has proved to be a semiconductor with an intrinsic electric conductivity of 2×10^{-5} S/cm. A comparison of the spectroscopic properties of the ladder polymer with those of the model compounds such as 5-methylphenoxathiinium triflate and phenoxathiin discloses π-electron delocalization over the methylsulfonio linkages, demonstrating the efficacy of the ladderization for p−π/d−π interactions in arylsulfonium moieties. This synthetic approach permits the thio and alkylsulfonio ladder linkages for a variety of phenyl ethers to form in high yields.

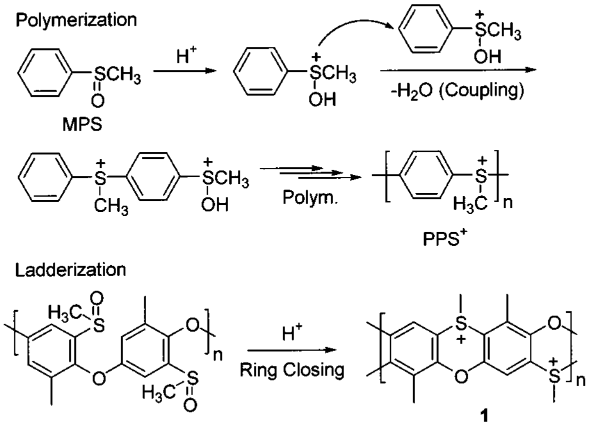
Introduction

Herein we report a novel synthetic approach to preparing π-conjugated laddertype poly(phenylene oxide)s containing methylsulfonio linkages and demonstrate the synthetic utility of aryl sulfoxides as the precursor for heterocyclic compounds. The synthetic concept consists of a polymer-analogous condensation of aryl sulfoxides as outlined in Scheme 1. This type of reaction yields a soluble ladder polymer **1** with benzenetetrayl repeating units bridged by oxo and sulfonio groups. Specifically, the spectroscopic results reveal the π-electron delocalization over the methylsulfonio moiety in the ladder polymer.

The interest in rigid-rod ladder (ribbon) polymers,[1] especially in the π-conjugated acene series,[2] has persisted over several decades due to their potential application as materials with thermal, mechanical, and chemical stability,[3] optical nonlinearity,[4] and electric conductivity upon oxidative or reductive doping.[5] The classical methods available for the synthesis of the ladder polymers are (1) a concerted route with repetitive cycloadditions,[6] which typically involve a regiospecific Diels−Alder cyclization,[7] and (2) a multistep route in which the single-stranded precursor can undergo polymer-analogous cyclization reactions.[8] Recently, some effective polymer-analogous reactions of pendant functional groups have been devised to provide π-conjugated ladder polymers, such as the Schiff base formation between alternating amine and ketone moieties[9a−d] and electrophilic cyclization utilizing 4-alkoxyphenylethynyl groups.[9e−g]

We have developed the chemistry to prepare a variety of linear alkylsulfoniophenylene polymers using aryl sulfoxides as monomers.[10] In particular, we have established that methyl phenyl sulfoxide (MPS) undergoes self-polycondensation in CF_3SO_3H under suitable conditions to produce poly(methylsulfonio-1,4-phenylene triflate) (PPS^+) in 100% yield (Scheme 1).[11] The protonated sulfoxide (hydroxylmethylphenylsulfonium cation) electrophilically attacks the terminal phenyl ring (Swern reaction of aryl sulfoxides)[12] to exclusively produce linear, high molecular-weight PPS^+. Interestingly, PPS^+ is highly soluble in organic polar solvents and even in H_2O.[13] Thus, it seems reasonable to suppose that a soluble, defect-free polymer **1** should be obtained when the same reaction is employed as the polymer-analogous reaction. The synthesis of **1** hinges on the use of the prepolymer poly(*p*-phenylene oxide) bearing *o*-methylsulfenyl groups (**3b**) as the key intermediate, which is prepared by copper-catalyzed oxidative polymerization of an *o*-methylsulfenylated phenol with O_2 followed by oxidation with H_2O_2 (Scheme 2). Although a large number of studies have been made on the oxidative

Scheme 1



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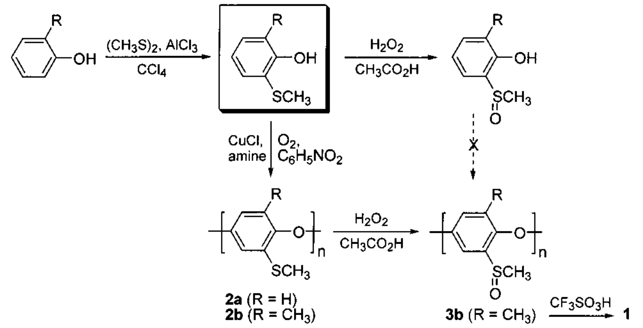
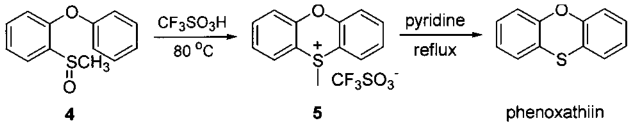
Scheme 2



Scheme 3



polymerization of phenols 2,6-disubstituted with alkyl[14] and aryl[15] groups and halogen atoms,[16] the oxidative polymerization of alkylsulfenylated phenols is unprecedented to our knowledge.

A further important issue is to resolve the problem of the inherent low solubility of the π-conjugated ladder polymers, which renders their structure elucidation and practical application very difficult. Indeed, rigid skeletons require flexible alkyl substituents to improve their solubility and processability, sacrificing the crystallinity and intermolecular interactions.[17] Therefore, the synthesis of a new definable and characterizable π-conjugated ladder backbone is an important subject of study. Our principal findings include the facts that the conversion of **3b** to **1** give rises to a distinct bathochromic shift in the longest wavelength absorption and a drastic increase in the intrinsic electric conductivity. Thus, the issue for **1** has to do with whether the benzene ring could resonate through the cationic site and develop a π-conjugated ladder framework. The delocalization of the electron density into the low-lying vacant 3d orbitals of sulfur has been proposed in sulfur ylides[18] ($R_2S^+{-}^-CR'_2 \leftrightarrow R_2S{=}CR'_2$) to rationalize the stabilization of the negative charge of the carbanion by the adjacent sulfur, though the preferred geometry of the carbon and sulfur atoms indicates that sulfur ylides do not contain an appreciable C=S bond character.[19] On the other hand, the p−π/d−π overlap and charge delocalization of arylsulfonium moiety into the aromatic ring has been found in the dihalo(pentafluorophenyl)sulfonium cation,[20] 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,[21] which 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 an inductive effect.[22] The lower pK_a of *p*-(dimethylsulfonio)phenol (7.30) than that of *p*-(trimethylammonio)phenol (8.35) is also indicative of the p−π/d−π interaction in the arylsulfonium moieties,[23] which should contribute to the stabilization of the conjugate base through the quinoid resonance form. In analogy to these observations, the NMR spectroscopic studies of **1** and a model compound, 5-methylphenoxathiinium triflate, 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 framework. This may be 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[24] and the extension of the π-conjugation length via the vacant *p*-orbital of a boron atom.[25]

Results and Discussion

Synthesis and Structure of a Model Compound (5). To confirm the ring-closing reaction by the Swern condensation of aryl sulfoxides, a model reaction was carried out (Scheme 3). 2-(Methylsulfinyl)phenyl phenyl ether (**4**) was prepared by the Ullmann ether synthesis. The admixture of phenol and 2-(methylsulfinyl)bromobenzene at 160 °C under basic conditions in the presence of a copper catalyst afforded **4** in 80% yield. Upon the exposure of **4** to CF_3SO_3H, a methylsulfonio linkage was formed that forced the two benzene units into planarity. The ring-closing reaction did not proceed at room temperature and required heating at 80 °C. The product, 5-methylphenoxathiinium triflate (**5**), was quantitatively obtained in 97% isolated yield. Triflic acid, the strongest monobasic acid, was found to be the most effective for the quantitative reaction. The product from intermolecular condensations was not detected when the reaction was carried out under dilution conditions.

An alternative synthetic route to **5** was provided by the superacid-induced transmethylation[26] with methyl formate and phenoxathiin, which yielded **5** in 95% yield (see Experimental Section). Conversely, the treatment of **5** with nucleophilic reagents such as pyridine resulted in the conversion of the methylsulfonio linkage to a sulfide bond yielding phenoxathiin quantitatively (Scheme 3).

Although a number of crystal structures of the sulfonium salts have been reported, such as those of the dihalosulfonium salts[27] and the aurated sulfonium salt,[28] no systemized study has been reported on those of the arylsulfonium salts, to the best of our knowledge. In attempts to obtain typical parameters for the bond lengths and angles and the torsional angles of the annulated arylsulfonium compounds, the product **5** was subjected to X-ray crystallographic analysis. Layering the acetone solution of **5** with diethyl ether afforded colorless needlelike crystals suitable for an X-ray diffraction study (Table 1) which revealed the structure of **5** as shown in Figure 1. The S(1) atom covalently bonded with the three carbon atoms extends 0.829 Å above the C(1)C(2)C(13) plane. The arrangement of the four atoms represents a typical trigonal-pyramidal structure. The S(1)−C(1) bond length (1.813 Å) is comparable with the value of typical alkylsulfonium compounds.[29] It is known that the bond length between the sulfur and the phenyl carbon is indicative of the oxidation state of the sulfur atom (Table 2). The S(1)−C(2) and S(1)−C(13) bond lengths (1.766 and 1.768 Å, respectively) are slightly longer than the C−S bond length of phenoxathiin[30] (1.75 Å) due to the decrease in the electron density of the 3p 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.

Table 1. Summary of X-ray Crystallographic Data for 5

emp form	$C_{14}H_{11}F_3S_2O_4$	absn coeff μ	3.85 cm^{-1}
fw	364.35	$2\theta_{max}$ (deg)	55.0
cryst syst	orthorhombic	no. of reflns cold	4112
space group	*P*nma (no. 62)	no. of unq reflns	4111
a (Å)	23.928(2)	no. of obsd reflns	2186 [$I > 3.00\sigma(I)$]
b (Å)	18.881(2)	params	249
c (Å)	6.961(2)	refln/param ratio	8.78
V (Å^3)	3144(1)	*R*	0.054
Z	8	R_w	0.044
density (calcd)	1.539 g/cm^3	goodness-of-fit	2.82
crystal size (mm)	0.1 × 0.1 × 1.2	max peak in diff map	0.77 e^-/Å^3
radiation	MoKα (λ = 0.71069 Å)	min peak in diff map	−0.57 e^-/Å^3

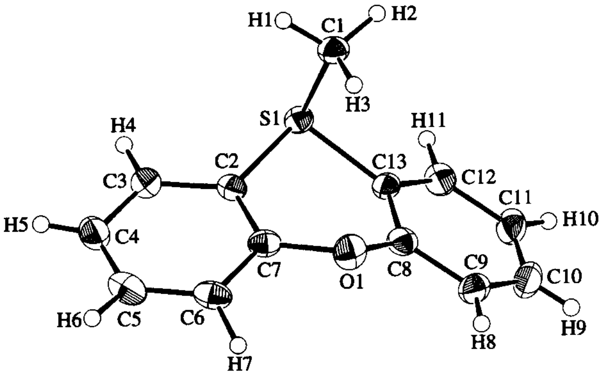


Figure 1. ORTEP view (30% probability ellipsoids) of **5**.

Table 2. Selected Bond Lengths and Angles for 5 Characterized by X-ray Crystallography[a]

atoms	bond length, Å	atoms	bond length, Å
S(1)−C(1)	1.813(5)	S(1)−C(2)	1.766(4)
S(1)−C(13)	1.768(4)	O(1)−C(7)	1.393(5)
O(1)−C(8)	1.377(5)		

atoms	angle, deg	atoms	angle, deg
C(1)−S(1)−C(2)	101.3(2)	C(1)−S(1)−C(13)	100.7(2)
C(2)−S(1)−C(13)	98.3(2)	S(1)−C(2)−C(7)	119.9(4)
S(1)−C(13)−C(8)	119.3(4)	O(1)−C(7)−C(2)	122.7(4)
C(7)−O(1)−C(8)	118.0(3)	O(1)−C(8)−C(13)	123.0(4)

[a] Estimated standard deviations are given in parentheses.

In ^1H NMR, a deshielding effect of 0.68 ppm is observed for the CH_3S^+- atoms in **5** relative to the $CH_3S(O)$- atoms in the precursor **4** (Figure 2). This effect is rationalized by considering an enhanced electron-withdrawing (inductive) effect of the sulfur atom upon the conversion of the sulfoxide into the sulfonium. Interestingly, the CH_3S^+- resonance of **5** in ^{13}C NMR appears at a higher magnetic field (δ = 36.8 ppm) than the $CH_3S(O)$- resonance of **4** (δ = 42.3 ppm).

The optical absorption spectra of **5** and phenoxathiin were recorded in CH_3CN (Figure 3a). The shortening of the (phenyl)C−S bond upon the conversion of **5** to phenoxathiin is reflected in the bathochromic shift of the *B* band[32] near 300 nm, which can be ascribed to the enhanced auxochromic effect of the sulfide bond relative to that of the sulfonium center.

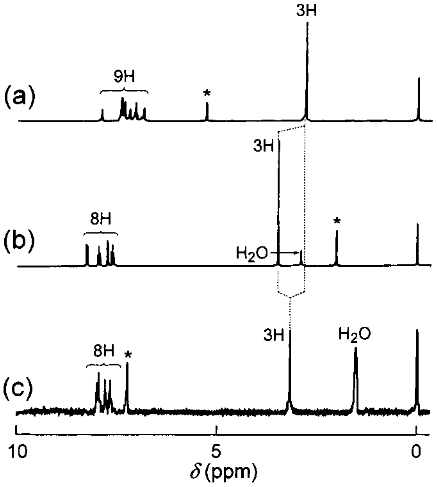


Figure 2. ^1H NMR spectra of (a) **4** in CD_2Cl_2, (b) **5** in acetone-d_6, and (c) **5** in CF_3SO_3H. (a, b) TMS was used as the internal standard. (c) A $CDCl_3$ solution of TMS was used as the external standard, which was placed near the sample solution by use of a double tube. Residual proton signals in the deuterated solvents are marked with asterisks.

Monomer Synthesis. We have already established that methylsulfenyl groups are conveniently introduced into a variety of aromatic compounds by the superacidified reaction with dimethyl sulfoxide (DMSO) (Swern reaction of sulfoxides)[8,10,13] followed by the treatment with nucleophilic reagents such as pyridine. However, phenol and cresol gave undesired *p*-methylsulfenylated phenols as major products in this reaction. In attempts to synthesize the *o*-substituted phenols, we turned to the methylsulfenylation of phenols by the Friedel−Crafts reaction with dimethyl disulfide in the presence of $AlCl_3$. The reaction proceeded at temperatures higher than 40 °C, and the desired products were obtained in the highest yield (ca. 50%) when the reaction was carried out in *m*-dichlorobenzene at 100 °C for 5 h. The products were most conveniently prepared and isolated with CCl_4 as the solvent at 80 °C for 1 h (see Experimental Section). The *p*-substituted phenols became the major products in solvents such as C_2H_5OH and CH_3CN or with a prolonged time of reaction. At higher temperatures, cresol was eventually converted to 2-(methylsulfenyl)toluene.

The oxidation of methylsulfenyl to methylsulfinyl groups was accomplished by the treatment with H_2O_2 in the presence of CH_3CO_2H. The product, the *o*-methylsulfinylated phenols, were obtained quantitatively in 98% isolated yield. Further oxidation to the undesired *o*-methylsulfonylated phenols did not take place when an equimolar amount of H_2O_2 was used as the oxidant.

Synthesis of Precursor Polymers. Attempts to polymerize the *o*-methylsulfinylated phenols with a copper catalyst and O_2 met with failure (Table 3). 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 turned to the polymerization of the *o*-methylsulfenylated phenols. Thus, polymer **3b** was prepared as outlined in Scheme 2.

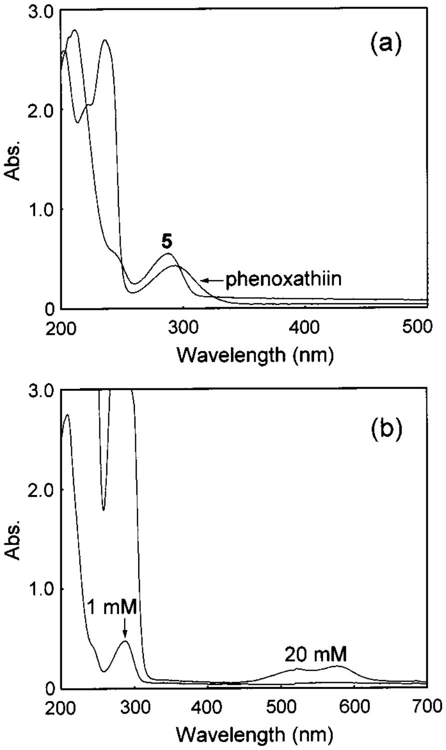


Figure 3. Absorption spectra of (a) the model compounds **5** (1 mmol/L) and phenoxathiin (1 mmol/L) in CH_3CN and (b) **5** (1 and 20 mmol/L) in CF_3SO_3H. The optical path length was 0.1 cm.

The oxidative polymerization of the monomers with a copper catalyst bearing a variety of amine ligands was examined (Table 3). A linear polymer **2b** was obtained from 2-methyl-6-(methylsulfenyl)phenol with a Cu−tmeda catalyst (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) under O_2. In particular, a relatively high molecular weight polymer ($M_w = 35\,000$, $M_n = 10\,000$) was obtained with a ligand/Cu ratio of 10 with nitrobenzene as the solvent. On the other hand, polymerization in CH_3OH gave the lower molecular weight **2b** due to the precipitation of the oligomer during the reaction; the product ($M_w = 4000$, $M_n = 2000$) was also employed to give **1** with a higher solubility in organic solvents by taking advantage of the low molecular weight (vide infra).

The oxidative polymerization of 2-(methylsulfenyl)phenol with the copper catalyst and O_2 gave polymer **2a** with lower yields and molecular weights (Table 3). ^1H NMR revealed that the product involved oxy-1,2-phenylene units and branched structure in addition to the oxy-1,4-phenylene units, which is undesirable for the subsequent ring-closing reaction.

The synthesis of a defect-free polymer **1** requires the quantitative conversion of both the sulfinylation of **2b** and the ring-closing of **3b**. A variety of oxidants were examined to oxidize the pendant methylsulfenyl groups in **2b** (Table 4). The oxidation of polymer **2b** with an equimolar amount of H_2O_2 in CH_3CO_2H at room temperature with CH_2Cl_2 as a solvent effected the high-yielding conversion of methylsulfenyl to methylsulfinyl groups without the formation of the undesired methylsulfonyl groups (Table 4). Gel-permeation chromatographic (GPC) analysis of **3b** revealed that no molecular weight degradation occurred during the sulfinylation. Further oxidation to methylsulfonyl groups tended to occur in the presence of excess H_2O_2 or at elevated temperatures. Other oxidants such as nitric acid and iodosobenzene resulted in the lower yielding conversion to the sulfoxide.

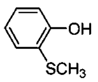
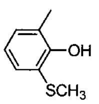
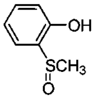
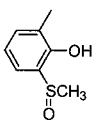
In ^1H NMR of **3b**, there is no CH_3S- or $CH_3S(O)_2$- resonance (Figure 4a); these typically appear near $\delta = 2.3$ and 3.2 ppm, respectively. The linear oxy-1,4-phenylene structure of **3b** is corroborated by the two distinct peaks at $\delta = 6.80$ and 7.26 ppm ascribed to the phenyl protons.

Ring-Closing Reaction. The exposure of **3b** to CF_3SO_3H at 80 °C under dilution conditions induced the polymer-analogous ring-closing reaction of the pendant methylsulfinyl groups to afford the planarized polymer **1**, which was soluble in acidic media such as CF_3SO_3H and fairly soluble in organic solvents such as DMSO. Polymer **1** is obtained as a black powder whose defect-free structure is confirmed by cross-polarization magic-angle spinning (CP/MAS) and ^1H NMR. In the CP/MAS spectra (Figure 5a,b), the CH_3S^+- resonance of **1** ($\delta = 29.1$ ppm) appears at a higher magnetic field than the $CH_3S(O)$- resonance of **3b** ($\delta = 42.4$ ppm), consistent with the spectral change upon the conversion of **4** to **5**. In addition, there is no remaining $CH_3S(O)$- resonance in the ^1H NMR spectra of the lower molecular-weight **1** (Figure 4b) (the higher molecular weight **1** is not sufficiently soluble in solvents to be clearly examined by NMR). The IR and NMR spectra indicate that intermolecular methylsulfonio linkages unlikely formed in **1**; at much higher concentrations (>10 mol/L), an insoluble and undefinable polymer network resulted due to the condensation of **3b**.

One could also suppose that the cyclization reaction does not necessarily occur selectively in the *para* position to the oxo functions. However, spectroscopic results showed no indication of *ortho* coupling. The experimental behavior is supported by the PM3 semiempirical MO calculation of the model compounds, where the net charges on the carbon atoms 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 (Figure 6). The regioselectivity in ladderization is also explained by steric effect. The cyclization at *ortho* position to the methylsulfonio group gives a considerably unstable structure in which hydrogen atoms of two methylsulfonio groups can collide with each other.

Spectroscopic Properties. The ^1H NMR spectra reveal that the CH_3S^+- atoms in **1** are deshielded by only 0.11 ppm compared to the $CH_3S(O)$- atoms in the precursor **3b**. The magnitude of the deshielding dramatically decreases for the ladder polymer. In fact, a deshielding effect of 0.68 ppm is observed for the methyl protons in **5** relative to those in **4** (Table 5). In the methylsulfoniophenylene polymer without the oxo linkage (PPS^+), the magnitude of the deshielding effect relative to the corresponding monomer (MPS) is even larger (1.1 ppm). On the other hand, a deshielding effect of ca. 0.9 ppm for the phenyl proton in **1** relative to **3b** is significantly larger than the deshielding effect of ca. 0.56 ppm for those in **5** relative to **4**. It follows that the decrease in the deshielding effect for the CH_3S^+- atoms in the case of the ladder polymer cannot be ascribed to the electron-donating effect of the methyl group on the benzene ring in **1**. These results can be rationalized only by considering a significant carbenium ion contribution to the resonance structure of **1** (Scheme 4), the charge

Table 3. Copper-Catalyzed Oxidative Polymerization of Phenols with O_2[a]

monomer[b]	ligand	[ligand]/[Cu][c]	product	yield (%)[d]	M_w[e]	M_n[e]
	pyridine	10		0		
	2,6-lutidine	10	**2a**	65	2400	1200
	tmeda[f]	10	**2a**	35	3500	1900
	pyridine	10		0		
	2,6-lutidine	10		0		
	tmeda	10	**2b**	98	35000	10000
	tmeda	20	**2b**	78	17000	6900
	tmeda	10[g]	**2b**	80	4000	2000
	pyridine	10		0		
	2,6-lutidine	10		0		
	tmeda	10		0		
	pyridine	10		0		
	2,6-lutidine	10		0		
	tmeda	10		0		

[a] Except where noted, solvent = nitrobenzene, room temperature, 12 h. [b] 0.25 mol/L. [c] Cu = CuCl (0.025 mol/L). [d] Insoluble part in methanol. [e] Determined by gel-permeation chromatography versus polystyrene standards. [f] *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine. [g] Solvent = methanol.

Table 4. Sulfinylation of 2b[a]

oxidant	solvent	concn (mol/L)	temp (°C)	time (h)	oxidation state (%)[b] sulfide	sulfoxide	sulfone	product
$H_2O_2 + CH_3CO_2H$	CH_2Cl_2	0.1	0	6	85	15	0	
	CH_2Cl_2	0.1	0	24	0	100	0	**3b**
	CH_2Cl_2	0.1	rt	24	0	100	0	**3b**
	CH_2Cl_2	2.5	0	24	0	0	100	c
	CH_2Cl_2	2.5	rt	24	0	0	100	c
	CCl_4	2.5	40	24	0	0	100	c
HNO_3 (70%)	CH_3CN		rt	24	50	41	9	
C_6H_5IO	CH_2Cl_2	0.12	rt	6	55	45	0	
	CH_2Cl_2	0.12	rt	24	30	70	0	

[a] 0.1 mol/L. [b] Determined by integration of ^1H NMR peaks near $\delta = 2.3$ (-SCH_3), 2.8 [-S(O)CH_3], and 3.2 ppm [-S(O)$_2$CH_3]. [c] Poly(oxy-2-methyl-6-methylsulfonyl-1,4-phenylene).

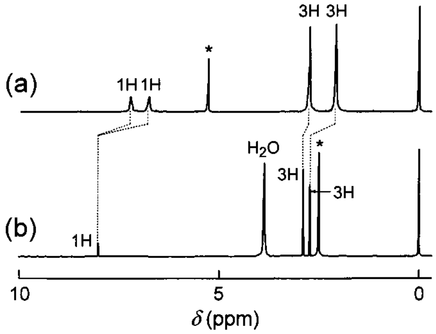


Figure 4. ^1H NMR spectra of (a) **3b** in CD_2Cl_2 and (b) the lower molecular weight **1** (see text) in DMSO-d_6. TMS was used as the internal standard. Residual proton signals in the deuterated solvents are marked with asterisks.

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 dihalo(pentafluorophenyl)sulfonium cations under strongly acidic conditions due to the charge delocalization into the pentafluorophenyl ring through p–π/d–π interactions.[20]

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** and diphenylmethylsulfonium hexafluoroantimoate,[11] the control of **5** without the oxo linkage between the two benzene rings. Obviously, the torsions of the best least-squares plane of the adjacent benzene units in **5** (34.72°) is smaller than that in the diphenylmethylsulfonium cation[11] (83.12°). In addition, while a comparison of crystal structures of phenoxathiin[30] and diaryl sulfides[28] [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 sulfide–C(phenyl) bond lengths, the S^+–C(phenyl) bond lengths in **5** are shorter than those of the diphenylmethylsulfonium cation (1.783 and 1.782 Å). Moreover, the smaller C–S–C bond angles in the diphenylmethylsulfonium cation[11] (103.6°) than in the diaryl sulfides[28] [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,[32] does not

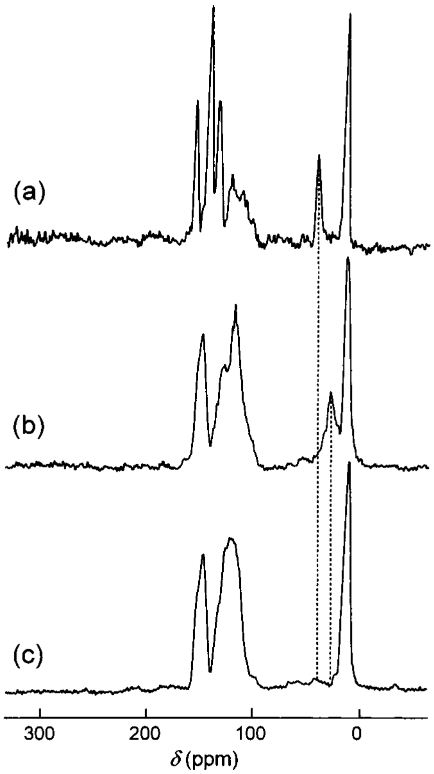


Figure 5. ^{13}C CP/MAS spectra of (a) **3b**, (b) **1**, and (c) **6**.

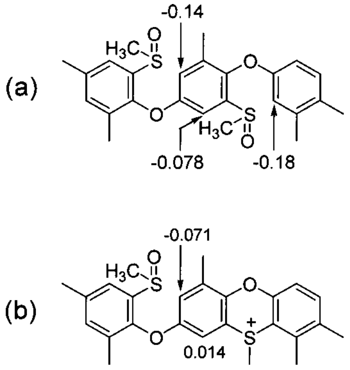


Figure 6. Carbon net charges of oxyphenylene trimer models for **3b** before (a) and during the course of ladderization (b) obtained by PM3 MO calculation.

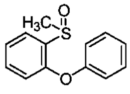
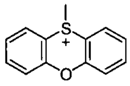
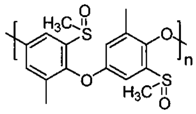
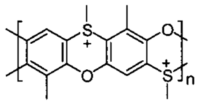
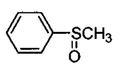
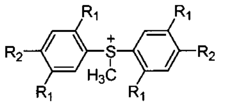
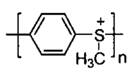
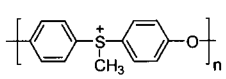
hold for the annulated compounds (**5**, 98.3°; phenoxathiin, 98°). These characteristics could be an indication that, with the planarized benzene rings in **5**, the π-electron density is faintly delocalized into the methylsulfonio linkage.

We hypothesized that the charge delocalization should be pronounced when the resulting carbenium cations are stabilized in a strongly acidic medium (Scheme 4). It was reported by Müllen and co-workers[8c] that CF_3SO_3H acts as a key dehydrating agent to allow the formation of a carbenium-containing π framework. In Figure 2c is shown the ^{1}H NMR of **5** dissolved in CF_3SO_3H, which reveals a decrease in the deshielding effect with the magnitude of 0.5 ppm for the CH_3S^+-atoms relative to those under neutral conditions consistent with the extensive charge delocalization into the aromatic rings. Additional evidence supporting this interpretation is given in Figure 3. In the absence of acid (Figure 3a), the methylation of phenoxathiin to **5** does not lead to any bathochromic shift of λ_{max}, which indicates that the methylsulfonio linkage and the sulfide linkage act as conjugation barriers. On the other hand, the CF_3SO_3H solution of **5** is deep blue and shows new absorption bands near $\lambda_{max} = 513$ and 578 nm (Figure 3b), due probably to the resonance structure (Scheme 4). No cation radical is detected in the electron spin resonance (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 **5**. The absorption band in the visible region is not attributable to the intramolecular charge-transfer transition because there is no indication of intermolecular donor–acceptor interactions[11] between the diphenylmethylsulfonium cation and diphenyl ether in CF_3SO_3H even at very high concentrations. It seems reasonable to suppose that **5** has a more planar conformation in strongly acidic medium than in the crystal state due to the enhanced carbenium ion contribution to the resonance form (Scheme 4). Neutralization of the CF_3SO_3H solution of **5** reinstates the ^{1}H NMR and optical absorption spectra identical to those in Figures 2b and 3a, respectively, ensuring the reversibility of the changes upon the superacidification of **5**.

Rigid planar conjugated systems are characterized by a distinct bathochromic shift of the longest wavelength absorption with the increasing number of fused aromatic subunits.[33] Furthermore, they generally show very sharp absorption edges due to their rigid character.[8b] The optical absorption data of the polymers (Figure 7a) were recorded in CH_3CN for **2b** and **3b** and in CF_3SO_3H for **1** and a partly ladderized polymer **1′** (see Experimental Section). The absorption band significantly red shifts upon completion of the ladderization (**1′** → **1**), which indicates 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 **1** is a broad shoulder near 600 nm, which is close to the absorption band of **5** under acidic conditions (Figure 3b). The featureless absorption edge tailing to ca. 940 nm may indicate that the contribution of the delocalized state to the resonance form of **1** (Scheme 4) is small and that π electrons cannot delocalize throughout the backbone, due probably to the relative stability of the localized quinoidal form. Nevertheless, the small optical band gap (1.3 eV) estimated from the tailing edge is comparable to those of other π-conjugated ladder polymers.[9]

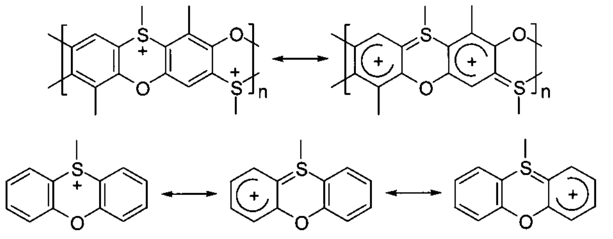
It must be noted that the electron delocalization through the ladder polymer backbone, rather than the mere planarization of the benzene rings, is responsible for the spectral changes upon ladderization. Preliminary results has been obtained to indicate that the molecular length, rather than the tetrasubstituted benzene units, mainly works on the tailing of the absorption edge of **1** under neutral conditions (Figure 7b); an unpurified two-unit model, derived from 1,4-bis[oxy(2-methylsulfinyl)-phenyl]benzene by the ring-closing reaction, showed λ_{max} at 298 nm without a significant tailing edge in neutral medium. Added support is also provided by the drastic change in the electronic properties upon the conversion of **1** into **6** (vide infra), a planarized analogue that is incapable of delocalization through the position occupied by the sulfide moiety; while **1** is a semiconductor with an intrinsic electric conductivity σ of 2×10^{-5} S cm^{-1}, **6** is an insulator ($\sigma < 10^{-11}$ S cm^{-1}). Polymer **1** and the model compound **5** show no emission signal; the sulfur atoms seem to play a role in the exciton quenching.

Table 5. ^{1}H and ^{13}C NMR Chemical Shifts of Methyl Groups Bound to Sulfur Atoms[a]

compound	abbr.	^{1}H	^{13}C	Ref.
	(4)	2.81[b]	42.3[b]	this work
	(5)	3.49[c] 2.99[e]	36.8[d] 36.0[e]	this work
	(3b)	2.78[b]	42.2 42.4[f]	this work
	(1)	2.89[d,g]	29.1[f]	this work
	MPS	2.72	43.82	10c
	($R_1 = R_2 = H$)	4.01[c] 3.83[d]	28.9[c] 26.9[d]	11
	($R_1 = H, R_2 = CH_3$)	3.63	28.9	
	($R_1 = CH_3, R_2 = H$)	3.57	27.5	
	PPS^{+}	3.85[h]	28.9[h]	11
	PPOS^{+}	3.67[i]	29.7[i]	13a

[a] δ values are given in parts per million (ppm). Excepts where noted, solvent = $CDCl_3$. [b] Solvent = CD_2Cl_2. [c] Solvent = acetone-d_6. [d] Solvent = DMSO-d_6. [e] Solvent = CF_3SO_3H. Standard (external) = TMS/$CDCl_3$. [f] CP/MAS. [g] Low molecular weight part. [h] Solvent = D_2O. [i] Solvent = CD_3CN.

Scheme 4



A comparison of the spectroscopic properties of the sulfonium cations under acidic and neutral conditions provides additional insights into the π-electron delocalization through the sulfonium center. In the first place, the lack of noticeable changes upon superacidification in the ^{1}H NMR and the optical absorption spectra of the diphenylmethylsulfonium cation and those of PPS^{+} may demonstrate, conversely, the efficacy of planarization by the oxo linkages in **5** and **1** for charge delocalization. In the second place, the lack of a noticeable difference between the spectroscopic properties of **1** in CF_3SO_3H and those in neutral medium (Figure 7b) indicates that the ladder framework also seems to play a role in the stabilization of the carbenium resonance forms. In the final place, while **1** is black, PPS^{+} is a white powder and colorless in both neutral and superacidic media.

Thermal Properties. Poly(phenylene sulfide) (PPS) and poly(2,6-dimethylphenylene oxide) (PPO) (Chart 1) are heteroatom-containing polymers with high chemical and thermal stability. PPS is slowly decomposed above 450 °C ($T_{d10\%} = 516$ °C), while PPO shows the onset of decomposition near 420 °C followed by a strong exothermic reaction accompanied by a rapid drop in weight of ca. 70% ($T_{d10\%} = 450$ °C).[34] These polymers are known to show two complementary types of solid-state properties. While PPS is a partly crystalline material ($T_g =$ 90 °C, $T_c = 137$ °C, and $T_m = 282$ °C),[35] PPO is mainly amorphous ($T_g = 205-220$ °C, $T_m = 267$ °C)[36] and completely miscible with polystyrene. We have already established that their linear hybrid poly(oxy-1,4-phenylenethio-1,4-phenylene) (PPOS) is a crystalline polymer with $T_m = 191$ °C, $T_g = 88$ °C, and $T_c = 137$ °C.[37] The T_m of PPOS is ca. 90 °C lower than that of PPS because of an increase in ΔS_m due to its lower molecular symmetry. The $T_{d10\%}$ of PPOS (535 °C)[37] is higher than that of PPS due to the higher binding energy of the ether bond than that of the thioether bond. The combination of PPS and PPO to compound **6** with phenoxathiin-type building blocks should result in a new material displaying interesting thermal properties. These include a high $T_{d10\%}$ due to the double-stranded, rigid, and planar structure. Indeed, it has been reported[38] that, among polypyromellitimides 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 diphenyl- or diphenyloxidetetracarboxylic acids show the same trend,[38] which is quite natural since the phenyl rings are attached by two bonds ensuring the high thermal stability of the diamine component.

The high-yielding conversion of **5** to phenoxathiin by the treatment with pyridine led us to examine the demethylation of **1**. The efficacy of this reaction for use in polymers has been demonstrated by the successful

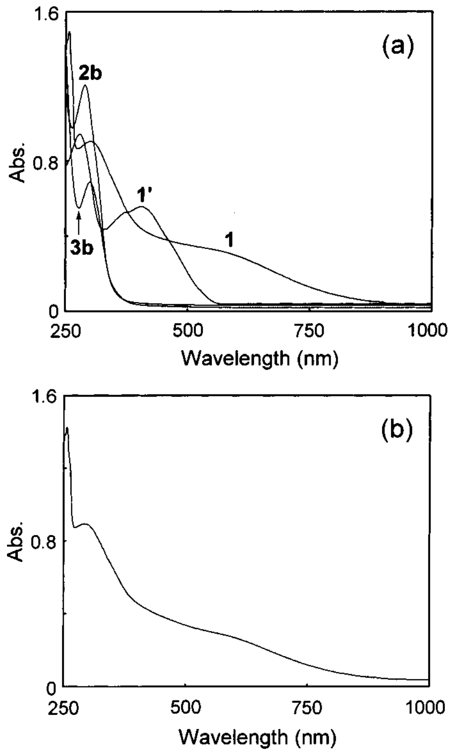
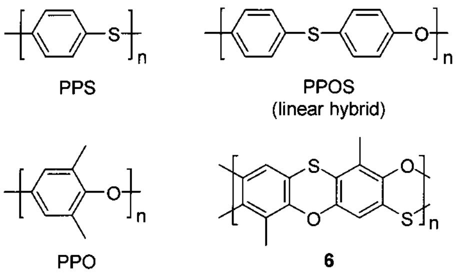


Figure 7. (a) Absorption spectra of the polymers (1 mmol unit/L) before ladderization (**2b** and **3b** in CH_3CN), during the course of the ladderization (**1′** in CF_3SO_3H), and after ladderization (**1** in CF_3SO_3H). (b) Absorption spectrum of the lower molecular weight **1** (see text) (1 mmol unit/L) in CH_3CN. The optical path length was 0.1 cm.

Chart 1



PPS

PPOS (linear hybrid)

PPO

6 (ladder-type hybrid)

conversion of PPS^+ to PPS.[10a–h] Polymer **1** was suspended in pyridine, which was refluxed for a sufficiently long time to ensure the completion of the demethylation reaction. The product is obtained as a pale brown powder. The absence of the $\mathit{C}H_3S^+$- resonance in CP/MAS (Figure 5c) and of the IR signals due to triflate anions establish the structure of **6**.

A comparison of the $T_{d10\%}$ values of the linear analogues, such as PPS, PPO, and PPOS, with that of **6** reveal the enhancement in stability against thermolysis by the ladder framework. Figure 7 shows the thermogravimetric analysis (TGA) curves of polymers **1** and **6** and their precursors. In the absence of O_2, polymers **2b** and **3b** show the onset of decomposition near 350 °C accompanied by a rapid drop in weight of ca. 30% (Figure 8a). In contrast, polymer **6** shows the onset of decomposition near 450 °C followed by only a slight weight loss (Figure 8b). The thermal stability of the ladder-type hybrid **6** ($T_{d10\%}$ = 555 °C) is even higher than that of the linear hybrid PPOS. Polymer **1** is more easily decomposed upon heating due to the weaker sulfonio linkages (Figure 8b).

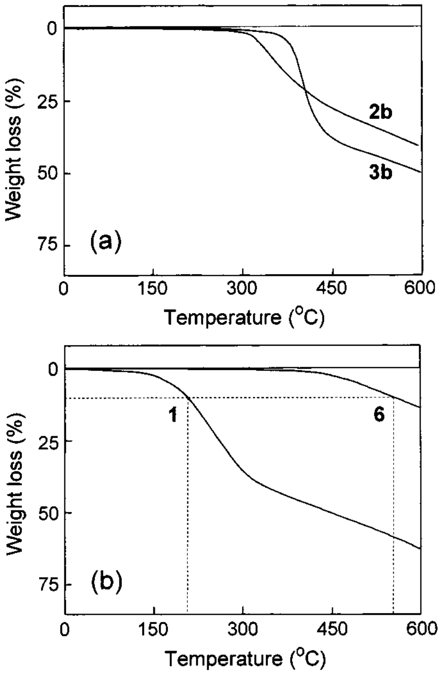


Figure 8. TGA curves of (a) the precursor polymers **2b** and **3b** and (b) the ladder polymers **1** and **6** under N_2. The dotted lines in panel b represent the temperature for a 10% weight loss ($T_{d10\%}$). The temperature was scanned from room temperature at a rate of 10 °C/min.

Polymers **1** and **6** both show no X-ray diffraction peak, revealing that they are amorphous. The DSC analysis shows no thermal transition before decomposition, indicating the lack of glass transition in the temperature range of interest due to the rigid structure.

Comparison with Previous Studies. The problem of improving the solubility of π-conjugated ladder polymers has frequently been addressed by derivatizing ladder structures with suitable side groups to destabilize the interchain interaction. On the other hand, one could also consider a polymer electrolyte structure as a candidate for a highly soluble ladder framework without such substituents. The first ladder polymer electrolyte, to our knowledge, is a polycarbenium with thioxanthylium-type repeating units reported by Müllen et al.,[8c] which was claimed to be isoelectronically related to poly[*n*]acenes. However, the characterization was impeded by an insufficient solubility in common solvents.[8d]

We previously reported the synthesis of two ladder polymers with methylsulfonio linkages by the polymer-analogous Swern condensation of aryl sulfoxides and demonstrated their solubility in protonic acids but failed to establish the π-electron delocalization into the sulfonio moiety due to the following reasons. First, we reported an oligo(*p*-phenylene) ladder containing sulfide and sulfonio linkages, but the extensive π-conjugation was ascribed rather to the planarization of the benzene rings than to the p−π/d−π interaction between the sulfonium moiety and the benzene ring.[8a] Then, a ladder polymer containing benzenetetrayl units bridged by imino and methylsulfonio groups, an analogue of **1** containing imino groups in place of the oxo linkages, was prepared from poly[imino-1,3-phenyleneimino-4,6-bis(methylsulfinyl)-1,3-phenylene].[8e] However, the optical band gap estimated from the tailing edge of the absorption spectrum (520 nm, 2.4 eV) indicated that the π-electron conjugation did not extend throughout the polymer chain. The localized intramolecular donor−

acceptor interaction between the imino and methylsulfonio moieties was also considered to play a role in the visible absorption.[8e,11] Taking into account the lack of such donor−acceptor interaction between oxo and methylsulfonio linkages, one can ascribe the smaller band gap in **1** only to the π-electron delocalization through the polymer backbone. MO calculations of **1** including the d-orbitals of sulfur, with a view to proving the p−π/d−π interaction, are the subject of our continuing research.

Conclusion

The polymer-analogous condensation of aryl sulfoxides is proposed as a convenient method to prepare the ladder polymer containing sulfonio linkages that force the consecutive aromatic units into planarity. The ladder polymer **1** has bathochromically shifted absorptions in the electronic spectrum. The bridging methylsulfonio units have a p−π/d−π interaction with the benzene rings, thus allowing for greater electron delocalization between the consecutive benzenetetrayl subunits. Because the delocalization of π-electrons through the sulfonium center is confirmed, the present approach represents a facile and potentially useful new class of ladder polymers.

Experimental Section

Materials. Commercial reagents of 2-bromobenzenethiol, iodomethane, phenol, *o*-cresol, dimethyl disulfide, $AlCl_3$, NaOH, HCl, CF_3SO_3H, the aqueous solution of H_2O_2, CH_3CO_2H, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 2,6-lutidine, CuCl, and deuterated solvents were used as received. The other solvents were purified by distillation prior to use.

Synthesis of the Model Compound 2-(Methylsulfinyl)phenyl Phenyl Ether (4). To an aqueous solution (40 mL) of NaOH (2.0 g, 50 mmol) were added 2-bromobenzenethiol (5.0 g, 26.5 mmol) and iodomethane (18.8 g, 0.132 mol) with vigorous stirring. The resulting white suspension was stirred at 40 °C for 12 h. Extraction with $CHCl_3$ followed by rotary evaporation afforded 2-(methylsulfenyl)bromobenzene in 98% yield as a dark brown liquid. ^1H NMR (CD_2Cl_2, TMS, ppm): δ 2.47 (s, 3H, SCH_3), 7.00−7.53 (m, 4H, ArH). ^{13}C NMR (CD_2Cl_2, TMS, ppm): δ 15.9 (SCH_3), 121.8, 125.7, 126.0, 128.8, 133.0, 140.2. IR (KBr, cm^{-1}): 3057 (m), 2984 (m), 2919 (νCH, s), 741 (δCH, s). MS: calcd for C_7H_7BrS, 201.95; found (*m*/*z*), 202 (M^+). To a solution of 2-(methylsulfenyl)bromobenzene (2.03 g, 10 mmol) in CH_2Cl_2 (50 mL) were added an aqueous solution of H_2O_2 (30%, 10 mL) and CH_3CO_2H (2 mL). The resulting mixture was stirred at rt for 24 h. Extraction with $CHCl_3$ followed by rotating evaporation and drying under vacuum afforded 2-(methylsulfinyl)bromobenzene in 97% yield as a dark brown liquid. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.81 (s, 3H, $SOCH_3$), 7.34−7.96 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 41.9 ($SOCH_3$), 118.3, 125.6, 128.7, 132.2, 132.9, 145.4. IR (KBr, cm^{-1}): 3059 (m), 2996 (m), 2914 (νCH, s), 1058 (νS=O, s), 758 (δCH, s). MS: calcd for C_7H_7BrOS, 217.94; found (*m*/*z*), 218 (M^+). A solution of 2-(methylsulfinyl)bromobenzene (1.1 g, 5.0 mmol), copper(I) chloride (0.495 g, 5.0 mmol), and sodium methoxide (0.54 g, 10 mol) in phenol (20 mL) was heated at 160 °C under N_2 for 24 h with constant stirring. After cooling, an aqueous solution of NaOH was added to the resulting solution to dissolve the unreacted sodium phenolate into an H_2O layer. Extraction with chloroform followed by a thorough washing with H_2O, dehydration with anhydrous Na_2SO_4, and rotary evaporation afforded a crude product in 80% yield as a dark brown liquid. Purification by silica gel column chromatography with $CHCl_3$ as the eluent gave **4** as a dark brown solid. Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.2; H, 5.21; S, 13.8. Found: C, 67.0; H, 5.18; S, 13.9. ^1H NMR (CD_2Cl_2, TMS, ppm): δ 2.81 (s, 3H, $SOCH_3$), 6.83−7.90 (m, 9H, ArH). ^{13}C NMR (CD_2Cl_2, TMS, ppm): δ 42.3 ($SOCH_3$), 117.6, 118.6, 119.7, 124.5, 124.9, 125.3, 130.5, 132.2, 136.6, 153.3, 156.0. IR (KBr, cm^{-1}): 3061 (w), 2920 (νCH, w), 1228 (νCOC, s), 1072 (νS=O, s), 754, 693 (δCH, s). MS: calcd for $C_{13}H_{12}O_2S$, 232.06; found (*m*/*z*), 232 (M^+).

Ring-Closing Reaction of 4. A solution of **4** (0.23 g, 1.0 mmol) in CCl_4 (2.0 mL) was added dropwise to CF_3SO_3H (5.0 mL) at rt with vigorous stirring. The resulting black solution was heated at 80 °C and stirred for 24 h. The reaction was quenched by pouring the solution into diethyl ether after cooling to precipitate 5-methylphenoxathiinium triflate (**5**) as a pale brown powder that was collected by filtration, washed thoroughly with diethyl ether, and dried under vacuum (97% yield). Anal. Calcd for $C_{14}H_{10}F_3O_4S_2$: C, 46.3; H, 2.77; S, 17.7. Found: C, 46.7; H, 2.69; S, 17.8. ^1H NMR (acetone-d_6, TMS, ppm): δ 3.49 (s, 3H, S^+CH_3), 7.60−8.25 (m, 8H, ArH). ^1H NMR (CF_3SO_3H, TMS/$CDCl_3$ in double NMR tube, ppm): δ 2.99 (s, 3H, S^+CH_3), 7.65−8.04 (m, 8H, ArH). ^{13}C NMR (DMSO-d_6, TMS, ppm): δ 36.8 (S^+CH_3), 107.0, 119.5, 126.1, 131.3, 135.7, 150.9. ^{13}C NMR (CF_3SO_3H, TMS/$CDCl_3$ in double NMR tube, ppm): δ 36.0 (S^+CH_3), 104.88, 104.93, 122.39, 126.92, 130.06, 136.67, 152.36, 152.41. IR (KBr, cm^{-1}): 3023 (m), 2930 (νCH, s), 1222 (νCOC, s), 758 (δCH, s), 638 (νCF, s). UV−vis (CH_3CN, nm): λ_{max} 212, 288. UV−vis (CF_3SO_3H, nm): λ_{max} 208, 288, 513, 578.

Demethylation of 5. The dark brown solution of **5** (0.35 g, 1.0 mmol) in pyridine (10 mL) was refluxed for 24 h with constant stirring. After cooling, the solution was neutralized with HCl. Extraction with $CHCl_3$ followed by rotating evaporation and drying under vacuum gave phenoxathiin in 98% yield as a pale brown solid. Anal. Calcd for $C_{12}H_8OS$: C, 72.0; H, 4.03; S, 16.0. Found: C, 71.9; H, 4.01; S, 15.9. ^1H NMR ($CDCl_3$, TMS, ppm): δ 6.98−7.25 (m, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 117.8, 120.4, 124.5, 126.8, 127.8, 152.1. IR (KBr, cm^{-1}): 2924 (νCH, m), 1226 (νCOC, s), 751 (δCH, s). MS: calcd for $C_{12}H_8OS$, 200.03; found (*m*/*z*), 200 (M^+). UV−vis (CH_3CN, nm): λ_{max} 202, 294.

Methylation of Phenoxathiin. To a solution of phenoxathiin (2.0 g, 10 mmol) and methyl formate (1.2 g, 20 mmol) in CH_2Cl_2 (7.5 mL) was added CF_3SO_3H (5.0 mL). The resulting purple solution was stirred at rt for 12 h. The reaction was quenched by pouring the solution into diethyl ether to precipitate **5**, which was collected by filtration, washed with diethyl ether, and dried under vacuum (95% yield).

Monomer Synthesis. 2-Methyl-6-(methylsulfenyl)phenol was prepared by the Friedel−Crafts reaction of *o*-cresol with dimethyl disulfide as follows. To a solution of $AlCl_3$ (160 g, 1.2 mol) in CCl_4 (300 mL) was added a solution of *o*-cresol (108 g, 1.0 mol) and dimethyl disulfide (113 g, 1.2 mol) in CCl_4 (200 mL). The solution boiled as the reaction progressed and was then refluxed under N_2 for 1 h. After the reaction, a light-yellow CCl_4 solution was separated from the hot reaction mixture by use of a separatory funnel. The addition of H_2O followed by extraction with $CHCl_3$, dehydration with anhydrous Na_2SO_4, and rotary evaporation afforded a mixture of 2-methyl-6-(methylsulfenyl)phenol, 2-methyl-4-(methylsulfenyl)phenol, 2-methyl-4,6-bis(methylsulfenyl)phenol, 2-(methylsulfenyl)toluene, and unreacted *o*-cresol. Distillation of the mixture (5 mmHg, 75 °C) gave a crude product that still contained 2-(methylsulfeyl)toluene and *o*-cresol as contaminants. The crude product was dissolved in an aqueous solution of NaOH, and undissolved 2-(methylsulfenyl)toluene was filtered out. The filtrate was neutralized with HCl and extracted with $CHCl_3$. The extract was washed thoroughly with H_2O, dehydrated with anhydrous Na_2SO_4, and rotary-evaporated to yield a mixture of *o*-cresol and the product. Purification by silica gel column chromatography with $CHCl_3$ as the eluent afforded 2-methyl-6-(methylsulfenyl)phenol (10 g) as a light yellow liquid. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.26 (s, 3H, CH_3), 2.28 (s, 3H, SCH_3), 6.78 (s, 1H, OH), 6.74−7.31 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 16.3 (CH_3), 19.9 (SCH_3), 120.3, 120.6, 124.3, 132.0, 132.3, 154.6. IR (KBr, cm^{-1}): 3397 (νOH, s), 2912 (νCH, s), 1339 (δOH, m), 1233 (νCO, s), 769 (δCH, m). MS: calcd for $C_8H_{10}OS$, 154.23; found (*m*/*z*), 154 (M^+).

2-(Methylsulfenyl)phenol was prepared from phenol and dimethyl disulfide by a similar method as follows. To a solution of phenol (47.1 g, 0.5 mol) in CCl_4 (50 mL) were added $AlCl_3$ (66.7 g, 0.5 mol) and dimethyl disulfide (47.1 g, 0.5 mol). The resulting yellow solution was refluxed for 2 h. The addition of H_2O followed by extraction with $CHCl_3$, dehydration with anhydrous Na_2SO_4, and rotary evaporation afforded the crude product. Purification by distillation (5 mmHg, 75 °C) followed by silica gel column chromatography with $CHCl_3$ as the eluent afforded 2-(methylsulfenyl)phenol in 80% yield as a transparent liquid. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.31 (s, 3H, SCH_3), 6.75 (s, 1H, OH), 6.84−7.50 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 114.7 (SCH_3), 120.6, 121.0, 130.5, 134.5, 155.9. MS: calcd for C_7H_8OS, 140.03; found (*m/z*), 140 (M^+).

2-Methyl-6-(methylsulfinyl)phenol was prepared by the oxidation of 2-methyl-6-(methylsulfenyl)phenol with H_2O_2 as follows. To a solution of 2-methyl-6-(methylsulfenyl)phenol (1.54 g, 10 mmol) in CH_2Cl_2 (50 mL) were slowly added 30% H_2O_2 (10 mL) and CH_3CO_2H (2 mL). The resulting mixture was vigorously stirred at rt for 24 h. Extraction with $CHCl_3$ followed by rotary evaporation and drying under vacuum afforded 2-methyl-6-(methylsulfinyl)phenol in 98% yield as a dark brown liquid. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.26 (s, 3H, CH_3), 2.94 (s, 3H, $SOCH_3$), 6.77−7.31 (m, 3H, ArH), 10.45 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 15.3 (CH_3), 41.72 ($SOCH_3$), 119.2, 122.0, 122.3, 128.9, 134.0, 157.9. IR (KBr, cm^{-1}): 3448 (νOH, m), 3061, 2922 (νCH, m), 1053 (νSO, s), 761 (δCH, m). MS: calcd for $C_8H_{10}O_2S$, 170.23; found (*m/z*), 170 (M^+).

2-(Methylsulfinyl)phenol was prepared by the oxidation of 2-(methylsulfenyl)phenol as follows. To a solution of 2-(methylsulfenyl)phenol (7.01 g, 50 mmol) in CH_2Cl_2 (100 mL) were slowly added 30% H_2O_2 (50 mL) and CH_3CO_2H (10 mL). The resulting mixture was vigorously stirred at rt for 24 h. Extraction with $CHCl_3$ followed by rotary evaporation and drying under vacuum afforded the crude product, which was purified by recrystallization from a solution in $CHCl_3$ and hexane to give 2-(methylsulfinyl)phenol in 90% yield as a white powder. Anal. Calcd for $C_7H_8O_2S$: C, 53.8; H, 5.16; S, 20.5. Found: C, 53.7; H, 5.20; S, 20.3. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.96 (s, 3H, $SOCH_3$), 6.90−7.39 (m, 4H, ArH), 10.24 (s, 1H, OH). MS: calcd for $C_7H_8O_2S$, 156.02; found (*m/z*), 156 (M^+).

Oxidative Polymerization. To a solution of 2-methyl-6-(methylsulfenyl)phenol (1.54 g, 10 mmol) in nitrobenzene (20 mL) was added a solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.16 g, 10 mmol) and CuCl (0.099 g, 1.0 mmol) in nitrobenzene (20 mL). Upon mixing, the color of the solution became dark brown. The resulting solution was stirred under O_2 for 12 h. After the reaction, the solution was poured into CH_3OH (200 mL) containing 5% HCl to precipitate the product, which was collected by filtration, washed with CH_3OH, and dried under vacuum to yield **2b** in 98% yield as a white powder. Anal. Calcd for C_8H_8OS: C, 63.1; H, 5.30; S, 21.1. Found: C, 63.3; H, 5.28; S, 21.0. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.07 (s, 3H, CH_3), 2.32 (s, 3H, SCH_3), 6.38 (d, 1H, ^4J = 2.4 Hz, ArH), 6.59 (d, 1H, ^4J = 2.4 Hz, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 14.6 (CH_3), 16.8 (SCH_3), 110.1, 113.0, 132.6, 134.4, 143.5, 155.1. IR (KBr, cm^{-1}): 2979, 2918, 2855 (νCH, m), 1590, 1458 (νC═C, s), 1186 (νCOC, s), 753 (δCH, m). GPC (DMF, PS standard): M_n, 10 000; M_w, 35 000. UV−vis (CH_3CN, nm): λ_{max} 290.

A lower molecular-weight **2b** was obtained in 25 wt % yield as an off-white powder when the same reaction was performed in CH_3OH instead of nitrobenzene. Anal. Calcd for C_8H_8OS: C, 63.1; H, 5.30; S, 21.1. Found: C, 63.0; H, 5.36; S, 20.8. ^1H NMR ($CDCl_3$, TMS, ppm): δ 2.06 (s, 3H, CH_3), 2.32 (s, 3H, SCH_3), 6.39 (d, 1H, ^4J = 2.4 Hz, ArH), 6.58 (d, 1H, ^4J = 2.4 Hz, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 14.5 (CH_3), 16.8 (SCH_3), 110.2, 113.0, 132.5, 134.4, 143.4, 155.1. IR (KBr, cm^{-1}): 2981, 2915, 2850 (νCH, m), 1589, 1455 (νC═C, s), 1181 (νCOC, s), 751 (δCH, m). GPC (DMF, PS standard): M_n, 2000; M_w, 4000.

Sulfinylation of 2b. Polymer **2b** was oxidized with H_2O_2 to **3b** as follows. To a solution of **2b** (0.76 g, 5 mmol unit) in CH_2Cl_2 (50 mL) were added 30% H_2O_2 (5.0 mL) and CH_3CO_2H (1.0 mL). The resulting mixture was vigorously stirred at rt for 24 h. After the reaction, the mixture was rotary-evaporated to replace the solvent with $CHCl_3$. The resulting solution was poured into hexane to precipitate the product, which was collected by filtration, washed thoroughly with hexane and H_2O, and dried under vacuum to give **3b** in 100% yield as a white powder. Anal. Calcd for $C_8H_8O_2S$: C, 57.1; H, 4.79; S, 19.1. Found: C, 56.9; H, 4.79; S, 19.5. ^1H NMR (CD_2Cl_2, TMS, ppm): δ 2.12 (s, 3H, CH_3), 2.78 (s, 3H, $SOCH_3$), 6.80 (s, 1H, ArH), 7.26 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, ppm): δ 16.5 (CH_3), 42.2 ($SOCH_3$), 119.8, 120.3, 134.4, 141.4, 142.2, 155.3. CP/MAS (ppm): δ 16.3, 42.4, 122.0, 134.5, 142.7, 155.9. IR (KBr, cm^{-1}): 3011, 2968, 2904 (νCH, m), 1183 (νCOC, s), 1056 (νSO, s), 752 (δCH, m). UV−vis (CH_3CN, nm): λ_{max} 300. GPC (DMF, PS standard): M_n, 11 000; M_w, 39 000.

Ladderization. Polymer **3b** (0.17 g, 1 mmol unit) was dissolved in CH_2Cl_2 (2.0 mL). The solution was added dropwise to CF_3SO_3H (10 mL) at rt with vigorous stirring. The resulting black solution was stirred at 80 °C for 24 h. After the reaction, the homogeneous solution was poured into diethyl ether to precipitate a black powder, which was collected by filtration, washed with diethyl ether, aqueous NaOH, and H_2O repeatedly, and dried under vacuum to yield **1** (0.27 g). Anal. Calcd for $C_9H_7F_3O_4S_2$: C, 36.0; H, 2.35; S, 21.4. Found: C, 36.1; H, 2.33; S, 21.6. CP/MAS (ppm): δ 15.2 (CH_3), 29.1 (S^+CH_3), 119.4, 122.0, 128.6, 130.7, 135.5, 148.7. IR (KBr, cm^{-1}): 3023, 2930 (νCH, m), 1222 (νCOC, s), 1161, 637 (νCF, m), 859, 761 (δCH, m). UV−vis (CF_3SO_3H, nm): λ_{max} 200, 256, 302. The partly ladderized polymer **1′** was obtained when the reaction was quenched for 5 h. UV−vis (CF_3SO_3H, nm): λ_{max} 278, 374, 404.

Sulfinylation of the lower molecular weight **2b** (M_n = 2000, M_w = 4000) followed by ladderization by the same method yielded the lower molecular weight **1**, which was soluble in DMSO. Anal. Calcd for $C_9H_7F_3O_4S_2$: C, 36.0; H, 2.35; S, 21.4. Found: C, 35.8; H, 2.29; S, 21.9. ^1H NMR (DMSO-d_6, TMS, ppm): 2.73 (s, 3H, CH_3), 2.89 (s, 3H, S^+CH_3), 7.95 (s, 1H, ArH). IR (KBr, cm^{-1}): 2931 (νCH, m), 1261 (νCOC, s), 1171, 640 (νCF, m), 859, 761 (δCH, m).

Demethylation of 1. Polymer **1** (1.5 g, 3.3 mmol unit) was dispersed in pyridine (100 mL), which was refluxed for 1 week. The resulting pale brown powder was collected by filtration, washed thoroughly with CH_3OH, and dried under vacuum to give **6** in 100% yield (0.9 g). Anal. Calcd for C_7H_4OS: C, 61.7; H, 2.96; S, 23.5. Found: C, 61.9; H, 2.94; S, 22.9. CP/MAS (ppm): δ 13.8, 123.4, 148.0. IR (KBr, cm^{-1}): 2920 (νCH, m), 1267 (νCOC, s), 850 (δCH, m).

Measurements. ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-LA500 (500 MHz ^1H, 125 MHz ^{13}C) spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. ^{13}C CP/MAS spectra were obtained on a Jeol GSX-400 spectrometer. Infrared spectra were obtained on a Jasco FT-IR 5300 spectrometer with potassium bromide pellets. UV−vis spectra were recorded on a Shimadzu UV-2100 spectrometer. Thermogravimetry and differential thermal analysis were performed on a Seiko TG-DTA 220 instrument at a heating rate of 10 °C/min under nitrogen at a flow rate of 300 mL/min. A 5 mg sample was used for each thermal analysis. Molecular weight measurements were done by gel-permeation chromatography (GPC) on a Shimadzu LC-9A liquid chromatograph equipped with a SPD-6AV UV−vis spectrophotometric detector set at 275 nm. DMF containing 1 wt % LiBr was used as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed on a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained on a Shimadzu GCMS-QP5050 spectrometer.

X-ray Crystallography. Colorless needlelike crystals of **5** were grown from acetone solutions of the desired compound after layering with diethyl ether. Following microscopic examination in air, a suitable crystal was mounted on a glass fiber at room temperature. All measurements were done on a Rigaku AFC7R diffractometer with a 7.5 kW rotating-anode generator and graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). Unit cell parameters and an orientation matrix for data collection were determined by least-squares refinements with the setting angles of 25 carefully centered reflections in the range $28.70° < 2\theta < 29.96°$. The data were collected at a temperature of 23 °C by the ω-2θ scan technique to a maximum 2θ value of 55.0°. Scans were done at a speed of 16.0°/min (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (up to two scans). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. An empirical absorption correction based on the azimuthal scans of several reflections was applied that resulted in transmission factors ranging from 0.89 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for the secondary extinction was applied (coefficient $= 4.61690 \times 10^{-7}$).

Structure Solution and Refinement. The structure was solved by direct methods (SHELXS86)[39] and expanded by Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement[40] was based on 2186 observed reflections [$I > 3.00\sigma(I)$] and 249 variable parameters and converged with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ as listed in Table 1. The plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The data collection and structure solution parameters and conditions are listed in Table 1. The selected bond lengths and angles are listed in Table 2. All calculations were performed with the teXsan crystallographic software package from Molecular Structure Corp.[41]

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Supporting Information Available: Five tables giving atomic coordinates, anisotropic displacement parameters, and equivalent isotropic thermal parameters for **5**. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For reviews: (a) Schlüter, A.-D. *Adv. Mater.* **1991**, *3*, 282. (b) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1990**, *2*, 649. (c) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. (d) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (e) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853.

(2) (a) Debad, J. D.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 2476. (b) Dai, Y.; Katz, T. J.; Nichols, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2109. (c) Dai, Y.; Katz, T. J. *J. Org. Chem.* **1997**, *62*, 1274. (d) Yoshizawa, K.; Yahara, K.; Tanaka, K.; Yamabe, T. *J. Phys. Chem. B* **1998**, *102*, 498. (e) Notario, R.; Abboud, J.-L. M. *J. Phys. Chem. A* **1998**, *102*, 5290. (f) Slawik, M.; Petelenz, P. *J. Chem. Phys.* **1997**, *107*, 7114. (g) Snow, A. W. *Nature* **1981**, *292*, 40.

(3) (a) Murakami, M.; Yoshioka, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1649. (b) Ruud, C. J.; Wang, C.; Baker, G. L. *Synth. Met.* **1997**, *84*, 363.

(4) (a) Günter, P. *Nonlinear Optical Effects and Materials*; Springer: Berlin, Germany, 2000. (b) Strassner, T.; Weitz, A.; Rose, J.; Wudl, F.; Houk, K. N. *Chem. Phys. Lett.* **2000**, *321*, 459.

(5) (a) Suh, M. C.; Jung, Y.; Kwak, J.; Shim, S. C. *Synth. Met.* **1999**, *100*, 195. (b) Ago, H.; Tanaka, K.; Yamabe, T.; Takegoshi, K.; Terao, T.; Yata, S.; Hato, Y.; Ando, N. *Synth. Met.* **1997**, *89*, 141. (c) Nakata, M.; Kobayashi, A.; Saito, T.; Kobayashi, H.; Takimiya, K.; Otsubo, T.; Ogura, F. *Chem. Commun.* **1997**, 593. (d) Arai, E.; Fujiwara, H.; Kobayashi, H.; Kobayashi, A.; Takimiya, K.; Otsubo, T.; Ogura, F. *Inorg. Chem.* **1998**, *37*, 2851.

(6) (a) Kim, O.-K. *J. Polym. Sci., Polym. Lett.* **1985**, *23*, 137. (b) Schmit, J.-P. N.; Davidson, K.; Iraqi, A. *Synth. Met.* **1999**, *101*, 100.

(7) (a) Kintzel, O.; Münch, W.; Schlüter, A.-D. *J. Org. Chem.* **1996**, *61*, 7304. (b) Godt, A.; Enkelmann, V.; Schlüter, A.-D. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1680. (c) Wegener, S.; Müllen, K. *Macromolecules* **1993**, *26*, 3037.

(8) (a) Haryono, A.; Miyatake, K.; Natori, J.; Tsuchida, E. *Macromolecules* **1999**, *32*, 3146. (b) Scherf, U.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489. (c) Scherf, U.; Bohnen, A.; Müllen, K. *Makromol. Chem.* **1992**, *193*, 1127. (d) Forster, M.; Annan, K. O.; Scherf, U. *Macromolecules* **1999**, *32*, 3159. (e) Freund, T.; Scherf, U.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2424. (f) Freund, T.; Müllen, K.; Scherf, U. *Macromolecules* **1995**, *28*, 547. (g) Miyatake, K.; Hay, A. S.; Mitsuhashi, F.; Tsuchida, E. *Macromolecules* **2001**, *34*, 2385.

(9) (a) Tour, J. M.; Lamba, J. J. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935. (b) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 9624. (c) Yao, Y.; Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 2805. (d) Yao, Y.; Tour, J. M. *Macromolecules* **1999**, *32*, 2455. (e) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895. (f) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578. (g) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Org. Chem.* **1998**, *63*, 1676.

(10) (a) Haryono, A.; Yamamoto, K.; Shouji, E.; Tsuchida, E. *Macromolecules* **1998**, *31*, 1202. (b) Miyatake, K.; Yamamoto, K.; Yokoi, Y.; Tsuchida, E. *Macromolecules* **1998**, *31*, 403. (c) Tsuchida, E.; Shouji, E.; Yamamoto, K. *Macromolecules* **1993**, *26*, 7144. (d) Tsuchida, E.; Yamamoto, K.; Shouji, E. *Macromolecules* **1993**, *26*, 7389. (e) Tsuchida, E.; Suzuki, F.; Shouji, E.; Yamamoto, K. *Macromolecules* **1994**, *27*, 1057. (f) Tsuchida, E.; Yamamoto, K.; Shouji, E.; Katoh, J.; Matsuo, M.; Kamiya, H. *Macromolecules* **1994**, *27*, 7504. (g) Yamamoto, K.; Shouji, E.; Suzuki, F.; Kobayashi, S.; Tsuchida, E. *J. Org. Chem.* **1995**, *60*, 452. (h) Yamamoto, K.; Kobayashi, S.; Shouji, E.; Tsuchida, E. *J. Org. Chem.* **1996**, *61*, 1912. Polymers containing nitrogen atoms have been reported by Müllen et al. See (i) Leuninger, J.; Wang, C.; Soczka-Guth, T.; Enkelmann, V.; Pakula, T.; Müllen, K. *Macromolecules* **1998**, *31*, 1720. (j) Leuninger, J.; Wang, C.; Soczka-Guth, T.; Müllen, K. *Synth. Met.* **1999**, *101*, 681. (k) Leuninger, J.; Uebe, J.; Salbeck, J.; Gherghel, L.; Wang, C.; Müllen, K. *Synth. Met.* **1999**, *100*, 79.

(11) Miyatake, K.; Oyaizu, K.; Nishimura, Y.; Tsuchida, E. *Macromolecules* **2001**, *34*, 1172.

(12) (a) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165. (b) Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819.

(13) (a) Tsuchida, E.; Yamamoto, K.; Miyatake, K.; Nishimura, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2843. (b) Yamamoto, K.; Miyatake, K.; Nishimura, Y.; Tsuchida, E. *Chem. Commun.* **1996**, 2099.

(14) For a review: Hay, A. S. *J. Polym. Sci., Part A* **1998**, *36*, 505.

(15) Hay, A. S.; Dana, D. E. *J. Polym. Sci., Part A* **1989**, *27*, 873.

(16) (a) Oyaizu, K.; Kumaki, Y.; Saito, K.; Tsuchida, E. *Macromolecules* **2000**, *33*, 5766. (b) Kubo, M.; Itoh, Y.; Tsuji, M.; Oda, N.; Takeuchi, H.; Itoh, T. *Macromolecules* **1998**, *31*, 3469. (c) Ikeda, R.; Tanaka, H.; Uyama, H.; Kobayashi, S. *Macromolecules* **2000**, *33*, 6648.

(17) (a) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549. (b) Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **2000**, *104*, 2953.

(18) Trost, B. M.; Melvin, L. S. *Sulfur Ylides*; Academic Press: London, 1975.

(19) Cremlyn, R. J. *An Introduction to Organosulfur Chemistry*; John Wiley & Sons: Chichester, England, 1996.

(20) Minkwitz, R.; Preut, H.; Sawatzki, J. *Z. Anorg. Allg. Chem.* **1989**, *569*, 158.

(21) (a) Olah, G. A.; Laali, K. K.; Wang, Q.; Surya Prakash, G. K. *Onium Ions*; John Wiley & Sons: New York, 1998. (b) Olah, G. A.; Surya Prakash, G. K.; Nakajima, T. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 812.

(22) Olah, G. A.; Nakajima, T.; Surya Prakash, G. K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 811.

(23) (a) Bordwell, F. G.; Boutan, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 1058. (b) Oae, S.; Price, C. C. *J. Am. Chem. Soc.* **1958**, *80*, 3425. (c) March, J. *Advanced Organic Chemistry*; Wiley-Interscience: New York, 1992.

(24) Olah, G. A.; Grant, J. L. *J. Org. Chem.* **1977**, *42*, 2237.

(25) (a) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112. (b) Matsumi, Y.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776.

(26) (a) Miyatake, K.; Yamamoto, K.; Endo, K.; Tsuchida, E. *J. Org. Chem.* **1998**, *63*, 7522. (b) Miyatake, K.; Endo, K.; Tsuchida, E. *Macromolecules* **1999**, *32*, 8786.

(27) (a) Minkwitz, R.; Nowicki, G.; Perut, H. *Z. Anorg. Allg. Chem.* **1989**, *573*, 185. (b) Minkwitz, R.; Bäch, B.; Perut, H. *Z. Naturforsch. B: Chem. Sci.* **1994**, *49*, 881.

(28) Jones, P. G.; Sheldrick, G. M.; Hadicke, E. *Acta Crystallogr.* **1980**, *B36*, 2779.

(29) Price, C. C.; Oae, S. *Sulfur Bonding*; Ronald Press: New York, 1962.

(30) Hosoya, S. *Acta Crystallogr.* **1966**, *20*, 429.

(31) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Componds*; John Wiley & Sons: New York, 1991.

(32) Oae, S. *Organic Chemistry of Sulfur*; Field, L., Ed.; Plenum Press: New York, 1977.

(33) Anton, U.; Müllen, K. *Macromolecules* **1993**, *26*, 1248.

(34) $T_{d10\%}$ = temperature for 10% weight loss in thermogravimetry, T_m = melting point, T_c = crystallization temperature, T_g = glass transition temperature.

(35) (a) Cheng, S. Z. D.; Wu, Z. Q.; Wunderlich, B. W. *Macromolecules* **1987**, *20*, 2802. (b) Hill, H. W., Jr.; Short, J. N. *CHEMTECH* **1972**, *2*, 481.

(36) (a) Hay, A. S. *J. Polym. Sci. A* **1998**, *36*, 505. (b) Karasz, F. E.; O'Reilly, J. M. *Polym. Lett.* **1965**, *3*, 561. (c) Karasz, F. E.; Bair, H. E.; O'Reilly, J. M. *J. Polym. Sci. A-2* **1968**, *6*, 1141.

(37) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Miyatake, K. *Macromolecules* **1993**, *26*, 4113.

(38) Koton, M. M.; Sazanov, Y. N. *J. Therm. Anal.* **1975**, *7*, 165.

(39) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985.

(40) Least-squares function minimized: $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o)]^{-1}$.

(41) teXsan Crystal Structure Analysis Package, Molecular Structure Corporation, 1985 and 1992.

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