

**Synthesis of Poly(1,4-phenylene sulfide) from Diphenyl Disulfide
and its Oxidative Polymerization Mechanism**

ジフェニルジスルフィドからの
ポリ(1,4-フェニレンスルフィド)合成とその酸化重合機構

Waseda University
Graduate School of Advanced Science and Engineering
Department of Applied Chemistry, Research on Polymer Chemistry

July 2016

Fuyuki Aida

相田 冬樹

Promoter: Prof. Dr. Hiroyuki Nishide
Referees: Prof. Dr. Kenichi Oyaizu
Assoc. Prof. Dr. Sejiro Hosokawa

Preface

Poly(1,4-phenylene sulfide) (PPS) is an engineering plastic and is used all over the world. Because of its excellent heat resistance, mechanistic strength and electric insulation, PPS is molded into various parts, which are used mainly in the automobile and electric industries. Casings of ignition coils, reflectors of head lamps, pistons for hydraulic transmissions and impellers for cooling water were representative applications of PPS in the automobile industry. Insulators of transistors, lamp cases for projectors and components for microwave ovens are examples of electric application. According to the marketing report by Fuji Keizai Co. Ltd. in 2012, production volume of PPS was estimated to be 100,000 metric tons in 2017, with an annual increase of 7%. Thus, PPS is a very attractive target for chemical industries.

PPS is produced from *para*-dichlorobenzene and sodium sulfide via polycondensation eliminating NaCl, under severe conditions (250 °C, 400 kPa) in *N*-methylpyrrolidone, called the Phillips method. Though there is a NaCl washing process with water in the Phillips method, the PPS contains a certain amount of chlorine. Remaining NaCl degrades the electric insulation of PPS. Utilizing halogen-free materials is extremely favored in the electric industry because very toxic dioxins are considered to be formed when the halogen-containing materials combust. In this case, the halogen is defined as chlorine and bromine. Low concentration of the halogen is quite an important quality of PPS. Therefore, PPS manufacturers make an effort to reduce the chlorine, based on the above mentioned two reasons.

Polymer Chemistry Laboratory at Waseda University reported oxidative polymerization of diphenyl disulfide (PhSSPh) as an alternative preparation of PPS. The polymerization only formed water as a by-product, without forming any salt. The polymerization was catalyzed by the vanadyl-strong acid catalyst, which did not contain chlorine or bromine. As the monomer, PhSSPh also did not contain any chlorine; the PPS obtained via the polymerization was halogen-free, theoretically. Besides, the polymerization proceeded under quite a mild condition at an ambient temperature and ambient pressure of oxygen. Thus, PPS synthesis via the oxygen oxidative-polymerization of PhSSPh is quite attractive.

However, there remain unsolved issues in the oxygen oxidative-polymerization of PhSSPh. A stoichiometric amount of water is formed during the polymerization. Since water decomposes the vanadyl catalyst, the polymerization requires expensive acid anhydrides to quench the water. This is the first unsolved issue. The second one is long reaction time: it generally takes more than 20 hours, to complete the polymerization. The third one is the low molecular weight of the obtained PPS, compared with those of conventional PPS. To conquer

these unsolved issues, improvements to the oxygen oxidative-polymerization are eagerly anticipated.

In this thesis, the author focused on synthesis of PPS and studied the oxidative polymerization mechanism to overcome the unsolved issues. The author paid attention to polymerization conditions, mainly the reaction temperature, to remove the water. The author observed the catalytic cycle to solve the issue of long reaction time. In the oxygen oxidative-polymerization, an electron is transferred from PhSSPh to oxygen via a vanadyl catalyst, which is reduced by PhSSPh and re-oxidized by oxygen. The author thought polymerization under pressurized oxygen conditions would accelerate the re-oxidation of a vanadyl catalyst. The author also considered that utilizing an oxidant, which added another catalytic cycle between PhSSPh and oxygen, would accelerate oxidation of PhSSPh or re-oxidation of a vanadyl catalyst. The author also investigated increasing molecular weight via elucidation of the polymerization mechanism.

The author reviews, in Chapter 1, carbon-sulfur bond formations, which are quite important for organic chemistry and polymer chemistry, utilizing elemental sulfur, sulfur-containing radicals, anions, cations and their synthetic equivalents. Electrophilic reactions of sulfur cationic species are mainly described in the review, showing addition to olefins and substitution to aromatic rings. The review concerns a series of oxidative-polymerizations of diaryl disulfides, including PhSSPh, and synthesis of heteropolyacenes, utilizing sulfonium electrophiles derived from sulfoxides. Chapters 2–4 depict investigations of solvent- and acid anhydride-free oxygen oxidative-polymerization, the chemical structure of the obtained PPS, the polymerization mechanism for increasing molecular weight and the selectivities to determine the chemical structure, and enhancements of catalytic activities for accelerating the polymerizations. Chapter 5 describes a palladium-catalyzed stereoselective reductive Mizoroki-Heck reaction to synthesize 5-*exo*-aryl-2-norbornene from aryl chloride and 2,5-norbornadiene, as one of the applications for utilizing a transition metal catalyst. Under a non-reductive condition, successful synthesis of benzocyclobutene-fused norbornene from the same raw materials is also described. The last chapter concludes this thesis and discusses the future prospects of PPS synthesis via oxygen oxidative-polymerization, including potential applications of the polymerization.

Fuyuki Aida

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Chapter 1

General Introduction:

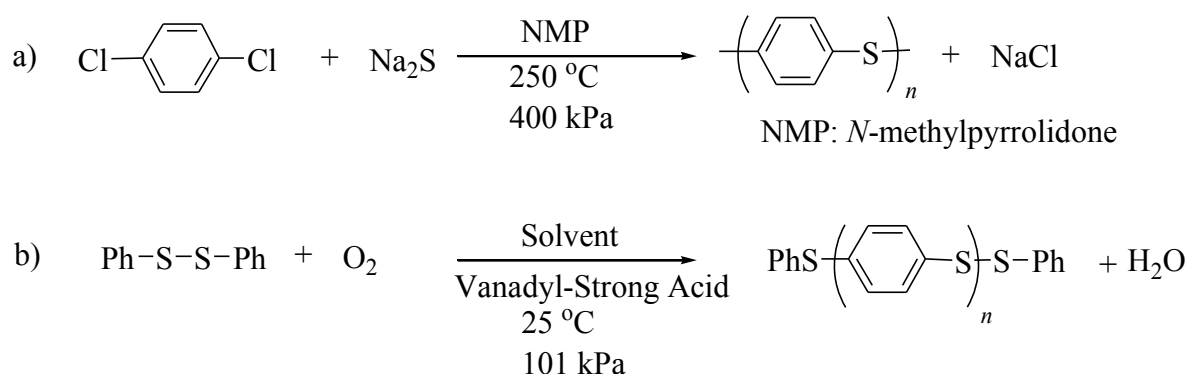
Overview of Carbon-Sulfur Bond Formation by Focusing on Sulfur-containing Cationic Species

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1-1. Introduction

Poly(1,4-phenylene sulfide) (PPS) is produced as shown in Scheme 1-1a, known as the Phillips method.¹ Its alternative method, developed by Polymer Chemistry Laboratory at Waseda University, is oxygen oxidative-polymerization of diphenyl disulfide (PhSSPh), as shown in Scheme 1-1b.² The propagation of the polymers is carbon-sulfur (C-S) bond formation.



Scheme 1-1. Preparation of PPS. a): Phillips method. b): oxidative polymerization of PhSSPh.

There are varieties of sulfur-containing chemicals and polymers besides PPS. One of the most important chemical reactions for preparing those chemicals and polymers is the C-S bond formation. As general introduction to this thesis, the recent progress on C-S bond formation is reviewed, utilizing sulfur-containing radicals, anions, cations, and their synthetic equivalents, including activation by organometallic compounds.

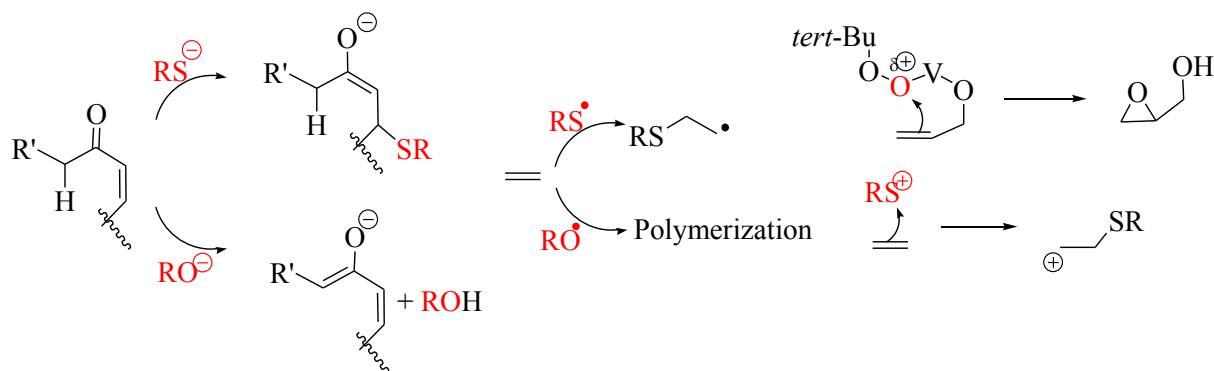
Sulfur and sulfur-containing chemicals are widely used all over the world. One of their major applications is manufacturing rubber industry.³ Typically, a synthetic styrene-butadiene rubber (SBR) is vulcanized to mechanically strengthen the pristine soft materials for use as automobile tires. Elemental sulfur (S₈), thioureas, mercaptothiazoles, and mercaptobenzoimidazoles are used for the vulcanization of SBR and as additives for stabilizing the rubber.¹ Vulcanization involves crosslinking of rubbery substances, typically having carbon-carbon double bonds. When SBR is vulcanized with sulfur and additives, C-S bonds are considered to be formed mainly at allylic positions.

As represented by PPS, polythioether sulfone, and polyether sulfone (PES), sulfur-containing polymers are known as engineering plastics and are used as base resins in

various kinds of industries. PPS and PES contain C-S bonds in their main chains, and are typically produced by polycondensation process. For example, PPS is prepared from *p*-dichlorobenzene and sodium sulfide (Na_2S).¹ In this case, the C-S bond formation corresponds to the propagation reaction of the polymer.

Another type of commercialized sulfur-containing chemicals is categorized as fine chemicals, such as pharmaceuticals and agrochemicals. Generally, they have various kinds of sulfur-containing functional groups, such as thiol, sulfide, disulfide, sulfoxide, sulfone, thioester, thiourethane, thiazole, dithiolane, and thiophene; therefore the target-oriented approaches to those chemicals have spawned a variety of synthetic reactions.² Indeed, there are plenty of methods to form the C-S bond, utilizing S_8 , sulfur cations, sulfur anions, sulfur radicals, and their synthetic equivalents. Also, there are a lot of effective methods for the C-S bond formation, utilizing transition metal catalysts via activation of carbon-halogen (C-X), sulfur-hydrogen (S-H), and carbon-hydrogen (C-H) bonds.⁵

Although sulfur and oxygen are the same 16 group elements, their reactivity is quite dissimilar. In general, sulfur-containing molecules have lower ionization potentials and higher electron affinities than those of oxygen-containing analogues. Sulfur-containing molecules are more easily reduced and oxidized than the oxygen-containing counterparts, and hence the sulfur-containing reagents are expected to show unique properties. Representative reactions utilizing sulfur anions, radicals and cations are summarized in Scheme 1-1. Alcoholates RO^- act as a base, but thiolates RS^- give Michael addition products with methyl vinyl ketone analogues. Alkoxy radicals $\text{RO}\cdot$ derived from peroxides have quite high reactivity and are typically used as an initiator for the radical polymerization of olefins, but $\text{RS}\cdot$ radicals provide addition products with olefins. As for cationic oxygen species, it is less easy to find examples of oxonium reagents RO^+ , which are however used in particular organic synthesis to form carbon-oxygen (C-O) bonds. Generally, cationic species exhibit electrophilic reactivities. Katsuki-Sharpless epoxidation by a titanium complex and *t*-butyl hydroperoxide could be the examples of the electrophilic reactions by oxygen-containing reagents (Scheme 1-2).^{6,7} Sulfoniums RS^+ and their synthetic equivalents can add to olefins to give sulfide compounds. A typical difference between the oxygen- and sulfur-containing molecules is the stability of peroxides (ROOR) and disulfides (RSSR). For example, diphenyl disulfide (PhSSPh) can be stored under an ambient temperature, but peroxides are explosive and are thus recommended to be stored in a refrigerator to avoid decomposition.



Scheme 1-2. Representative reactions of oxygen and sulfur species.

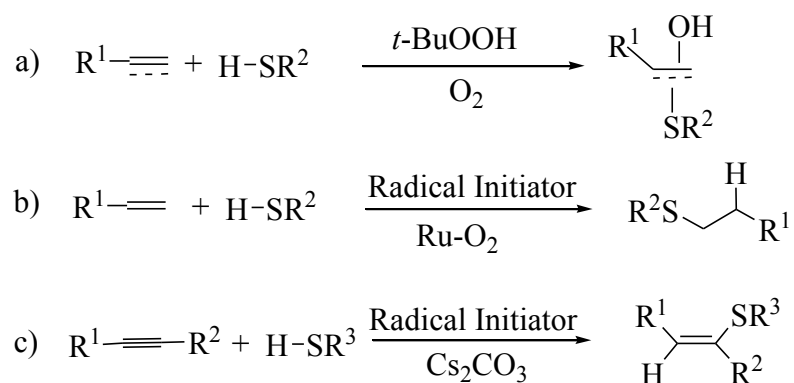
Among the synthetic methods for the C-S bond formation, sulfur cations and their synthetic equivalents show quite unique electrophilic reactions. Our group has been pursuing for electrophilic substitution reactions utilizing sulfonium cations, such as bis(phenylthio)phenyl sulfonium cation ($\text{PhS}(\text{PhSSPh})^+$),⁸ mainly for the PPS synthesis via oxidative polymerization. This type of sulfonium cation has also been utilized in electrophilic addition to various kinds of olefins. The present review describes recent developments in the C-S bond formation, especially focusing on the RS^+ electrophiles, showing their prospects in organic and polymer synthesis. Reactivities of sulfur-containing radicals and anions were also reviewed concisely with a view to emphasize the synthetic utility of the sulfonium electrophiles

1-2. A Brief Overview on Sulfur-Containing Radicals, Anions, and Their Coupling Reactions

The unique organic chemistry of the sulfur-containing molecules originates from their low ionization potentials and high electron affinities, compared with those of the oxygen-containing molecules. The sulfur-containing molecules can thus act both as nucleophiles and electrophiles, which results in sharp contrast from the reactivity of the oxygen-containing analogues.

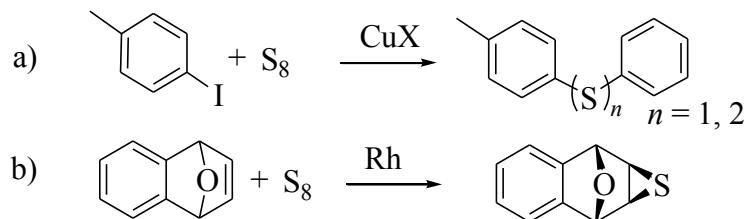
Radical oxygen species (i.e. the $\text{RO}\cdot$ radicals) are highly reactive and used as initiators for radical mediated reactions. Because of the high reactivity, it is quite hard to utilize the $\text{RO}\cdot$ radicals for the C-O bond formation. In contrast to the $\text{RO}\cdot$ radical, $\text{RS}\cdot$ radicals are frequently employed as a convenient synthetic tool for the C-S bond formation. Recently, oxidative radical hydrosulfurization of styrenes and alkynes were reported, which proceeded

via activation with a peroxide radical initiator to give regioselective products, β -hydroxysulfides and α -thioaldehydes, respectively (Scheme 1-3a).^{9,10} The regioselectivities found for styrene and alkyne were completely different. In the presence of the radical initiator, triethylboran and catechol, a thiol-ene coupling reaction^{11a} proceeded between allylether and thiol.^{11b} Another type of the radical-mediated thiol-ene reaction was also reported, utilizing a ruthenium photoredox catalyst (Scheme 1-3b).¹² In the presence of the radical initiator, stereoselective hydrothiolation of alkynes was accomplished, which was catalyzed by cesium carbonate (Scheme 1-3c).¹³



Scheme 1-3. Representative C-S bond formation reactions utilizing $\text{RS}\cdot$ radicals.

The simplest and most economical sulfur source is S_8 , which is recovered from oil refineries. There have been many attempts to utilize S_8 for organic synthesis, but reactivity or selectivity is generally insufficient. Recently, good examples of utilizing S_8 for organic synthesis were reported. Aryliodide and S_8 gave diaryl sulfide and diaryl disulfide selectively, in the presence of a copper catalyst and a base (Scheme 1-4).¹⁴ Under full conversion of iodotoluene, Cu-LiOH and Cu-AcONa systems selectively gave ditolyl sulfide and the corresponding disulfide, respectively (Scheme 1-4a). Another curious example of utilizing S_8 is the synthesis of *exo*-1,2,7,8-tetrahydro-2,7-epoxynaphtho[2.3-*b*]thiirane from 7-oxabenzonorbornadiene, in the presence of rhodium catalyst and 4-ethynyltoluene (Scheme 1-4b).¹⁵ Further investigation of selective reactions utilizing economically attractive S_8 is greatly prompted by these studies.¹⁶



Scheme 1-4. Representative C-S bond formation reactions utilizing S₈.

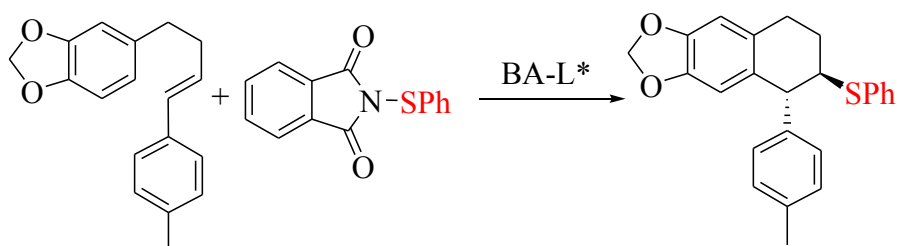
Because of the enhanced stability of the RS \cdot radical species compared with that of the RO \cdot radicals, the selectivities of the reactions in Scheme 1-2 were relatively high. As radical reactions typically require an initiative step prompted by heating, light irradiation and other external stimuli, the reaction conditions tend to be harsh which may give rise to side reactions to lower the selectivity. Generally, ionic reactions proceed under milder conditions than is required for the radical reactions, resulting in a much higher selectivity. The advantages of using the ionic reactions have been found in many types of ionic and/or catalytically activated sulfur-containing reagents as follows.

As representative anionic sulfur-containing species, RS $^-$ can proceed nucleophilic attack to C=C double bonds of methyl vinyl ketone analogues (Scheme 1-2, left), but RO $^-$ forms their enolates. Because RS $^-$ are soft base, they add to the soft carbon at the β -position to give thia-Michael addition products. Thus, the thia-Michael addition is regarded as the characteristic reaction of the sulfur-containing anions. In the presence of a catalytic amount of Et₃N, thia-Michael addition of RSH to conjugated cyclohexenone was accomplished.¹⁵ Thioboration of α,β -unsaturated ketones and aldehydes gave vinylborate analogues having a sulfide bond at the β -position, even without base or metal.¹⁸ To quinones, a silver-catalyzed addition of diphenyl disulfide (PhSSPh) was reported (Scheme 1-5a).¹⁹ These are typical examples of the thia-Michael addition to electron-deficient olefins. Metal-activated RSH can add to electron-sufficient olefins, such as vinyl ethers and enamines, to give sulfide derivatives.²⁰ Similarly, transition metal-catalyzed RSH addition to C=C double bonds proceeds with palladium,²¹ rhodium,²² actinoid,²³ and zirconium catalysts.²⁴ As a quite unfamiliar metal catalyst in organic synthesis, calcium-catalyzed RSH addition to alkyne gave dithioacetals (Scheme 1-5b).²⁵ Iron-catalyzed cyclization of alkynols with PhSSPh yielded 3,4-bis(phenylthio)-2,5-dihydrofuran derivatives (Scheme 1-5c).²⁶ Another type of the C-S bond formation is a nucleophilic reaction with the C-O bond cleavage of epoxides or carbonates. Enantioselective epoxide cleavage with RSH catalyzed by a gallium lithium chiral

1-3. Sulfur-containing Cationic Species and Their Electrophilic Reactions

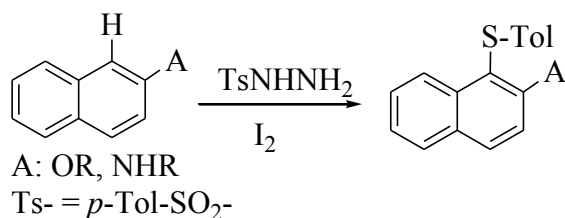
As for the cationic sulfur-containing reagents, sulfonium ions RS^+ and their synthetic equivalents undergo electrophilic reactions, while RO^+ is rarely utilized for the C-O bond formation. Here, the electrophilic reactions of RS^+ and their synthetic equivalents are reviewed with an emphasis placed on their usefulness in the synthesis of aromatic molecules and polymers.

When phenylsulfenophthalimide was reacted with styrene derivative in the presence of a catalytic amount of Brønsted acid (BA) and a chiral biphenyl derivative ligand, formally the PhS^+ was added to the C=C double bond of styrene at the initial stage of the reaction. The PhS -added cationic intermediate underwent the Friedel-Crafts (FC) electrophilic substitution onto the aromatic ring of catechol, which gave the optically active PhS -coupled tetrahydronaphthalene derivative (Scheme 1-6).³³



Scheme 1-6. PhS^+ cation-mediated asymmetric synthesis.

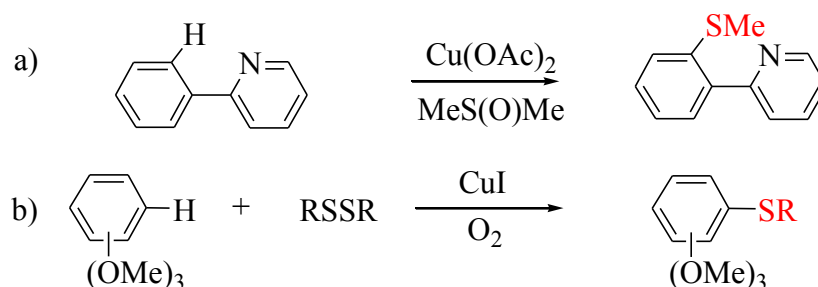
Arylsulfonyl hydrazines were utilized as the thiolation source of naphthols/naphthylamines with iodine.³⁴ The report demonstrated that a $TolS^+$ cation added to the naphthalene derivatives, via ditolyl disulfide formation from tolylsulfonyl hydrazines and iodine (Scheme 1-7).



Scheme 1-7. Electrophilic substitution by $Tol-S^+$ cation generated from tosyl hydrazine.

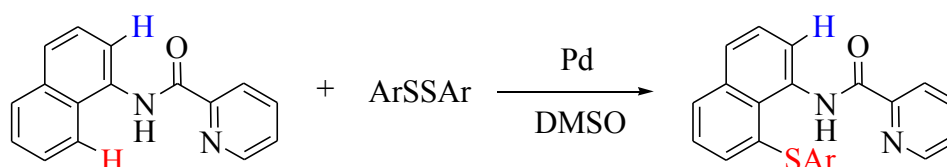
Dimethyl sulfoxide (DMSO) has also been applied as the source of the methylthio group. Methylthiolations of arenes and heteroarenes were reported (Scheme 1-8a).³⁵ DMSO was

decomposed thermally to give MeSH and formaldehyde. Subsequently, the actual reactive precursor, MeSSMe was formed which then added to the aromatic ring. The formation of disulfide was described as follows: $2\text{MeSH} + \text{DMSO} \rightarrow \text{MeSSMe} + \text{MeSMe} + \text{H}_2\text{O}$. The presence of the cationic mechanism was suggested in the reaction of 2-phenylpyridine and copper species, AcOCu-SMe complex, which was derived from MeSSMe and $\text{Cu}(\text{OAc})_2$. The methylthiolation proceeded selectively at the *ortho*-position of the phenyl ring. The copper-containing intermediate was stabilized by the pyridine group, which most likely formed a five-membered ring. The reaction was uninhibited by 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), which suggested the MeS^+ -based mechanism rather than the radical mediated reaction. Additional examples of the similar copper-utilizing reactions (*vide infra*) demonstrated their synthetic utility. Copper-catalyzed thiolation to the C-H bond of trimethoxybenzene was accomplished, utilizing disulfide compounds under oxidative conditions (Scheme 1-8b).³⁶ Copper-mediated C-H activation/C-S cross coupling reaction between heterocycles and thiol was established.³⁷ The C-S bond formation via the C-H bond functionalization has been reviewed.³⁸



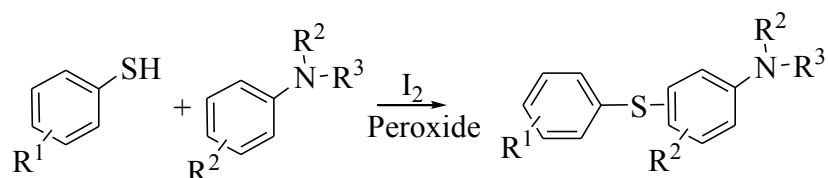
Scheme 1-8. RS^+ cation-mediated reactions generated from DMSO and RSSR.

Similar electrophilic thiolation to aromatic rings by PhSSPh was reported (Scheme 1-9).³⁹ The disulfide PhSSPh was activated by a palladium or a nickel complex to yield a PhS-M-SPh (M: Pd or Ni) derivative as the oxidative addition product. To stabilize the organometallic complex, formation of a metallacycle with the heteroatom was favored. Regioselectivity was derived from the five-membered metallacycle.



Scheme 1-9. Palladium-catalyzed arylthiolation by diaryl disulfide.

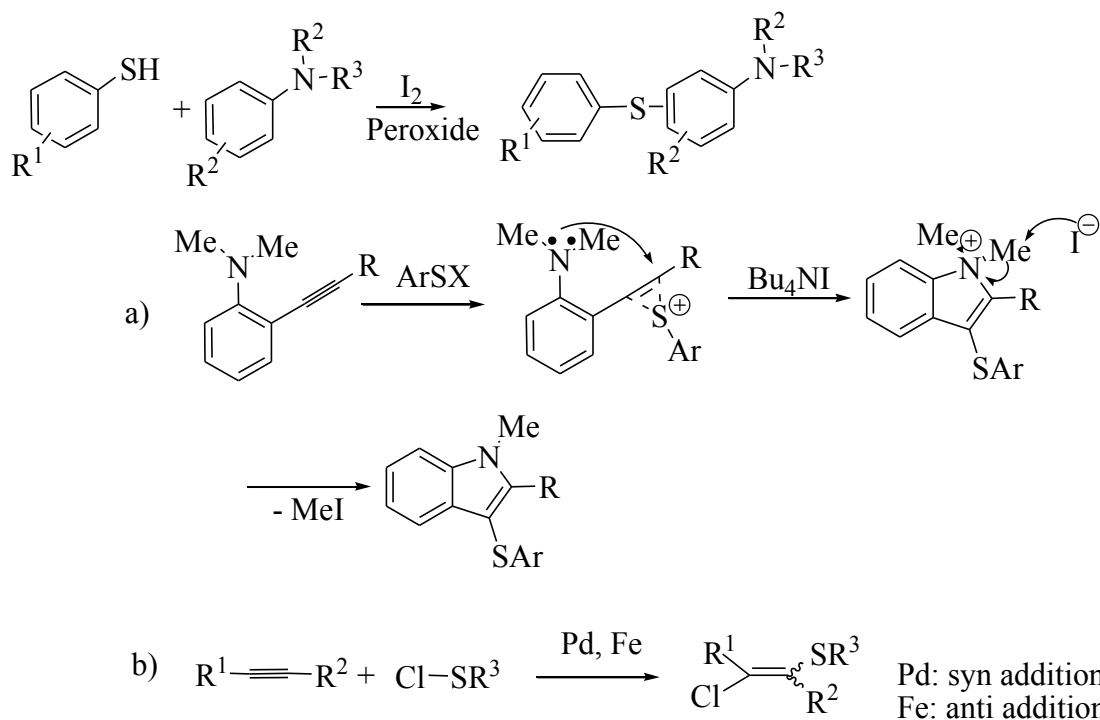
Metal-free iodine-catalyzed direct arylation of substituted anilines was reported, which gave diaryl sulfides in the presence of a peroxide (Scheme 1-10).⁴⁰ Diaryl disulfide was formed via the oxidation of the arylthiol by iodine, and the resulting iodine was re-oxidized by the peroxide.



Scheme 1-10. Direct arylation of substituted anilines with thiols.

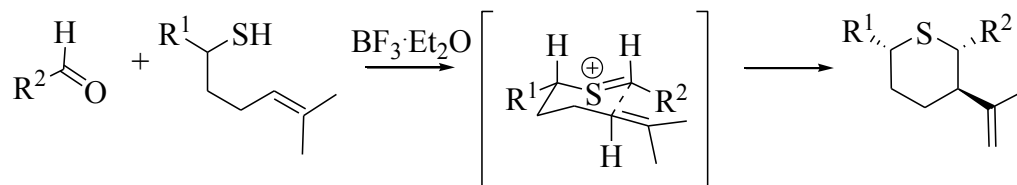
Disulfide compounds, including those generated *in-situ*, are easily available and are thus quite useful as the RS^+ sources for the C-S bond formation.

Another type of RS^+ source is RSX (X: halogen). Arylsulfide substituted indole synthesis was reported, employing a reaction between $ArSCl$ and aniline derivative bearing an alkyne bond with ammonium halides via RS^+ addition to the alkyne (Scheme 1-11a).⁴¹ The RSX and the terminal or inner alkyne derivatives gave vinylsulfide compounds with transition metal catalysts (Scheme 1-11b).⁴²



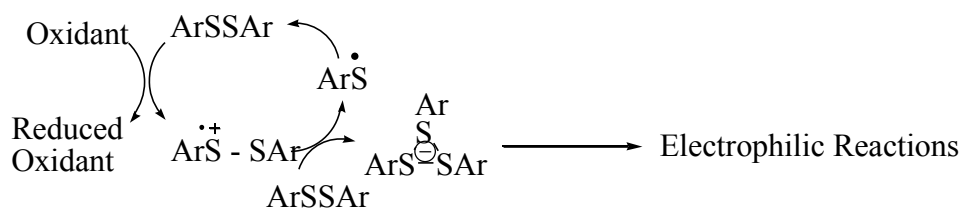
Scheme 1-11. RSX addition reactions to alkyne derivatives.

Another type of the sulfur-containing cationic reagent is a thionium cation ($R=S^+-R$), which mediated the reaction to synthesize substituted tetrahydropyrans via thionium-ene cyclization (Scheme 1-12).⁴³



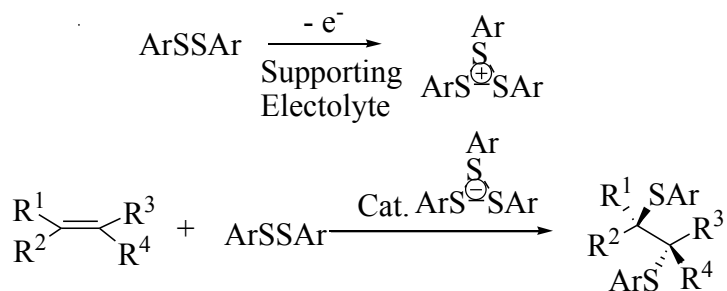
Scheme 1-12. Thionium type cation intermediated cyclization.

Sulfonium ions have much larger varieties than oxonium ions, giving rise to many types of electrophilic reactions in addition to the above-mentioned reactions utilizing RS^+ and their equivalents. Different from oxygen, sulfur forms three-membered sulfonium cations $RS(RSSR)^+$ from RS^+ and $RSSR$. Oxidation of disulfides by electrolysis and with chemical oxidants such as quinones and vanadium(V) compounds gives their radical cations $RSS^+\cdot R$. The radical cation reacts with another neutral disulfides to yield the $RS(RSSR)^+$ cation and $RSSR$ which is produced by the coupling of the eliminated $RS\cdot$ radicals. The three-membered sulfonium cations possess high electrophilic reactivity and have been applied for organic synthesis (Scheme 1-13). The three-membered cationic structure was identified using a more inert $MeS(MeSSMe)^+$ cation ($R = Me$) by NMR under low temperature.⁸



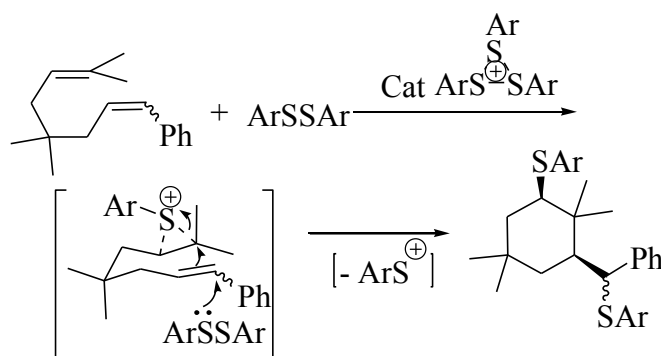
Scheme 1-13. Sulfonium cations produced by the oxidation of diaryl disulfide.

As one of the applications utilizing the sulfonium cation, addition of an electrochemically generated $ArS(ArSSAr)^+$ cation to olefin was reported, which gave 1,2-bisthiolated compounds (Scheme 1-14).⁴⁴



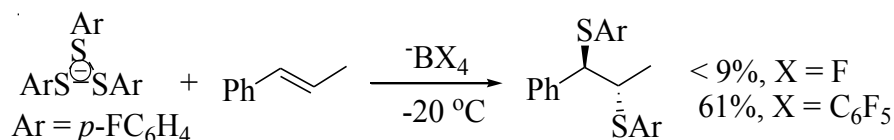
Scheme 1-14. Bisthiolation of olefin using the sulfonium cation.

Application of this reaction to 1-phenyl-4,4,7-trimethyl-1,6-octadiene resulted in yielding a cyclohexane derivative as the final product, which proceeded via the six-membered ring transition state (Scheme 1-15). This bis-thiolation was applied to various kinds of olefins, such as styrenes and cycloalkenes. It may be noted that the bis-thiolation was strongly affected by the steric hindrance of olefin. 1-Methylcyclohexene gave bis-thiolated product in ca. 70% yield, but both *trans*- and *cis*-stilben showed lower yields of less than 40%.^{44b}



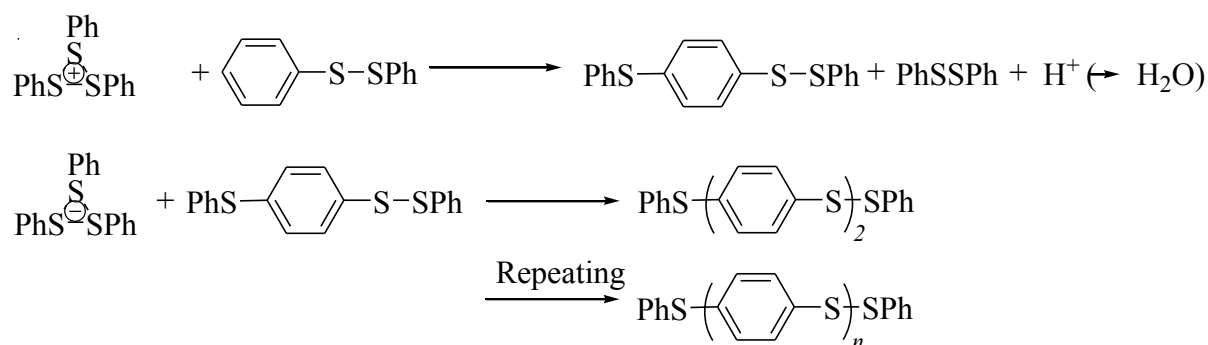
Scheme 1-15. Sulfonium cation-catalyzed bisthiolation of 1,6-diolefin.

Interestingly, a counter anion of the sulfonium salt was reported to dominate the overall reactivity of the electrophilic reactions. When tetrabutylammonium tetrakis(pentafluorophenyl)borate ($\text{Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4$) was used as a supporting electrolyte, *trans*-1-phenyl-1-propene and ArSSAr ($\text{Ar} = p\text{-FC}_6\text{H}_4$) gave a 1,2-bis-thiolated compound in 61% yield, but the replacement of the $\text{B}(\text{C}_6\text{F}_5)_4^-$ salt with a tetrafluoroborate (Bu_4NBF_4) significantly reduced the yield down to less than 9% (Scheme 1-16).^{44b} The effect of the BF_4^- ion was ascribed to the stabilization of the cationic intermediates, most probably by chemical bond formation with the fluorine atom, to reduce its reactivity. The apparent anion effect gave insight into the nature of the borate in the case of the polymerization of PhSSPh .⁴⁵



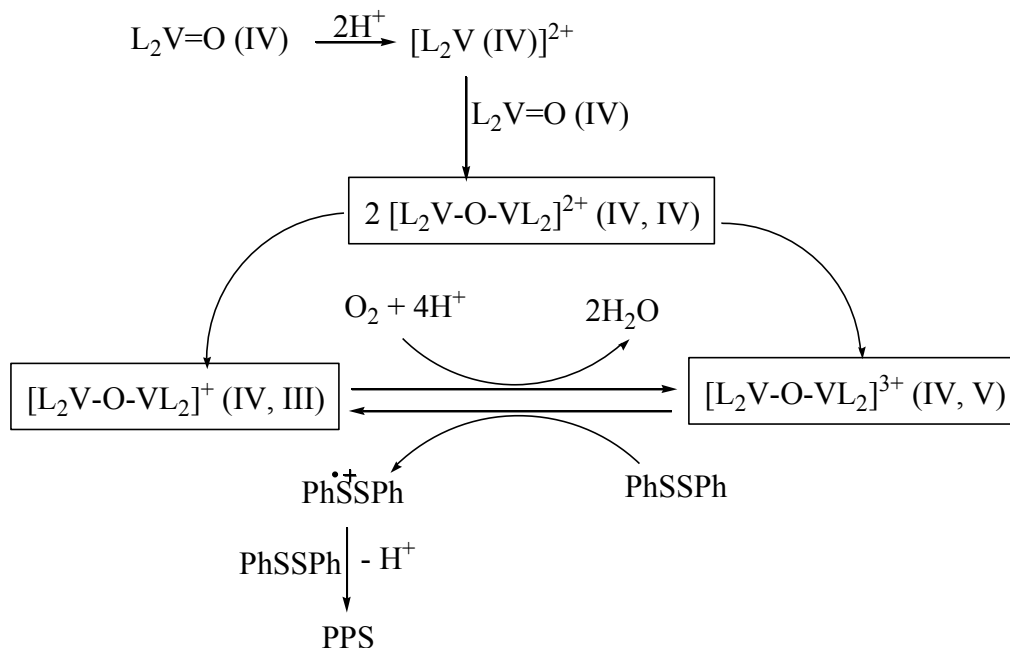
Scheme 1-16. Activation and deactivation of the sulfonium cation by borate anions.

In addition to the electrochemical oxidation, vanadyl-catalyzed autoxidation and chemical oxidation with quinones have been found to convert disulfide into the sulfonium cation. Around 20 years ago, our group discovered a synthetic route to PPS via the oxidative polymerization of PhSSPh.⁴⁶ The sulfonium cation underwent condensation at the aromatic group via an electrophilic FC substitution to form the thioether bond. The reaction of PhSSPh with the corresponding sulfonium cation PhS(PhSSPh)⁺ yielded PhS-C₆H₄SSPh as the condensed product with the elimination of H⁺ and PhSSPh. This thioether bond formation was repeated until all of the disulfide molecules were consumed to yield a polymer, PhS-(C₆H₄S)_{*n*}-SPh, which was regarded as a polythiophenylene (PPS) bearing a disulfide bond at the end. The eliminated H⁺ was consumed in the reduction of O₂ to H₂O according to O₂ + 4H⁺ + 4e⁻ → 2H₂O, when O₂ was used as the oxidant (Scheme 1-17).



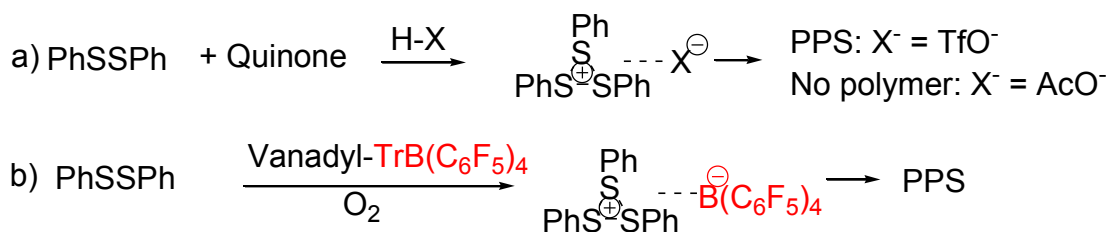
Scheme 1-17. PPS synthesis via FC substitution by the sulfonium cation.

An important aspect of the reaction in Scheme 16 is the capability of catalysis by oxovanadium(IV) or vanadyl (V^{IV}=O) complexes for the O₂ oxidation of the disulfide. The V=O complex has to be activated with a strong acid to form the active form of the catalyst, [V-O-V]²⁺.⁴⁷ The catalyst allowed the 4-electron reduction of O₂ to H₂O without producing the partially reduced active oxygen species, which contributed to enhance the selectivity of the reaction. The catalytic mechanism is illustrated in Scheme 1-18.⁴⁸



Scheme 1-18. Vanadyl-catalyzed PPS synthesis, based on the 4-electron reduction of O₂ (L = β-diketonato ligand).

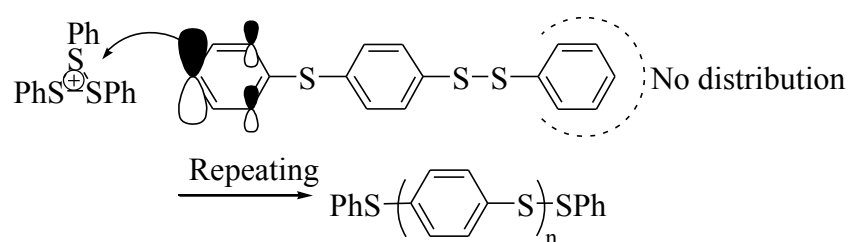
As chemical oxidants for the polymerization of the disulfide, quinones bearing electron-withdrawing groups such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 2,3,5,6-tetrabromo-*p*-benzoquinone (bromanil), and vanadium(V) oxide have also been found to yield PPS. In both cases of using the chemical oxidants and the vanadyl-catalyzed O₂ oxidation, a strong acid was essential for the polymerization. Strong acids, such as trifluoromethanesulfonic acid (TfOH) and perfluoroalkylsulfonic acids, were the initial proton source to activate the vanadyl catalyst as well as the stabilizer of the cationic species with their conjugated bases. As weak acids such as acetic acid (AcOH) significantly retarded the polymerization, it has so far been considered that strong protic acids should be essential (Scheme 1-19a). However, we have recently found that the polymerization proceed even in the absence of the strong acid, as far as the reactivity of the electrophile is maintained. Interestingly, a catalytic amount of triphenylmethyl cation tetrakis(pentafluorophenyl)borate (TrB(C₆F₅)₄) activated the vanadyl complex to catalyze the O₂-oxidative polymerization of PhSSPh (Scheme 1-19b) without the use of the pricy strong acids.⁴⁵ Enhanced reactivity of the electrophile at higher temperatures (160 °C) allowed the use of triphenylmethyl tetrafluoroborate (TrBF₄). These results suggested that the polymerization was dominated by the reactivity of the conjugate base, rather than the proton concentration.⁴⁵



Scheme 1-19. Reactivity of the sulfonium salt dominated by the nature of the counter ion.

As illustrated in Scheme 1-16 and 1-17, the eliminated proton was converted into H₂O during the O₂-oxidative polymerization. Because H₂O decomposed the active form of the catalyst [V-O-V]²⁺, very pricy strong acid anhydrides such as trifluoroacetic anhydride have been regarded as essential. We recently solved this problem using molten PhSSPh as the monomer by maintaining the temperature above 100 °C under O₂ flow conditions, where the eliminated H₂O was efficiently removed by evaporation. This led to the establishment of the first anhydride- and solvent-free process of the oxidative polymerization to yield PPS.⁴⁹

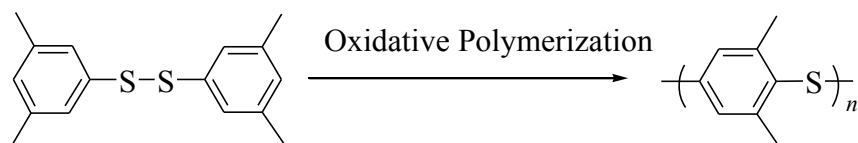
The obtained PPS had pure thio-1,4-phenylene structure which was evidenced by spectroscopic analyses. The *para* selectivity was supported by computational calculation.^{8,49,50} The obtained PPS contained a disulfide bond at the terminal position, which was suggested by the characteristic thermal dimerization behavior giving rise to double the molecular weight with the elimination of PhSSPh. Calculation results also supported the terminal disulfide functionality, based on the comparison of the HOMO levels and the shapes of their lobes in PhSSPh and PhS-(C₆H₄S)-SPh (Scheme 1-20).^{49,51}



Scheme 1-20. Origin of the selectivity to produce the thio-1,4-phenylene chain.

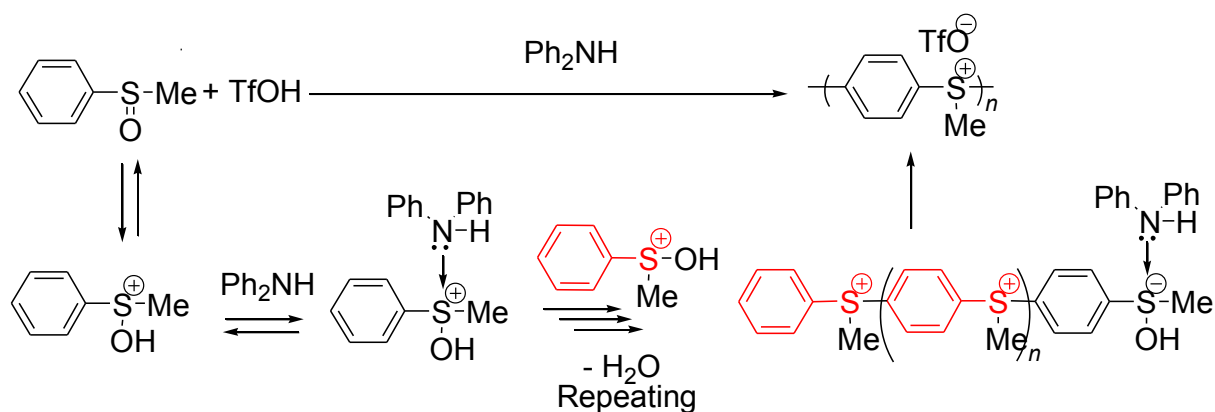
It may be added that the reaction has been expanded to those with many kinds of diaryl disulfides (ArSSAr) to yield poly(1,4-arylene sulfide)s (PAS), typically for those containing methyl groups at the phenyl ring except the *para* position of the disulfide bond (Scheme 1-21). The PAS, derived from bis(3,5-dimethylphenyl) disulfide, showed a higher glass transition temperature of $T_g = 185$ °C than that of PPS (85 °C),⁵² with the capability of wet processing by virtue of the enhanced solubility in common organic solvents. The PAS was completely

compatible with polystyrene (PS) showing continuous changes in T_g according to the PAS/PS composition, which was characteristic to the miscible polymeric blends.⁵³



Scheme 1-21. PAS synthesis via oxidative polymerization.

Besides the synthesis of PPS and PAS from disulfides, our group also reported a similar but different type of polymerization utilizing methyl phenyl sulfoxide (PhS(O)Me) as the monomer under TfOH-acidified conditions, giving poly(methylsulfonio-1,4-phenylene triflate) (Scheme 1-22).⁵⁴ A relevant mechanism of the polymerization that proceeded via the aromatic electrophilic substitution of the hydroxyl methyl phenyl sulfonium ion has been proposed.



Scheme 1-22. Polymerization of methyl phenyl sulfoxide via the sulfonium ion

Availability of the sulfonium electrophile derived from the sulfoxide has been demonstrated by the successful synthesis of heteropolyacenes. Intramolecular condensation of 2-methylsulfinylphenyl phenyl ether followed by the treatment with pyridine produced phenoxathiin. Polymer-analogous reaction of poly(arylene oxide)s containing the sulfinyl functionality yielded the corresponding heterocyclic ladder polymer containing the phenoxathiinium-type building blocks via the ring closure and the demethylation.⁵⁵ A heteropolyacene with phenothiazinium repeating units was similarly obtained from the corresponding prepolymer.⁵⁶

The synthetic utility of the sulfonium ions RS^+ and their equivalents as reagents is thus widely spread, especially for those in electrophilic additions and substitutions. The highly selective and robust nature of the sulfonium ions should lead to the further development of organosulfur chemistry, employing them as one of the key reagent.

As the above described, the wide reactivity of the organosulfur reagents permits the use of the radical, anionic, and cationic mechanism, in contrast to those for oxygen-containing molecules which are mainly based on the anionic mechanism. Progress of the chemistry of the C-S bond formation has been depending on the development of new reagents as the sulfur source, as typically represented by the sulfonium electrophile for the synthesis of sulfur-containing polymers. Exploring the chemistry of the organosulfur compounds, in terms of the C-S bond formation, should lead to unraveling the new synthetic route and the material science of sulfur-containing chemicals.

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Chapter 1

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Chapter 2

Selective 1,4-Thiophenylene Chain Formation in Oxidative Polymerization of Diphenyl Disulfide

- 2-1. Introduction
 - 2-2. Oxygen-Oxidative Polymerization at Elevated Temperature and Thermal Curing
 - 2-3. Polymerization Mechanistic Study by Relationship between Reaction Time and Polymer Yield
 - 2-4. Polymerization Mechanistic Study by Computational Calculation
 - 2-5. Experimental Section
 - 2-6. Conclusion
- References

2-1. Introduction

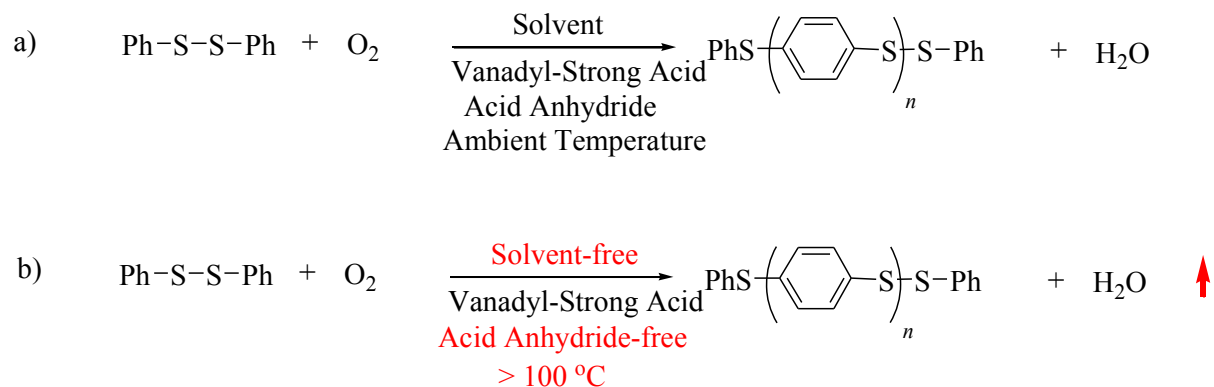
Poly(1,4-phenylene sulfide) (PPS) is categorized as an engineering plastic, because of its excellent mechanical, thermal and electric properties.¹ Commercially, PPS is produced by the polycondensation of *p*-dichlorobenzene and Na₂S eliminating NaCl under relatively severe conditions at a high temperature and pressure, using *N*-methylpyrrolidone as a solvent.² This particular solvent is essential because of the need to dissolve PPS during chain propagation which is inherently insoluble in common organic solvents.

In ca. 20 years ago, Tsuchida and Yamamoto found an alternative route to yield PPS via oxidative polymerization of diphenyl disulfide (PhSSPh) at room temperature (Scheme 2-1a).³⁻⁶ This method attracted much attention at that time, because of the capability of using oxygen or air as the convenient ultimate oxidant, based on the establishment of a vanadyl complex-strong acid catalyst as the electron mediator.⁷ Indeed, the reaction was reminiscent of the copper-catalyzed oxidative polymerization of 2,6-dimethylphenol which was successfully commercialized as the industrial process of polyphenylene ether production.^{8,9} However, the oxidative polymerization for PPS has not so far been adopted as the industrial process, mainly because of the limited molecular weights of ca. 10³ for the product and the low cost performance due to the inherent need to use very pricy dehydrating agent such as trifluoroacetic anhydride to maintain the activity of the sulfonium electrophile.^{10,11}

Recently, a breakthrough for one of these problems has been being anticipated, based on the finding that molten diphenyl disulfide with a melting point of $T_m = 61$ °C undergo polymerization above 100 °C with the evaporation of H₂O as the reduced species of O₂, giving rise to the first anhydride-free process of the oxidative polymerization (Scheme 2-1b). This high-yielding reaction not only suggests the robustness of the catalyst and the propagating sulfonium electrophile at the moderately elevated temperatures, but also the possibility of developing the PPS production through a highly atom-economical process, which have prompted us to study on the mechanism dominating the polymerization.

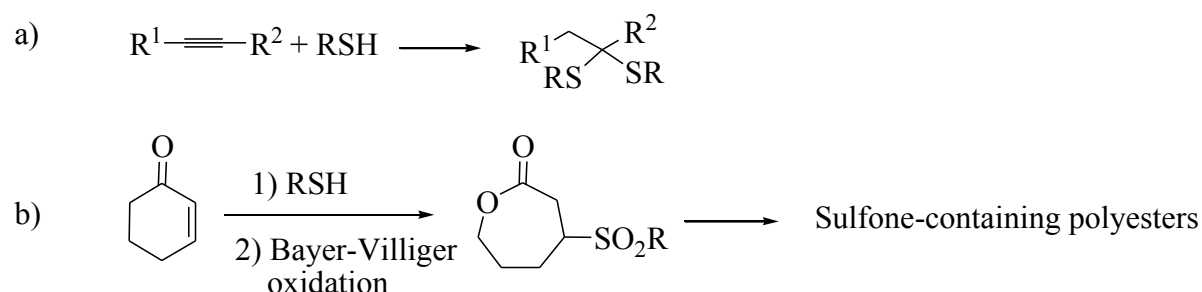
In previous studies, it was reported that the oxidative polymerization of diphenyl disulfide proceeded via the electrophilic aromatic substitution with the oxidized species of the disulfide which was identified to be a bis(phenylthio)phenyl sulfonium (PhS(PhSSPh)⁺) ion.¹⁰ In the present study, it is most likely that the sulfonium electrophile similarly acts as the propagating species, considering that the undesired nucleophilic attack by H₂O should be suppressed by elimination from the reaction mixture through evaporation above 100 °C.

Poly(1,4-phenylene sulfide) (PPS) Synthesis via Oxidative Polymerization of Diphenyl Disulfide: Mechanistic Insight into the Selective Formation of 1,4-Thiophenylene Chain



Scheme 2-1. PPS synthesis via oxidative polymerization of PhSSPh. a): under room temperature. b): above 100 °C.

Chemistry of sulfur-containing molecules in organic synthesis has been focused on thiolates (RS^-) as nucleophiles, as typically represented by bis-hydrothiolation of thiols to alkyne using calcium catalyst¹² (Scheme 2-2a) and thia-Michael addition of RS^- to cyclohexenone followed by lactone formation and ring-opening polymerization to yield sulfone-containing polyesters (Scheme 2-2b).¹³

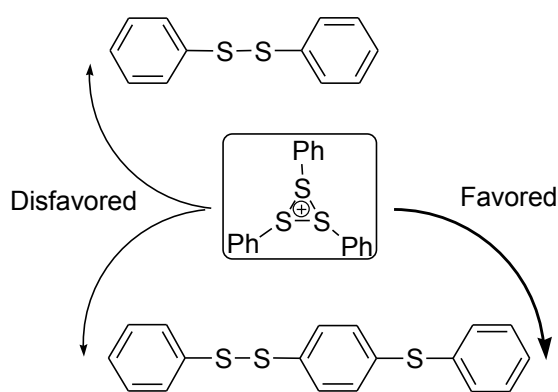


Scheme 2-2. Representative thiolates addition reactions.

Sulfonium electrophiles (RS^+) have been employed under dehydrated conditions, such as the addition of $\text{ArS}(\text{ArSSAr})^+$ electrochemically produced from disulfides to olefin via cationic chain reaction mechanism.¹⁴ Using phenylsulfenophthalimide as the PhS^+ source, enantioselective intramolecular carbosulfonylation has been reported.¹⁵ The sulfonium electrophile was also employed in the synthesis of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene perchlorate) by the condensation of methyl (4-phenylthio)phenyl sulfoxide, which was expanded to many kinds of polysulfonium

synthesis including those for heteropolyacenes.¹⁶ These kinds of reactions mediated sulfonium electrophiles are summarized in Chapter 1.

A remarkable aspect of the oxidative polymerization of PhSSPh under the molten conditions is the selectivity of the aromatic substitution expected for the $\text{PhS}(\text{PhSSPh})^+$ electrophile, which leads to the formation of a linear thio-1,4-phenylene chain with a disulfide bond at one of the chain end as evidenced by spectroscopic methods, thermal curing properties,¹⁷ and unique behaviors of polycondensation (vide infra). The selectivity, as illustrated in Scheme 2-3, is summarized as a chain propagation that mainly occurs at the phenyl ring of the thioether end rather than the disulfide end.



Scheme 2-3. Selectivity of the sulfonium electrophile during the oxidative polymerization of PhSSPh.

2-2. Oxygen-Oxidative Polymerization at Elevated Temperature and Thermal Curing

The oxidative polymerization was typically carried out as follows. A mixture of PhSSPh (**1**) (20.0 g, 92 mmol) and a catalytic amount of TfOH (10 mol%, 9.2 mmol) and vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) (5 mol%, 4.6 mmol) kept at 100 °C was stirred under 1 atm O_2 for 80 h. The mixture was cooled to room temperature and a portion of the cooled mixture (3.2 g) was then poured into 50 ml of CH_2Cl_2 . The precipitate was washed with methanol and H_2O and dried in vacuo to give the product in 60% yield. The linearity of the product was suggested by the presence of C-H out-of-plane vibration for adjacent two hydrogens found at 820 cm^{-1} in the IR spectrum and the absence of those for isolated hydrogens at tri- or tetra-substituted phenylenes that typically appear at 840 and 880 cm^{-1} (Figure 2-1).³

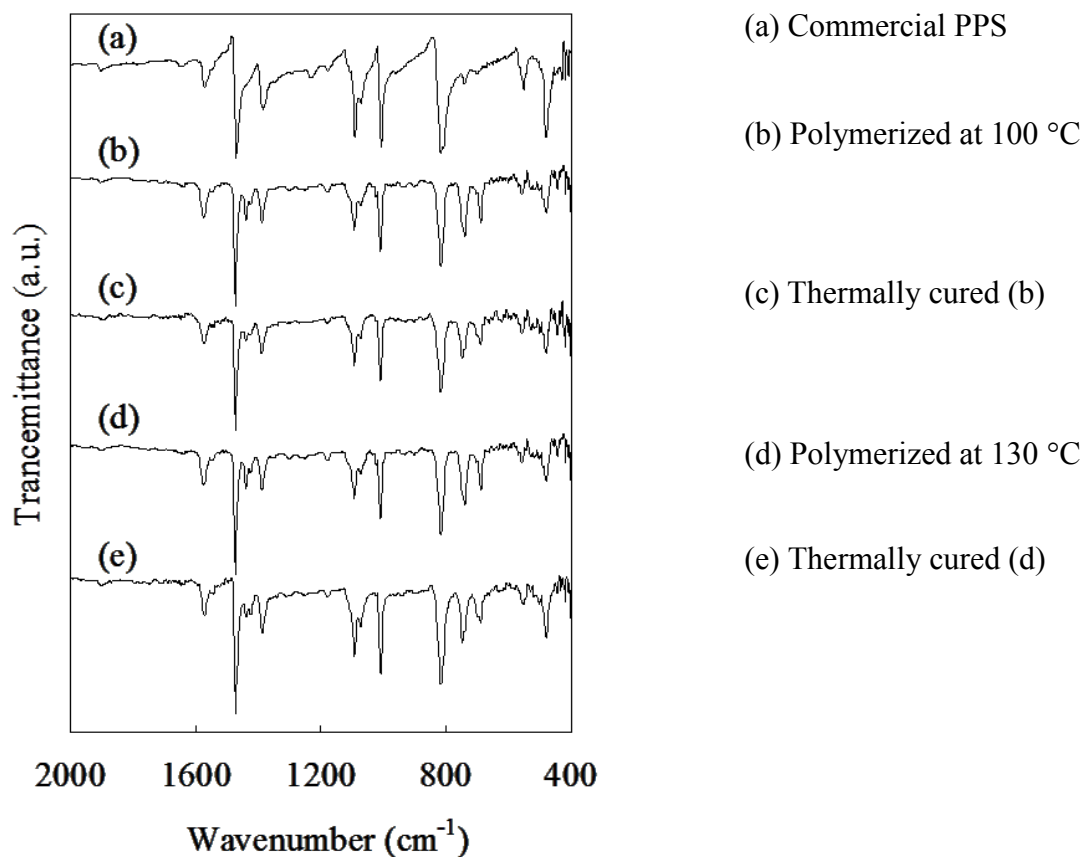
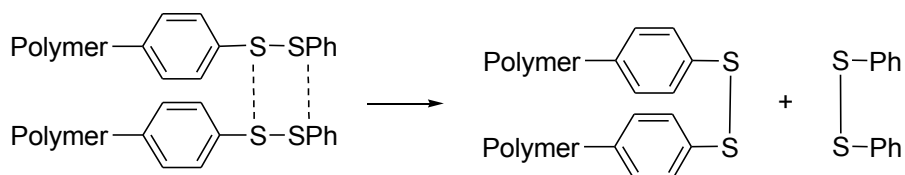


Figure 2-1. IR spectra for the polymer samples.

High-temperature GPC analysis of the product before and after the thermal curing¹⁷ which was performed at 270 °C for 40 h in *m*-terphenyl revealed that the molecular weight doubled by the curing with the elimination of **1** as a result of the rearrangement of the disulfide bond (Scheme 2-4 and Table 2-1). The lack of absorption at 840 and 880 cm^{-1} for the cured polymer gave an evidence for the selective coupling between the polymeric thiophenoxyl radical.



Scheme 2-4. Curing of PPS bearing a disulfide bond at the terminal position.

Table 2-1. Thermal curing of PPS obtained by oxidative polymerization

Polymerization		Curing		M_n^a	M_w^a
Temperature / °C	Time / h	Temperature / °C	Time / h		
100	60	None		1000	1500
		270	40	1800	4500
130	10	None		1300	2300
		270	40	1700	3700

^aDetermined by high temperature GPC at 210 °C with α -chloronaphthalene as an eluent and polystyrene as an external standard.

The curing under a reduced pressure at 310 °C for 1 h without solvent converted the initial polymer (reprecipitated from NMP, 34 mg, $M_n = 980$) into the cured product (31 mg, $M_n = 1600$) with the vaporization of eliminated **1** which was determined by GC-MS analysis. The weight loss of 3 mg was reasonably ascribed to the evaporated **1** (14 μ mol), considering the mean molar mass of the cured product (ca. 19 μ mol). These unique curing behaviors demonstrated the presence of the disulfide bond placed at the end of the chain.

2-3. Polymerization Mechanistic Study by Relationship between Reaction Time and polymer yield

Despite the polycondensation reaction eliminating H_2O ,¹⁸ the chain propagation behavior during the polymerization of **1** under the molten bulk conditions at 160 °C with the $VO(acac)_2-C_2HF_4SO_3H$ catalyst significantly deviated from that of the step-growth mechanism.¹¹ Indeed, such deviation has been found for oxidative polymerization of phenols such as 2,6-dimethylphenol yielding the “reactive intermediate”.¹⁹ In the present case, the molecular weight and the polymer yield seemed to increase linearly with the reaction time (Table 2-2, Figure 2-2), suggesting that the addition of the monomeric sulfonium electrophile to the chain end dominated the reaction, rather than the coupling of the oligomers although they also possessed the disulfide functionality at the chain end. The selective electrophilic substitution as shown in Scheme 2-1 is regarded as a unique chain growth-type polycondensation which is suggestive of the “living-like” behavior. Saturation of yield and molecular weight after 15–20 h most likely suggested the establishment of an equilibrium for polymerization and depolymerization. It may be added that such a behavior was also found for $VO(TPP)$ instead of $VO(acac)_2$ as the catalyst (Table 2-3, Figure 2-3). The “living-like”

character indicated a further increase in molecular weight by reducing the catalyst/monomer ratio, which will be reported elsewhere.

Table 2-2. Oxidative Polymerization of PhSSPh at 160 °C under oxygen^a

Time / h	Yield / %	$T_m / ^\circ\text{C}^b$	M_n^c	M_w^c
8	48	140	720	1140
10	61	140	790	1330
15	82	197	1250	2670
25	80	207	1790	4860
50	73	200	1680	4320

^a[VO(acac)₂]/[CHF₂CF₂SO₃H]/[Monomer] = 0.05/0.05/1. ^bDetermined by DSC.

^cMeasured by high temperature GPC

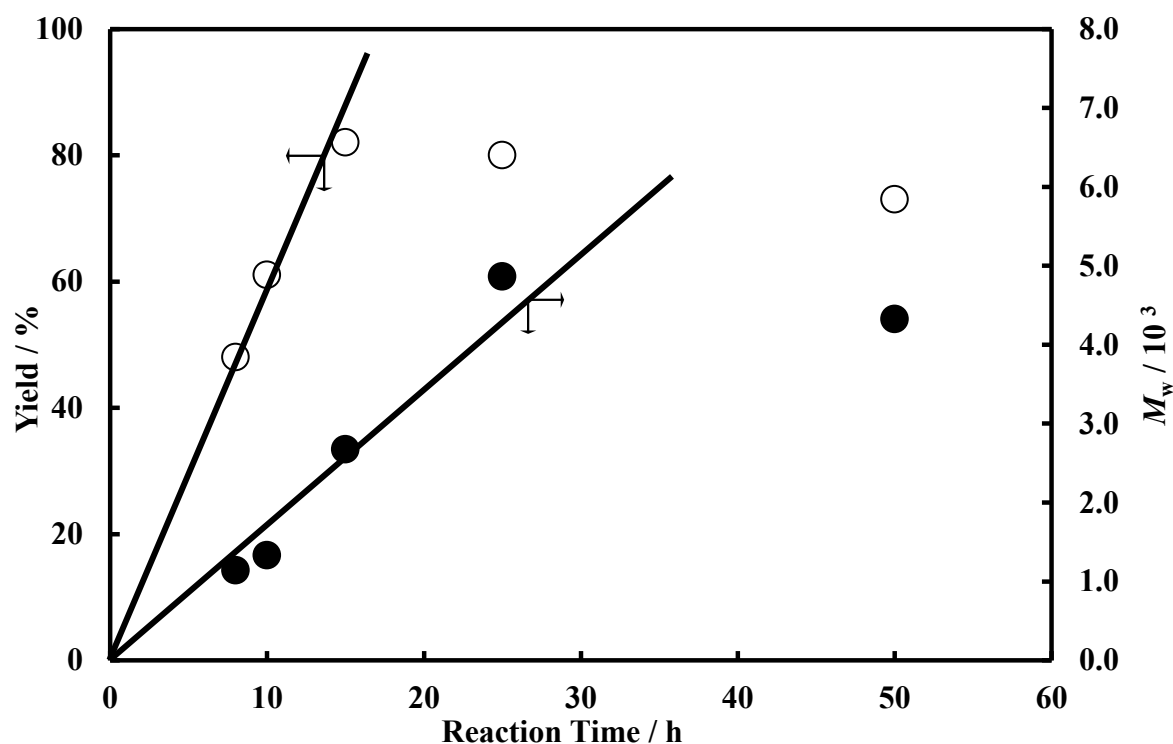


Figure 2-2. Linear relationship between reaction time vs. polymer yield (○) and weight-averaged molecular weight (M_w) (●) found for the early stage of the polymerization.

Table 2-3. Oxidative Polymerization of PhSSPh at 160 °C under oxygen^a

Time / h	Yield / %	$T_m / ^\circ\text{C}^b$	M_n^c	M_w^c
15	15		1000	1300
25	32		1100	1600
35	73	193	1500	2100
50	82	200	1500	2400

^a[VO(TTP)]/[Monomer] = 0.01, [CHF₂CF₂SO₃H]/[Monomer] = 0.01. ^bDetermined by DSC. ^cMeasured by high temperature GPC.

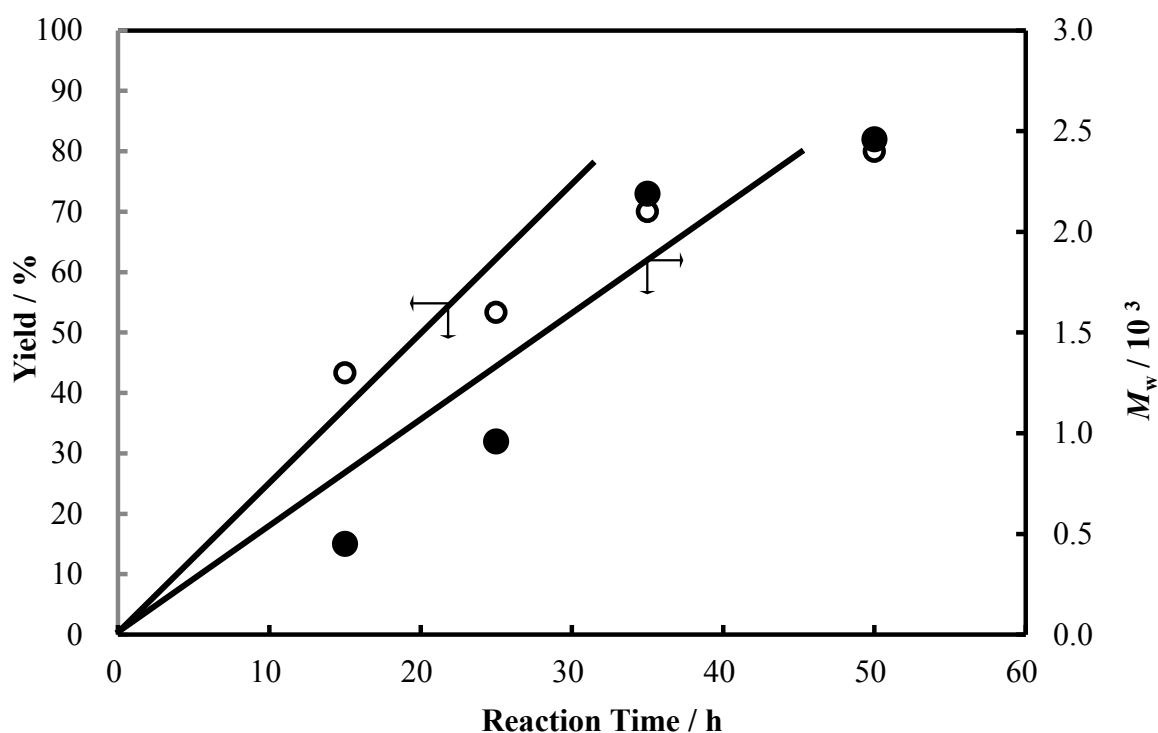


Figure 2-3. Relationship between reaction time & polymer yield and M_w ; polymer yield (○), M_w (●).

2-4. Polymerization Mechanistic Study by Computational Calculation

An account for the characteristic selectivity of the sulfonium electrophile is given by HOMO-LUMO levels and their distribution estimated by a computational method.²⁰ Oxidative polymerization proceeds by the Friedel-Crafts (FC) electrophilic substitution between the $\text{PhS}(\text{PhSSPh})^+$ ion and **1** or its polymerized product, $\text{PhS}(\text{C}_6\text{H}_4\text{S})_n\text{SPh}$. The key molecular orbitals are the LUMO of the sulfonium cation and the HOMO of **1** or

$\text{PhS}(\text{C}_6\text{H}_4\text{S})_n\text{SPh}$. The HOMO of **1** and the model oligomer $\text{PhS}(\text{C}_6\text{H}_4\text{S})\text{SPh}$ (**2**) are shown in Figure 2-4. The oligomer **2** has a higher HOMO level than **1**, which supported the selective FC reaction to the oligomer rather than to the monomer. Actually, the oligomer **2** has many positions to accept the FC reaction, but there is no distribution of HOMO on the benzene ring of the disulfide end. This character most likely gave rise to the selective substitution at the terminal phenyl ring of the thioether end rather than that at the disulfide end, resulting in the presence of the disulfide bond at one of the chain end.

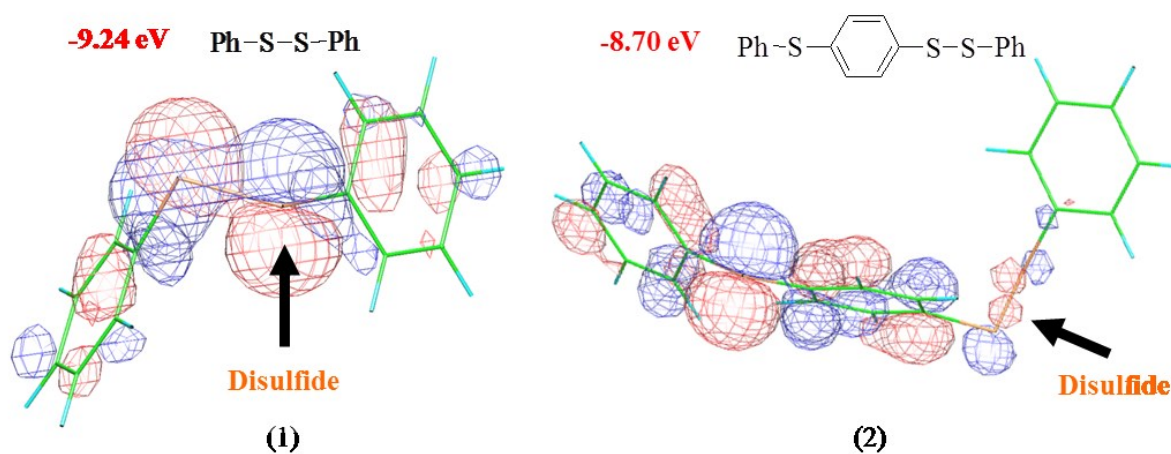


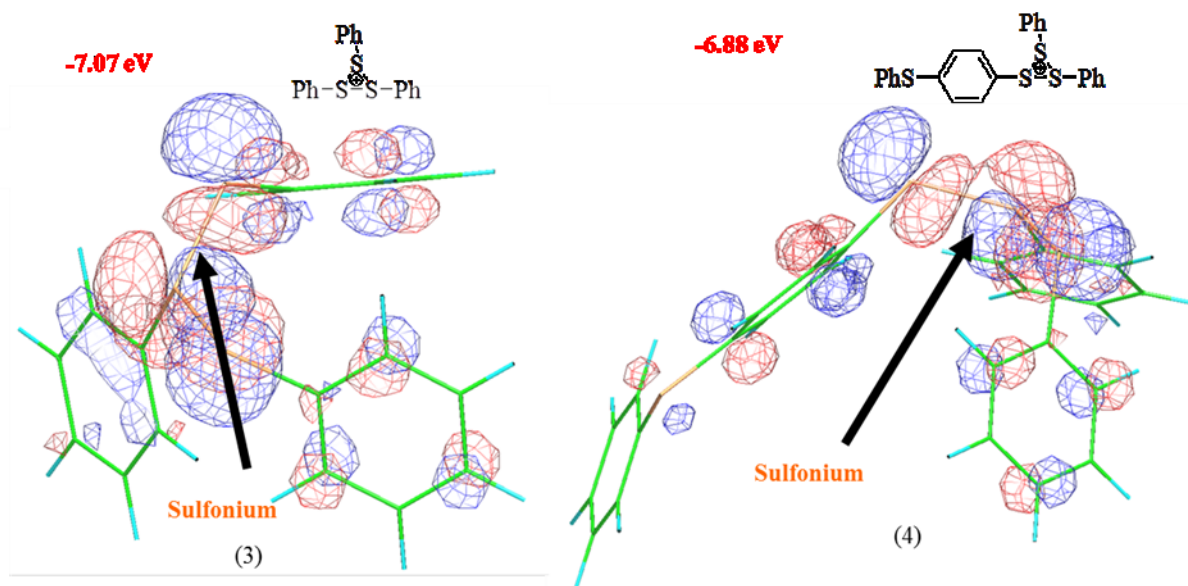
Figure 2-4. HOMO levels and shapes of PhSSPh (**1**) and the oligomer model (**2**).

As for the position selectivity, Tsuchida and Yamamoto previously reported the *para* selectivity using thioanisole as a model compound based on AM1 calculation.²⁰ Similarly, we calculated the populations of *ortho*, *meta* and *para* positions in HOMO of **1** and **2** by using PM3 Hamiltonian (Table 2-4). The *para* position of both compounds showed the highest distribution among the three positions. Added support for the position selectivity is found in previous reports of Tsuchida showing no example of the substitution at the *ortho* position for several kinds of sulfonium electrophiles,²¹ which has been attributed to the steric effect of the bulky sulfonium cation that should favor the *para* position over the *ortho* position.

Table 2-4. Population of HOMO on the *o*-, *m*- and *p*-positions of the phenyl group in **1** and the thiophenyl group in **2**

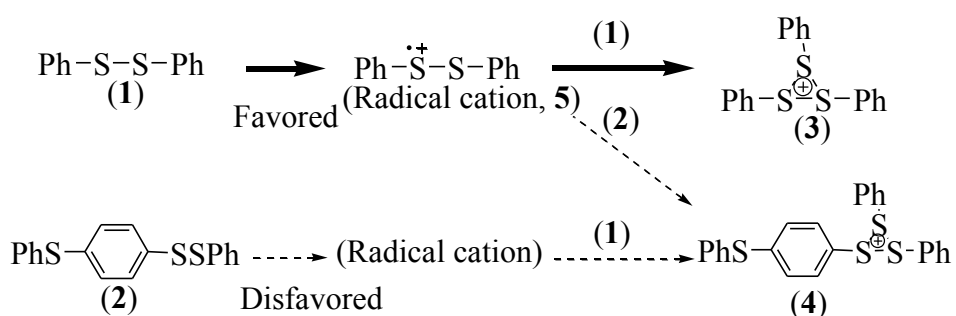
Compound	<i>ortho</i>	<i>meta</i>	<i>para</i>
PhSSPh (1)	0.039	0.019	0.092
PhS(C₆H₄S)SPH (2)	0.031	0.005	0.038

Figure 2-5 shows the LUMO level and shape of the PhS(PhSSPh)⁺ cation (**3**) and the oligomeric sulfonium ion, PhS(C₆H₄S)(PhSSPh)⁺ (**4**). Both LUMO apparently localized on the sulfonium cation, so one could state that the reactivity of the electrophiles are dominated by their energy levels. As the LUMO accepts the HOMO attack, the LUMO in lower levels shows higher reactivity. The monomeric ion **3** possessed a lower LUMO level than the oligomeric ion **4**, showing the inert character of the oligomeric electrophile compared with **3**. These results suggest that the “chain growth-type” reaction proceeds in the oxidative polymerization of **1** via the selective reaction of **3** and the oligomers such as **2**.

**Figure 2-5.** LUMO levels and shapes of PhS(PhSSPh)⁺ (**3**) and the oligomeric sulfonium ion **4**.

An account for the origin of the selectivity and the process of polymerization is given as follows. The oxidative polymerization is initiated with the oxidation of **1** by the vanadyl catalyst.^{20c)} The oxidized product, a radical cation **5** and **1** produce the electrophile **3**. The inert sulfonium ion **4**, produced by the oxidation of the oligomer **2** followed by the similar

process, and possibly by the addition of **5** to the oligomer (Scheme 2-3), is less dominative. It may be added that the oxidation of the oligomer **2** could be disfavored over that of the monomer **1** because of the very small distribution of HOMO around the disulfide bond, although the electron-donating character of the additional thiophenyl group reduces the ionization energy. The HOMO-1 of the oligomer **2** distributed around the disulfide bond, but its energy level (-9.32 eV) was lower than that of **1**. These results were also indicative of the polymerization mechanism in which the oxidation of the monomer **1** prevails to yield **3** that attacks the thioether end of the oligomer while the disulfide end remains unreacted. Formation of sulfonium cation was estimated as followed (Scheme 2-5).



Scheme 2-5. Estimated mechanism of the selective substitution with the sulfonium electrophiles.

2-5. Experimental Section

The oxygen-oxidative polymerization of **1** proceeds via the chain growth-type polycondensation mechanism in which the monomer adds to the polymer at the *para* position of the phenyl ring of the thioether end, remaining the disulfide functional group at the other end of the chain. The unique mechanism should allow various types of thiophenylene functionalization, which are the topic of our continuous research. Diphenyl disulfide (PhSSPh), oxovanadium(IV) acetylacetonate (VO(acac)₂), triflic acid (TfOH), tetrafluoroethanesulfonic acid (CHF₂CF₂SO₃H), *m*-terphenyl, *m*-Dichlorobenzene and *N*-methylpyrrolidone (NMP) were purchased from TCI and used as received. Infrared spectra were obtained using a Jasco FT-IR 410 spectrometer with sodium chloride plates. Melting points (*T_m*) were recorded using DSC (Seiko Instruments Inc. Differential Scanning Calorimeter DSC-220), scanned 20 to 310 °C (rate 20 °C/min) with alpha-alumina as reference. Molecular weight measurements were done by gel permeation chromatography

using an AGILENT PL-220 1-chloronaphthalene as the eluent. Calibration was done with polystyrene standards. MO calculation was done on Dell computer (Inspiron 1720) by using the PM3 method of Fujitsu MO Compact.

Oxygen-oxidative polymerization

To a 100-ml three neck flask, PhSSPh (20.0 g), VO(acac)₂ (5 mol%) and TfOH (10 mol%) were introduced. The mixture was heated and stirred mechanically (100 rpm) at 100 °C for 60 h under oxygen flow. The resultant mixture was cooled to room temperature and 3.1787 g of the cooled mixture was dispersed in 50 ml of CH₂Cl₂. To mixture of MeOH and *c*-HCl (95:5 in v/v, total 300 ml), the CH₂Cl₂ dispersion was added. The precipitate was collected and washed with MeOH, H₂O and MeOH again thoroughly. The solid was dried in vacuo. The yield was 60%. Molecular weights for the obtained PPS, measured with a high temperature GPC apparatus, together with the analytical data, are shown in Figure 2-1 and Table 2-2 (sample (b) in Figure 2-1).

DDQ-oxidative polymerization

To a 100-ml three neck flask, PhSSPh (3.27 g, 15 mmol), DDQ (15 mmol) and CHF₂CF₂SO₃H (10 mol%) were introduced. The mixture was heated and stirred mechanically (100 rpm) at 130 °C for 10 h under air. The resultant mixture was cooled to room temperature and dispersed in 50 ml of CH₂Cl₂. To a mixture of MeOH and *c*-HCl (95:5 in v/v, total 300 ml), the CH₂Cl₂ dispersion was added. The precipitate was collected and washed with MeOH, KOH aq (0.05 M), H₂O and MeOH again thoroughly. The solid was dried in vacuo. The yield was 90%. The PPS was characterized using the high temperature GPC. IR spectrum is shown in Figure 2-1 (sample (d)).

Thermal curing in terphenyl

To a 10-ml test tube, 0.500 g of PPS and 2.50 g of *m*-terphenyl were introduced. The mixture was heated at 160 °C for 30 min for dissolving with small volume of nitrogen bubbling. Then the heated mixture was kept at 270 °C for 40 h with nitrogen bubbling. The resultant mixture was dispersed in 25 ml CH₂Cl₂. The CH₂Cl₂ dispersion was poured into a mixture of 150 ml of MeOH and *c*-HCl (95:5 in v/v). The precipitate was washed with MeOH, H₂O and MeOH thoroughly. The molecular weights for the purified PPS were measured with a high temperature GPC. IR spectrum is shown in Figure 2-1 (samples (c) and (e)). All of the product exhibited benzene C-H out-of-plane vibration at 820 cm⁻¹, while no

peak at 840 and 880 cm^{-1} attributed to the tri- and tetra substituted benzene C-H vibrations was observed.

Bulk thermal curing (Solution polymerization)

To a 500-ml three neck flask, PhSSPh (24.9 g), VO(acac)₂ (0.5 mol%), TfOH (0.5 mol%) and *m*-Dichlorobenzene (142 g) were introduced. The mixture was heated and stirred mechanically (300 rpm) at 194 °C for 4 h under air flow (140 ml/min). The resultant mixture was cooled to room temperature. To mixture of MeOH and *c*-HCl (95:5 in v/v, total 1000 ml), the dichlorobenzene slurry was added. The precipitate was collected and washed with MeOH (200 ml, 3 times). The washed PPS (3 g) was added to 50 ml of NMP and the mixture was heated to 170 °C for 4 h. After confirming turning to a clear solution, the NMP solution was slowly cooled to room temperature. The precipitate was collected, washed with MeOH (50 ml, 3 times) and dried in vacuo.

(Bulk curing)

The purified PPS (33.6 mg, M_n 980) was introduced to Kugelrohr and heated 310 °C for 1 h, with cold trap at 1 kPa. The thermally cured PPS (30.7 mg, M_n 1600) and a small amount of volatile were obtained. The volatile was determined as PhSSPh by GC and GCMS analyses.

Oxidative polymerization at 160 °C (Figure 2-2 and Table 2-2)

To a 100-ml three neck flask, PhSSPh (20.0 g), VO(acac)₂ (5 mol%) and CHF₂CF₂SO₃H (5 mol%) were introduced. The mixture was heated and stirred mechanically at 160 °C under oxygen atmosphere. At 8, 10, 15, 25 and 50 h after the reaction was initiated, around 1 g of a mixture was taken out of the flask. The mixture was dispersed in 50 ml of CH₂Cl₂. To a mixture of MeOH and *c*-HCl (95:5 in v/v, total 300 ml), the CH₂Cl₂ dispersion was added. The precipitate was collected and washed with MeOH, H₂O and MeOH again thoroughly. The purified PPS was characterized by measuring the molecular weights and T_m .

Oxidative polymerization at 160 °C (Figure 2-3 and Table 2-3)

To a 100-ml three neck flask, PhSSPh (20.0 g), VO(TPP) (5 mol%) and CHF₂CF₂SO₃H (5 mol%) were introduced. The mixture was heated and stirred mechanically at 160 °C under an oxygen atmosphere. At 8, 10, 15, 25 and 50 h after the reaction was initiated, around 1g of the reaction mixtures were taken out of the flask. The each reaction mixture was dispersed in 50 ml of CH₂Cl₂. To a mixture of MeOH and *c*-HCl (95:5 in v/v, total 300 ml), the CH₂Cl₂

dispersion was added. The precipitate was collected and washed with MeOH, H₂O and MeOH again thoroughly. The purified PPS was characterized by measuring the molecular weights and T_m .

2-6. Chapter Conclusion

The oxygen-oxidative polymerization of **1** proceeds via the chain growth-type polycondensation mechanism in which the monomer adds to the polymer at the *para* position of the phenyl ring of the thioether end, remaining the disulfide functional group at the other end of the chain. The unique mechanism should allow various types of thiophenylene functionalization, which are the topic of our continuous research.

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Chapter 3

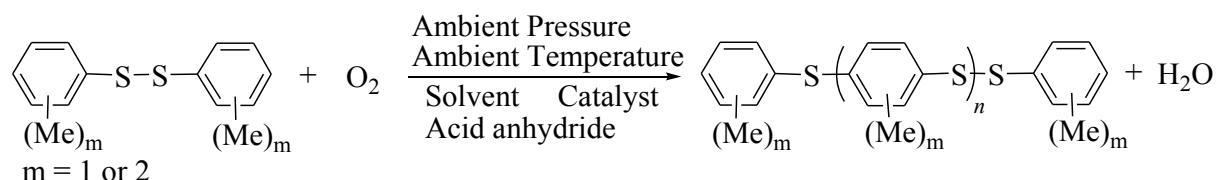
Vanadyl-Triphenylmethylium Borate Catalyzed Oxidative Polymerization of Diphenyl Disulfide

- 3-1. Introduction
- 3-2. Optimization of Catalyst Combination
- 3-3. Optimization of Polymerization Conditions for High Molecular-Weight PPS
- 3-4. Experimental Section
- 3-5. Conclusion

References

3-1. Introduction

Poly(1,4-phenylene sulfide) (PPS) is one of engineering plastics, having excellent mechanical, thermal and electrical properties.¹ Commercially available PPS is produced by the solution polycondensation of *para*-dichlorobenzene and Na₂S under high temperatures and pressure in *N*-methylpyrrolidone eliminating NaCl (Phillips method).² In ca. 20 years ago, Tsuchida and Yamamoto reported oxygen-oxidative polymerization of diaryl disulfides (ArSSAr) for poly(arylene sulfide) (PAS) preparation under ambient temperatures and pressure without forming salt.³ This method was quite attractive because oxygen or air could be used as the oxidative agent (Scheme 3-1).⁴

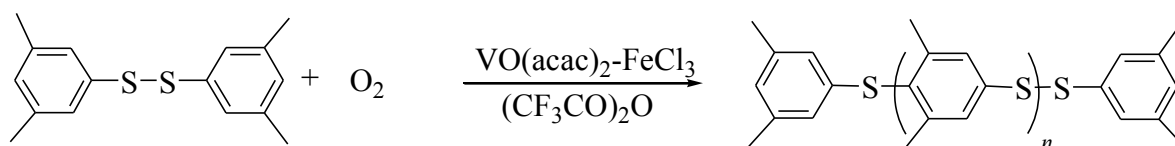


Scheme 3-1. Oxidative polymerization of ArSSAr.

However, this method required expensive dehydrating agent, such as acid anhydride, to keep the activity of the vanadyl catalyst and the sulfonium electrophile by removing water that was formed during the polymerization as a by-product. Recently, we developed a new method without using dehydrating agent by setting molten diphenyl disulfide, especially above 100 °C to evaporate water.⁵

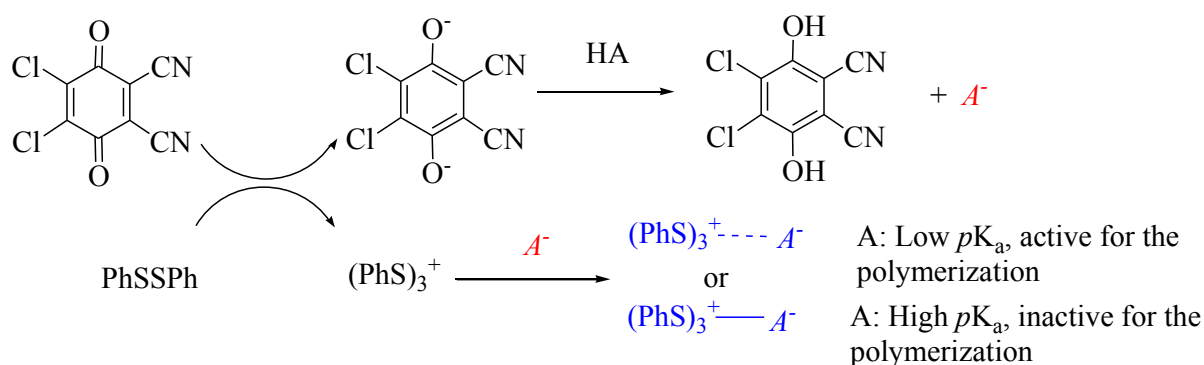
For the oxidative polymerization, a strong acid (e.g. trifluoromethanesulfonic acid (TfOH)) has been required to activate the vanadyl (e.g. VO(acac)₂, where acac⁻ is the acetylacetonato ligand) catalyst. However, the use of the strong acid is undesired in commercial production, because of the need to employ quite expensive glass-lined materials or any other anti-caustic material to suppress corrosion by the strong acid. Regarding a strong acid-free polymerization of diaryl disulfide, we reported vanadyl-Lewis acid (e.g. FeCl₃) catalytic system.⁶ However, to reach a high yield, around 20 mol% of FeCl₃ and 2 equivalent of dehydrating agent were required under the reported conditions (Scheme 3-2).⁶ Without the dehydrating agent, the polymer was given only in a low yield. Using the FeCl₃-AlCl₃ system under an argon atmosphere, a similar results of the polymerization of diphenyl disulfide was reported,⁷ but the FeCl₃-AlCl₃ system rather acted as a chemical oxidizing agent without the catalytic activity and the obtained polymer had a large amount of Al, Fe and chlorine even

after washing. Until now, there has been no effective method for vanadyl catalyzed oxygen-oxidative polymerization of diphenyl disulfide without using the strong acids.



Scheme 3-2. Strong acid-free oxidative polymerization of ArSSAr.

Oxidative polymerization of diaryl disulfide is also possible by various oxidants, without using the vanadyl catalyst. Representatively 2,3-dichloro-5,6-dicyano-*para*-benzoquinone (DDQ), 2,3,5,6-tetrachloro-*para*-benzoquinone (chloranil), and 2,3,5,6-tetrabromo-*para*-benzoquinone (bromanil) are the effective oxidants. This method does not require oxygen or air, but a stoichiometric amount of the oxidant is needed. Even in this case, the strong acid is essential to activate the oxidant.^{6,8} For example, TfOH ($pK_a = -5.5$), CF_3COOH (0.3), and CCl_3COOH (0.8) with DDQ gave the polymer, but a weak acid such as acetic acid ($AcOH$) (4.8) was not effective (Scheme 3-3).⁸

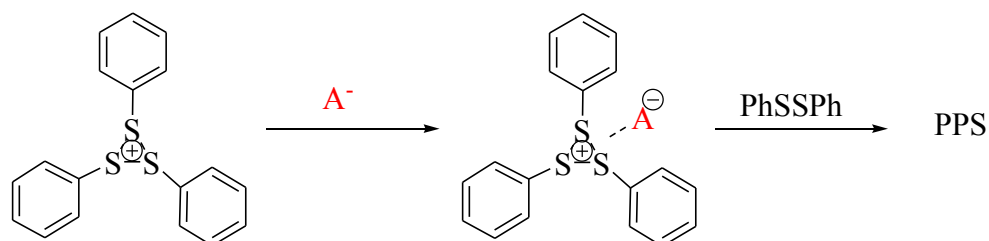


Scheme 3-3. Polymerization of PhSSPh by DDQ-the acid oxidation.

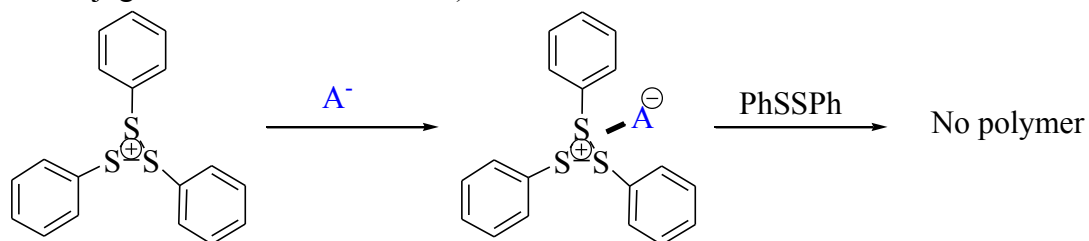
We suppose that the strong acid contributes to the stabilization of the bis(phenylthio)phenyl sulfonium cation as the active species of the polymerization which should decompose by nucleophilic attack under less acidic conditions.⁹ DDQ is reduced to a dianion form of 2,3-dichloro-5,6-dicyano-*para*-hydroquinone (DDH), and finally to DDH by the protonation with the acid. If acid were used just as a proton source, weak acid should also be applied with DDQ. However the combination of DDQ and the weak acid does not proceed the polymerization, so that the strong acid is considered to have roles not only as the proton source. The quinones have the more positive reduction potential for $Q + 2H^+ + 2e^- \rightarrow QH_2$

and thus the more enhanced oxidizing ability under the stronger acidic conditions, which should be the principal reason that strong acid is essential for the polymerization. The conjugate base of the weak acid has strong nucleophilicity and may form chemical bond or interact with the key intermediate, the sulfonium cation. Then the sulfonium cation should be decomposed or deactivated as the electrophile. On the contrary, the conjugate base of the strong acid has very low nucleophilicity and seems to stabilize the sulfonium cation as the counter ion, which is the second reason that strong acid is essential (Scheme 3-4). We anticipated that the strong acid when employed with the quinones in the polymerization of the disulfides had the roles of both protonation and stabilization of the sulfonium cation because of the low nucleophilicity.

a) (A^- : Conjugated base of **a strong acid**)



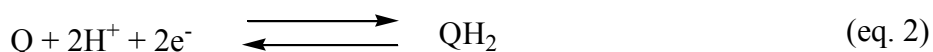
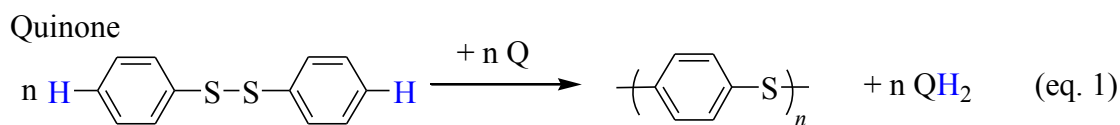
b) (A^- : Conjugated base of **a weak acid**)



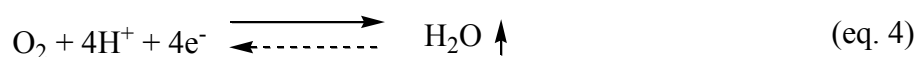
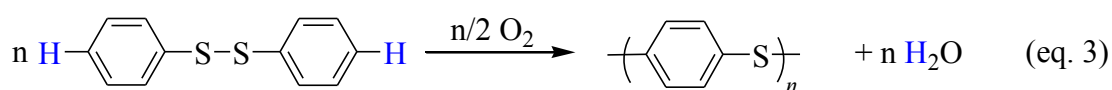
Scheme 3-4. Stabilization of sulfonium cation by conjugated bases of acids.

In case of using oxygen as an oxidant, strong acid is also essential, according to the redox equation (eq. 4 in Scheme 3-5). Although the redox reaction of oxygen is inherently reversible, water is removed by evaporation under moderately elevated temperatures, especially above 100 °C, so that protons are eliminated from the reaction mixture as they are generated via Friedel-Crafts reaction during the polymerization according to $A^+ + H-Ar \rightarrow A-Ar + H^+$. This reaction stoichiometry suggested that only a catalytic amount of proton should be needed under the moderately elevated temperature conditions. As Lewis acids can activate the vanadyl complex (vide infra), we anticipated that the strong acid-free oxygen-oxidative

polymerization of disulfides should be achieved by choosing suitable counter ions of the sulfonium electrophile.



Oxygen: An incentive of this work



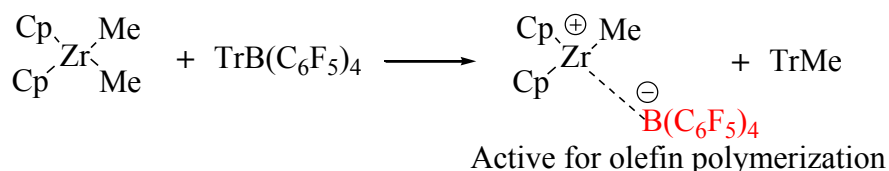
Scheme 3-5. Oxidative Polymerization of PhSSPh with Quinone or Oxygen.

In the case of using the vanadyl-complex-strong-protic-acid catalytic system, we estimate a polymerization mechanism as follows. The vanadyl (V=O) compound and the strong protic acid form a binuclear μ -oxo vanadium complex (V-O-V), via forming a vanadyl dimer (V-O-V=O) and eliminating H₂O.^{3c} The V-O-V complex oxidizes the PhSSPh monomer to undergo the oxidative polymerization. The reduced V-O-V complex is re-oxidized with oxygen to regenerate the V-O-V=O complex to accomplish the catalytic cycle. For the vanadyl to act as the catalyst, the activation with the strong acid is essential to form the catalytically active V-O-V complex from two molecules of the V=O unit (see Scheme 1-17).

We reported one of the representative form of the V-O-V complex, [V(salen)-O-V(salen)][BF₄]₂, which was formed by the reaction between [VO(salen)] and TrBF₄. The dinuclear complex was isolated and identified by elemental analysis and fast atom bombardment mass spectroscopy (FABMS).^{3c} The μ -oxo bridged structure was revealed by crystallography, employing a single crystal of the dinuclear complex obtained as a triiodide salt.^{3h,10} This indicates that the Tr⁺ cation has an ability to form the activated vanadyl species, V-O-V, from two molecules of V=O eliminating TrOTr.

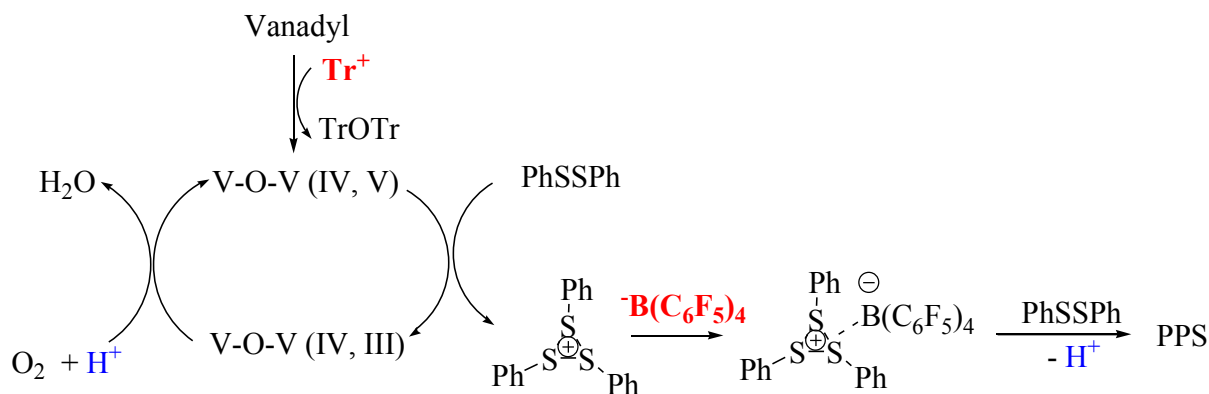
Regarding the stabilization of the cationic species, a less nucleophilic or non-coordinating anion is considered to be effective. For example, bis(cyclopentadienyl)dimethylzirconium (Cp₂ZrMe₂) is a typical olefin polymerization catalyst and activated with TrB(C₆F₅)₄ to form a zwitterionic active species Cp₂ZrMe⁺-B(C₆F₅)₄⁻, with eliminating TrMe (Scheme 3-6).¹¹ The anion, B(C₆F₅)₄⁻ has a very big ionic diameter and exists near the active cationic species,

Cp_2ZrMe^+ , without forming a chemical bond. Then, Cp_2ZrMe^+ can be stabilized by $\text{B}(\text{C}_6\text{F}_5)_4^-$ and exists almost as a naked cation which is considered to be highly active for the olefin polymerization. Similarly, it is anticipated that if this kind of non-coordinating anion stabilizes the sulfonium cation, oxidative polymerization should proceed via the activation of the vanadyl catalyst.



Scheme 3-6. Stabilization of the cationic Cp_2ZrMe^+ by the non-coordinating anionic $\text{B}(\text{C}_6\text{F}_5)_4^-$.

Actually, there is no report of using $\text{B}(\text{C}_6\text{F}_5)_4^-$ or any other non-coordinating anion for the oxidative polymerization of the disulfide, but there are a few reports on the stabilization of an electrogenerated sulfonium cation, $\text{ArS}(\text{ArSSAr})^+$, with a botate anion.¹² According to the report, ArSSAr and 1-phenyl-1-propene gave 1,2-diarylthioxy-1-phenylpropane in a high yield, when $\text{Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4$ was used as a supporting electrolyte. On the contrary, Bu_4NBF_4 showed a low reactivity, probably because of the high nucleophilicity of BF_4^- to interact with the sulfonium cation. The report^{12a} noted that “The use of BF_4^- somewhat stabilizes A and B.” Here, both A and B are cationic compounds containing sulfur. The stabilization seems to represent the formation of a chemical bond with the sulfonium cation, and the reactivity is lost by the stabilization. They noted nothing about the particular case of the oxidative polymerization. We previously examined the similar effects of anions using Bu_4NClO_4 , Bu_4NBF_4 and Bu_4NPF_6 as the supporting electrolytes of an electro-oxidative polymerization, but the polymer yields remained low.⁹ It could be reasoned that these kind of anions, ClO_4^- , BF_4^- and PF_6^- , should form chemical bonds or interact with the sulfonium cation because of their moderate nucleophilicity. As $\text{B}(\text{C}_6\text{F}_5)_4^-$ stabilizes the sulfonium cation and Tr^+ activates the vanadyl complex, $\text{TrB}(\text{C}_6\text{F}_5)_4$ is considered to have an essential characteristics to proceed the catalytic oxidative polymerization of the disulfide. Here we report the first strong protic acid-free oxygen-oxidative polymerization using the vanadyl catalyst with $\text{TrB}(\text{C}_6\text{F}_5)_4$ (Scheme 3-7).



Scheme 3-7. Concept of the strong protic acid-free oxygen oxidative-polymerization with $\text{TrB}(\text{C}_6\text{F}_5)_4$.

3-2. Optimization of Catalyst Combination

Initially, we examined the catalytic activity of $\text{TrB}(\text{C}_6\text{F}_5)_4$ combined with $\text{VO}(\text{acac})_2$. As we expected, we succeeded in the first strong acid-free oxygen-oxidative polymerization of the disulfide (Table 3-1, entry 1). It seems reasonable to suppose that Tr^+ activated $\text{VO}(\text{acac})_2$ forming V-O-V and that $\text{B}(\text{C}_6\text{F}_5)_4^-$ stabilized the sulfonium cation. ^1H NMR analysis of the obtained polymer was impeded by the lack of solubility in any solvents. However, the linearity of the polymer was supported by the presence of IR absorption at 820 cm^{-1} ascribed to the C-H out-of-plane vibration of adjacent (i.e. 1,4-phenylene) protons and the lack of those for isolated (i.e. crosslinked phenylene) protons near 860 cm^{-1} (see Figure 3-2). The newly established acid-free catalytic system worked as well as the conventional $\text{TfOH-VO}(\text{acac})_2$ system and gave PPS in a higher yield and T_m compared with the conventional system (entry 2 and 3). On the other hand, $\text{TrBF}_4\text{-VO}(\text{acac})_2$ gave only oligomers having undetectable T_m (entry 4). The $\text{TrBF}_4\text{-VO}(\text{salen})$ and $\text{TrBF}_4\text{-VO}(\text{TPP})$ combinations gave no polymer (entries 5 and 6). The Tr^+ cation of TrBF_4 seemed to activate $\text{VO}(\text{acac})_2$ based on the specific bathochromatic changes in color from the pale green of $\text{VO}(\text{acac})_2$ to the dark brown of the VOV complex. The tetrafluoroborate ion (BF_4^-) is considered to form a $[\text{V-O-V}](\text{BF}_4)_2$ salt, which is however inactive as the catalyst for the polymerization because of the quenching with BF_4^- of the bis(phenylthio)phenyl sulfonium ion categorized as a soft acid in the hard and soft acids and bases (HSAB) theory.

Contrary to our expectation, a catalytic system of TrBF_4 and $\text{VO}(\text{salen})$ or $\text{VO}(\text{TPP})$ gave PPS at $160\text{ }^\circ\text{C}$ (entries 8 and 9). The BF_4^- ion should be less associative at elevated temperatures where pK_a is lowered according to the van't Hoff's equation and thus less nucleophilic, giving rise to the catalysis of the polymerization. On the other hand, the

VO(acac)₂-TrBF₄ catalyst did not proceed the polymerization, which suggested that the BF₄⁻ ion was still nucleophilic to decompose the active form of VO(acac)₂ (entry 7). The bidentate acetylacetonato ligand is less coordinative than the tetradentate porphyrin and salen ligands. Catalysis by the VO(salen) and VO(TPP) is most likely ascribed to the enhanced stability of their dinuclear derivatives^{3a,c,e,f} in the presence of TrBF₄ (entries 8 and 9).

In a case of using TrB(C₆F₅)₄, both VO(acac)₂ and VO(TPP) gave higher molecular-weight PPS under 160 °C conditions (entries 10 and 11) compared with the product obtained under 100 °C. The enhanced catalytic activity is likely to be ascribed to the more acidic character of TrB(C₆F₅)₄ at higher temperatures.

Table 3-1. Oxidative polymerization of PhSSPh at 100 °C

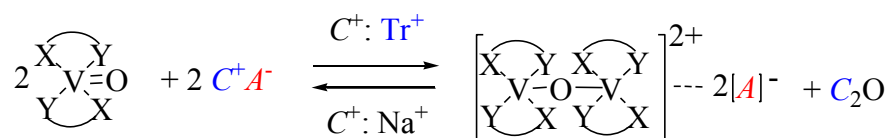
Entry	Vanadyl	Additive(s)	Yield / %	<i>T</i> _m ^{a)} / °C	<i>M</i> _n ^{b)}	<i>M</i> _w ^{b)}
1	VO(acac) ₂	TrB(C ₆ F ₅) ₄	68	160	850	1400
2	VO(acac) ₂	TfOH	44	155		
3 ^{c)}	VO(acac) ₂	TfOH	36	155	1300	1800
4	VO(acac) ₂	TrBF ₄ ^{d)}	17			
5	VO(salen)	TrBF ₄ ^{d)}	0			
6	VO(TPP)	TrBF ₄ ^{d)}	3			
7 ^{e)}	VO(acac) ₂	TrBF ₄ ^{d)}	6			
8 ^{e)}	VO(salen)	TrBF ₄ ^{d)}	69	202	850	1700
9 ^{e)}	VO(TPP) ^{e)}	TrBF ₄ ^{f)}	65	195	1300	1800
10 ^{e)}	VO(TPP) ^{e)}	TrB(C ₆ F ₅) ₄ ^{f)}	64	195	1500	2100
11 ^{e)}	VO(acac) ₂	TrB(C ₆ F ₅) ₄ ^{d)}	76		1100	2700
12	VO(acac) ₂	TfOH-NaOTf ^{g)}	3			
13	VO(acac) ₂	TfOH-NaBPh ₄ ^{h)}	3			
14 ⁱ⁾	VO(acac) ₂	TrB(C ₆ F ₅) ₄	0			

Catalyst: Vanadyl 5 mol% - Additive 5 mol%, Reaction time 20 h, Under oxygen.

^{a)}Determined by DSC. ^{b)}Measured by high temperature GPC. ^{c)}Reaction time 60h, 1 mol% of vanadyl and additive were used. ^{d)}10 mol%. ^{e)}Reaction temperature, 160 °C. ^{f)}1 mol%. ^{g)}TfOH 5 mol%, NaOTf 5 mol%. ^{h)}TfOH 5 mol%, NaBPh₄ 10 mol%. ⁱ⁾Under nitrogen.

Results in entries 12 and 13 demonstrated that the polymerization was inhibited by Na⁺. TfONa was insoluble and NaBPh₄ was soluble in molten PhSSPh, and both compounds

obstructed the polymerization. Under nitrogen, the polymerization did not proceed, resulting in the recovery of the monomer in an almost 100% yield (entry 14). The vanadyl complexes are activated by the oxophilic character of the Lewis acidic cation (C^+) as the activator (Scheme 3-8). In the case of using Tr^+ as the activator, the catalytically active V-O-V complex is easily formed as a result of the strongly oxophilic character and thus the formation of a highly stable Tr_2O . This stabilization is not accomplished with the less oxophilic Na^+ to give Na_2O which could disproportionate with A^- (Scheme 3-8). In addition to this negative effect of Na^+ , BPh_4^- might also react with the sulfonium cation because of its high nucleophilicity. This is reminiscent of the case of $Cp_2ZrMe^+-BF_4^-$ or $Cp_2ZrMe^+-BPh_4^-$ systems for the olefin polymerization, with which the catalysis is not accomplished as a result of the nucleophilic character of these anions (Figure 3-1).



(VO(acac)₂, VO(salen), VO(TPP))

Scheme 3-8. Mechanism of activation of the vanadyl compound with [C^+A^-].

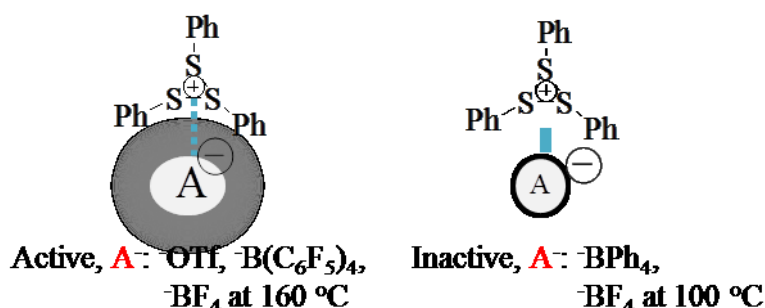


Figure 3-1. Enhanced stability of the sulfonium electrophile with less coordinative counter ions.

3-3. Optimization of Polymerization Conditions for High Molecular-Weight PPS

To obtain a high molecular-weight PPS in a good yield, the effects of the amount of the catalyst and reaction time were examined. A high polymer yield was accomplished with 5 mol% of the VO(acac)₂-TrB(C₆F₅)₄ catalyst, but its molecular weight was quite low (Table 3-2, entry 1). As shown by the results in entry 2, an even smaller amount of VO(TPP) gave a

higher molecular-weight PPS than that in entry 1. A prolonged time of the reaction (40 h, entry 3) resulted in a high molecular weight, as compared with that obtained after 20 h (entry 2). A further reaction up to 60 h did not affect the molecular weight and the yield of the product (entry 3 and 4). Interestingly, in entry 6, a less amount of the catalyst (0.25 mol%) reacted for 70 h gave a higher molecular-weight polymer above 5000 in M_w , which was in agreement with the behavior of the polymerization characterized as the “living-like” polycondensation in our recent report.⁵ The presence of two melting points in the DSC thermogram is reasoned by the possible mechanism for the equilibrium between the polymerization and the depolymerization.⁵ Long duration of the reaction does not always give PPS with a high yield and a high molecular weight. Comparison of the results for entry 3 with that for 4 in Table 2 indicates that the polymerization proceeded to give a high T_m polymer, but the depolymerization concurred to produce the lower M_w byproduct and in lower yield. Unraveling the nature of the polymerization-depolymerization equilibrium and the further structural analysis by e.g. CP/MAS NMR are the topics of our continuous research.

Table 3-2. Oxidative polymerization of PhSSPh at 160 °C

Entry	VO(acac) ₂ / mol%	TrB(C ₆ F ₅) ₄ / mol%	RT / h	Yield / %	T_m ^{a)} / °C	M_n ^{b)}	M_w ^{b)}
1	5	5	25	92	190	330	1100
2	1 ^{c)}	1	20	64	195	1500	2100
3	1	1	40	79	176	1600	2800
4	1	1	60	75	174, 268	1500	2700
5	0.25	0.25	60	82	194	1900	3200
6	0.25	0.25	70	65	199	2300	4700

^{a)}Determined by DSC. ^{b)}Measured by high temperature GPC. ^{c)}VO(TPP).

3-4. Experimental Section

3-4-1. General

All solvents were purified by distillation, prior to use. PhSSPh, VO(acac)₂, TfOH, NaOTf, NaBPh₄, TrBF₄, and TrB(C₆F₅)₄ were obtained from Tokyo Kasei Co., and used without further purification. VO(TPP) was obtained from Wako Co., and used without further purification. VO(salen) was prepared as previously reported.¹³

3-4-2. Characterization

Molecular weight measurements were done by gel permeation chromatography using an AGILENT PL-220 with 1-chloronaphthalene as the eluent (1ml/min) at 210 °C. Calibration was done with polystyrene standards.

Melting points were recorded using differential scanning calorimeter (DSC, Seiko Instruments Inc. DSC-220), scanned 20 to 310 °C at a rate of 20 °C/min with alpha-alumina as the reference.

3-4-3. General Procedure for Polymerization

Entry 1 in Table 3-1

To a 50-ml of test tube, 545 mg of diphenyl disulfide (2.50 mmol), 33.2 mg of VO(acac)₂ (5 mol%) and 115 mg of TrB(C₆F₅)₄ (5 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried in vacuo to give purified PPS in 68% yield. Molecular weight measurement of the obtained PPS was found to be $M_n = 850$ g/mol and $M_w = 1400$ g/mol. Melting point was found to be 160 °C. Infrared spectrum was obtained using a Jasco FT-IR 410 spectrometer with sodium chloride plates.

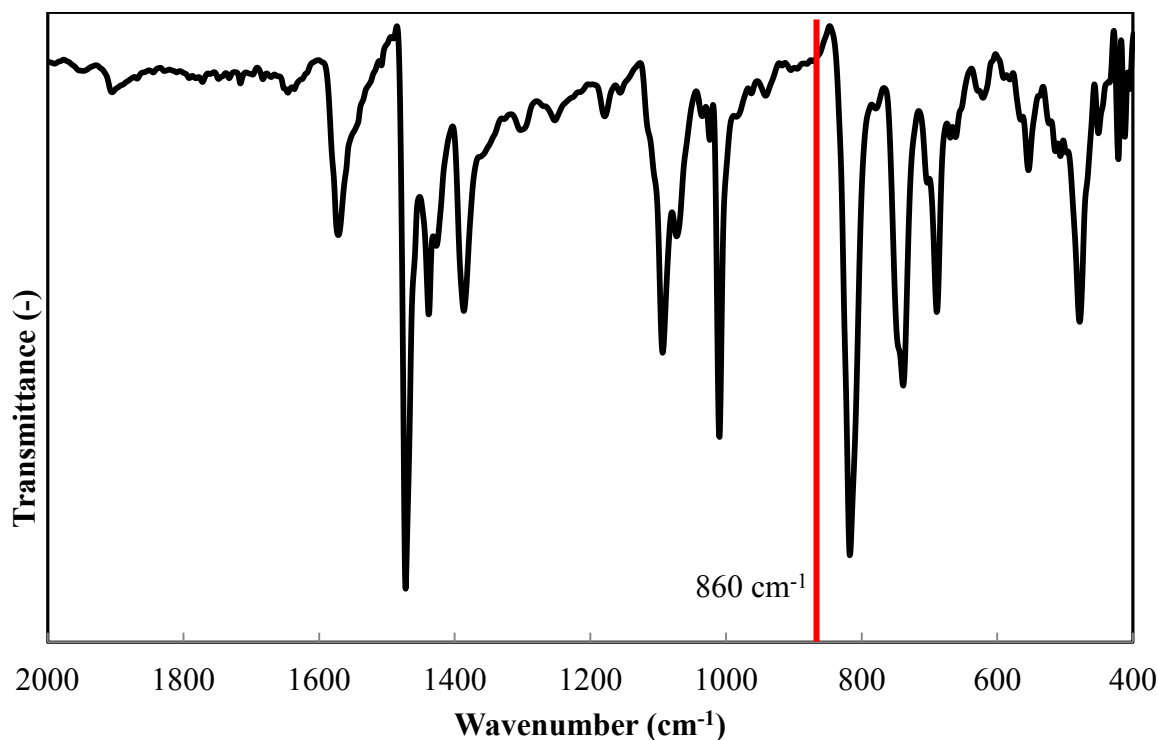


Figure 3-2. IR spectrum of Entry 1 sample.

Entry 2 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 66.3 mg of VO(acac)₂ (5 mol%) and 37.5 mg of TfOH (5 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 44% yield. Melting point was measured, $T_m = 155$ °C.

Entry 3 in Table 3-1

To a 100-ml of flask, 20.0 g of diphenyl disulfide (91.6 mmol), 0.242 g of VO(acac)₂ (1 mol%) and 80.3 μL of TfOH (1 mol%) were introduced. The mixture was stirred for total 100 hours at 100 °C, under 101 kPa of oxygen flow. 1 g of sample was taken at 40 and 60 hours. The 60-hour sample was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 36% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 155$ °C, $M_n = 1300$ and

$M_w = 1800$.

Entry 4 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 66.3 mg of VO(acac)₂ (5 mol%) and 165 mg of TrBF₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 17% yield.

Entry 5 in Table 3-1

To a 50-ml of test tube, 1.0875 g of diphenyl disulfide (5.00 mmol), 82.8 mg of VO(salen) (5 mol%) and 164 mg of TrBF₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). No precipitation was obtained.

Entry 6 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (4.98 mmol), 170 mg of VO(TPP) (5 mol%) and 164 mg of TrBF₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 3% yield.

Entry 7 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 66.4 mg of VO(acac)₂ (5 mol%) and 164 mg of TrBF₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 6% yield.

Entry 8 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 86.3 mg of VO(salen) (5 mol%) and 165 mg of TrBF₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 69% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 202$ °C, $M_n = 850$ and $M_w = 1400$.

Entry 9 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 33.9 mg of VO(TPP) (1 mol%) and 16.0 mg of TrBF₄ (1 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 65% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 195$ °C, $M_n = 1300$ and $M_w = 1800$.

Entry 10 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 33.9 mg of VO(TPP) (1 mol%) and 46.0 mg of TrB(C₆F₅)₄ (1 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 64% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 195$ °C, $M_n = 1500$ and $M_w = 2100$.

Entry 11 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 66.3 mg of VO(acac)₂ (5 mol%), 460 mg of TrB(C₆F₅)₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room

temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 76% yield. Melting point was not appeared. Molecular weight was measure and found to be as follows, $M_n = 1100$ and $M_w = 2700$.

Entry 12 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 66.4 mg of VO(acac)₂ (5 mol%), 37.5 mg of TfOH (5 mol%) and 43.0 mg of NaOTf (5 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 3% yield.

Entry 13 in Table 3-1

To a 50-ml of test tube, 1.09 g of diphenyl disulfide (5.00 mmol), 66.3 mg of VO(acac)₂ (5 mol%), 37.5 mg of TfOH (5 mol%) and 172 mg of NaBPh₄ (5 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 3% yield.

Entry 14 in Table 3-1

To a 50-ml of test tube, 545 mg of diphenyl disulfide (2.50 mmol), 33.2 mg of VO(acac)₂ (5 mol%) and 115 mg of TrB(C₆F₅)₄ (5 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C, under nitrogen. The reaction mixture was cooled to room temperature and poured into 50 ml of CH₂Cl₂. The solution was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). No precipitation was collected and the monomer was recovered in an almost 100% yield.

Entry 1 in Table 3-2

To a 100-ml of 3 necked flask, 20.0 g of diphenyl disulfide (91.6 mmol), 1.21 g of VO(acac)₂ (5 mol%) and 4.22 g of TrB(C₆F₅)₄ (5 mol%) were introduced. The mixture was stirred with

mechanical stirrer (100 rpm) for 25 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 100 ml of CH₂Cl₂. The dispersion was poured into 600 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 92% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 190$ °C, $M_n = 330$ and $M_w = 1100$.

Entry 2 in Table 3-2

Same as Entry 10 in Table 3-1, yield was 64%, $T_m = 195$ °C, $M_n = 1500$ and $M_w = 2100$.

Entry 3 in Table 3-2

To a 100-ml of 3 necked flask, 20.0 g of diphenyl disulfide (91.6 mmol), 0.243 g of VO(acac)₂ (1 mol%) and 0.844 g of TrB(C₆F₅)₄ (1 mol%) were introduced. The mixture was stirred with mechanical stirrer (100 rpm) for 40 hours at 160 °C, under 101 kPa of oxygen flow. 2.97 g of the reaction mixture was taken out and cooled to room temperature. The residual mixture was continued polymerization as entry 4. The taken out mixture was dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 79% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 176$ °C, $M_n = 1600$ and $M_w = 2800$.

Entry 4 in Table 3-2

The residual mixture at entry 3 was continued polymerization at the same condition for additional 20 hours (total 60 hours). The reaction mixture was cooled to room temperature and the cooled mixture was dispersed into 100 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 75% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 174$ and 268 °C, $M_n = 1500$ and $M_w = 2700$.

Entry 5 in Table 3-2

To a 100-ml of 3 necked flask, 20.0 g of diphenyl disulfide (91.6 mmol), 60.9 mg of VO(acac)₂ (0.25 mol%) and 0.211 g of TrB(C₆F₅)₄ (0.25 mol%) were introduced. The mixture

was stirred with mechanical stirrer (100 rpm) for 60 hours at 160 °C, under 101 kPa of oxygen flow. 1.97 g of the reaction mixture was taken out and cooled to room temperature. The residual mixture was continued polymerization as entry 6. The taken out mixture was dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 82% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 194$ °C, $M_n = 1900$ and $M_w = 3200$.

Entry 6 in Table 3-2

The residual mixture at entry 5 was continued polymerization at the same condition for additional 10 hours (total 70 hours). The reaction mixture was cooled to room temperature and the cooled mixture was dispersed into 100 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95 / 5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 65% yield. Melting point and molecular weight were measure and found to be as follows, $T_m = 199$ °C, $M_n = 2300$ and $M_w = 4700$.

3-5. Chapter Conclusion

A strong acid-free vanadyl-TrBR₄ catalyst for the oxygen-oxidative polymerization of PhSSPh was established. At 100 °C, the vanadyl-TrB(C₆F₅)₄ catalyst gave PPS in a good yield. The catalysis was ascribed to the efficient activation of the vanadyl complex with the Tr⁺ ion and the low reactivity of the B(C₆F₅)₄⁻ ion as the nucleophile, allowing the sulfonium cation to persist though the polymerization. At 160 °C, TrBF₄ also proceeded the polymerization with VO(TPP) and VO(salen), because of the enhanced Lewis acidity of TrBF₄ at the elevated temperature. A smaller amount of the catalyst gave a polymer with a high molecular weight of $M_w = 5000$.

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Chapter 4

Enhanced Catalytic Activity of Oxovanadium Complexes in Oxidative Polymerization of Diphenyl Disulfide

- 4-1. Introduction
 - 4-2. Oxygen-oxidative polymerization of PhSSPh catalyzed by VO(salen) at elevated temperatures
 - 4-3. Bromanil-assisted catalysis of oxygen-oxidative polymerization of PhSSPh by Vanadyl Complexes
 - 4-4. Experimental Section
 - 4-5. Conclusion
- References

4-1. Introduction

In polymer synthesis, organic reaction of sulfur-containing molecules has been paid much attention, because of their unique properties. In addition to utilizing various kinds of sulfur-containing monomers represented by thiophenes, C-S bond formation is quite useful to yield polymers. Thiolates (RS^-) as nucleophiles and sulfenyl cations (RS^+) as electrophiles are used for this purpose. The nucleophilic reaction of RS^- is typically represented by bis-hydrothiolation of thiols to alkynes to give thioacetals using calcium catalysts¹ and thia-Michael addition of RS^- to cyclohexenone followed by Baeyer-Villiger oxidation and finally giving sulfone-containing polyesters via ring-opening polymerization.² Sulfonium electrophiles (RS^+) have been employed under dehydrated conditions, such as the addition of electrochemically generated bis(arylthio)aryl sulfonium cation ($ArS(ArSSAr)^+$) to olefins to give 1,2-bis(arylthio)-substituted compounds via cationic chain reaction mechanism.³ Palladium-catalyzed intermolecular C-H chalcogenation of arenes with disulfides or diselenides has also been reported.⁴ Using phenylsulfenophthalimide as the PhS^+ source, Brønsted acid-chiral binaphthyl ligand system catalyzed carbosulfenylation of olefins enantioselectively and intramolecularly.⁵ The sulfonium electrophile, derived from the condensation of methyl (4-phenylthio)phenyl sulfoxide, was also used for the synthesis of poly(methylsulfonio-1,4-phenylenethio-1,4-phenylene trifluoromethanesulfonate).^{6a} The condensation was applied in many kinds of polysulfonium synthesis including those for heteropolyacenes.⁶ Recently, as represented by copper acetate-dimethyl sulfoxide (DMSO) promoted methylthiolation of arenes,⁷ β -hydroxysulfide synthesis via air oxidative hydroxysulfurization⁸ and dithioether synthesis from 1,3-dithianes via ring-opening and palladium catalyzed C-S bond formation have been reported.⁹ Sulfur chemistry is thus one of the hot topics in current organic chemistry relevant to polymer synthesis.¹⁰ However, catalytic system to produce the synthetically useful sulfonium electrophiles has been limited to those found in our previous research on the oxygen-oxidative polymerization of diphenyl disulfide catalyzed by $VO(acac)_2$.

Our research group has been focusing on the chemistry of $ArS(ArSSAr)^+$ electrophile, especially its formation and reactivity by catalytic oxidation of corresponding $ArSSAr$ using a vanadyl catalyst.¹¹ The chemical structure of the sulfonium cation, having three-membered sulfur ring, was determined by 1H and ^{13}C NMR of bis(methylthio)methyl sulfonium^{11e} (Figure 4-1) and *in situ* Raman spectroscopy of $ArS(ArSSAr)^+$ ($Ar = p\text{-FC}_6\text{H}_4$).^{3c}

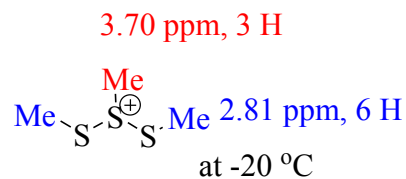


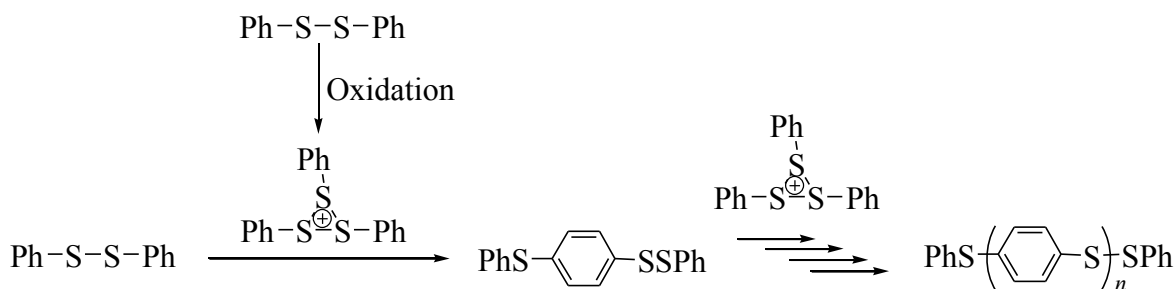
Figure 4-1. Determination of chemical structure of $\text{MeS}(\text{MeSSMe})^+$ by ^1H NMR.

This kind of sulfonium cation was applied to a poly(1,4-arylene sulfide) (PAS) synthesis, under oxidative conditions with the vanadyl catalyst and oxygen. In previous studies, it was reported that bis(phenylthio)phenyl sulfonium ($\text{PhS}(\text{PhSSPh})^+$) ion was identified to be the active species of the oxygen-oxidative polymerization of PhSSPh, propagating the “PhS” unit via Friedel-Crafts (FC) type electrophilic aromatic substitution (Scheme 4-1).¹² Vanadyl complexes, such as $\text{VO}(\text{acac})_2$ (acac⁻ is the acetylacetonato ligand), $\text{V}(\text{acac})_3$, bis(1-phenyl-2,4-pentanedionato)oxovanadium ($\text{VO}(\text{dbm})_2$), and (*meso*-tetraphenylporphyrinato)oxovanadium ($\text{VO}(\text{TPP})$), proceeded the oxygen-oxidative polymerization.^{11d} However, the inherent lability of the β -diketonato ligand such as acac⁻ has impeded to unravel the catalytic mechanism. The lack of the catalytic activity of $\text{VO}(\text{salen})$ (where salen²⁻ is an inert four-coordinate *N,N'*-ethylenebis(salicylideneaminato) ligand) with a more negative redox potential suggested that the overall activity of the catalyst was dominated by the oxidation of the monomer with the catalyst (Table 4-1, Scheme 4-1).

Table 4-1. Oxidative polymerization of PhSSPh with the vanadium catalysts^{11d}

Vanadium complexes	$E_{1/2}$ / V vs. Ag/AgCl	PPS Yield / %
$\text{VO}(\text{salen})$	0.5	0
$\text{V}(\text{acac})_3$	0.8	85
$\text{VO}(\text{acac})_2$	1.1	92
$\text{VO}(\text{TPP})$	1.5	95

We report here that the $\text{VO}(\text{salen})$ -catalyzed oxygen-oxidative polymerization of PhSSPh proceed at elevated temperatures, which revealed that the complex was sufficiently robust as a result of the inertness of the ligand and yet the reactivity of $\text{VO}(\text{salen})$ is significantly enhanced.



Scheme 4-1. Oxidative polymerization of PhSSPh via FC electrophilic reaction of the sulfonium cation.

H_2salen and its derivatives are quite stable compounds and are useful as inert tetradentate ligands for various metal ions. Ruthenium(III)-, iron(II)-, copper(II)- and oxovanadium(IV)-salen complexes are typically classified into highly stable and robust complexes, which can be used as catalysts for oxidative reactions with peroxides and other oxidants.¹³ Oxygen or air is the ultimate oxidant in biological systems and the most economical reagent for oxidation in organic synthesis. To reduce oxygen, four-electron and four-proton transfers are essential according to $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. The two-electron and two-proton transfers give rise to a hydroxide according to $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ which is often undesirable in the respiratory systems and the organic synthesis. So far, many kinds of organometallic complexes have been reported, showing various types of the multi-electron transfer processes.^{14,15} The above mentioned oxygen-oxidative polymerization of PhSSPh is one of the four-electron-transfer preferred reaction to give H_2O as the byproduct, because the hydroxide instantly oxygenates, rather than oxidates, the disulfide to yield the undesired sulfoxides and sulfones.^{11,12,15,16} Although VO(salen) did not show the catalytic activity for the polymerization under ambient conditions, the enhanced chemical robustness of VO(salen) and its oxidized $[\text{V}^{\text{VO}}(\text{salen})]^+$, suggested from the electrochemically almost totally reversible nature of the couple which is in sharp contrast to the quasi-reversible response obtained for $[\text{VO}(\text{acac})_2]^{0/+}$, clearly indicated the possibility of exploring more severe conditions with VO(salen) to undergo the four-electron transfer reaction.^{11d,16b}

The mediated oxidation of PhSSPh catalyzed by the vanadyl complexes requires that the redox potentials of the vanadyl complexes are located in-between the potential for the oxidation of PhSSPh near 1.7 V vs. Ag/AgCl and that for the four-electron reduction of oxygen near 0.5 V at room temperature. We previously reported that the potential range of 0.8-1.5 V for the vanadyl complex was appropriate to catalyze the polymerization.^{11d} VO(acac)₂ catalyzed the polymerization, because its redox potential was estimated near 1.1 V.^{11b} The lack of the catalytic activity of VO(salen) was ascribed to the negative redox potential for the $[\text{VO}(\text{salen})]^{0/+}$ couple at a half-wave potential of $E_{1/2} = 0.5$ V (Table 4-1).^{11d}

However, one could assume that the reactivity of those less oxidizing vanadyl complexes should be enhanced at elevated temperatures,¹⁷ according to the Nernst's equation which suggests that the redox potential shifts positively with the temperature (Figure 4-2).

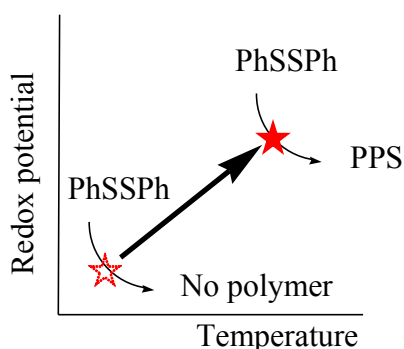


Figure 4-2. Assumption for enhancement of the reactivity at elevated temperatures.

We report here our successful attempt to enhance the catalytic activity at moderately elevated temperatures by applying a pressurized condition (ca. 0.45 MPa) to partially maintain the oxygen concentration. Another effective mean to enhance the catalytic activity is to combine an additional redox cycle to the oxovanadium(IV/V) couple. Effect of applying such multiple redox cycles formed in-between the monomer and oxygen has been examined in our previous work on the polymerization of bis(3,5-dimethylphenyl) disulfide using $\text{VO}(\text{acac})_2$ and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in the presence of trifluoroacetic acid ($\text{CF}_3\text{CO}_2\text{H}$) under ambient conditions with $(\text{CF}_3\text{CO})_2\text{O}$ in a halogenated hydrocarbon as a solvent.^{16a} This method of enhancing the catalytic activity proved to have an inherent advantage over just raising the reaction temperature, because of the capability of undergoing the polymerization under atmospheric pressure. In search of quinones that match the conditions to undergo the polymerization of the disulfide at moderately elevated temperatures, we have found that 2,3,5,6-tetrabromo-*p*-benzoquinone (bromanil) significantly enhance the catalytic activity of the vanadyl complexes to produce polymers in larger molecular weights.

4-2. Oxygen-oxidative polymerization of PhSSPh catalysed by VO(salen) at elevated temperatures

Cyclic voltammograms of VO(salen) were recorded at -10, 20, and 70 °C, which revealed the redox potentials ($E_{1/2}$) at 0.44, 0.47, and 0.56 V, respectively (Figure 4-3).

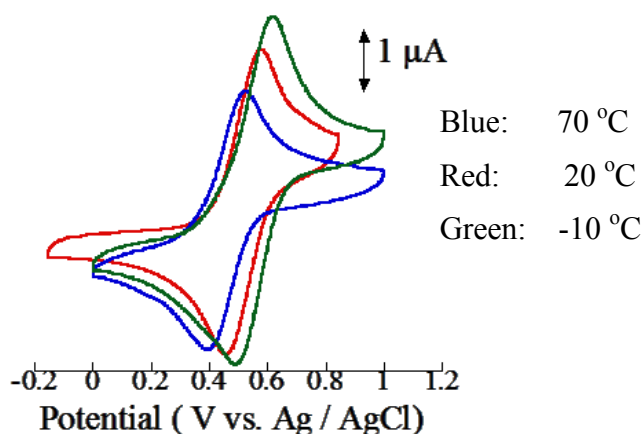


Figure 4-3. Cyclic voltammogram of VO(salen) under various temperatures.

Assuming a linearity of the formal potential with temperature, $E_{1/2}$ was extrapolated to be 0.60, 0.64, and 0.69 V at 100, 130, and 160 °C, respectively. The positive shift in the redox potential that came into the region of the proper range for the catalysis suggested that the oxygen-oxidative polymerization should proceed above 100 °C using VO(salen) as the catalyst (Figure 4-4).

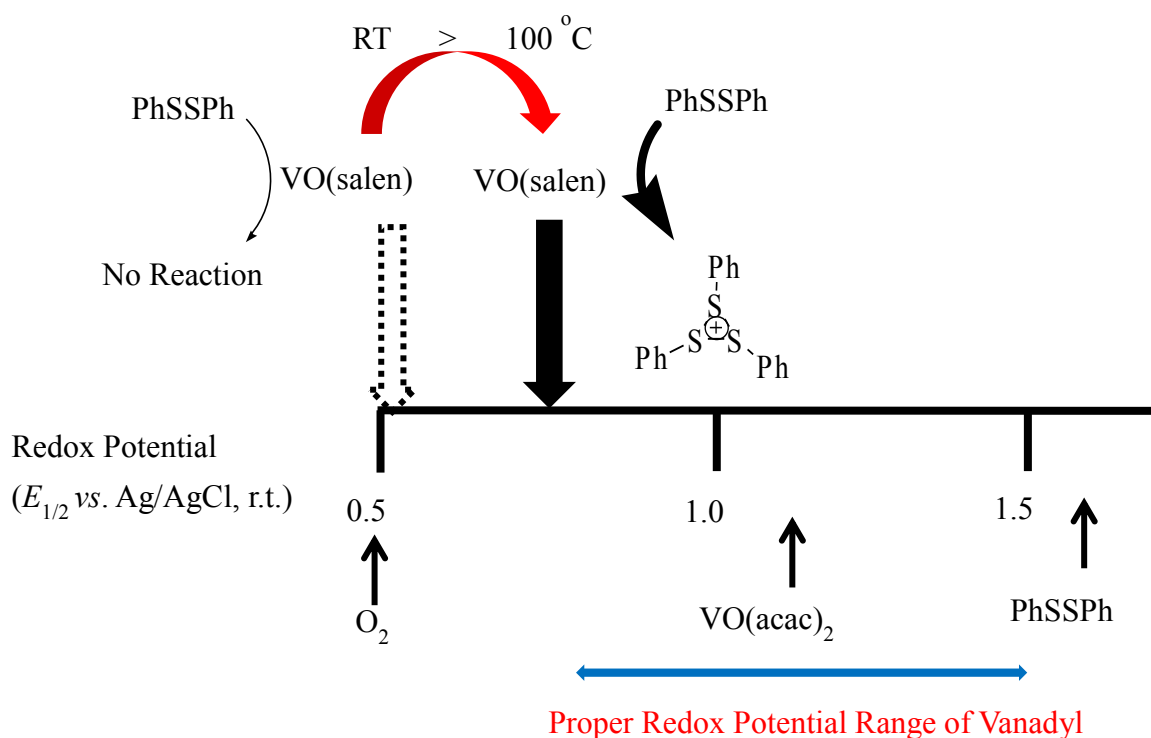


Figure 4-4. Potential diagram of the catalyst at elevated temperatures.

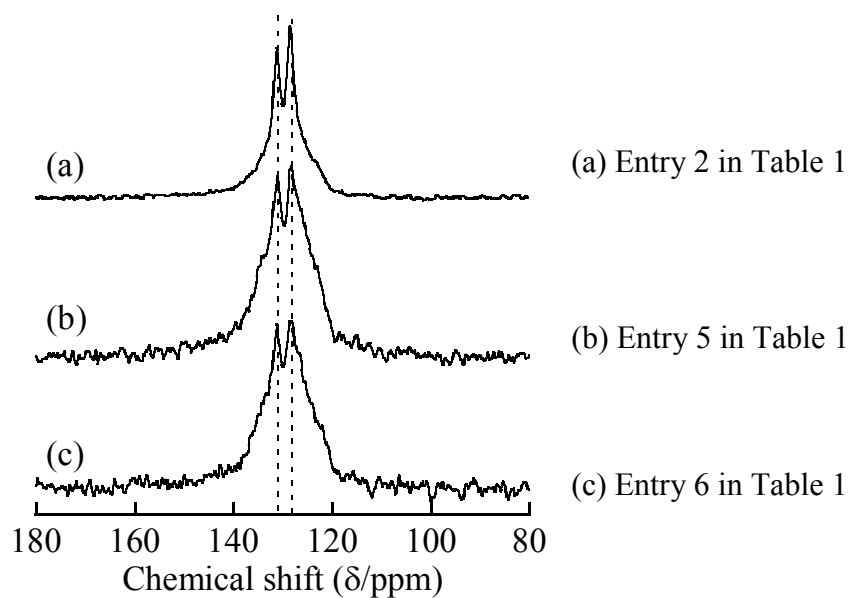
Table 4-2 showed the results of the oxygen-oxidative polymerization of the disulfide with the VO(salen) catalyst, which was inactive at a room temperature (entry 1) but gained activity at 100 °C (entry 2). Comparison between entries 2 and 4 suggested that higher reaction temperatures led to higher yields and melting points (T_m) of the products. Also, comparison between entries 3 and 6 indicated that the higher reaction temperatures resulted in higher yields and T_m of the products even in a shorter reaction time. Both the strong acid and the borate gave rise to the polymerization activity with VO(salen) (entries 4 and 5). Considering that the reactivity was limited by the equilibrated oxygen concentration which should be lowered at elevated temperatures, we adopted a pressurized condition (entry 7) to further enhance the reactivity. As expected, a higher molecular weight and T_m for the obtained PPS was accomplished with an even shorter time of the polymerization, compared with the results in entry 6. These results demonstrated the first catalysis of the oxidative polymerization of the disulfide by VO(salen) which has so far been regarded as inactive, suggesting that the electrochemical reversibility persisted at the elevated temperatures as a result of the inertness of the salen²⁻ ligand to give rise to the positive shift of the formal potential for the [VO(salen)]^{0/+} couple. The polymer obtained by this method was generally linear without branching or crosslinking as evidenced by the presence of only two carbon signals in the CP-MAS spectrum (Figure 4-5) corresponding to the structural symmetry and the IR peak at 820 cm⁻¹ ascribed to the C-H out-of-plane vibration of adjacent two hydrogens in the 1,4-phenylene unit (Figure 4-6),^{10,17,19} suggesting the highly selective catalysis by VO(salen). The present study is the first achievement of catalytic activity of VO(salen) for the polymerization of the disulfide, while the catalytic mechanism of the vanadyl catalyst has so far been determined with the complexes bearing the inert salen²⁻ ligand and yet the catalytic activity has so far been obtained only for those having labile acac⁻ and related ligands.^{11d} The results clearly demonstrated that the catalysis was accomplished by the incorporation of the multi-electron transfer process established for VO(salen).^{16e}

Table 4-2. Oxygen-oxidative polymerization of PhSSPh with VO(salen)^{a)}

Entry	Acid or borate (/ mol%)	Temp / °C	Time / h	Yield / %	T_m ^{b)} / °C	M_n ^{c)}	M_w ^{c)}
1 ^{d)}	TfOH (10)	RT	40	0			
2	TrB(C ₆ F ₅) ₄ (10)	100	20	52	149		
3 ^{e)}	CHF ₂ CF ₂ SO ₃ H (1)	130	80	70	163	1200	1600
4	TrB(C ₆ F ₅) ₄ (10)	160	20	69	254	880	1800
5	CHF ₂ CF ₂ SO ₃ H (10)	160	20	69	198	1500	3400
6 ^{e)}	CHF ₂ CF ₂ SO ₃ H (1)	160	40	82	175	1100	1500
7 ^{f)}	CHF ₂ CF ₂ SO ₃ H (1)	160	20	82	205	1800	4400

^{a)}5 mol% of VO(salen) was used. ^{b)}Determined by DSC. ^{c)}Measured by high temperature GPC. ^{d)}Data from reference 3a). ^{e)}1 mol% of VO(salen) was used.

^{f)}1 mol% of VO(salen) was used and oxygen pressure was 0.45 MPa.

**Figure 4-5.** CP-MAS spectra of the PPS.

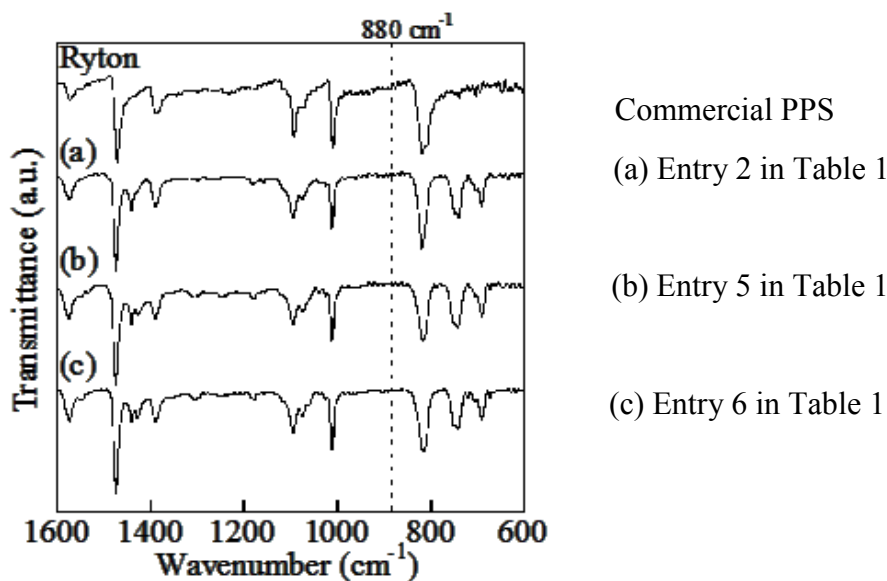


Figure 4-6. IR spectra of the PPS.

4-3. Bromanil-assisted catalysis of oxygen-oxidative polymerization of PhSSPh by Vanadyl Complexes

Under ambient temperature conditions, quinones such as DDQ and bromanil are known to enhance the reactivity of the VO(acac)₂-acid catalytic system for the oxygen-oxidative polymerization of PhSSPh or diaryl disulfide.^{16a} Assuming that the quinones should also enhance the reactivity of VO(salen), we turned to examine the catalysis by VO(salen) under moderately elevated conditions in the presence of the quinones. These quinones are good chemical oxidants to undergo the oxidative polymerization of PhSSPh when an equimolar amount of the oxidant is used.^{11a} A catalytic amount of them gave only a trace amount of the polymerized product as typically shown for the case of 2.5 mol% bromanil and 5 mol% CHF₂CF₂SO₃H with respect to the monomer after 4 h of the reaction (entry 1 in Table 4-3). It might be suggested that catalysis by bromanil was accomplished by placing the potential of bromanil near to an oxovanadium(IV/V) couple such as [VO(salen)]^{0/+}. An interesting aspect of the bromanil was found for the combination with VO(acac)₂ or VO(salen) at the moderately elevated temperatures, which demonstrated the catalytic activity even higher than those found for the conventional catalysis by VO(acac)₂ or VO(salen). When 2.5 mol% VO(acac)₂ was combined with the bromanil-acid system, the polymerization proceeded rapidly to give PPS in a 51% yield within 1 h (entry 2). Under the same conditions as in entry 2, a higher molecular-weight PPS was obtained in 82% yield after 4 h (entry 3). In the case of the conventional oxidative polymerization without bromanil, 5 mol% VO(acac)₂ and

$\text{CHF}_2\text{CF}_2\text{SO}_3\text{H}$ gave PPS in yields of only 22% after 1 h (entry 4) and 74% after 4 h (entry 5), which were much lower than those for the entries 2 and 3. Strong acids or borate compounds, such as $\text{CHF}_2\text{CF}_2\text{SO}_3\text{H}$ and $\text{TrB}(\text{C}_6\text{F}_5)_4$, were essential to activate the vanadyl compounds.¹⁹ Even for the oxidative polymerization with quinones, strong acids were found to be essential for stabilizing the key intermediate, sulfonium cation ($\text{PhS}(\text{PhSSPh})^+$).¹⁹ In the case of utilizing $\text{VO}(\text{salen})$ -acid catalytic system, bromanil similarly accelerated the oxidative polymerization (entries 6 and 7). These results gave insight into the nature of the catalysis which was dominated by the oxidation of the monomer and much improved by placing a second redox couple to enhance the overall reactivity under moderately elevated temperature conditions to yield PPS with a higher molecular weight than those with the conventional catalyst system. It was reported that redox potentials of quinones were positively shifted under acidic conditions.²⁰ Actually, the redox potential of bromanil ($E_{1/2} = -0.71$ and 0.11 V vs. Ag/AgCl , r.t.) was shifted to 0.1 and 0.5 V to show the irreversible reduction to yield the protonated product under acidified conditions (Figure 4-7, 4-8, 4-9). During the polymerization, the anionic species, such as the reduced forms of the quinones or the conjugated base of strong acids, were reported to stabilize the cationic species, typically the sulfonium cations.¹⁹ Bromanil turns to be an anionic species by reduction, so the reduced bromanil might be able to form complexes with the cationic vanadyl compounds. It may be suggested that the effective enhanced catalytic systems of the vanadyl-acid-bromanil triad was ascribed to the re-oxidation of the possibly newly formed complex between the vanadyl catalyst and the reduced bromanil. Further investigation of the mechanism is the topic of our continuous research.

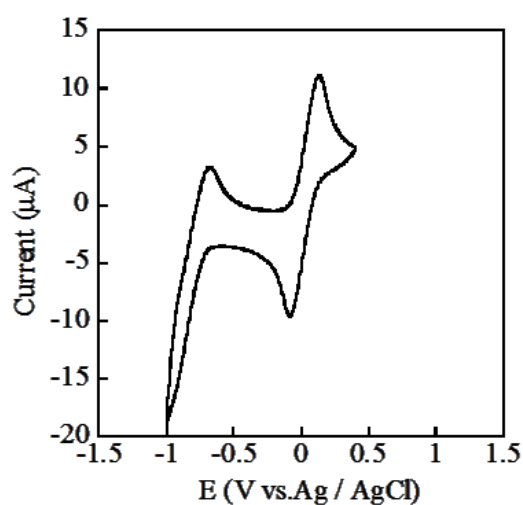


Figure 4-7. Cyclic voltammogram of bromanil under neutral condition.

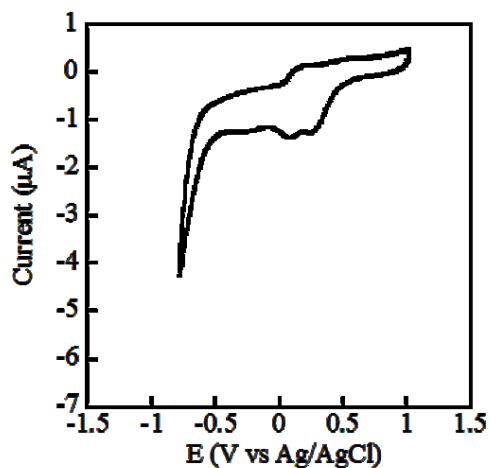


Figure 4-8. Cyclic voltammogram of bromanil with 2 molar of $C_2HF_4SO_3H$.

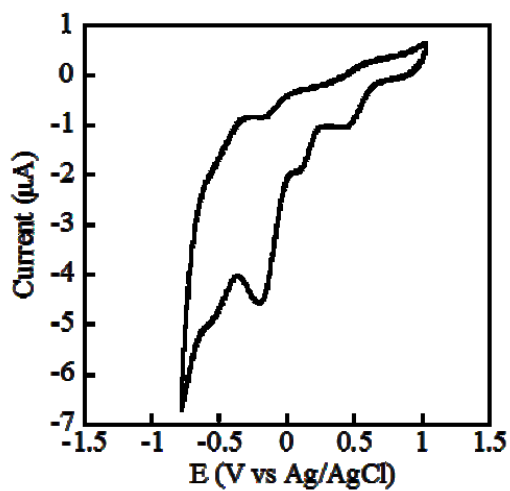


Figure 4-9. Cyclic voltammogram of bromanil with 5 molar of $C_2HF_4SO_3H$.

Table 4-3. Oxidative polymerization with vanadyl-oxidant system^{a)}

Entry	Vanadyl / mol%	Bromanil / mol%	Time / h	Yield / %	$M_n^{b)}$	$M_w^{b)}$
1 ^{c)}	0	2.5	4	Trace		
2	2.5 ^{d)}	2.5	1	51	900	1100
3	2.5 ^{d)}	2.5	4	82	1600	2400
4	5 ^{d)}	0	1	22	680	850
5	5 ^{d)}	0	4	74	1300	1600
6	2.5 ^{e)}	2.5	4	56	960	1300
7	5 ^{e)}	0	4	24		

^{a)}[CHF₂CF₂SO₃H]/[Vanadyl] = 2, oxygen atmosphere, polymerized at 160 °C.

^{b)}Determined by high temperature GPC. ^{c)}5 mol% of CHF₂CF₂SO₃H was used.

^{d)}VO(acac)₂ was used. ^{e)}VO(salen) was used.

4-4. Experimental Section

PhSSPh, VO(acac)₂, bromanil, TrB(C₆F₅)₄ (Tr⁺ = the triphenylmethylium cation), TfOH, and CHF₂CF₂SO₃H were obtained from Tokyo Kasei Co., and were used without further purification. VO(salen) was prepared as previously reported.¹⁸ Molecular weight measurements were done by gel permeation chromatography using an AGILENT PL-220 and 1-chloronaphthalene as the eluent (1 ml/min) maintained at 210 °C. Calibration was done with polystyrene standards. Melting points were recorded using differential scanning calorimeter (DSC, Seiko Instruments Inc. DSC-220), scanned 20 to 310 °C at a rate of 20 °C/min with alpha-alumina as the reference. Cyclic voltammetry was performed in 0.1 M solutions of tetrabutylammonium tetrafluoroborate (TBABF₄) in 1,2-dichloroethane with Pt working electrodes. The electrode potential of the working electrode was set versus the commercial Ag/AgCl reference electrode, and was scanned at a speed of 100 mV/s using an ALS/CH Instruments Electrochemical Analyzer (Model 660Dx) at -10, 20, and 70 °C. All potentials are shown with respect to this reference electrode.

Polymerization Procedure

Entry 2 in Table 4-1

To a 10-ml flask, 1.09 g of PhSSPh (4.98 mmol), 84.0 mg of VO(salen) (5 mol%), and 461 mg of TrB(C₆F₅)₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 100 °C,

under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS 52% yield. Melting point was measured and found to be $T_m = 149$ °C.

Entry 3 in Table 4-1

To a 100-ml flask, 20 g of PhSSPh (91.6 mmol), 0.305 g of VO(salen) (1 mol%), and 95.5 μ L 1,1,2,2-tetrafluoroethanesulfonic acid (1 mol%) were introduced. The mixture was stirred for 80 hour at 130 °C, under 101 kPa of oxygen flow. 1 g of the final reaction mixture was taken and cooled to room temperature. The cooled mixture was dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 70% yield. Molecular weight and melting point were measured and found to be as follows, $M_n = 1200$, $M_w = 1600$, and $T_m = 163$ °C.

Entry 4 in Table 4-1

To a 10-ml flask, 1.09 g of PhSSPh (5.00 mmol), 83.4 mg of VO(salen) (5 mol%), and 470 mg of TrB(C₆F₅)₄ (10 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 69% yield. Molecular weight and melting point were measured and found to be as follows, $M_n = 880$, $M_w = 1800$, and $T_m = 254$ °C.

Entry 5 in Table 4-1

To a 10-ml flask, 1.09 g of PhSSPh (5.00 mmol), 83.9 mg of VO(salen) (5 mol%), and 75.0 mg of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was stirred for 20 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 69% yield. Molecular weight and melting

point were measured and found to be as follows, $M_n = 1500$, $M_w = 3400$, and $T_m = 198$ °C.

Entry 6 in Table 4-1

To a 100-ml flask, 20.0 g of PhSSPh (91.7 mmol), 0.305 g of VO(salen) (1 mol%), and 95.5 μ L of 1,1,2,2-tetrafluoroethanesulfonic acid (1 mol%) were introduced. The mixture was mechanically stirred for 40 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH_2Cl_2 . The dispersion was poured into 1000 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H_2O , and MeOH thoroughly and dried under vacuum to give purified PPS in 82% yield. Molecular weight and melting point were measured and found to be as follows, $M_n = 1100$, $M_w = 1500$, and $T_m = 175$ °C.

Entry 7 in Table 4-1

To a 50-ml autoclave with Teflon® inner tube, 6.76 g of PhSSPh (31 mmol), 103 mg of VO(salen) (1 mol%), and 32.3 μ L of 1,1,2,2-tetrafluoroethanesulfonic acid (1 mol%) were introduced. The mixture was heated, pressurized with 0.45 MPa of oxygen and stirred for 20 hours at 160 °C. At every 1 hour, the reaction mixture was depressurized to ambient pressure and pressurized to 0.45 MPa again with oxygen. After the reaction, oxygen was depressurized and purged with nitrogen. Then the autoclave was cooled down to room temperature. The reaction mixture was dispersed into 50 ml of CH_2Cl_2 and the dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H_2O , and MeOH thoroughly and dried under vacuum to give PPS in 82% yield. Molecular weight and melting point were measured and found to be as follows, $M_n = 1800$, $M_w = 4400$, and $T_m = 205$ °C.

Entry 1 in Table 4-2

To a 10-ml flask, 1.09 g of PhSSPh (4.99 mmol), 52.5 mg of bromanil (2.5 mol%), and 26.0 μ L of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH_2Cl_2 . The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, H_2O and MeOH thoroughly and dried under vacuum to give trace amount of polymer.

Entry 2 in Table 4-2

To a 10-ml flask, 1.09 g of PhSSPh (5.00 mmol), 33.1 mg of VO(acac)₂ (2.5 mol%), 53.0 mg of bromanil (2.5 mol%), and 26.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 1 hour at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with a glass filter. The solid was washed with MeOH, 0.1 N of aqueous KOH solution, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 51% yield. Molecular weight was measured and found to be as follows, $M_n = 900$ and $M_w = 1100$.

Entry 3 in Table 4-2

To a 10-ml flask, 1.0898 g of PhSSPh (4.99 mmol), 33.6 mg of VO(acac)₂ (2.5 mol%), 53.9 mg of bromanil (2.5 mol%), and 26.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, 0.1 N of aqueous KOH solution, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 82% yield. Molecular weight was measured and found to be as follows, $M_n = 1600$ and $M_w = 2400$.

Entry 4 in Table 4-2

To a 10-ml flask, 1.09 g of PhSSPh (4.99 mmol), 66.0 mg of VO(acac)₂ (5 mol%), and 52.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was stirred for 1 hour at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 22% yield. Molecular weight was measured and found to be as follows, $M_n = 680$ and $M_w = 850$.

Entry 5 in Table 4-2

To a 10-ml flask, 1.09 g of PhSSPh (5.00 mmol), 66.2 mg of VO(acac)₂ (5 mol%), and 52.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was

stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 74% yield. Molecular weight was measured and found to be as follows, $M_n = 1300$ and $M_w = 1600$.

Entry 6 in Table 4-2

To a 10-ml flask, 1.09 g of PhSSPh (5.0 mmol), 41.7 mg of VO(salen) (2.5 mol%), 53.0 mg of bromanil (2.5 mol%), and 26.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (5 mol%) were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, 0.1 N of aqueous KOH solution, H₂O and MeOH thoroughly and dried under vacuum to give purified PPS in 56% yield. Molecular weight was measured and found to be as follows, $M_n = 960$ and $M_w = 1300$.

Entry 7 in Table 4-2

To a 10-ml flask, 1.09 g of PhSSPh (5.00 mmol), 83.4 mg of VO(salen) (5 mol%), and 52.0 μL of 1,1,2,2-tetrafluoroethanesulfonic acid (10 mol%) were introduced. The mixture was stirred for 4 hours at 160 °C, under 101 kPa of oxygen flow. The reaction mixture was cooled to room temperature and dispersed into 50 ml of CH₂Cl₂. The dispersion was poured into 300 ml of MeOH-HCl mixture (MeOH/HCl = 95/5, in v/v). The precipitation was collected with glass filter. The solid was washed with MeOH, H₂O, and MeOH thoroughly and dried under vacuum to give purified PPS in 24% yield

Cyclic Voltammetry of VO(salen)

Cyclic voltammetry was performed in 0.1 M solutions of tetrabutylammonium tetrafluoroborate (TBABF₄) in 1,2-dichloroethane with Pt electrodes vs. Ag/AgCl at a scan speed of 100 mV/s, using an ALS / CH Instruments Electrochemical Analyzer (Model 660Dx), at -10, 20, and 70 °C (Table S1). Then correlation between temperature and redox potential ($E_{1/2}$) was determined as follows.

$$E_{1/2} (\text{V vs Ag/AgCl}) = 0.0015 \times (\text{Temp}, ^\circ\text{C}) + 0.4492$$

Table 4-3. Redox potential of VO(salen)

Temperature / °C	V / $E_{1/2}$, vs. Ag/AgCl
-10	0.44
20	0.47
70	0.56

Cyclic Voltammetry of bromanil

Cyclic voltammetry was performed 1 mM solution of bromanil in nitrobenzene with 0.1 M solutions of tetrabutylammonium tetrafluoroborate (TBABF₄), with Pt electrodes vs. Ag/AgCl at a scan speed of 100 mV/s, using an ALS/CH Instruments Electrochemical Analyzer (Model 660Dx), at ambient temperature.

Cyclic Voltammetry of bromanil under acidic conditions

Cyclic voltammetry was performed 1 mM solution of bromanil and 2 or 5 molars of C₂HF₄SO₃H in nitrobenzene with 0.1 M solutions of tetrabutylammonium tetrafluoroborate (TBABF₄), with Pt electrodes vs. Ag/AgCl at a scan speed of 100 mV/s, using an ALS/CH Instruments Electrochemical Analyzer (Model 660Dx), at ambient temperature.

4-5. Chapter Conclusion

The VO(salen)-catalyzed oxygen-oxidative polymerization of PhSSPh was successfully established above 100 °C. Pressurized oxygen further accelerated the oxidative polymerization and gave higher molecular weight products in high yield. The results demonstrated that the catalysis was dominated by the oxidation of the monomer rather than re-oxidation of the catalysis by oxygen, which was also supported by the enhanced reactivity of the vanadyl catalyst with Bromanil. Further modification of the catalyst with a view to yield a higher molecular-weight PPS is the topic of our continuous research.

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Chapter 5

Palladium-catalyzed 5-exo-Selective Reductive Mizoroki-Heck Reaction of Aryl Chlorides with 2,5-Norbornadiene

- 5-1. Introduction
 - 5-2. Screening of Palladium complexes for Reductive Mizoroki-Heck Reaction
 - 5-3. Determination of the Stereochemistry
 - 5-4. Effects of Solvents, Additives, and Amount of Catalyst in Reductive Mizoroki-Heck Reaction
 - 5-5. Reductive Mizoroki-Heck Reaction with Various Aryl Halides and Benzocyclobutene-fused Norbornene Synthesis
 - 5-6. Plausible Reaction Mechanism
 - 5-7. Experimental Section
 - 5-8. Conclusion
- References

5-1. Introduction

The author researched reductive Mizoroki-Heck reactions of 2,5-norbornadiene (NBD) and aryl chloride (Ar-Cl) for preparation of 5-*exo*-aryl-2-norbornene, as another application of utilizing transition metal catalysts. The research also related to the expansion of applicable compounds, which were mostly limited to aryl trifluoromethanesulfonic acid ester (Ar-OTf), aryl iodide (Ar-I), and aryl bromide (Ar-Br) for the reaction. Utilizing Ar-Cl was also related to its disuse of expensive acid anhydride, which was essential for preparing Ar-OTf. Vanadium compounds are only used for oxidative reactions, as shown in Chapters 2-4. On the contrary, palladium compounds show a variety of reactions, categorized as oxidations, reductions, hydrogenolysis, couplings, etc. In 2010, Professors Negishi, Suzuki, and Heck received the Nobel Prize, with their excellent works, palladium-catalyzed cross couplings. The palladium-catalyzed Mizoroki-Heck reaction, one of the coupling reactions, is a very useful synthetic tool for carbon-carbon bond formation. Ar-OTf, Ar-I, and Ar-Br are favorably used for the Mizoroki-Heck reaction because they are easily activated by a palladium catalyst. Ar-Cl is less expensive, compared to Ar-OTf, Ar-I, and Ar-Br. But Ar-Cl is hardly activated with a palladium catalyst. Therefore, investigation of Mizoroki-Heck reaction conditions for utilizing Ar-Cl is quite attractive and challenging. The author reports here a stereoselective reductive Mizoroki-Heck reaction between NBD and Ar-Cl to synthesize norbornene derivatives.

Norbornene and its derivatives are very attractive chemicals as versatile starting compounds of functionalized materials not only for academic research but also industrial use. One of the industrial usages is in the manufacture of high transparent polymers for optical materials. Particularly, norbornenes having a bulky aryl group at the *exo* position are expected to be in great demand as monomers for synthesizing optical materials because of their high transparency, negative birefringence, negative dispersion and high heat resistance properties.^{1,2,3} Norbornenes are easily synthesized with cyclopentadiene by Diels-Alder reaction. For example, maleic anhydride is an extremely good coupling partner with cyclopentadiene and *endo*-nadic anhydride is formed with nearly 100% selectivity in a quantitative yield. This *endo* selectivity is explained by so-called “endo rule”, the π - π interaction between cyclopentadiene and the p-orbitals in the carbonyl group.⁴ Even when styrene is employed as a dienophile, *endo*-5-phenyl-2-norbornene is dominantly formed. Therefore, *exo*-aryl-substituted norbornenes cannot be achieved by Diels-Alder reactions. Although a potential process is the isomerization of *endo*-norbornene but it requires harsh conditions and the yield is generally poor.

Generally, norbornenes show quite high *exo* selectivity regardless kinds of addition reactions.⁵ Among the possible addition reactions to the C=C double bond in norbornenes, Mizoroki-Heck reaction could be an effective candidate to get *exo*-norbornanes. Aryl bromide, iodide and triflate are widely used for Mizoroki-Heck reactions and reductive Mizoroki-Heck reactions can be conducted with suitable reducing reagents. In fact, treatment of 2-norbornene and 2,5-norbornadiene with phenyl iodide by palladium catalyst gives 2-phenylnorbornane and 5-phenyl-2-norbornene with excellent *exo*-selectivity.⁶ However, inexpensive chloride derivatives are greatly preferable for industrial use in economic point of view. Although several kinds of Mizoroki-Heck reactions of alkynes and olefins using aryl chlorides have been reported,^{7,8,9} reductive Mizoroki-Heck reactions using aryl chloride is unprecedented to our best knowledge.

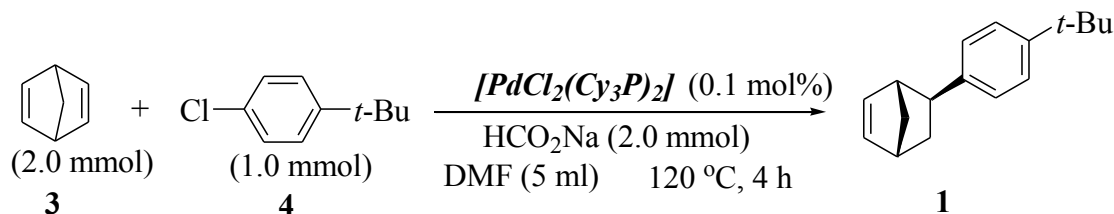
To get our target compound, 5-*exo*-(4-*tert*-butylphenyl)-2-norbornene (**1**) which is a monomer for the above mentioned characteristics, reductive Mizoroki-Heck reaction between 2,5-norbornadiene and 4-*tert*-butyl-1-halobenzene seems to be the most favorable combination. However, the reaction of 2,5-norbornadiene with phenyl iodide catalyzed by Pd(OAc)₂/Bu₄NCl/HCO₂K was reported to give *exo*-5-phenyl-2-norbornene only in 20% yield, because of subsequent further addition reaction to the target product.⁶ Similar reductive Mizoroki-Heck reaction of 2,5-norbornadiene with naphthyl bromide or pyrenyl bromide gave *exo*-5-naphthyl-2-norbornene or *exo*-5-pyrenyl-2-norbornene in insufficient yield (55% and 15%, respectively).¹⁰ Thus, effective synthetic method of *exo*-5-aryl-2-norbornene from 2,5-norbornadiene has been unexplored so far.

In this chapter, the author reports a new and feasible synthetic method of 5-*exo*-(4-*tert*-butylphenyl)-2-norbornene (**1**) and its derivatives by the reductive Mizoroki-Heck reaction using aryl chloride and 2,5-norbornadiene catalyzed by [PdCl₂(PCy₃)₂] (abbreviated as **Pd-Cy**). We also describe the formation of an *exo*-benzocyclobutene-fused norbornene, 6-*tert*-butyl-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene (**2**), which is also found during this study.

5-2. Screening of Palladium complexes for Reductive Mizoroki-Heck Reaction and Determination of the Stereochemistry

Initially, we screened the catalysts suitable for the reductive Mizoroki-Heck reaction of 2,5-norbornadiene (**3**) with 4-*tert*-butylphenyl chloride (**4**) in the presence of HCO₂Na as a

reductant. Under the optimized conditions of catalyst (0.1 mol % versus **4**), **3** (2.0 mmol), **4** (1.0 mmol), and HCO₂Na (2.0 mmol) in DMF at 120 °C for 4 h, only trace amount of **4** was consumed when [PdCl₂(dppm)], [PdCl₂(dppe)], [PdCl₂(dppp)], [PdCl₂(dppb)], [PdCl₂(PPh₃)₂], [PdCl₂(dppf)], and [Pd₂(dba)₃·CHCl₃] were used.¹¹ However, we found a promising preliminary result to give **1** in 30% conversion of **4** with **Pd-Cy**, based on GC analysis (Scheme 5-1).



Scheme 5-1. Palladium-catalyzed reductive Mizoroki-Heck reaction.

In order to determine the stereochemistry of the product **1**, as an authentic *endo* and *exo* mixture of 5-(4-*tert*-butylphenyl)-2-norbornene was synthesized by Diels-Alder reaction of cyclopentadiene with 4-*tert*-butylstyrene. Figure 5-1 clearly shows the present product **1** being the *exo*-form without formation of observable *endo*-**1**. Stereochemistry of norbornene derivatives can be determined by chemical shifts of ¹H NMR.^{2,12} In addition to NMR analysis, GC analysis was also effective to analyze *endo*- and *exo*-forms quantitatively.

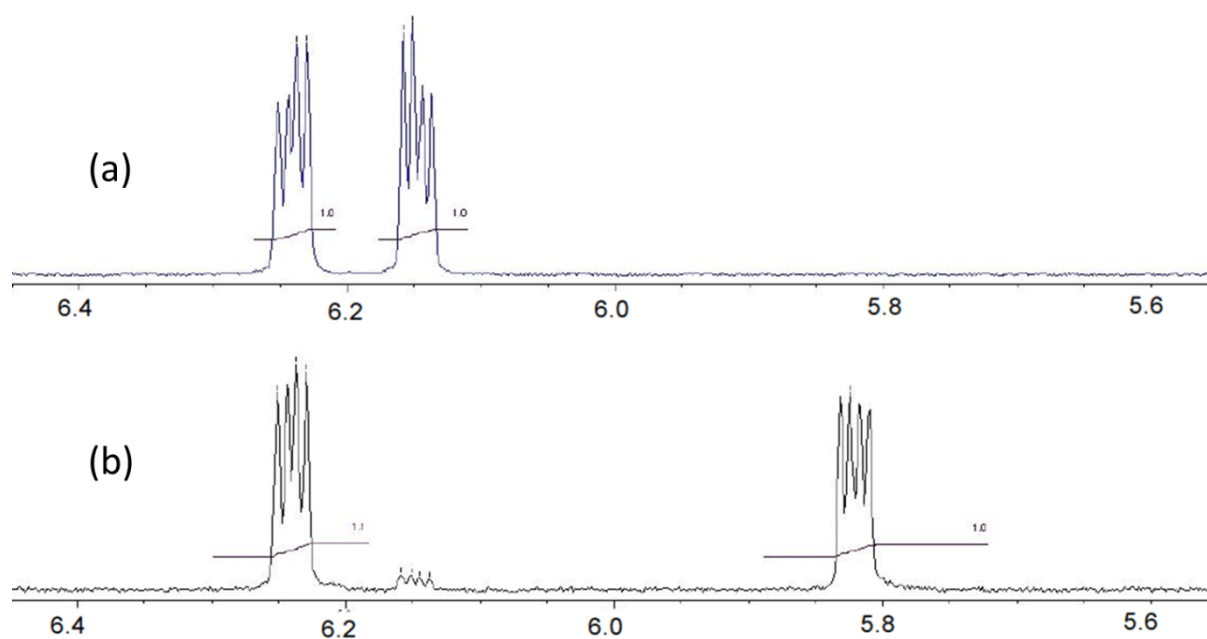


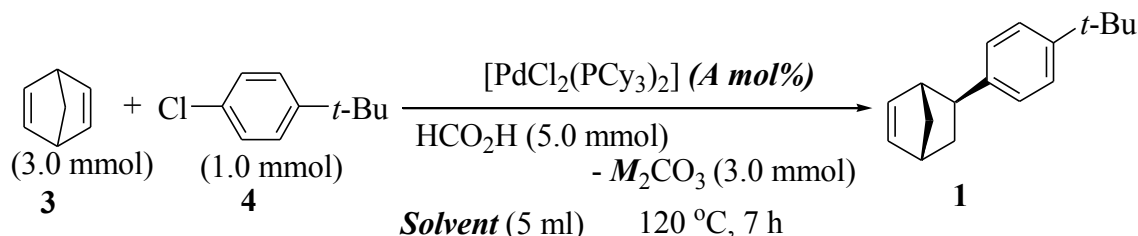
Figure 5-1. ¹H NMR spectra of 5-(4-*tert*-butylphenyl)-2-norbornenes. (a): the present product. (b): the *endo*-rich product involving small amount of the *exo*-isomer obtained by Diels-Alder

reaction.

5-3. Effects of Solvents, Additives, and Amount of Catalyst in Reductive Mizoroki-Heck Reaction

The effect of solvent and carbonate salts on this reaction in the presence of formic acid is summarized in Table 5-1. Higher *exo-1* selectivity can be achieved in amide solvents, particularly DMF, than in DMSO (Entries 1-3). Among carbonate salts tested, Cs₂CO₃ showed the highest conversion and selectivity (Entries 1, 4, and 5). Despite the complete conversion of **4** on using Na₂CO₃, only negligible amount of *exo-1* was produced (Entry 5). In this reaction, corresponding 5-*exo*-arylnorbornane was formed in 69% yield, suggesting further reduction of the target compound. We also screened HCO₂H-Et₃N in the absence of carbonate salts because the combination was reported to act as an effective reductant in a Pd-catalyzed system.¹³ However, HCO₂H-Et₃N resulted in low conversion and yield (Entry 6).

Table 5-1. Effects of solvents and additives on reductive Mizoroki-Heck reaction



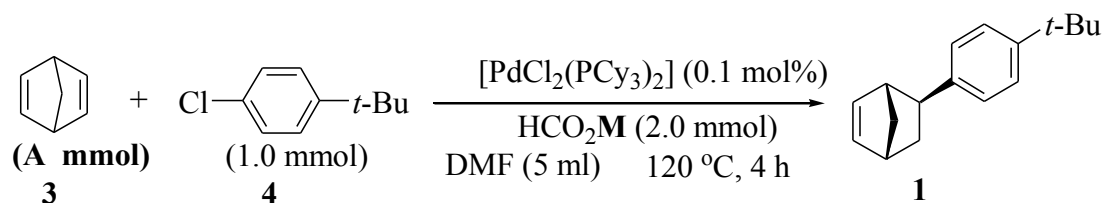
Entry	Sol.	M	A / mol%	Conv. / %	Select. / %	Yield / %
1	DMF	Cs ^a	3.0	100	73	73
2	DMA	Cs ^a	3.0	98	64	63
3	DMSO	Cs ^a	3.0	100	23	23
4	DMF	K	5.0	100	21	21
5	DMF	Na	5.0	100	1	1
6 ^b	DMF	None ^c	5.0	35	82	29

^a3.1 mmol was used. ^bReaction time was 4 h. ^cEt₃N (3.0 mmol) was used.

Formate salts such as HCO₂NH₄ are also potential reductants in a Pd-catalyzed system.¹⁴

The screening using several formate salts is summarized in Table 5-2. Same as HCO₂H-Et₃N, HCO₂NH₄ showed low conversion and yield. When HCO₂Na or HCO₂K was used, **1** was produced in high selectivity and yield (Entries 2 and 3). Although the HCO₂K system gave better selectivity than HCO₂Na, we focused on HCO₂Na from the economic point of view. In the presence of excess **3** (5.0 mmol), *exo*-**1** was produced in 85% yield using HCO₂Na (Entry 4). The author confirmed that using **Pd-Cy** as catalyst, HCO₂Na as the reducing agent, DMF solvent were the best combination for the reductive Mizoroki-Heck reaction.

Table 5-2. Effects of formates on reductive Mizoroki-Heck reaction

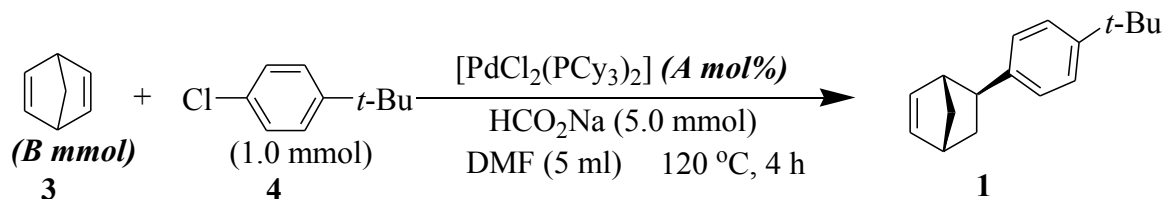


Entry	M	A / mmol	Conv. / %	Select. / %	Yield / %
1	NH ₄	2.0	23	89	20
2	Na	2.0	99	67	66
3	K	2.0	99	84	83
4 ^a	Na	5.0	100	85	85

^a3.0 mol% of Pd-Cy and 5.0 mmol of HCO₂Na were used.

With these promising results in hand, we have optimized the amount of **Pd-Cy** and **3** (Table 5-3). With 0.7 mol % of Pd-Cy, the reaction proceeded with excellent conversion, to give **1** in 92% yield. When the catalyst loading was increased to 3.0 mol %, **1** was given in 95% yield (Entry 5).

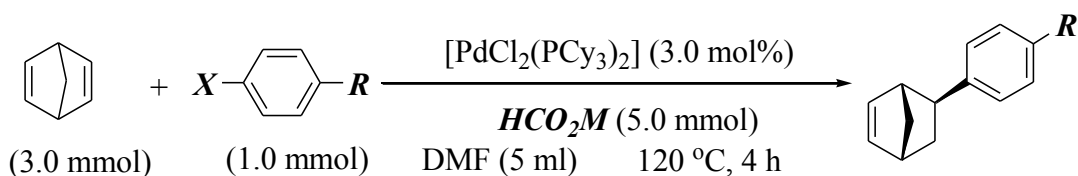
Table 5-3. Reductive Mizoroki-Heck reaction with various amounts of Pd-Cy and **3** versus **4**



Entry	A / mol%	B / mmol	Conv. / %	Select. / %	Yield / %
1	0.1	5.0	42	95	40
2	0.3	5.0	71	96	68
3	0.5	5.0	86	96	83
4	0.7	5.0	99	93	92
5	3.0	10.0	99	96	95

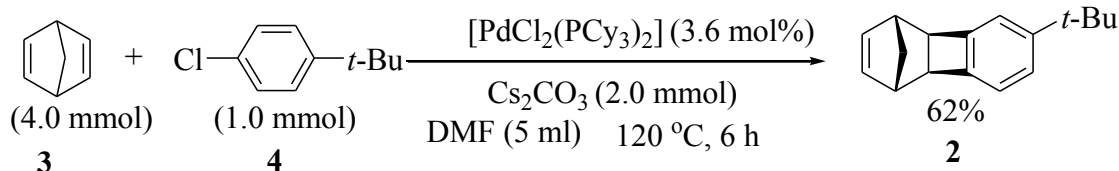
5-4. Reductive Mizoroki-Heck Reaction with Various Aryl Halides and Benzocyclobutene-fused Norbornene Synthesis

Next, we investigated a series of aryl halides for the reductive Mizoroki-Heck reaction. The conversion of aryl halide, *exo*-norbornene's selectivity, and yield are summarized in Table 5-4. As a typical example, we used electron-deficient 4-nitrophenyl halide and electron-donating 4-methoxyphenyl halide in this reaction. The present catalytic system showed tolerance for these substituents, and aryl chloride gave similar results to aryl bromide.

Table 5-4. Reductive Mizoroki-Heck reaction with various aryl halides

Entry	X	R	M	Conv. / %	Select. / %	Yield / %
1	Br	NO ₂	K	100	72	72
2	Cl	NO ₂	Na	100	86	86
3	Br	OMe	K	100	89	89
4	Cl	OMe	Na	83	83	69

When Cs₂CO₃ was used with **Pd-Cy** in the absence of reducing reagent, benzocyclobutene-fused norbornene, 6-*tert*-butyl-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene (**2**) was formed in 62% (Scheme 5-2). The NMR analysis of **2** showed the stereochemistry of **2** being the *exo*-form, according to the plausible reaction mechanism (Scheme 5-3).

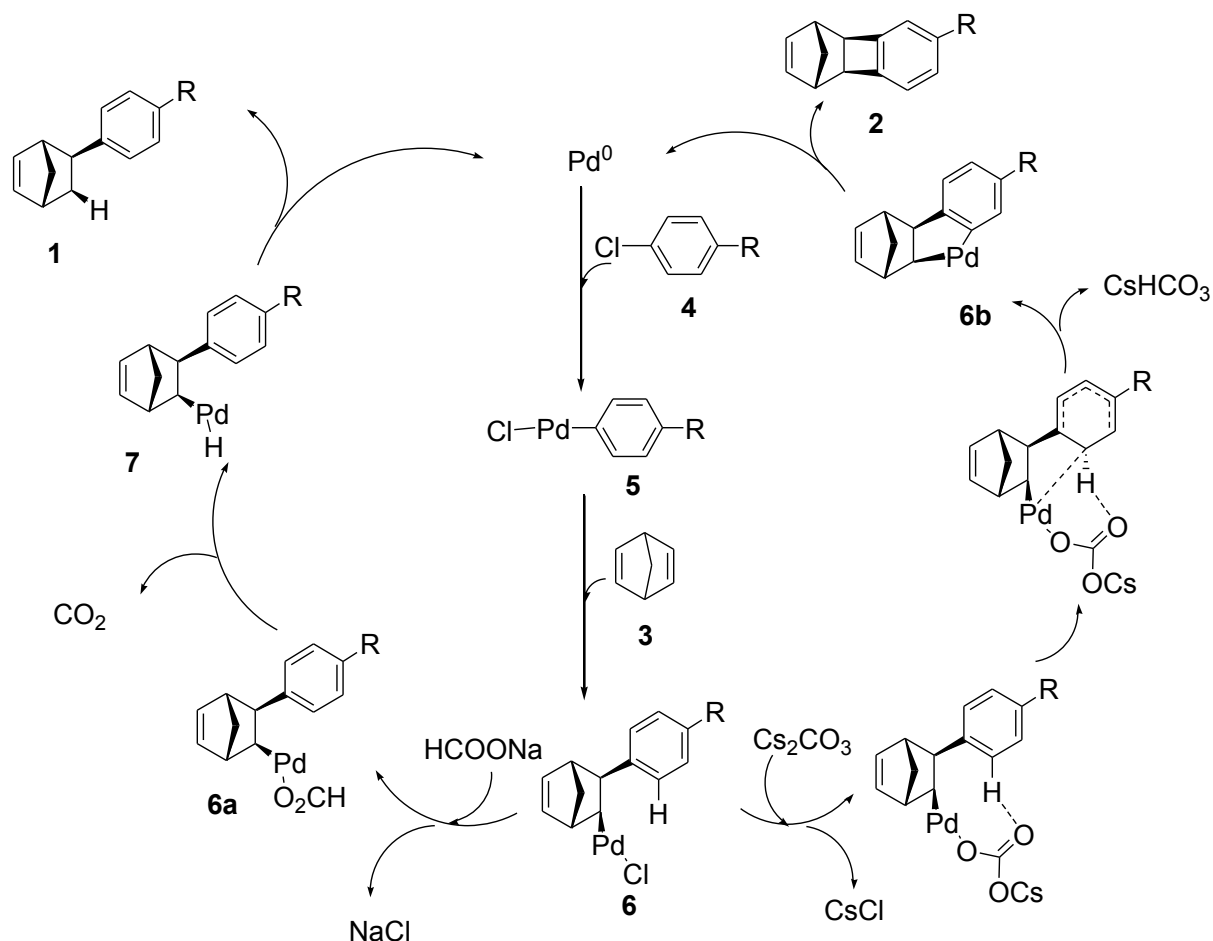
**Scheme 5-2.** Benzocyclobutene-fused norbornene synthesis.

5-5. Plausible Reaction Mechanism

Similar benzocyclobutene-fused norbornenes have been reported in the Mizoroki-Heck reaction,^{15,16} where the key palladacycle intermediates such as **6b**, are formed by orthopalladation of β-arylated norbornylpalladium.¹⁷⁻²⁶

The present reaction mechanism is consistent with Scheme 5-3.^{19,20,22,24,26,27} A Pd(II) species is readily reduced to Pd(0) by a suitable reductant.^{28,29} The oxidative addition of aryl chloride to Pd(0) gives an intermediate **5**. The basic PCy₃ ligand probably promotes the oxidative addition step. Then, norbornadiene inserts *exo* face selectively into the resulting Pd-C bond.⁵ This insertion reaction produces the key intermediate **6**. The resulting chloride ligand is replaced by formate and subsequent decarboxylation yields the hydridopalladium(II)

7. Finally, the reductive elimination releases the *exo*-arylated norbornene **1**. In the absence of a reducing agent, the chloride in **6** is replaced by a carbonate in the presence of Cs_2CO_3 . Such carbonate fragment in Pd(II) is reported to abstract an aromatic proton from the adjacent aryl group by the concerted metalation-deprotonation (CMD) mechanism.²⁷ Finally, the reductive elimination at **6b** produces **2**.^{15,16}



Scheme 5-3. Plausible reaction mechanism. In this Scheme, Pd stands for Pd(PCy₃)_n species.

5-6. Experimental Section

Solvents, aryl halides and Et₃N were used after purification by distillation, stored under nitrogen. HCO₂H, its salt and palladium complexes were used as received. ¹H NMR and ¹³C NMR spectra were recorded on Oxford Instruments (500 MHz) or JEOL (JMT 400 MHz) or Agilent (600 MHz). Chemical shifts are referred to TMS (CDCl₃). Quantitative analysis was done with GC with internal standard.

GC: GL Science GC-4000

Column: Agilent Technology HP-5, Length 30 m, ID 0.32 mm, Thickness 0.25 μm

Oven Condition: 50 $^{\circ}\text{C}$ (hold for 10 min), 5 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$ (hold for 10 min)

Flow rate: 0.5 mL/min (Helium)

General Procedure: Reductive Mizoroki-Heck Reaction

To a 30 ml of two necked flask, Pd catalyst, HCO_2M (M: H, Na, K), Base (Cs_2CO_3 , K_2CO_3 , Na_2CO_3 , Et_3N), X- $\text{C}_6\text{H}_4\text{-R}$ (1 mmol), and 2,5-norbornadiene were introduced. 5 ml of solvent (DMF, DMA, DMSO) was added to the mixture under nitrogen. The resultant mixture was heated at 120 $^{\circ}\text{C}$ and stirred for 4-7 hours. The mixture was cooled to ambient temperature and poured into 30 ml of water. The combined mixture was extracted with diethyl ether (50 ml, 3 times). The organic layer was washed with water and brine. The washed organic layer was dried over MgSO_4 , filtered and condensed in vacuo. The residue was analyzed via GC quantitatively, using internal standard. Also the residue was chromatographed on SiO_2 with hexane-ethyl acetate. The purified compound was determined its chemical structure with NMR analysis.

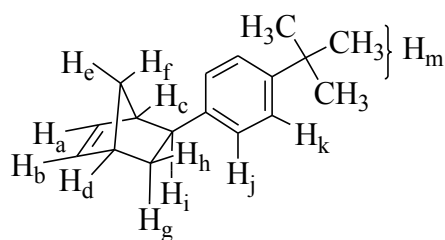
$$\text{Conversion} = [\text{A} - \text{B}] / \text{A}$$

A : Introduced X- $\text{C}_6\text{H}_4\text{-R}$

B : Unreacted X- $\text{C}_6\text{H}_4\text{-R}$

Spectral data***exo*-5-(4-*tert*-Butylphenyl)-2-norbornene [$\text{C}_{17}\text{H}_{22}$] (1)**

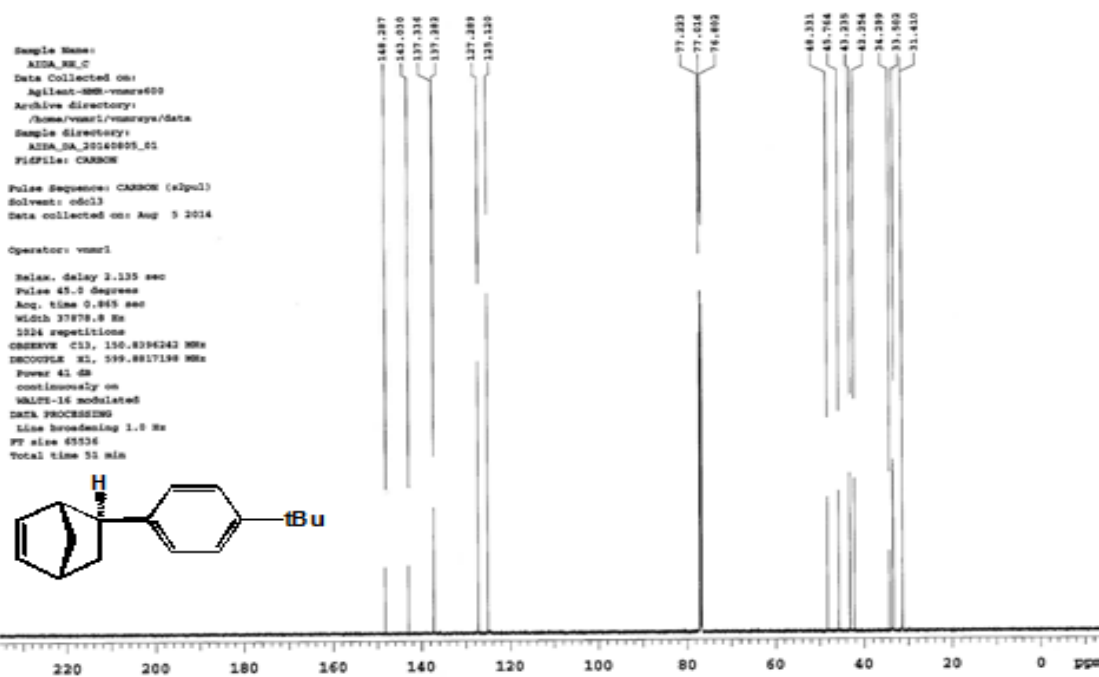
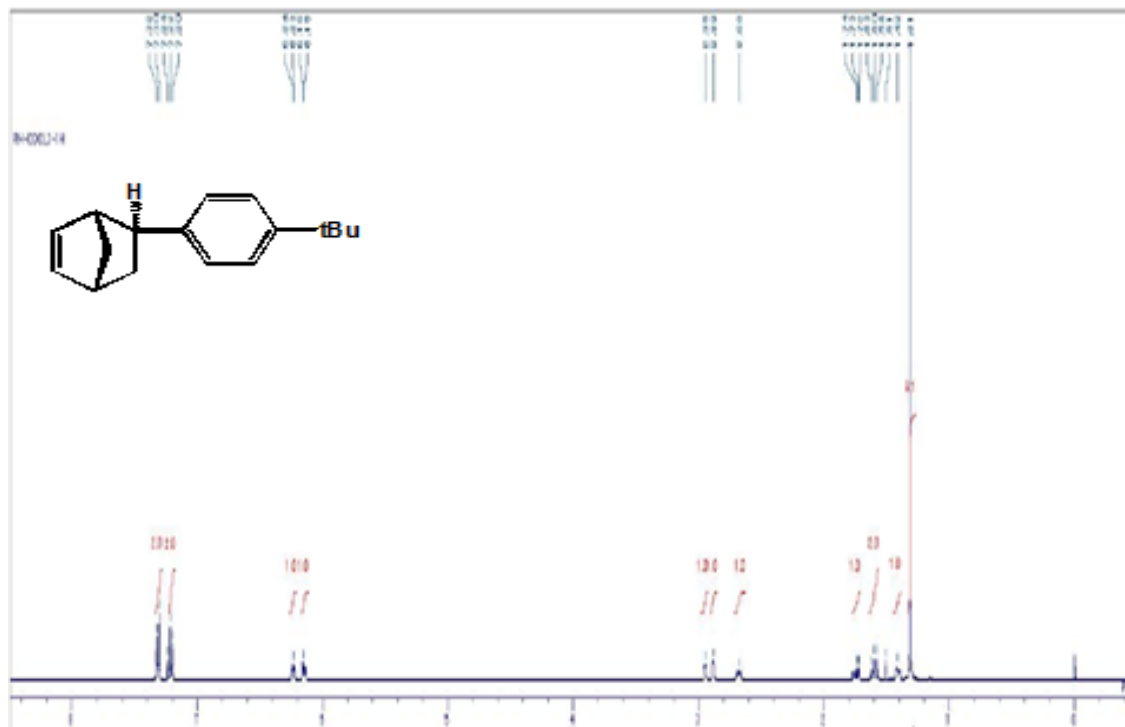
^1H NMR (CDCl_3 , 600 MHz): δ 1.31 (9 H, s, H_m), 1.42 (1 H, m, H_e), 1.51 (1 H, m, H_f), 1.60 (1 H, m, H_g), 1.73 (1 H, m, H_h), 2.68 (1 H, m, H_i), 2.89 (1 H, m, H_c), 2.95 (1 H, m, H_d), 6.16 (1 H, dd, $J = 3.5$ and 8.5 Hz, H_a), 6.23 (1 H, dd, $J = 3.5$ and 8.5 Hz, H_b), 7.22 (2 H, d, $J = 12$ Hz, H_k), 7.30 (2 H, d, $J = 12$ Hz, H_j)



^{13}C NMR (CDCl_3 , 600 MHz): δ 31.4, 33.5, 34.3, 42.3, 43.2, 45.8, 48.3, 125.1, 127.3, 137.3, 137.3, 143.0, 148.3

Palladium-catalyzed 5-exo-Selective Reductive Mizoroki-Heck Reaction of Aryl Chlorides with 2,5-Norbornadiene

FAB-MS: calc. for $[C_{17}H_{23}]^+$: 227.1794; found 227.1795.



Supplemental information determining stereochemistry of norbornene derivatives via ^1H NMR analysis¹²

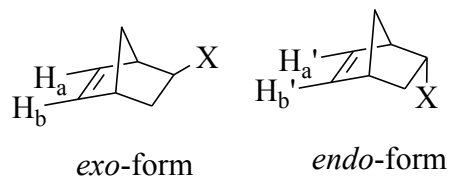
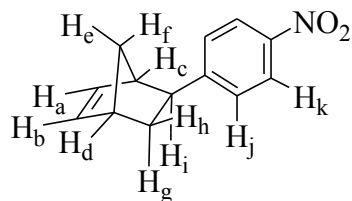


Table 5-5. Chemical Shifts of norbornene derivatives

X	exo / ppm		endo / ppm	
	H _a	H _b	H _a '	H _b '
CO ₂ Me	6.10	6.14	5.92	6.18
COMe	6.13	6.15	5.85	6.15
OMe	5.90	6.16	5.97	6.33
NH ₂	5.95	6.17	6.05	6.44

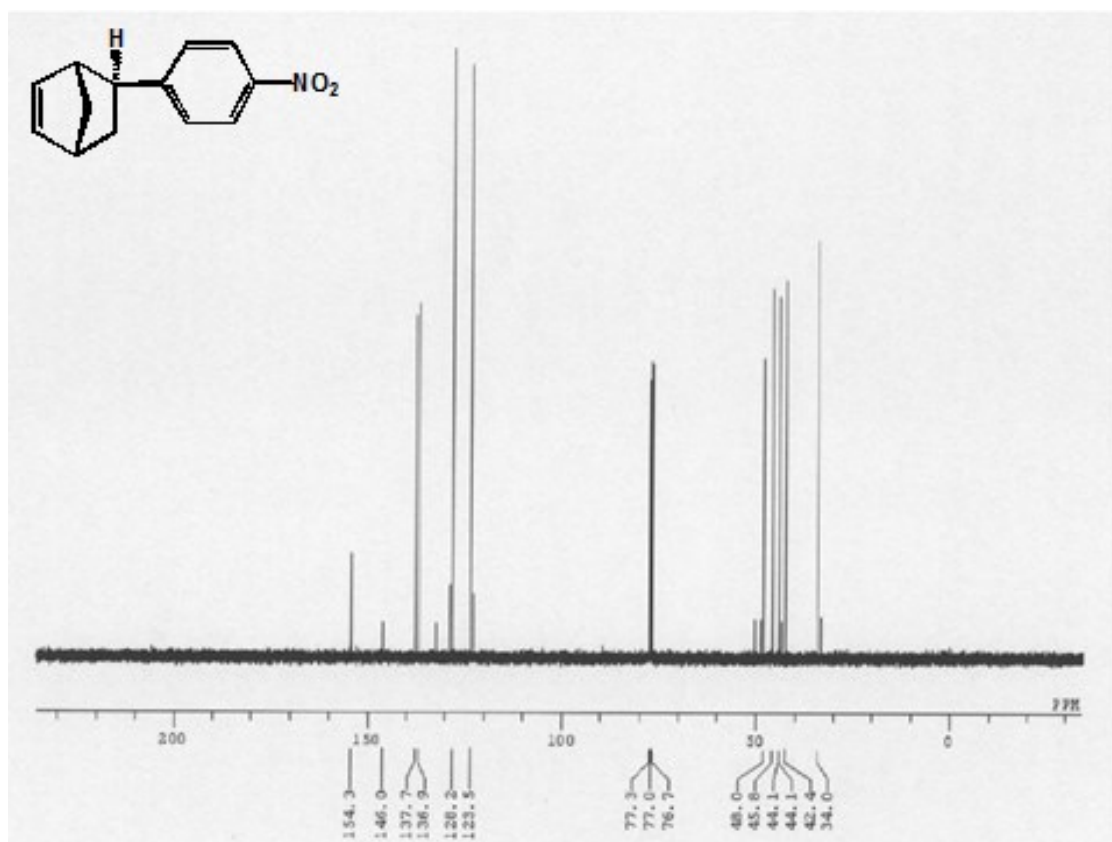
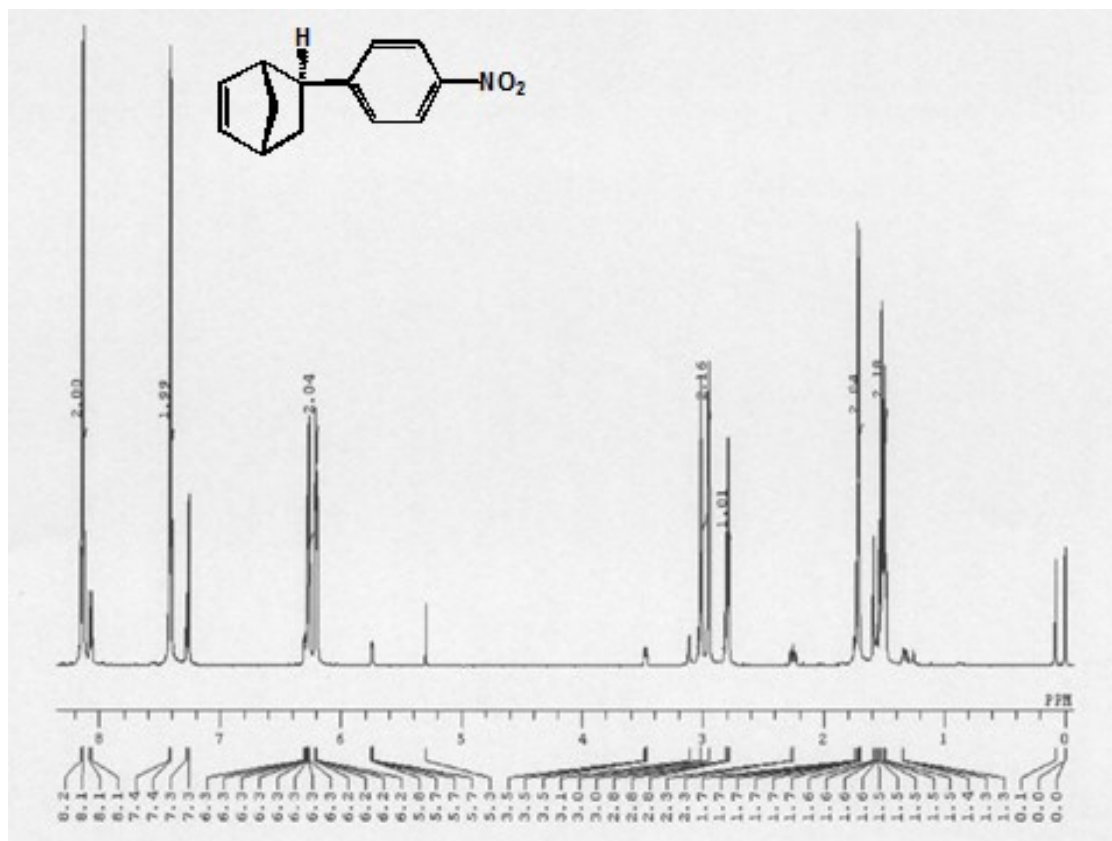
***exo*-5-(4-Nitrophenyl)-2-norbornene**

^1H NMR (CDCl₃, 400 MHz): δ 1.4 (1 H, H_f), 1.5 (1 H, H_e), 1.6 (1 H, H_h), 1.7 (2 H, H_g), 2.8 (1 H, H_i), 2.9 (1 H, H_c), 3.0 (1 H, H_d), 6.2 (1 H, H_a), 6.3 (1 H, H_b), 7.4 (2 H, H_j), 8.2 (2 H, H_k)



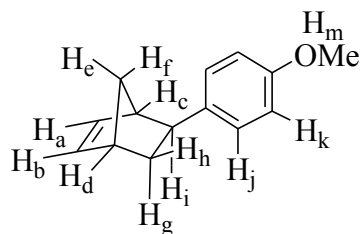
^{13}C NMR (CDCl₃, 400 MHz): δ 34.0, 42.4, 44.1, 45.0, 48.0, 123.5, 128.2, 136.9, 137.7, 146.0, 154.3

Palladium-catalyzed 5-exo-Selective Reductive Mizoroki-Heck Reaction of Aryl Chlorides with 2,5-Norbornadiene

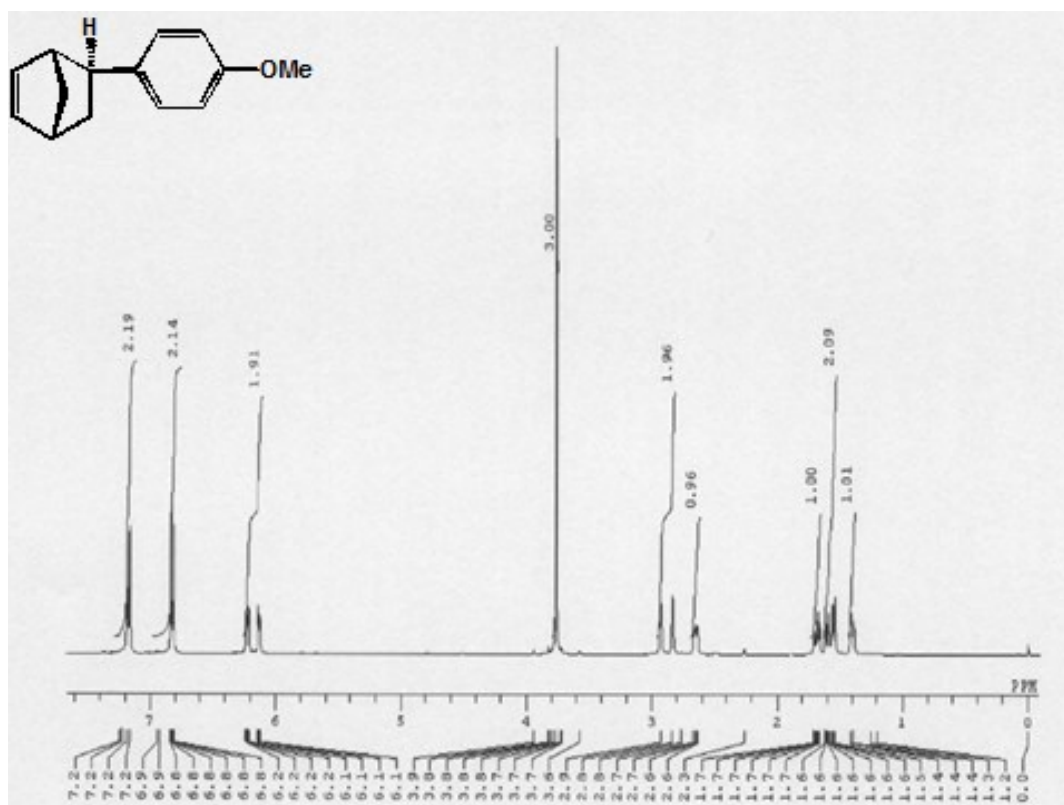


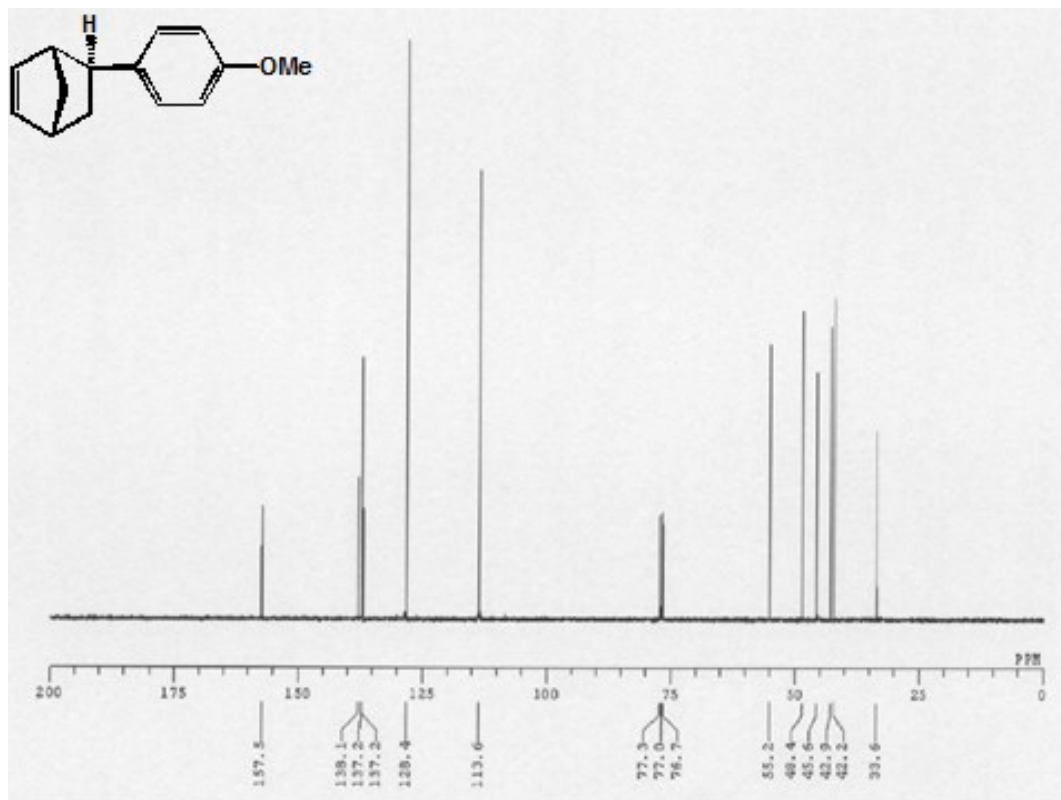
exo-5-(4-Methoxyphenyl)-2-norbornene

^1H NMR (CDCl_3 , 400 MHz): δ 1.2 (1 H, H_f), 1.3 (1 H, H_e), 1.6 (1 H, H_h), 1.7 (1 H, H_g), 2.6 (1 H, H_i), 2.8 (1 H, H_c), 2.9 (1 H, H_d), 3.8 (3 H, H_m), 6.1 (1 H, H_a), 6.2 (1 H, H_b), 6.9 (2 H, H_j), 7.2 (2 H, H_k)



^{13}C NMR (CDCl_3 , 400 MHz): δ 33.6, 42.2, 42.9, 45.6, 48.4, 55.2, 113.6, 120.4, 137.2, 137.3, 138.1, 157.5





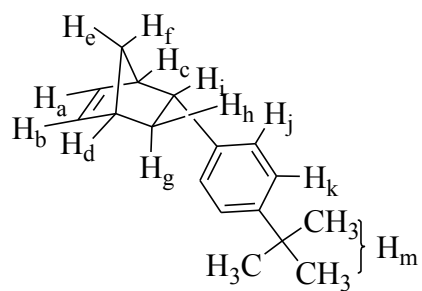
Diels-Alder Reaction

To a 600-ml of autoclave, dicyclopentadiene (8.65 g), 4-*tert*-butylstyrene (10.5 g), and mixed xylene (100 ml) were introduced. The mixture was heated at 160 °C for 6 hours. The mixture was cooled down to ambient temperature and the cooled mixture was condensed in vacuo. The resultant mixture was purified via column chromatography with hexane-ethyl acetate to give 5-(4-*tert*-butylphenyl)-2-norbornene in 20% yield. The purified compound was determined its chemical structure with NMR analysis.

Spectral data

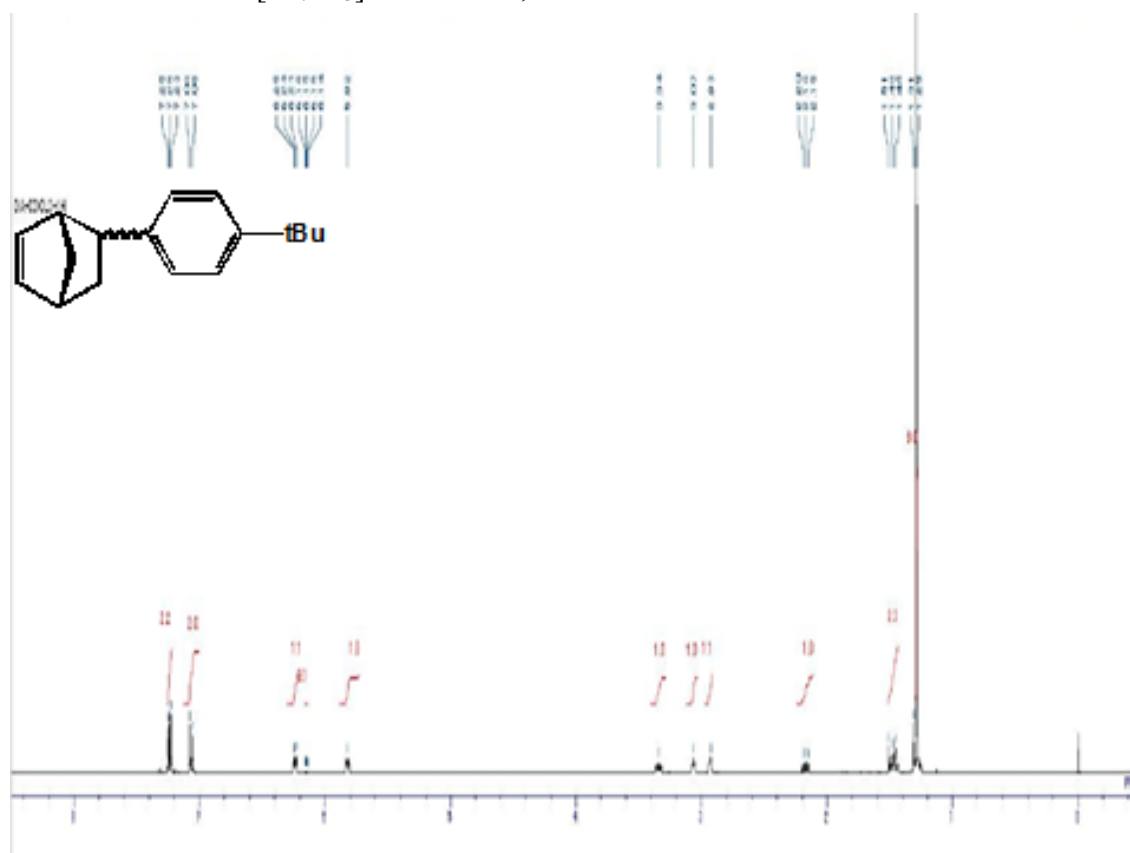
5-(4-*tert*-butylphenyl)-2-norbornene (*exo* : *endo* = 1 : 9) [C₁₇H₂₂]

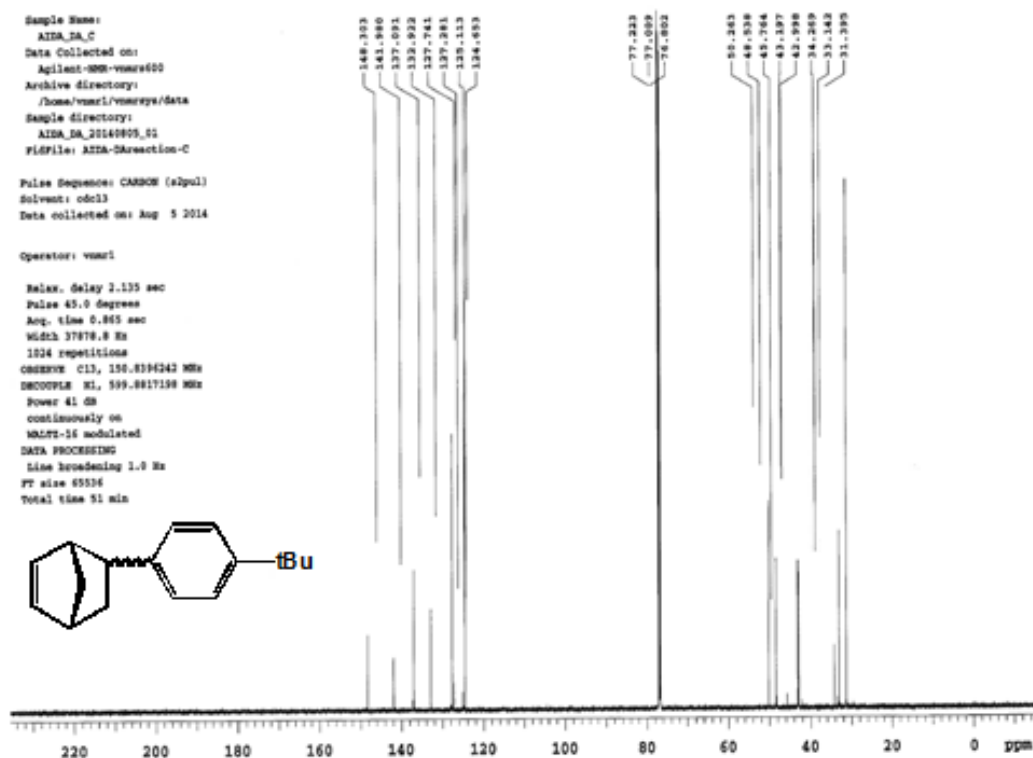
¹H NMR (CDCl₃, 600 MHz): δ 1.29 (9 H, s, H_m), 1.31 (1 H, m, H_e), 1.46 (1 H, m, H_f), 1.51 (1 H, m, H_g), 2.16 (1 H, m, H_h), 2.93 (1 H, m, H_c), 3.07 (1 H, m, H_d), 3.34 (1 H, m, H_i), 5.82 (0.9 H, dd, *J* = 3.5 and 8.5 Hz, H_a, *endo*), 6.16 (0.1 H, *exo*), 6.24 (1 H, dd, *J* = 3.5 and 8.5 Hz, H_b), 7.06 (2 H, d, *J* = 12 Hz, H_k), 7.25 (2 H, d, *J* = 12 Hz, H_j)



¹³C NMR (CDCl₃, 600 MHz): δ 31.4, 33.1, 34.3, 43.0, 43.2, 45.8, 48.5, 50.3, 124.7, 125.1, 127.3, 127.7, 132.9, 137.1, 142.0, 148.3

FAB-MS: calc. for [C₁₇H₂₃]⁺: 227.1794; found 227.1795.





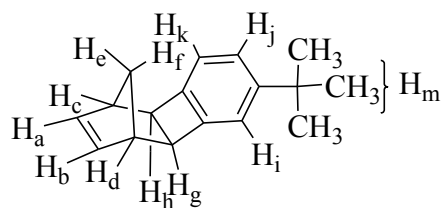
6-tert-Butyl-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene [C₁₇H₂₀] (2)

To a 30 ml of two necked flask, 26.3 mg of [PdCl₂(PCy₃)₂], 667.8 mg of Cs₂CO₃ were introduced. To the mixture, 5 ml of DMF, 168.7 mg of 4-tert-butyl-1-chlorobenzene, 368.6 mg of 2,5-norbornadiene and 170 mg of diethyleneglycohol (internal standard) were added. The mixture was stirred for 6 hours at 120 °C. The mixture was cooled to ambient temperature and poured into 30 ml of water. The combined mixture was extracted with ether (50 ml, 3 times). The organic layer was washed with water and brine. The washed organic layer was dried over MgSO₄, filtered and condensed in vacuo. The residue analyzed via GC quantitatively, using internal standard. Also the residue was chromatographed on SiO₂ with hexane-ethyl acetate to give 6-tert-butyl-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene (2) in 62% yield. The purified compound was determined its chemical structure with NMR analysis.

Spectral Data

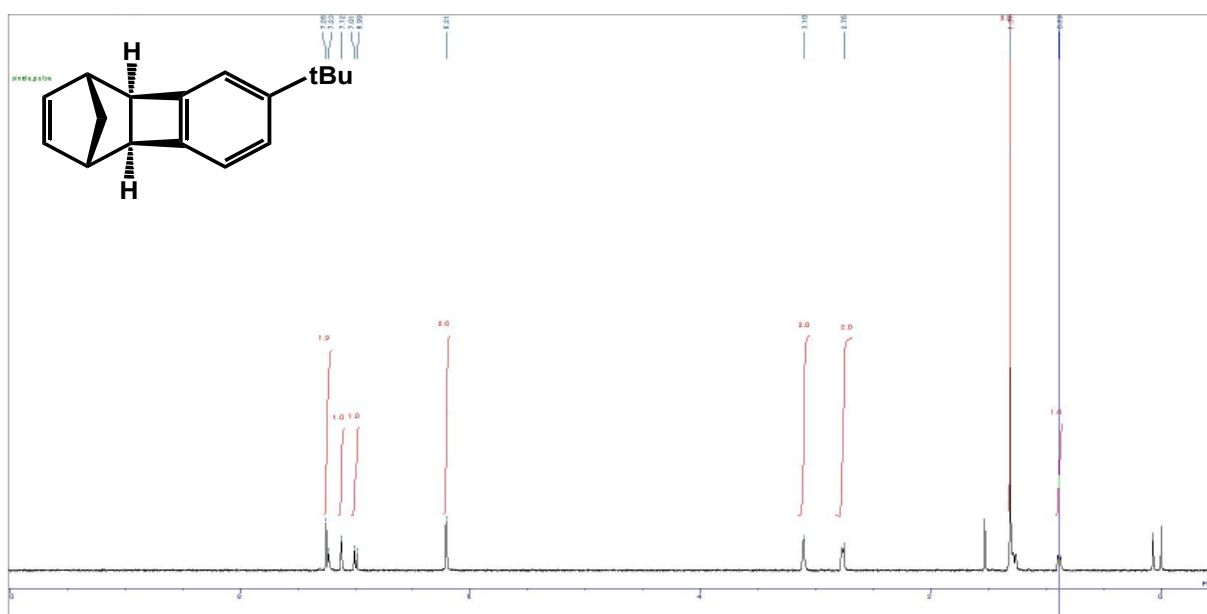
6-tert-butyl-1,4,4a,8b-tetrahydro-1,4-methanobiphenylene

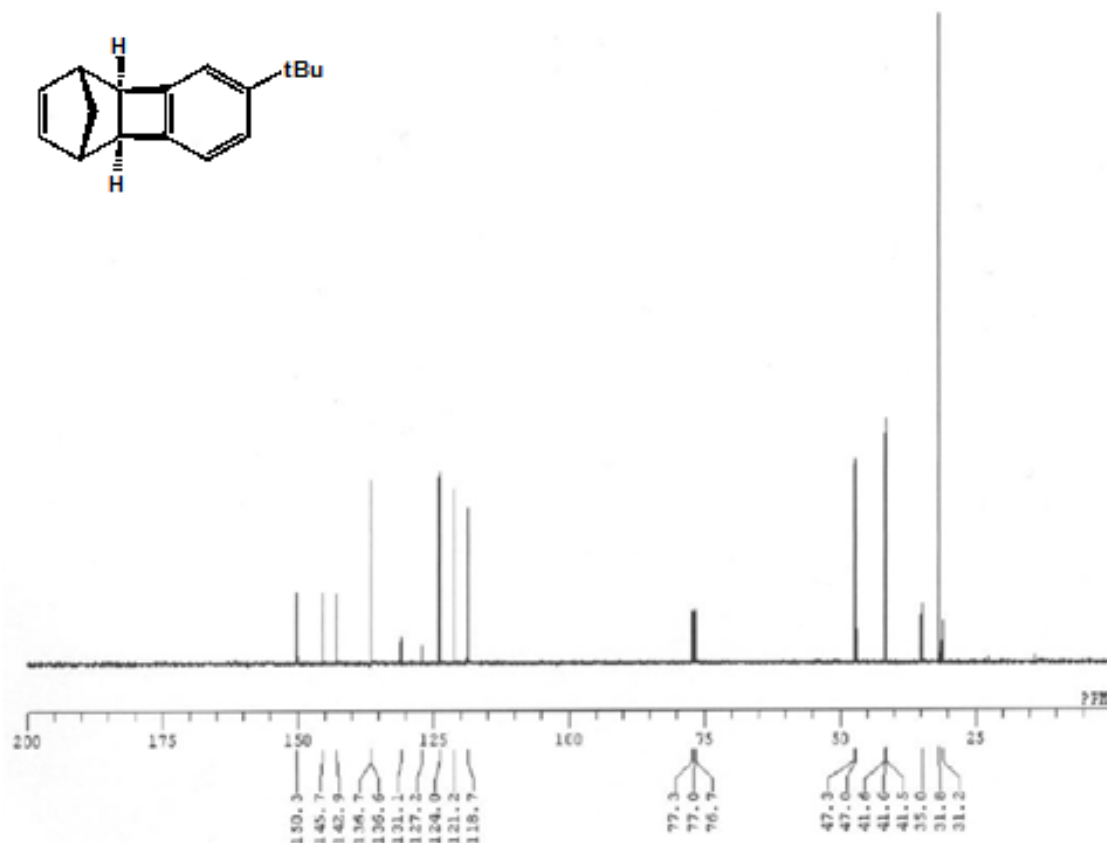
¹H NMR (CDCl₃, 600 MHz): δ 0.89 (1H, m, H_e), 1.31 (9H, s, H_m), 1.31 (1H, m, H_f), 2.76 (2H, m, H_g and H_h), 3.10 (2H, m, H_d and H_e), 6.21 (2H, s, H_a and H_b), 7.01 (1H, d, *J* = 11.0 Hz, H_j), 7.12 (1H, s, H_i), 7.20 (1H, d, *J* = 11.0 Hz, H_k)



^{13}C NMR ($CDCl_3$, 600 MHz): δ 31.6, 35.0, 41.5, 41.6, 41.7, 47.0, 47.3, 110.7, 121.2, 124.0, 136.6, 136.7, 142.9, 145.7, 180.3

FAB-MS: calc. for $[C_{17}H_{20}]^+$: 224.1560; found 224.1560





5-7. Chapter Conclusion

In summary, the reductive Mizoroki-Heck reaction, an effective synthetic method of *exo*-5-(4-*tert*-butylphenyl)-2-norbornene (**1**) from 2,5-norbornadiene and 4-*tert*-butylphenyl chloride, was established. Under the optimized conditions in DMF at 120 °C for 4 hours with [PdCl₂(PCy₃)₂] (3.0 mol%)/HCO₂Na (5.0 mmol), the target *exo*-norbornene **1** was successfully synthesized in 95% yield (99% conversion, 96% selectivity).

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 - 11 dppm: 1,1-bis(diphenylphosphino)methane; dppe: 1,2-bis(diphenylphosphino)ethane; dppp: 1,3-bis(diphenylphosphino)propane; dppb: 1,4-bis(diphenylphosphino)butane; dppf: 1,1'-diphenylphosphinoferrocene; dba: dibenzylideneacetone.
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Chapter 6

Conclusion and Future Perspectives

6-1. Conclusion

6-2. Future Perspectives

6-2-1. High molecular weight PPS

6-2-2. Copolymerization of PhSSPh and ArSSAr

6-2-3. Synthetic applications of sulfonium cations

References

6-1. Conclusion

In this thesis, the author described synthesis of poly(1,4-phenylene sulfide) (PPS) and mechanistic exploration of the oxygen oxidative-polymerization of diphenyl disulfide. In this chapter, the important conclusions derived from this study were summarized.

In Chapter 2, the first solvent- and acid anhydride-free oxygen oxidative-polymerization of diphenyl disulfide (PhSSPh) was successfully carried out at a moderately elevated temperature (above 100 °C). The polymerization mechanism was regarded as a chain growth-type polycondensation, suggesting a “living-like” one. The PPSs obtained under these conditions were identified to have disulfide bonds at the terminal position, by detecting the doubled molecular weight of PPS and PhSSPh via thermal curing. 1,4-Thiophenylene structure was confirmed by IR analysis. These results indicated that the active species, bis(phenylthio)phenyl sulfonium cation ($\text{PhS}(\text{PhSSPh})^+$) added to the *para* position of phenyl sulfide chain selectively, and the sulfur-sulfur-phenyl functional group remained at the terminal position. The experimental results were supported by computational calculation.

In Chapter 3, the first example of strong acid-free oxygen oxidative-polymerization of PhSSPh was established by the vanadyl-tripheylmethylum borate (TrBR_4) catalyst. When utilizing a strong acid with a vanadyl, a proton activates a vanadyl and a conjugated base of strong acid stabilizes cationic species. Triphenylmethylumtetrakis(pentafluorophenyl)borate ($\text{TrB}(\text{C}_6\text{F}_5)_4$) was found to be effective for the polymerization, because triphenylmethylum cation activated a vanadyl, the same role as a proton, and the borate anion, $\text{B}(\text{C}_6\text{F}_5)_4^-$, stabilized the $\text{PhS}(\text{PhSSPh})^+$. Along with the “living-like” behavior suggested in Chapter 2, the smaller amount of the catalyst gave a polymer with higher molecular weight.

In Chapter 4, activation of *N,N'*-(ethylenebis(salicylideneaminate))oxovanadium ($\text{VO}(\text{salen})$) was successfully accomplished at 100 °C to proceed the oxygen oxidative-polymerization of PhSSPh. $\text{VO}(\text{salen})$ was reported to be inert for the polymerization under ambient conditions, because its redox potential was outside of the suitable range to work as an oxidizing agent. At moderately elevated temperature conditions, the redox potential of $\text{VO}(\text{salen})$ was positively shifted enough to be in proper range for the polymerization. Enhancements of catalytic ability of vanadyl compounds, by pressurized oxygen and 2,3,5,6-tetrabromo-*para*-benzoquinone (bromanil), also successfully accelerated the oxygen oxidative-polymerization to give a high molecular weight of PPS.

In Chapter 5, palladium-phosphine complex-catalyzed reductive Mizoroki-Heck reactions were carried out under the same aim of organic synthetic applications utilizing transition metal catalysts and without using acid anhydride.

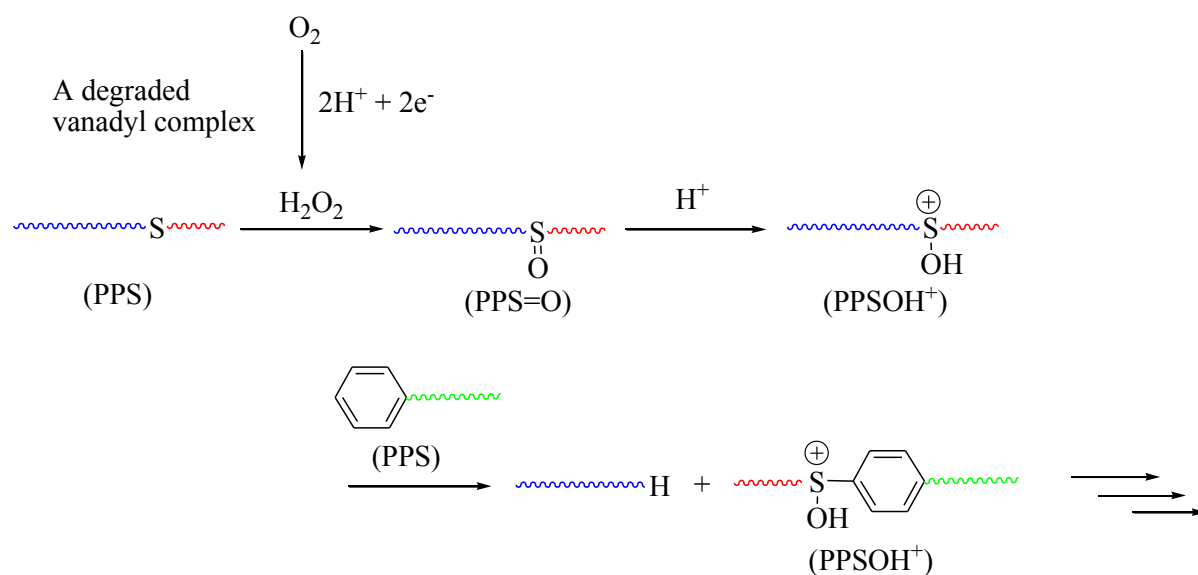
Dichlorobis(tricyclohexylphosphine)palladium(II) was successfully found to catalyze the Mizoroki-Heck reaction, between unreactive aryl chloride (Ar-Cl) and 2,5-norbornadiene (NBD), to give 5-*exo*-aryl-2-norbornene in excellent selectivity and yield in the presence of a reducing agent, represented by formates. In the absence of reducing agents, a benzocyclobutene-fused norbornene was obtained from Ar-Cl and NBD in the modest yield, plausibly via a concerted metalation-deprotonation mechanism.

6-2. Future Perspectives

6-2-1. High molecular weight PPS

The author anticipates that the PPS synthesis via the oxygen oxidative-polymerization will be developed into “kilogram scale” stage in near future. But until now, the M_w of the PPS obtained by the polymerization remains around 6×10^3 , still lower than that of commercially available PPS ($M_w > 20,000$). Further investigation of increasing molecular weight is crucial. Though the polymerization mechanism was regarded as a chain growth-type polycondensation, the polymer yield and the molecular weight reached a ceiling. There might be an equilibrium between polymerization and depolymerization, or any other cleaving reactions of polymer chains. To avoid undesired reactions is requisite for increasing the molecular weight.

Investigation of the undesired reaction mechanism seems to be the most important subject of future research. The author presumes that the undesired reactions could be caused by a degraded catalyst. Though these results are unpublished, the PPS obtained via the oxygen oxidative-polymerization contained a small amount of oxygen, according to an elementary analysis. During the polymerization, a vanadyl [$V^{IV}-O-V^V$] oxidizes PhSSPh and the reduced vanadyl ($[V^{IV}-O-V^{III}]$) is oxidized by O_2 . Then the total 4-electron reduction of O_2 is completed, by eliminating H_2O . If the vanadyl is converted to a different type of vanadium complexes, there may no longer be the 4-electron transfer by the vanadium complex. On the occasion of 2-electron reduction of O_2 , hydrogen peroxide (H_2O_2) could be formed, which could oxidize sulfides to sulfoxides or sulfones. As a protonated sulfoxide is a strong electrophile,¹ it could attack on an aromatic ring of the polymer chain. At the same time, the polymer chain may be cleaved to form PPS with low molecular weight (Scheme 6-1). To prevent the estimated undesired reaction, the author expects, for example, adding of a fresh catalyst could suppress the undesired reactions.



Scheme 6-1. Estimated mechanism of PPS cleavage caused by the degraded vanadyl complex.

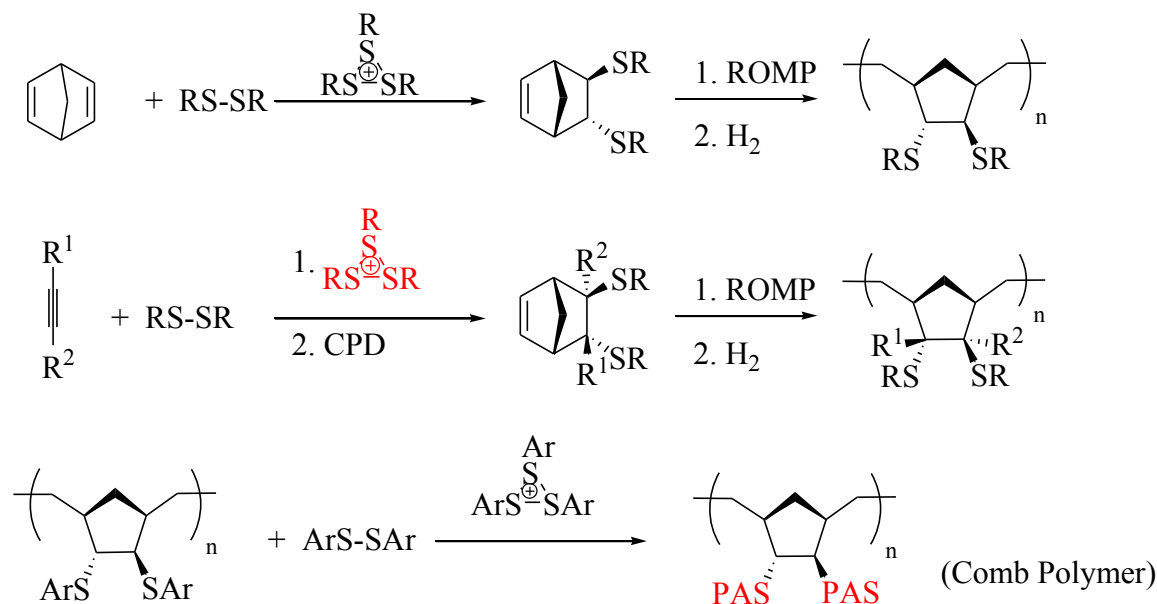
Based on the results in Chapters 2-4, enhancements of catalytic ability and study on the amount and timing of the added catalyst or monomer or oligomer would be effective to increase the molecular weight. Kinetics studies of the polymerization, the depolymerization, and any other cleaving reactions of polymer chain, are very important, because the elementary reactions are functions of the reaction temperature and the concentrations of monomer, oligomer, catalyst, and oxygen. The ideal condition, for accelerating the polymerization and suppressing the undesired reactions, could be found by adjusting the above mentioned factors.

6-2-2. Copolymerization of PhSSPh and ArSSAr

A small amount of 1-alkene (e.g. 1-butene, 1-hexene and 1-octene) is copolymerized with ethylene to improve properties, especially the transparency and moldability of polyethylene. The copolymer is called “linear low density polyethylene” (LLDPE). Poly(1,4-arylene sulfides) (PASs) are obtained via oxidative polymerization of diaryl disulfides (ArSSAr). ArSSAr (Ar = monomethyl or dimethyl substituted phenyl) gave similar redox potentials as that of PhSSPh,² so ArSSAr could be co-polymerized with PhSSPh. PAS was reported to be an amorphous transparent polymer,² but in contrast, PPS was a crystalline polymer. Similar to LLDPE, the copolymer of PhSSPh and ArSSAr could be a transparent polymer. The copolymer may have high heat resistance, in addition to transparency, because T_g of PAS is higher than that of PPS.³ Thus, the copolymer could have unique properties.

6-2-3. Synthetic applications of sulfonium cations

As one of applications of utilizing sulfonium cations, the following polymers, shown in Scheme 6-3, are attractive. Because of high sulfur concentration in the polymers having cycloolefin structure, the polymer is suspected to be highly transparent and have a high refractive index. An electrophilic bisalkylthiolation^{4,5} of dialkyl disulfide to alkynes or 2,5-norbornadiene can be applied to prepare the monomers (2,3-bisalkylthio-5-norbornene). The norbornene can be converted to its polymer via ring opening metathesis polymerization. Through oxidative-polymerization of diaryl disulfide to the polymer, poly(arylene sulfides) chain can be grown on “SAr” of the polymer forming a comb polymer, which is expected to have new characteristics because of mixture of polyolefin and polyarylene sulfide structure.



Scheme 6-3. Plausible preparative procedure of sulfur containing cycloolefin polymers.

As the described above, the oxidative-polymerization has a wide range of applications. The author anticipates that the applications could become a reality through further developments of the polymerization technique.

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List of Publications

1. Fuyuki Aida, Yohei Takatori, Daichi Kiyokawa, Kentaro Nagamatsu, Hiroyuki Nishide, Kenichi Oyaizu, “Poly(1,4-phenylene sulfide) (PPS) Synthesis via Oxidative Polymerization of Diphenyl Disulfide: Mechanistic Insight into the Selective Formation of 1,4-Thiophenylene Chain”, *Chemistry Letters* **2015**, *44*, 767.
2. Fuyuki Aida, Souske Yamaguchi, Yohei Takatori, Kentaro Nagamatsu, Daichi Kiyokawa, Kenichi Oyaizu, Hiroyuki Nishide, “Vanadyl-TrBR₄-Catalyzed Oxidative Polymerization of Diphenyl Disulfide”, *Macromolecular Chemistry and Physics* **2015**, *216*, 1850.
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4. Fuyuki Aida, Kenichi Oyaizu, “Emerging Organosulfonium Electrophiles as Unique Reagents for Carbon-Sulfur Bond Formation: Prospects in Synthetic Chemistry of Organosulfur Compounds”, *Chemistry Letters (Highlight Review)* **2016**, *45*, 102.
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1. Hiroyuki Nishide, Kenichi Oyaizu, Fuyuki Aida, Takaya Matsumoto, “Method for manufacture of polyarylene sulfide with improved molecular weight”, WO 2013133424.
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1. Fuyuki Aida, Hisashi Sone, Ryuhei Ogawa, Takeharu Hamaoka, and Isao Shimizu, “Palladium-catalyzed 5-*exo*-Selective Reductive Mizoroki-Heck Reaction of Aryl Chlorides with 2,5-Norbornadiene”, 62nd Symposium on Organometallic Chemistry, P3-68 (2015. 9, Osaka, Japan).

Acknowledgements

The present thesis is the collection of the studies, which have been carried out under the direction of Professor Dr. Hiroyuki Nishide and Professor Dr. Kenichi Oyaizu, Department of Applied Chemistry in Waseda University, during 2014-2016. The author expresses the greatest acknowledgement to Professor Dr. Hiroyuki Nishide and Professor Dr. Kenichi Oyaizu for their invaluable suggestions, uncountable pieces of advice, discussion, and continuous encouragements throughout this work. The author thanks Associate Professor Dr. Seijiro Hosokawa for his effort as a member of the judging committee for the doctoral thesis.

The author also expresses his sincere gratitude to Professor Dr. Yoshinori Nishikitani (Waseda Univ.) for his valuable advice and encouragements.

The author feels very indebted to all active collaborators, Mr. Souske Yamaguchi, Mr. Shota Otani, Mr. Yohei Takatori, Mr. Daichi Kiyokawa, Mr. Kentaro Nagamatsu, Mr. Shota Tani, Mr. Keisuke Shinomiya, Mr. Minato Aoki, Mr. Naoto Takasu, Mr. Tomoya Yamazaki, and Ms. Yoko Tanaka. Without their efforts, the thesis could not be accomplished.

The author expresses his acknowledgement to all members in Nishide-Oyaizu laboratory.

The author also expresses his sincere gratitude to Professor Dr. Nobuhiro Kanomata (Waseda Univ.), Professor Dr. Kazuo Nagasawa (Tokyo Univ. of A & T), Professor Dr. Masafumi Hirano (Tokyo Univ. of A & T), Professor Dr. Fumitoshi Kakiuchi (Keio Univ.) , Professor Dr. Akiharu Satake (Tokyo Univ. of Science) and former Professor Dr. Tadashi Nakata (Tokyo Univ. of Science) for their encouragements to pursue a Ph.D.

The author expresses his gratitude to all members of JX Nippon Oil & Energy Corporation. Especially, he expresses great thanks to Dr. Jinichi Igarashi for his encouragement for studying chemistry as a doctoral thesis on weekends. The author also expresses great thanks to Mr. Yukinori Kude for his support of the collaborative work between Waseda University and JX Nippon Oil & Energy Corporation.

The author also expresses his gratitude to the late Professor Dr. Isao Shimizu (Waseda Univ.) for his encouragement to study chemistry again as a doctoral thesis. Without his guidance, the author could not have had much interest in organic chemistry. Regretfully, he passed away on October 30th in 2014. The author expresses heartfelt condolence for him.

Finally, the author would like to express his hearty gratitude to his family and friends. Their mental support reassured him.

July 2016
Fuyuki Aida