

Review

NOVEL SYNTHESIS OF POLYARYLENESULFONIUM CATIONS THROUGH A MULTI-ELECTRON TRANSFER PROCESS*

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Abstract The oxidative polymerization of aryl sulfoxides provides a novel polysulfonium compound, poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene cation) in quantitative yield. The polymerization proceeds efficiently in an acidic solution under atmospheric conditions. Oxygen, chemical and electrochemical oxidations are available. Vanadyl acetylacetonate and cerium ammonium nitrate act as an effective catalyst for the oxygen oxidative polymerization. The polymerization mechanism involves multielectron oxidation of the sulfides followed by successive electrophilic substitution. The resulting polyarylenesulfonium cations are useful as a soluble precursor for the synthesis of high molecular weight ($M_w > 10^5$) poly(thio arylene)s.

Keywords Oxidative polymerization; Multi-electron transfer; Sulfonium cation; Poly(thio phenylene)

INTRODUCTION

There has been considerable interest in direct oxidation of sulfides for the preparation of sulfoxides. Numerous catalysts have been known as oxygenase-like models in the formation of sulfoxides by the oxidation of sulfide compounds with oxygen, where the mechanism likely involves a one-electron transfer process^[1]. Traditionally, sulfonium compounds have been synthesized with low conversion by the alkylation of the sulfides with iodoalkanes in the presence of an equimolar amount of silver salt, by the protonation of sulfoxides, or by the treatment of alkyl sulfoxides with alkyl

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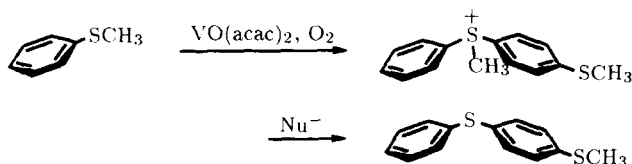
Grignard reagents^[2]. Recently, we reported that N,N'-ethylenebis (salicylideneaminate)oxovanadium undergoes a two-electron transfer at 0.5 V (vs Ag/AgCl) through disproportionation in acidic media^[3]. Oxovanadium acetylacetonate (VO(acac)₂) could be employed as a two-electron mediator in the oxidation of an aryl sulfide because of its suitably high redox potential (1.1 V vs Ag/AgCl).

The polymerization via selective oxidation utilizing oxygen as the oxidant presents potentially a desirable low-cost method for upgrading the value of raw materials. The most successful example is the oxidative polymerization of 2,6-dimethylphenol to yield poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) using a copper/amine catalyst in an oxygen atmosphere at room temperature^[4]. Our studies on the preparation of poly(thio-1,4-phenylene) (PTP), which is an excellent thermostable engineering plastic^[5], have revealed that thiophenol or diphenyl disulfide is oxidatively polymerized to PTP via a cationic mechanism by electrochemical or chemical oxidations^[6~9]. The oxovanadium catalyst acts as an efficient catalyst for the O₂-oxidative polymerization of diphenyl disulfide^[10]. The polymerization provides very pure PTP in high yield but of low molecular weight because of the insolubility of PTP in dichloromethane at room temperature.

This review proposes a new synthetic method for the preparation of high molecular weight PTP via a soluble precursor under mild conditions, which overcomes the synthetic difficulties presented by poor solubility^[11]. In the course of oxidation of monomeric aryl sulfides as a model, we have succeeded in the synthesis of unsymmetric arylalkylsulfonium salts by the oxygen-mediated oxidative coupling catalyzed by an oxovanadium complex through a multi-electron transfer process. The reaction involves not only a new catalytic system for the oxidation of sulfides by an electron-transfer analogous to that of an oxidase model but also the direct formation of unsymmetric aryl sulfides via sulfonium compounds. The oxidation reaction of sulfides is also applicable for the synthesis of high molecular weight polyarylene-sulfonium salts. The polymerization of 4-methylsulfinyldiphenyl sulfide efficiently provides poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) as a soluble poly(sulfonium cation) in the presence of trifluoromethanesulfonic acid. That is, a new transformation from an aryl sulfoxide to a polysulfonium compound has been achieved. Further investigation revealed that 4-methylsulfinyldiphenyl sulfide could be polymerized to poly(sulfonium cation) by oxygen-oxidation catalyzed with cerium ammonium nitrate (CAN) or by electro- or chemical oxidation. This polymerization method provides a novel and convenient synthetic route to high molecular weight PTP ($M_w > 10^5$) via a soluble precursor.

OXIDATIVE COUPLING OF ALKYL ARYL SULFIDES DRIVEN BY THE SPLITTING REACTION OF OXYGEN

The oxidative coupling of thioanisole with oxygen can be catalyzed by $\text{VO}(\text{acac})_2$ in the presence of tetrabutylammonium perchlorate, trifluoromethanesulfonic acid and trifluoroacetic anhydride in dichloromethane to yield the corresponding dimeric aryl sulfonium perchlorate (Scheme 1). During the reaction, quantitative oxygen uptake has been observed. For each mole of oxygen consumed, 2.0 mol of the product is formed. The combination of 500 MHz COSY ^1H -NMR and ^{13}C -NMR and IR spectroscopy permitted identification of the sulfonium structure of the product. In the NMR spectra, signals (^1H -NMR: $\delta = 3.65$; ^{13}C -NMR $\delta = 28.4$) attributed to the methylsulfonio group appeared at a lower magnetic field than those of the methylsulfenyl group ($\delta = 2.45$ and 14.6, respectively).

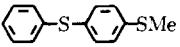
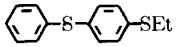
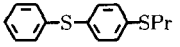
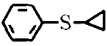
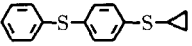
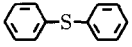
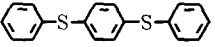
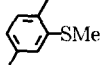
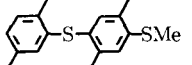
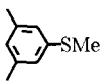
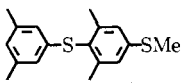
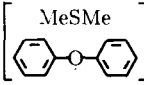
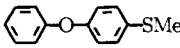


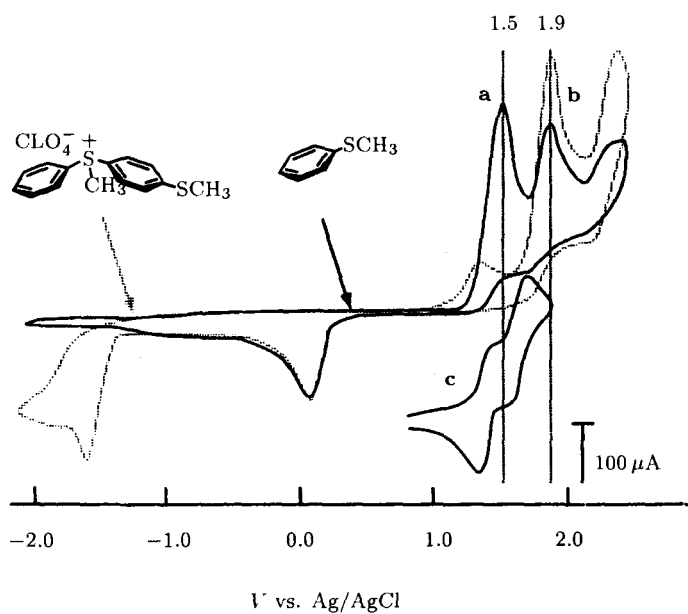
Scheme 1

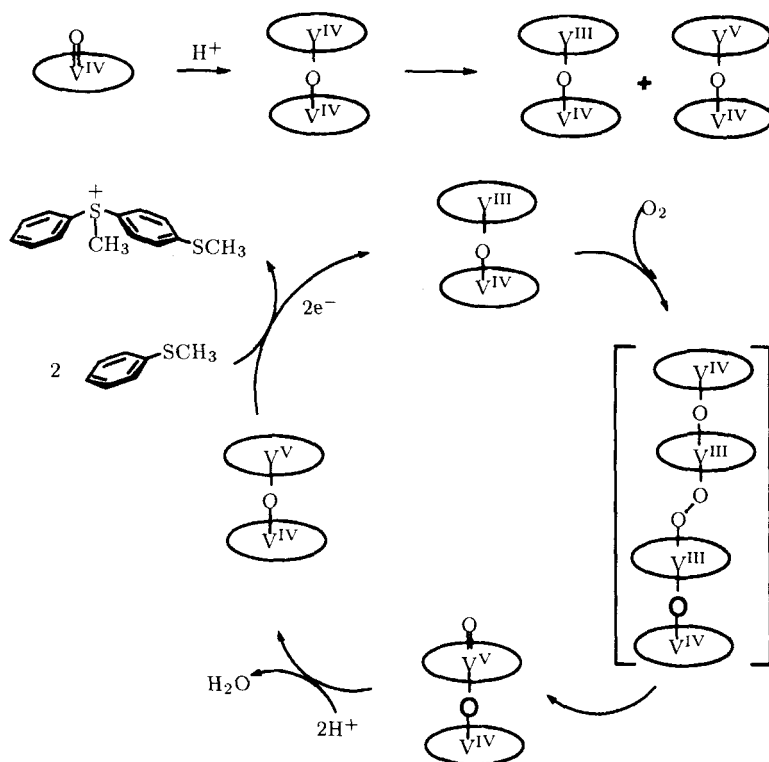
The demethylation of 4-methylsulfonyldiphenyl methyl sulfonium perchlorate was carried out in pyridine at reflux temperature for 1 h. The reaction proceeds quantitatively to give 4-methylsulfonyldiphenyl sulfide in 96% yield. It should be noted that the dimeric sulfide product is obtained in-situ by treating the oxidation mixture with excess pyridine. Table 1 summarizes the results of the oxidative coupling reaction of aryl sulfides. The alkyl aryl sulfides with a lower oxidation peak potential produce the corresponding dimeric aryl sulfides in high yield. The electron-donating alkyl substituents promote the coupling reaction because the reaction is based on electrophilic aromatic substitution. Diphenyl sulfide is not available due to its higher oxidation potential (1.7 V) than the alkyl aryl sulfides. Cyclopropyl phenyl sulfide is not also available because of the side reaction, elimination of a labile methyne proton from the sulfonium product.

Thioanisole has an irreversible oxidation peak potential at 1.5 V (vs Ag/AgCl) (Fig.1). The isolated dimeric sulfonium compound, 4-methylsulfonyldiphenyl methyl sulfonium perchlorate has a higher oxidation peak potential at 1.9 V. Substitution of the sulfonio group on the phenylene ring causes an increase in the oxidation potential due to its electron withdrawal property. It would be reasonable that the

Table 1 Oxidative coupling of alkyl aryl sulfides catalyzed by VO(acac)₂

Reactant	Epa (V) ^a	Product	Yield (%) ^b	MS (m/z)
	1.5		100	232
	1.4		84	246
	1.5		100	250
	1.3		trace	258
	1.7		0	—
	1.2		100	289
	1.2		100	289
	1.3		8	216

a. V vs. Ag/AgCl in CH₃CN; b. determined by GC**Fig.1** Cyclic voltammograms of (a) thioanisole, (b) 4-methylsulfenyldiphenyl methyl sulfonium perchlorate and (c) VO(acac)₂ in acidic CH₂Cl₂



Scheme 2

dimeric sulfonium cation is not oxidized by the oxovanadium catalyst. No oxygen consumption was observed under the same reaction conditions for the sulfonium compound. The redox potential ($E_{1/2}$) of $\text{VO}(\text{acac})_2$, which is ascribed to the redox couple between $\text{V}(\text{IV})/\text{V}(\text{V})$, is 1.1 V in dichloromethane. In an anaerobic acidic environment, two reversible redox couples were located at very close potentials (1.4 and 1.6 V) and can be assigned to $\text{V}(\text{III})/\text{V}(\text{IV})$ and $\text{V}(\text{IV})/\text{V}(\text{V})$, respectively^[12], which was measured by cyclic voltammetry. This result supports the idea that a two-electron transfer is facilitated due to the small potential separation between the two redox couples^[13].

The oxidative coupling of aryl sulfides with oxygen occurs through two redox couples that bridge the large potential gap between oxygen and the substrates. The oxovanadium catalyst acts as an excellent electron mediator in the catalytic reaction. The catalyst is oxidized by oxygen to a high-valent vanadyl(V) species. The resulting active cationic species of aryl sulfides derived from the oxidation by vanadyl(V) reacts electrophilically with the phenylene ring of another sulfide substrate to form the dimeric sulfonium cation. The resulting vanadium (III) species is reoxidized

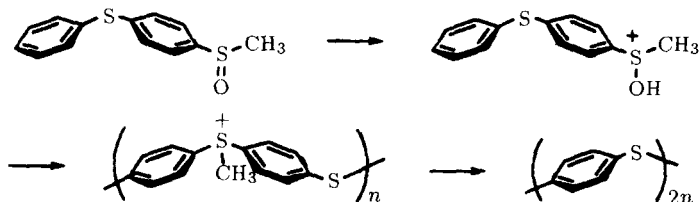
to vanadyl(V) by oxygen (Scheme 2). The μ -oxo vanadium dinuclear complex is formed in strongly acidic nonaqueous media, which would play an important role in the catalytic system. The catalytic cycle involves coordination of O_2 to the dinuclear $[V^{IV}OV^{III}]^+$ cation through which oxidation to $[V^{IV}OV^VO]^+$ takes place accompanying the splitting reaction of O_2 . The $VOVO^+$ cation is deoxygenated to produce the high-valent $[V^{IV}OV^V]^{3+}$ complex which would act as a two-electron oxidant for the substrate (thioanisole) regenerating the low-valent starting complex $[V^{IV}OV^{III}]^+$.

ACID-PROMOTED POLYMERIZATION OF ARYL SULFOXIDE FOR THE SYNTHESIS OF POLYARYLENESULFONIUM CATIONS

In order to confirm the formation of sulfonium-containing polyaromatics by the oxidation of aryl sulfides via sulfoxides, a model reaction of thioanisole and methyl phenyl sulfoxide was carried out. The reaction proceeds efficiently and gives 4-methylsulfinyldiphenyl methyl sulfonium cation quantitatively as a stable salt. The predominant unsymmetric aryl sulfide formation using the sulfoxide-acid system through the electrophilic substitution reaction is applicable to diphenyl ether, diphenyl sulfide, and naphthalene derivatives. Computational calculation by the PM3^[14] method for the 4-methylsulfinyldiphenyl methyl sulfonium cation indicates that the sulfonium cation possesses a higher LUMO energy level (-4.3 eV) than that of a trityl cation (LUMO -6.3 eV). This suggests that the sulfonium cation exists more stably than the trityl cation and can be isolated as a salt.

The polymerization process involves the self-condensation of 4-methylsulfinyldiphenyl sulfide in a strong acid by an electrophilic substitution reaction. 4-Methylsulfinyldiphenyl sulfide was polymerized in trifluoromethanesulfonic acid at room temperature for 24h to produce the polymer quantitatively (Scheme 3). The mixture was poured into water to precipitate the polymer as a triflate salt. The resulting polymer is isolated as a white powder having the empirical formula $C_{13}H_{11}S_2CF_3SO_3$, which is soluble in sulfolane, nitrobenzene, dimethyl sulfoxide, acetone, acetonitrile and formic acid. The existence of the methyl group and a counter anion in the resulting polymer was confirmed by the IR spectrum, where strong absorption bands at 1258, 638(ν_{C-F}), 1161, 1067($\nu_{S=O}$), and 3086, 3023(ν_{C-H}) cm^{-1} were observed. In the 500MHz COSY $^1H-^{13}C$ NMR spectrum (Fig.2), a methyl group is observed at

$\delta = 3.78$ and 28.9 , respectively, whose chemical shifts are at a lower magnetic field than those of the methylsulfonyl group. The 1,4-phenylene structure was confirmed by the absorption at 816cm^{-1} in the IR spectrum, AB quartet peaks in the ^1H -NMR spectrum and four typical peaks in the ^{13}C -NMR spectrum. These spectroscopic data support the formation of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate).



Scheme 3

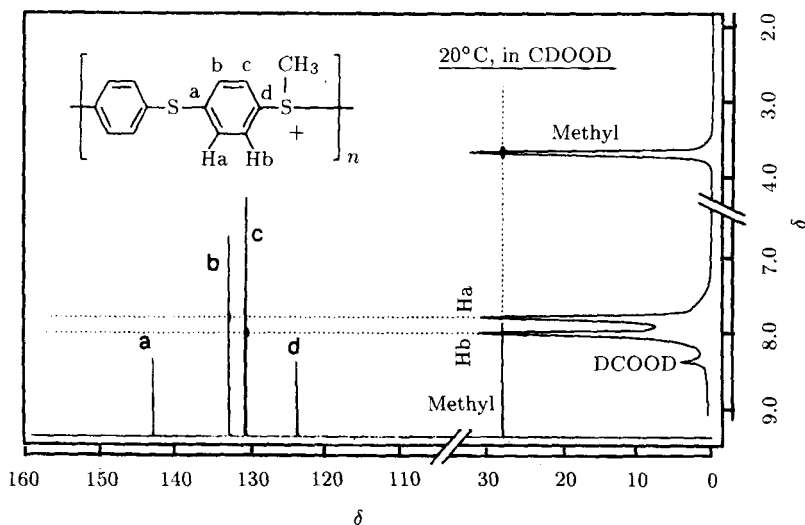


Fig.2 COSY ^1H - ^{13}C -NMR spectrum of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene triflate) in DCOOD at 20°C

The polymerization is influenced by the acidity of the mixture and is accelerated by dehydration using phosphorus pentoxide. The sulfoxide bond is polarized as S^+O^- due to the presence of the empty d orbital of sulfur. Attack on the negatively charged oxygen atom is facilitated by electrophiles. The activated sulfoxide is well-known for use as an electrophile (Swern method)^[15]. The polymerization of the sulfoxide compound is initiated via the sulfonium cation as an active species by protonation on the oxygen of the sulfoxide bond. The active species electrophilically substitutes on the phenylene ring to eliminate water.

The demethylation of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene salt)

was carried out in refluxed pyridine for 5 h. The polysulfonium salt is soluble in pyridine at room temperature, and a white insoluble powder precipitated on heating the solution. N-Methylpyridinium triflate was isolated quantitatively from the reaction mixture. The usual work-up gave a white powder of the demethylated polymer with the empirical formula of C_6H_4S . The polymer shows the same IR spectrum and CP/MAS ^{13}C -NMR spectra as the commercially available PTP Rytton V1 (virgin polymer produced by the Phillips method). No absorption bands attributed to methyl, sulfone, and sulfoxide bonds are detected in the IR spectrum. The demethylation is complete without main chain degradation. The two-center energy calculated by the PM3 method supports the result that the $H_3C-S^+ <$ bond (-14.8 eV) is the most cleavable in the diphenylmethylsulfonium structure ($Ph-S^+$, -15.9 eV).

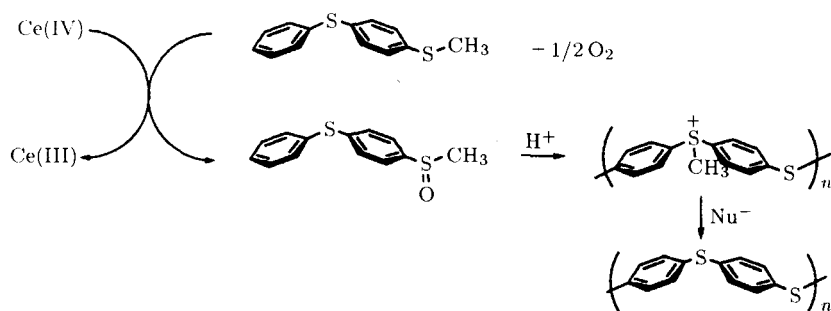
The resulting PTP has a high molecular weight of $M_w = 2.5 \times 10^5$ determined by high-temperature GPC at 210°C in 1-chloronaphthalene as an eluent calibrated with polystyrene standards. The polymerization not only enables high-molecular-weight PTP formation but also efficient synthesis of poly(thio arylene)s with high crystallinity. The precursor method also provides poly(oxy-1,4-phenylenethio-1,4-phenylene) with $M_w = 4 \times 10^4$.

OXYGEN-OXIDATIVE POLYMERIZATION OF ARYL SULFIDES

It is well-known that thioanisole is oxidized with oxygen in the presence of a catalytic amount of $Ce(NH_4)_2(NO_3)_6$ (CAN) under high pressure to yield methyl phenyl sulfoxide^[16]. When the reaction is conducted in methanesulfonic acid, the Ce-catalyzed oxidation of thioanisole proceeds under ambient atmosphere and a 22% yield of 4-methylsulfonyldiphenyl sulfide and a 78% yield of 4-methylsulfinyldiphenyl sulfide are obtained after the treatment with pyridine for the demethylation. Control experiments reveal that thioanisole dimerizes in the presence of a catalytic amount of CAN under acidic conditions. The reaction gives 4-methylsulfonyldiphenyl methyl sulfonium cation quantitatively via the formation of methyl phenyl sulfoxide. 4-Methylsulfonyldiphenyl sulfide is produced by the demethylation of 4-methylsulfonyldiphenyl methyl sulfonium cation, and 4-methylsulfinyldiphenyl sulfide is produced by the demethylation of 4-methylsulfinyldiphenyl methyl sulfonium cation which is formed by the O_2 oxidation of 4-methylsulfonyldiphenyl methyl sulfonium cation. The O_2 oxidation is influenced by the acid used. In a weak acid such as acetic

acid, the coupling reaction does not occur because the formed sulfoxide could not be activated enough to react electrophilically with a phenylene ring. The predominant formation of the dimers supports the fact that Ce(IV) acts as good catalyst for the oxidation of the aryl sulfide in a strong acid and that the resulting sulfoxide is allowed to electrophilically react with another substrate to form the sulfonium cation in high yield.

On the basis of these model reactions, the polymerization of 4-methylsulfinyldiphenyl sulfide was carried out in methanesulfonic acid in an oxygen atmosphere in the presence of a catalytic amount of CAN. During the polymerization water formed should be removed to maintain high enough acidity for the successive electrophilic substitution reaction. Among the several dehydrating agents examined, P_2O_5 showed good activity. The polymerization proceeds rapidly with the quantitative uptake of oxygen to give the poly(sulfonium cation). The oxidation of 1 mol of the monomer consumed $1/2$ mol of O_2 to give 1 mol of the sulfoxide. Oxygen is essential for the polymerization. The possible polymerization mechanism is shown in Scheme 4. 4-Methylsulfinyldiphenyl sulfide resulting from the oxidation of 4-methylsulfinyldiphenyl sulfide is protonated in methanesulfonic acid. 4-Methyl(hydroxy)sulfoniumdiphenyl sulfide as an active species electrophilically attacks the phenylene ring of another monomer. The successive coupling reaction gives the polyarylenesulfonium cation which was isolated as a white resin by precipitation from 60% perchloric acid.



Scheme 4

After the demethylation of the polysulfonium salt, PTP is isolated as a white powder in 100% yield. The molecular weight of the resulting PTP was determined to be 2.0×10^5 (Table 2). DSC measurement shows that $T_m = 260^\circ\text{C}$, $T_g = 93^\circ\text{C}$, and $T_c = 158^\circ\text{C}$ (Fig.3). T_m did not change upon annealing at 200°C , implying the absence of acid contamination. The molecular weight of the resulting PTP depends on the reaction temperature. A higher polymerization temperature at 70°C results

in a decrease in the molecular weight.

Table 2 Oxidative polymerization of 4-methylsulfonyldiphenyl sulfide

t (h)	T (°C)	Conc (mol/L)	M_w	T_m (°C)
25	20	0.5	33000	261
25	20	1.0	204000	259
70	20	0.5	104000	260
70	2	1.0	41000	260

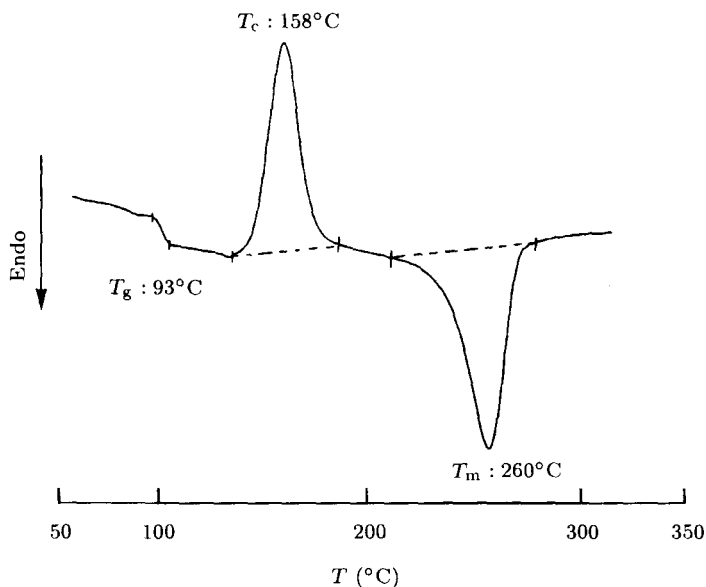


Fig.3 DSC thermogram of poly(thio phenylene) prepared by the oxidative polymerization of 4-methylsulfonyldiphenyl sulfide via polyarylenesulfonium cation

POLYMERIZATION OF ARYL SULFIDE THROUGH A MULTI-ELECTRON OXIDATION PROCESS

The use of multi-electron oxidants for the oxidative polymerization of aryl sulfides does not give the sulfoxide products but the polyarylenesulfonium cations directly via a cation radical mechanism. 4-Methylsulfonyldiphenyl sulfide was chemically oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone under acidic conditions at room temperature. During the polymerization, 2,3-dichloro-5,6-dicyano-1,4-hydroquinone precipitated out as a reduction product. After 20 h, the polyarylenesulfonium salt was isolated as a white power by precipitation from perchloric acid.

The molecular weight of the resulting PTP after demethylation is 9.5×10^3 .

Electro-oxidation is also available for the polymerization. A control experiment for the electro-oxidation of thioanisole in sulfolane in the presence of LiClO_4 (1.4V vs Ag/AgCl , in CH_3CH) resulted in the formation of dimeric 4-methylsulfonyldiphenyl methyl sulfonium perchlorate in 88% yield. The oxidation of thioanisole through an electron-transfer reaction results in predominant formation of the aryl sulfonio bond. The electro-oxidative polymerization of 4-methylsulfonyldiphenyl sulfide also yields the poly(sulfonium cation). On the basis of coulometry, it is estimated that 2F/mol are required for the polymerization in a stepwise oxidative coupling of 4-methylsulfonyldiphenyl sulfide by an electron transfer mechanism.

REFERENCES

- [1] Riley, D.P., Smith M.R., Correh, P.E., *J. Am. Chem. Soc.*, **1988**, *110*, 177
- [2] (a) Roush, D.M., Price, E.M., Templeton, L.K., Templeton, D.H., Heathcock, C.H., *J. Am. Chem. Soc.*, **1979**, *101*, 2971. (b) Yamamoto, K., Shouji, E., Nishide, H., Tsuchida, E., *J. Am. Chem. Soc.*, **1993**, *115*, 5819. (c) Anderson, K.K., Caret, R.L., Kerup-Nielsen, I., *J. Am. Chem. Soc.*, **1974**, *96*, 8020
- [3] (a) Yamamoto, K., Oyaizu, K., Iwasaki, N., Tsuchida, E., *Chem. Lett.*, **1993**, 1223. (b) Tsuchida, E., Yamamoto, K., Oyaizu, K., Iwasaki, N., Anson, F.C., *Inorg. Chem.*, **1994**, *33*, 1056
- [4] Hay, A.S., Blanchard, H.S., Endres, G.F., Eustance, J.W., *J. Am. Chem. Soc.*, **1958**, *81*, 6335
- [5] (a) Edmonds, J.T., Jr., Hill, H.W., Jr., *U.S. Pat.*, 3354129, **1967**. (b) Campbell, R.W., Edmonds, J.T., *U.S. Pat.*, 4038259, **1977**. (c) Hill, H.W., Jr., *Ind. Eng. Chem., Prod. Res. Div.*, **1979**, *18*, 252
- [6] Yamamoto, K., Tsuchida, E., Nishide, H., Yoshida, S., Park, Y.S., *J. Electrochem. Soc.*, **1992**, *139*, 2401
- [7] Yamamoto, K., Jikei, M., Oi, K., Nishide, H., Tsuchida, E., *J. Polym. Sci., Part A*, **1991**, *29*, 1359
- [8] Tsuchida, E., Yamamoto, K., Jikei, M., Shouji, E., Nishide, H., *J. Macromol. Sci., Chem.*, **1991**, *11*, 1285
- [9] Yamamoto, K., Yoshida, S., Nishide, H., Tsuchida, E., *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 3655
- [10] Tsuchida, E., Yamamoto, K., Jikei, M., Nishide, N., *Macromolecules*, **1989**, *22*, 4138
- [11] Yamamoto, K., Shouji, E., Nishide, H., Tsuchida, E., *Macromolecules*, **1993**, *115*, 5819
- [12] Bonadis, J.A., Butler, W.M., Pecoraro, V.L., Carrano, C., *Inorg. Chem.*, **1987**, *26*, 1218
- [13] Rechardson, D.E., Taube, H., *Inorg. Chem.*, **1981**, *20*, 1278
- [14] Stewart, J.J.P., *J. Comput. Chem.*, **1989**, *10*, 221
- [15] Mancuso, A.J., Swern, D., *Synthesis*, **1981**, 165
- [16] Riley, D.P., Correh, P.E., *J. Chem. Soc., Chem. Commun.*, **1986**, 1097