# New $\pi$-Conjugated Polyelectrolyte Composed of Alkylphenoxathiinium-Type Repeating Units

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## Introduction

Development of a novel $\pi$-conjugated polymer backbone is an important subject of polymer chemistry. Here we report the synthesis and characterization of a new $\pi$-conjugated aromatic polyelectrolyte (**1**) containing alkyldiarylsulfonium groups in the backbone which forms a flexible thin film and shows an electrical semiconductivity after doping. The polymer is viewed as an unprecedented carbon−sulfur analogue of polyacene and yet soluble in a wide range of organic solvents.

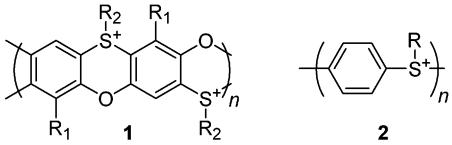
Polyelectrolytes containing $\lambda^4$-alkylsulfanyliumdiyl-bridged aromatic groups[1] are interesting macromolecules because they are soluble synthetic precursors for an engineering plastic poly(*p*-phenylene sulfide) (PPS),[2−12] photoacid generators,[13] key compounds for the photochemical recycling process of PPS,[14,15] permselective anion-exchanging resins,[16] polyelectrolytes with wide potential windows,[16−18] and versatile alkylating reagents.[19] The polymers possess $\pi$ electrons localized at the aromatic rings, and hence they usually behave as electrical insulators. On the other hand, we recently reported on spectroscopic evidences regarding the delocalization of $\pi$ electrons into the $\lambda^4$-methylsulfanyliumdiyl group in a 5-methylphenoxathiinium salt.[20] On the basis of the resonance effect, a ladder-type backbone **1** (Chart 1) comprising 5-alkylphenoxathiinium-type repeating units is considered to provide an extended $\pi$-conjugated system to allow delocalization of the $\pi$ electrons along the chain. In this report, we calculate and analyze the band electronic and geometric structure of **1** at the PM5 level of theory and compare them to the structure of poly(alkylsulfonio-1,4-phenylene) (**2**).[9,11] The origin of the lower band gap for **1** than that for **2** is discussed in view of geometric changes imposed by the fused ring structure.

## Experimental Section

**Materials.** All reagents were obtained from Kanto Chemical Co. or Tokyo Kasei Co. and used without further purification. 2-*tert*-Butylsulfenyl-6-methylphenol was prepared from 2-bromo-6-methylphenol by the lithiation with *n*-butyllithium followed by the reaction with di-*tert*-butyl disulfide. All solvents were purified by distillation prior to use.

**Poly(oxy-2-methyl-6-*tert*-butylsulfinyl-1,4-phenylene).** To a solution of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (1.16 g, 10.0 mmol) and CuCl (0.0990 g, 1.00 mmol) in nitrobenzene (20 mL) was added a solution of 2-*tert*-butylsulfenyl-6-methylphenol (1.93 g, 10.0 mmol) in nitrobenzene (20 mL). The resulting solution was stirred at 40 °C for 72 h under $O_2$. The product, poly(oxy-2-*tert*-butylsulfenyl-6-methyl-1,4-phenylene), was isolated from the solution by pouring the solution into methanol (500 mL) containing 5% HCl. Yield: 76%. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 1.25 (s, 9H), 2.15 (s, 3H), 6.71 (s, 1H), 6.73 (s, 1H). IR (KBr, cm$^{-1}$): 3021, 2940 ($\nu_{CH}$), 1172 ($\nu_{COC}$), 774 ($\delta_{CH}$). The molecular weight of the product was $M_w = 1 \times 10^4$ ($M_w/M_n = 2.5$). Then, the polymer (0.195 g, 1.00 mmol unit) was dissolved in $CH_2Cl_2$ (10 mL). To the solution was added an aqueous solution of 30% $H_2O_2$ (1.0 mL). The mixture was stirred at room temperature, to which was slowly added acetic acid (0.5 mL). The mixture was heated to 40 °C with constant stirring for 24 h. The resulting mixture was poured into methanol (500 mL) to give poly(oxy-2-*tert*-butylsulfinyl-6-methyl-1,4-phenylene) as a white precipitate (1.95 g). Yield: 93%. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 1.35 (s, 9H), 2.13 (s, 3H), 6.93 (s, 1H), 7.18 (s, 1H). IR (KBr, cm$^{-1}$): 2988, 2956 ($\nu_{CH}$), 1060 ($\nu_{S=O}$), 1172 ($\nu_{COC}$).

**Chart 1. Ladder-Type (1) and Linear (2) Alkylsulfonioarylene Polymers**



**Polymer 1 ($R_1$ = Methyl, $R_2$ = *tert*-Butyl).** Poly(oxy-2-*tert*-butylsulfinyl-6-methyl-1,4-phenylene) (0.210 g, 1.00 mmol unit) was dissolved in $CH_2Cl_2$ (2 mL). The solution was added to triflic acid (10 mL) with constant stirring. The mixture was stirred at 80 °C for 24 h. The product was isolated by pouring the resulting solution into diethyl ether (500 mL) and was obtained as a dark brown powder (0.31 g). Yield: 91%. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 1.63 (s, 9H), 2.78 (s, 3H), 7.82 (s, 1H). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 15.4, 36.7, 59.9, 109.4, 120.8, 121.6, 127.0, 145.3, 146.1. IR (KBr, cm$^{-1}$): 2998, 2936 ($\nu_{CH}$), 1172, 651 ($\nu_{CF}$), 764 ($\nu_{CH}$).

**Measurements.** $^1$H NMR spectra were recorded on a JEOL JNM-LA500 spectrometer. Infrared spectra were obtained using a Jasco FT-IR 410 spectrometer. Molecular weight measurements were done by GPC using a TOSOH LS-8000 instrument. THF was used as an eluent. Calibration was done with polystyrene standards.

**Computational Methods.** We calculated the structure of the periodic fused ring system **1** ($R_1$ = H, $R_2$ = methyl) that involved as units the 5-methylphenoxathiinium groups. We also calculated the structure of **2** (R = methyl) as the control compound. Polymer models were constructed using translation vectors to represent boundary conditions along the chain. Polymer models with insufficient crystal lattice size can lead to erroneous results. We concluded that the unit cell containing eight sulfur atoms (16 fused rings for **1**) was long enough to estimate the structure of the infinite chain. Sufficiently large unit cells containing 10 sulfur atoms (20 fused rings for **1**) were employed for the band calculation, which were constructed using the WinMAKPOL program from Fujitsu Co. Geometry optimization was performed using the PM5 method.[21] The WinMOPAC 3.5 program package from Fujitsu Co. was used for the PM5 calculations. Although we did not limit our theoretical investigation to a planar conformation, the converged structure of **1** showed nearly coplanar geometries for benzene units. The electronic structures were obtained by performing PM5 geometry optimizations followed by band calculations. The WinBZ program involved in the WinMOPAC 3.5 package was used for the band calculation. After the geometry optimization, the distances of the translation vectors were 49.4 and 52.9 Å for **1** and **2**, respectively. It is known that Hartree−Fock calculations without correcting the electron correlation effects generally overestimates the band gap of polymers. In the present report, the absolute values for the calculated band gaps did not have significance because we did not include electron correlation. However, observed qualitative

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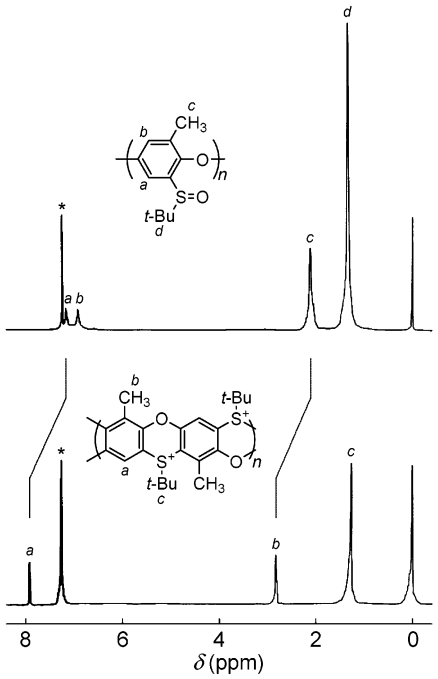


**Figure 1.** $^1$H NMR spectral changes accompanied by the ring-closing reaction of the prepolymer, poly(oxy-2-*tert*-butylsulfinyl-6-methyl-1,4-phenylene). Solvent ($CDCl_3$) peaks are shown as asterisks. TMS was used as the internal standard.

trends sufficed for providing insights into the difference between the electronic states of **1** and **2**.

## Results and Discussion

As the key intermediate to synthesize **1**, poly(phenylene oxide) having pendant *tert*-butylsulfenyl groups at the ortho positions were prepared by the copper-catalyzed oxidative polymerization of the corresponding monomer with $O_2$. The *o*-*tert*-butyl-sulfinylated phenols did not oxidatively polymerize with the copper catalyst because of the higher oxidation potentials and/or the undesired coordination of the sulfoxide group to the copper catalyst. The oxidation of the resulting polymer with peracetic acid successfully converted the *tert*-butylsulfenyl groups to the corresponding sulfinyl groups without the formation of the undesired sulfonyl groups. The superacidified condensation (Swern reaction) of the resulting precursor polymer induced the polymer-analogous ring-closing reaction to yield **1** ($R_1$ = methyl, $R_2$ = *tert*-butyl). In this reaction, the protonated sulfoxide (the *tert*-butylhydroxyphenylsulfonium ion) electrophilically attacked at the adjacent benzene ring to produce the required ladder-type polymer. The product was obtained as a dark brown powder and was soluble in $CHCl_3$, acetone, $CH_3CN$, and DMSO. Interestingly, there was no remaining C*H*$_3$S(O) resonance in the $^1$H NMR spectrum (Figure 1), suggesting the completion of the ring closure. The IR and NMR spectra indicated that intermolecular $\lambda^4$-*tert*-butylsulfanyliumdiyl linkages unlikely formed in **1**. The remarkably simple NMR spectrum without any end-group signal demonstrates that the proposed synthetic process successfully gives a structure-defined and relatively high-molecular-weight product.[20]

A significant difference was noticed between the electronic properties of **1** and **2**. The polymer **2** can be regarded as an analogue of **1** but is incapable of provoking the $\pi$-electron delocalization through the $\lambda^4$-alkylsulfanyliumdiyl groups as shown below. While both polymers formed flexible films, **1** was a semiconductor with an intrinsic electrical conductivity ($\sigma$) of $4 \times 10^{-5}$ S cm$^{-1}$, but **2** was an insulator ($\sigma < 10^{-10}$ S cm$^{-1}$). Moreover, the thin film of **1** showed a significant increase in $\sigma$ after $I_2$ doping ($\sigma \approx 10^{-2}$ S cm$^{-1}$), which suggested the formation of a $\pi$-conjugated system. An analogous polymer **1** with $\lambda^4$-methylsulfanyliumdiyl linkages ($R_1 = R_2$ = methyl)[20] does not form a good film and shows a lower conductivity after $I_2$ doping ($\sigma = 5 \times 10^{-5}$ S cm$^{-1}$), which demonstrates the efficacy of introducing the *tert*-butyl group in **1** to reveal the $\pi$-conjugated property.

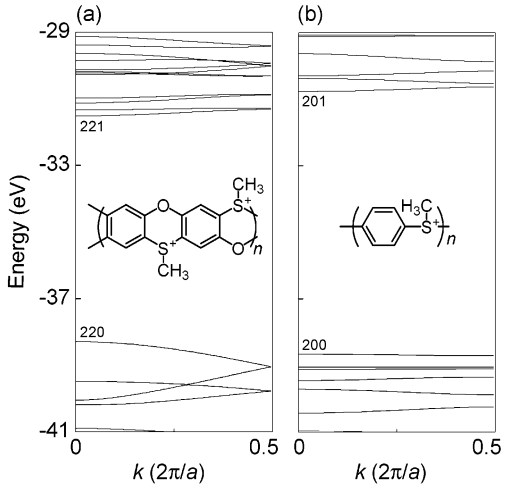


**Figure 2.** PM5-calculated band electronic structures for (a) **1** and (b) **2**.

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 electrical conductivity. The effect of ladderization for electron delocalization through the $\lambda^4$-alkylsulfanyliumdiyl groups was supported by the results of MO calculations. We show in Figure 2 the band electronic structures of **1** ($R_1$ = H, $R_2$ = methyl) and **2** (R = methyl). The HOCO (the highest occupied crystal orbital) and the LUCO (the lowest unoccupied crystal orbital) consisted of the $p_z$ orbitals vertical to the benzene rings. The band gap ($E_g$) corresponded to the direct transition at $k = 0$. The PM5 calculated band gap for **1** was 6.79 eV. In comparison with the absolute values of the band gaps for $\pi$-conjugated polymers such as polythiophene ($E_g \approx 1.5-2.0$ eV),[22,23] the PM5 SCF value for **1** was high due mainly to the neglect of the electron correlation effects. The PM5 calculated band gap for **2** was 7.90 eV, which was even higher than that of **1** by 1.1 eV. For many polymers, it has been suggested that the correlation effects result only in an almost constant shift of the electronic levels by 3−4 eV.[24] According to this assumption, one could roughly approximate more reliable band gaps of 2.8−3.8 eV for **1** and 3.9−4.9 eV for **2**.

The lower band gap for **1** was attributed to the lower LUCO ($\phi_{221}$) level, which originated from the symmetry-allowed interaction between the $p_z$ orbital of the sulfur atom and the two carbon atoms adjacent to the sulfur atom. As shown in Figure 3, the LUCO of **1** was stabilized in energy by this bonding interaction. On the other hand, the optimized geometry for **2** revealed that the torsional angle between the adjacent benzene rings amounted to 77°, in which case the $p_z$ orbital of one of

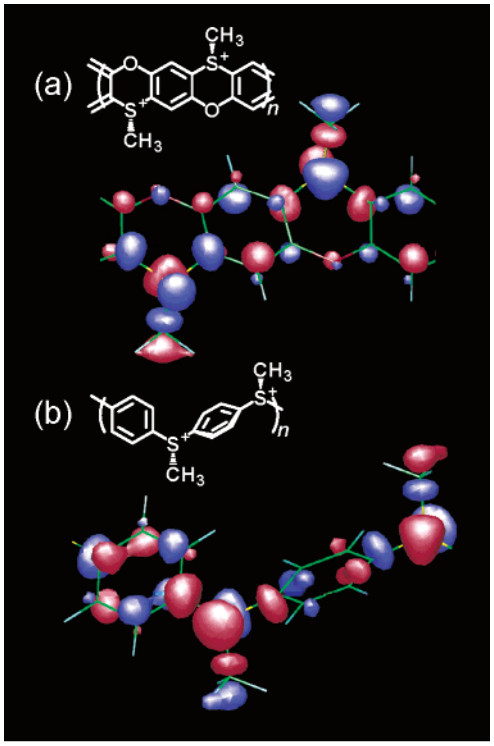


**Figure 3.** PM5-calculated optimized geometries and the lowest unoccupied crystal orbitals for (a) **1** and (b) **2**.

the two carbon atoms adjacent to the sulfur atom could no longer interact with the $p_z$ orbital of the sulfur atom. The low band gap for **1** was also attributed to a significant increase in the HO bandwidth ($\phi_{220}$) as shown in Figure 2, which suggested that $\pi$ electrons in **1** were delocalized into the sulfur atom as a result of the planarized structure.

## Conclusion

The polymer-analogous condensation of aryl sulfoxides was employed as a convenient method to prepare the ladder-type polymer containing $\lambda^4$-alkylsulfanyliumdiyl linkages in the backbone that force the consecutive aromatic rings into planarity. The bridging $\lambda^4$-alkylsulfanyliumdiyl groups allowed for the electron delocalization between the aromatic subunits to give the $\pi$-conjugated system, which was suggested by the film properties and supported by the MO calculations. The reduction of the band gap from that of poly(alkylsulfonio-1,4-phenylene) was attributed to an increase in the planarity of the molecular geometry, which stabilized the LUMO through the symmetry-allowed bonding interaction between the $p_z$ orbitals of the sulfur atom and those of the adjacent carbon atoms.

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## References and Notes

(1) For a review, see: Tsuchida, E.; Oyaizu, K. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 15−47.
(2) Tsuchida, E.; Shouji, E.; Yamamoto, K. *Macromolecules* **1993**, *26*, 7144−7148.
(3) Yamamoto, K.; Shouji, E.; Nishide, H.; Tsuchida, E. *J. Am. Chem. Soc.* **1993**, *115*, 5819−5820.
(4) Shouji, E.; Nishimura, S.; Yamamoto, K.; Tsuchida, E. *Chem. Lett.* **1994**, 403−406.
(5) Haryono, A.; Yamamoto, K.; Shouji, E.; Tsuchida, E. *Macromolecules* **1998**, *31*, 1202−1207.
(6) Shouji, E.; Yamamoto, K.; Tsuchida, E. *Chem. Lett.* **1993**, 1927−1930.
(7) Yamamoto, K.; Shouji, E.; Suzuki, F.; Kobayashi, S.; Tsuchida, E. *J. Org. Chem.* **1995**, *60*, 452−453.
(8) Tsuchida, E.; Suzuki, F.; Shouji, E.; Yamamoto, K. *Macromolecules* **1994**, *27*, 1057−1060.
(9) Miyatake, K.; Oyaizu, K.; Nishimura, Y.; Tsuchida, E. *Macromolecules* **2001**, *34*, 1172−1179.
(10) Wang, L. X.; Soczka-Guth, T.; Havinga, E.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1495−1499.
(11) Tsuchida, E.; Yamamoto, K.; Miyatake, K.; Nishimura, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2843−2845.
(12) Yamamoto, K.; Miyatake, K.; Nishimura, Y.; Tsuchida, E. *Chem. Commun.* **1996**, 2099−2100.
(13) Tsuchida, E.; Yamamoto, K.; Shouji, E.; Haryono, A. *Chem. Commun.* **1996**, 2091−2092.
(14) Haryono, A.; Miyatake, K.; Tsuchida, E. *Macromol. Chem. Phys.* **1999**, *200*, 1257−1267.
(15) Miyatake, K.; Endo, K.; Tsuchida, E. *Macromolecules* **1999**, *32*, 8786−8790.
(16) Oyaizu, K.; Nakano, H.; Natori, J.; Tsuchida, E. *J. Electroanal. Chem.* **2001**, *498*, 232−236.
(17) Dewi, E. L.; Nakano, H.; Oyaizu, K.; Nishide, H.; Tsuchida, E. *J. Macromol. Sci.* **2003**, *A40*, 37−47.
(18) Dewi, E. L.; Oyaizu, K.; Nishide, H.; Tsuchida, E. *J. Power Sources* **2003**, *115*, 149−152.
(19) Shouji, E.; Nishimura, S.; Yamamoto, K.; Tsuchida, E. *Polym. Adv. Technol.* **1994**, *5*, 507−512.
(20) Oyaizu, K.; Mikami, T.; Mitsuhashi, F.; Tsuchida, E. *Macromolecules* **2002**, *35*, 67−78.
(21) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220.
(22) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: New York, 1999.
(23) Hotta, S. Molecular Conductive Materials: Polythiophenes and Oligothiophenes. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: Chichester, 1997; Vol. 2, pp 309−387.
(24) Jürimäe, T.; Strandberg, M.; Karelson, M.; Calais, J.-L. *Int. J. Quantum Chem.* **1995**, *54*, 369−379.

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