Macromolecules 1993, *26*, 3432–3437

Oxovanadium-Catalyzed Oxidative Polymerization of Diphenyl Disulfides with Oxygen

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Received January 21, 1993; Revised Manuscript Received March 23, 1993

ABSTRACT: Oligo(*p*-phenylene sulfide) is synthesized through oxygen oxidative polymerization of diphenyl disulfide catalyzed by vanadyl acetylacetonate. The mechanistic studies reveal that two redox cycles [V(III)/V(IV) and V(IV)/V(V)] give rise to catalysis through a 2-electron transfer between diphenyl disulfide and molecular oxygen. The VO catalysts act as an excellent electron mediator to bridge a 1.0-V potential gap between the oxidation potential of disulfides and the reduction potential of oxygen. The VO-catalyzed oxygen oxidative polymerization provides pure oligo(*p*-phenylene sulfide)s containing an S–S bond. The polymeric product is of low molecular weight due to the insolubility of poly(*p*-phenylene sulfide) under these experimental conditions.

Introduction

Facile oxidative polymerization utilizing the abundant and cheap oxidant oxygen to make aromatic polymers such as high-performance engineering plastics and electroconductive polymers provides a desirable clean process for upgrading the value of a material, *e.g.*, the commercial production of poly(2,6-dimethyl-1,4-phenylene oxide) through oxygen oxidative polymerization of 2,6-dimethylphenol with a copper amine catalyst.[1,2]

Vanadium complexes are of considerable interest not only in complex chemistry but also as redox catalysts and in molecular oxygen chemistry. The redox chemistry of vanadium complexes (3, 4, and 5 valence) bridges a large potential gap between oxygen and aromatic compounds with high oxidation potential such as diphenyl disulfide, pyrrole, thiophene, and benzene. It is an excellent electron mediator because the V(III) and V(V) whose redox potentials are located in the potential gap act as powerful reducing and oxidizing agents.

Our present work reveals that a novel catalysis by vanadyl complexes is applicable to the synthesis of oligo(*p*-phenylene sulfide) (OPS) containing a S–S bond by an oxygen oxidative polymerization of diphenyl disulfide through electron transfer. Poly(*p*-phenylene sulfide) (PPS) possesses high chemical resistance, good moldability, and electrical conductivity when doped, even when it is of low molecular weight. OPSs can also provide many grades[4] of PPS when mixed or reacted with PPS; *i.e.*, low molecular weight PPS improves the moldability due to the lower melt flow index. Commercially available PPS has been prepared by high-pressure and high-temperature processes,[5–9] *e.g.*, polycondensation of sodium sulfide and *p*-dichlorobenzene.[10]

We report here our successful attempts to synthesize OPSs through oxygen oxidative polymerization catalyzed by vanadyl complexes. Spectroscopic and electrochemical studies of vanadyl complexes in an acidic environment were performed to examine the electron-transfer mechanism.

Experimental Section

Materials. Diphenyl disulfide (99%, Kantoh Chemical Co.) was purified by recrystallization from ethanol, dried *in vacuo* for 1 day at 30 °C, and obtained as white needles (mp 59 °C). Bis(2,5-dimethylphenyl) disulfide was prepared in alkaline methanol by the oxidation of the corresponding thiophenol with I_2. Bis(3,5-dimethylphenyl) disulfide was prepared by the Leuckart reaction[11] from the corresponding aniline as a starting material. The structures of these monomers were confirmed by spectroscopic measurements before the polymerization. The purities of the disulfides were over 99.8% as measured by gas chromatography. 1,1,2,2-Tetrachloroethane, dichloromethane, and nitromethane were purified by distillation twice in the usual manner. Bis(2,4-pentanedionato)oxovanadium(IV) ($VO(acac)_2$, vanadyl acetylacetonate) was obtained from Tokyo Kasei Co. and recrystallized from benzene. Bis(1-phenyl-2,4-butanedionato)oxovanadium ($VO(Bzac)_2$), (tetraphenylporphinato)oxovanadium (VOTPP), and tris(2,4-pentanedionato)vanadium ($V(acac)_3$) were synthesized by previously reported methods.[12–14] Trifluoromethanesulfonic acid was obtained from 3M Co. with 97% purity and was used under a dry argon atmosphere without further purification. Trifluoroacetic acid and its anhydride (reagent grade) were obtained from Kantoh and were used with the same treatment as trifluoromethanesulfonic acid. Tetrabutylammonium trifluoromethanesulfonate (Aldrich Co.) was used as a supporting electrolyte after recrystallization from dichloromethane–ether and drying *in vacuo* for 1 day at 100 °C.

Polymerization Procedure. A typical procedure was as follows. Vanadyl acetylacetonate (0.066 g, 5 mmol/L), trifluoromethanesulfonic acid (0.075 g, 10 mmol/L), and trifluoroacetic anhydride (2.1 g, 0.2 mol/L) were dissolved in 1,1,2,2-tetrachloroethane (40 mL) in a closed vessel maintained at 20 °C. The vessel was kept airtight. The mixture was stirred for 1 h under a dry argon atmosphere before polymerization. The atmosphere in the vessel was then replaced by oxygen. A solution of diphenyl disulfide (1.09 g, 0.1 mol/L) in 1,1,2,2-tetrachloroethane (10 mL) was added.

The reaction was carried out for 40 h under an oxygen atmosphere with constant stirring at 20 °C. During the polymerization, a white powder precipitated in the solution. After the reaction, the mixture was poured into 200 mL of methanol containing 5% hydrochloric acid. The precipitate was collected and washed repeatedly with methanol and water.

The polymerization of bis(3,5-dimethylphenyl) disulfide and bis(2,5-dimethylphenyl) disulfide was carried out under the same conditions. In this polymerization trifluoroacetic acid was used instead of trifluoromethanesulfonic acid. The concentration of the acid was 1 mol/L (1.14 g).

Data for poly(*p*-phenylene sulfide): CP-MAS ^{13}C NMR δ 129.1, 131.5 (phenyl C); IR (KBr, cm^{-1}) 3050 (ν_{C-H}), 1393, 1470, 1570 ($\nu_{C=C}$), 818 (δ_{C-H}), 480, 550, 690, 740, 1010, 1070, 1090; X-ray diffraction pattern (Cu Kα) 2θ = 19, 21; MS (*m/e*) 756, 648, 540,

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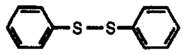
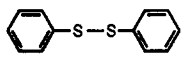
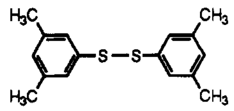
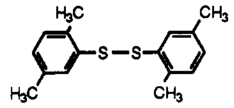
0024-9297/93/2226-3432$04.00/0

Table I. VO-Catalyzed Oxidative Polymerization of Diphenyl Disulfides at 20 °C under Acidic Environments

monomer	oxidation peak potential (V vs Ag/AgCl)	solvent	acid	T_g (°C)	OPS yield (wt %)	OPS $\bar{M}_w$
	1.65	$(CHCl_2)_2$	CF_3SO_3H	58	92	5450
	1.65	CH_2Cl_2	CF_3COOH	-	76	1890
	1.4	CH_2Cl_2	CF_3COOH	198	93	9200
	1.5	CH_2Cl_2	CF_3COOH	298	98	6790

434, 326, 218, 110; M_w = 5450, M_n = 1050; T_m = 220, 224 °C, T_{ch} = 119 °C, T_g = 58 °C.[15] Anal. Calcd for C_6H_4S: C, 66.67; H, 3.7; S, 29.63. Found: C, 66.81; H, 3.65; S, 29.12.

Data for poly(2,6-dimethylphenylene sulfide): ^{13}C NMR ($CDCl_3$, ppm, 400 MHz) δ 125.1, 127.2, 140.1, 144.3 (phenyl C), 21.9 (methyl C); ^1H NMR ($CDCl_3$, ppm, 400 MHz) δ 6.7 (s, 2H), 2.3 (s, 6H); IR (KBr, cm^{-1}) 2850, 2920, 2950, 2975, 3040, (ν_{C-H}), 1370, 1450, 1570 ($\nu_{C=C}$), 860, 880 (δ_{C-H}); MS (m/e) 682, 544, 408; M_w = 9200; T_g = 198 °C. Anal. Calcd for C_8H_2S: C, 70.54; H, 5.92; S, 23.54. Found: C, 70.47; H, 5.93; S, 23.50.

Data for poly(2,5-dimethylphenylene sulfide): CP MAS ^{13}C NMR δ 124, 132, 141 (phenyl C), 20 (methyl C); IR (KBR, cm^{-1}) 2850, 2910, 2960 (ν_{C-H}), 1450, 1470, 1590 ($\nu_{C=C}$), 880 (δ_{C-H}); MS (m/e) 544, 408; M_w = 6790; T_g = 298 °C. Anal. Calcd for C_8H_2S: C, 70.54; H, 5.92; S, 23.54. Found: C, 70.44; H, 5.98; S, 23.45.

Kinetics of Oxygen Oxidative Polymerization. The oxygen consumption was determined as follows. Vanadyl acetylacetonate (0.033 g, 2.5 mmol/L), trifluoromethanesulfonic acid (0.038 g, 5 mmol/L), and trifluoroacetic anhydride (2.1 g, 0.2 mol/L) were dissolved in 1,1,2,2-tetrachloroethane (40 mL) in a closed vessel maintained at 20 °C and were mixed for 1 h until a steady state was reached under a dry argon atmosphere. A similar vessel equipped with a manometer and a buret was connected to it with a tube. The atmosphere in the vessel was replaced by oxygen. The whole instrument was kept airtight. A solution of diphenyl disulfide (1.09 g, 0.1 mol/L) in 1,1,2,2-tetrachloromethane (10 mL) was added. 1,1,2,2-Tetrachloromethane was carefully added from a buret to the second vessel to keep the pressure at 1 atm. Oxygen consumption was measured from the net amount of tetrachloromethane added during the reaction.

Electrochemical Measurements. Electrochemical measurements were carried out in a two-compartment electrochemical cell kept under a dry argon atmosphere. A platinum disk (28.3 mm^2) and platinum wire (ϕ = 0.2 mm, l = 200 mm) were used as the working and auxiliary electrodes, respectively. The reference electrode consisted of an Ag/AgCl electrode in dichloromethane solution containing 0.1 mol/L tetrabutylammonium trifluoromethanesulfonate. The electrode junction was a small soft glass cracked bead sealed into a Pyrex tube and was positioned in a Luggin capillary in the cell assembly. The electrode potential was determined at 0.21 V vs NHE by the adjustment with a ferrocene–ferrocenium(+) redox couple. The potential and current density were controlled by a Nikko Keisoku DPGS-1 dual potentiogalvanostat and a Nikko Keisoku NFG-3 function generator. The voltammograms were recorded on a Graphtec WX2400 *X–Y* recorder. The disk electrode was rotated by a Nikko Keisoku SC-5 motor speed controller in rotating disk voltammetry. Cyclic voltammetry was measured at a scanning rate of 50 mV/s. In rotating disk voltammetry, the rotating rate of the electrode was 1000 rpm and the scanning rate was 5 mV/s. Chronopotentiometry was carried out at a current density of -200 $\mu A/cm^2$ controlled by the above instruments.

Measurements. The ^{51}V NMR spectrum was obtained on a JEOL 400-MHz FT-NMR GXS400. Neat $VOCl_3$ was used as a reference sample of 0 ppm. The conventional CP-MAS spectrum was obtained by spin-locked cross-polarization established through a Hartman–Hahn method conition[16] in the same NMR spectrometer. Infrared spectra were determined on a JASCO FT-IR 5300 having 2-cm^{-1} resolution using a potassium bromide pellet. UV–vis spectra were obtained on a SHIMAZU UV-2100 spectrophotometer connecting a NEC Vm-3 computer. Melting points were determined on a SEIKO thermal analyzer SSC/550 with a heating rate of 20 °C/min. In the case of the resulting OPS the sample for the heating scan (ca. 10 mg) was melted at 265 °C for 2 min and then quenched on a metal block cooled in dry ice, giving the T_g, the crystallization from the glass, T_{ch}, and T_m. The molecular weight of the polymer was measured using high-temperature GPC (Senshu Scientific Co. Ltd., SSC VHT-7000) with 1-chloronaphthalene as an eluent. Shoudex GPC columns (AT-80M/s) were used for the analysis. The operating temperature was 200 °C with a flow rate of 1.0 mL/min of 1-chloronaphthalene. The detector was a UV–vis spectrophotometer (Senshu Scientific Co. Ltd., S-3750, 354 nm). The purity of the polymer was analyzed by inductively coupled plasma emission spectroscopy (ICAP-575II, Nippon Jarrell-ash Co., Ltd.). Mass spectra were obtained using an ionization energy of 20 eV on a JEOL Model JMS-DX300 spectrometer.

Results and Discussion

Structures. In our attempts to catalyze the oxygen oxidative polymerization of diphenyl disulfide to oligo(*p*-phenylene sufide) (OPS) through an electron transfer (Table I), a catalytic amount of vanadyl acetylacetonate ($VO(acac)_2$) was allowed to react with diphenyl disulfide in the presence of acids such as trifluoromethanesulfonic acid and trifluoroacetic anhydride[17] in dichloromethane under air at room temperature. A white powder separated out over time. The polymer was isolated in >95% total yield (dichloromethane-insoluble part ca. 85% of the total) as a white, highly pure powder having the empirical formula $C_6H_4S_1$.

The polymer does not contain a detectable amount of vanadium, as confirmed by inductively coupled plasma emission spectroscopy. The PPSs prepared by a polycondensation procedure are usually contaminated with metal salt and nitrogen.[18,6,10] However, the oxidative polymerization provides pure PPS without salt contamination (Na ion <5 ppm).

An OPS structure composed of a 1,4-phenylene unit as the main structure was confirmed by spectroscopic measurements (Figure 1). The absorption band at 820 cm^{-1} attributed to the C–H out-of-plane vibration of 1,4-substituted benzene was observed, but no absorption at 840 and 880 cm^{-1} ascribed to tri- and tetrasubstituted benzene was observed. Absorption bands at 750 and 777 cm^{-1} have been identified quantitatively for the meta and ortho isomers, respectively, in PPS.[8] In the obtained oligomer these bands were not detected in the 700–800-cm^{-1} region except at 740 cm^{-1} in spite of the low molecular weight. These results indicate a linear or 1,4-conjugated phenylene sulfide structure. IR spectroscopy in the

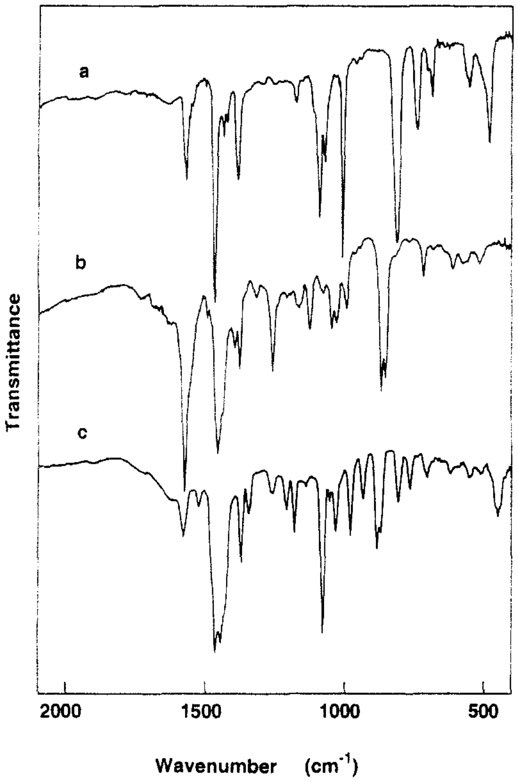


Figure 1. IR spectra of OPS (a), oligo(2,6-dimethylphenylene sulfide) (b), and oligo(2,5-dimethylphenylene sulfide) (c).

1000–1150-cm^{-1} region reveals significant and diagnostic differences between the cyclic and the linear PPS.[19,20] This region of the spectrum also shows that the resulting polymer does not contain detectable sulfoxide and sulfone structures.[21] No thianthrene structure is detected by IR.[22] The solid-state ^{13}C NMR reveals two main peaks at 129.1 and 131.5 which are ascribed to the quaternary and tertiary carbons of the resulting polymer, respectively. This result also supports the idea that the polymer is constructed by thiophenylene units as a main structure.

The OPS was reduced by lithium aluminum hydride in dichloromethane in order to address the existence of the S–S bond in the oligomer. The reduction product shows the new absorption at 2550 cm^{-1}, which is ascribed to the mercapto group. This indicates that the OPS chain contains a S–S bond.[23] The OPS is available for formation of a block copolymer or a cross-linking agent. The details will be reported in the near future.[24]

This VO-catalyzed polymerization not only enables efficient OPS formation at room temperature but is also applicable to the synthesis of alkyl-substituted OPSs (Table I). For example, bis(3,5-dimethylphenyl) disulfide and bis(2,5-dimethylphenyl) disulfide yield oligo(2,6-dimethylphenylene sulfide) (OMS) and oligo(2,5-dimethylphenylene sulfide), respectively. The IR spectrum of the OMS agrees with that of well-defined poly(2,6-dimethyl-1,4-phenylene sulfide) prepared by polycondensation from (4-bromo-2,6-dimethylthiophenoxy)copper salt. IR absorption bands between 800 and 900 cm^{-1}, which are ascribed to an isolated C–H out-of-plane vibration on the benzene ring, are significant for identifying the phenylene conjugation. Two absorption bands at 870 and 854 cm^{-1} are observed in the IR (Figure 1). Disubstituents at the 2,6-positions of the thiophenylene ring result in 90° rotation of the phenylene plane in alternate benzene units, just as for poly(2,6-dimethylphenylene oxide) (PPO).[25] The two bands are caused by the different environments of the C–H bond because the phenylene sulfide unit, 2,6,3′,5′-tetramethylphenylene sulfide, is not a C_{3v} symmetric structure.

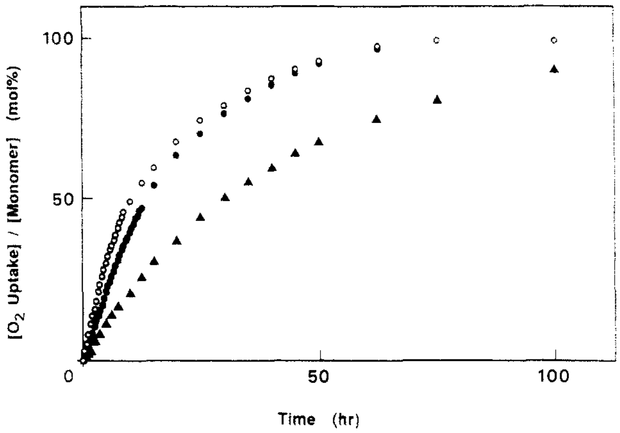


Figure 2. The VO-catalyzed oxygen oxidative polymerization of diphenyl disulfide at 20 °C in 1,1,2,2-tetrachloroethane in the presence of CF_3SO_3H (1 atm of O_2 pressure, $C_2H_2Cl_4$ (50 mL) with [disulfide] = 0.05 mol/L, [CF_3SO_3H] = 0.01 mol/L, [$(CF_3CO)_2O$] = 0.2 mol/L, and sub/cat. = 20): diphenyl disulfide (▲), bis(3,5-dimethylphenyl) disulfide (●), bis(2,5-dimethylphenyl) disulfide (○).

The disulfide bond in the chain was confirmed by reduction of the oligomer with triphenylphosphine in the presence of water. A new absorption band at 2563 cm^{-1}, which was assigned to the vibration of S–H, appears in the IR spectrum of the reduced oligomer. The ^1H NMR spectrum of the reaction mixture shows two peaks at 3.3 and 3.4 ppm after the reduction, which are attributed to the mercapto proton of 3,5-dimethylthiophenol and that of reduced oligomer, respectively. These results indicate that a disulfide bond exists in the oligomer. The obtained oligomer in the earlier stage of the polymerization contains a disulfide at the end of a chain. The disulfide bond in the chain is also available as a functional group.[26]

Oxidative Polymerization. In the presence of VO(acac)$_2$, the polymerization is accompanied by a quantitative oxygen uptake (Figure 2). Oxygen is essential for the polymerization of diphenyl disulfides. For each mole of oxygen consumed, 2.0 mol of PPS is generated.

The initial rate of the oxygen uptake (V_0) was measured at various partial pressures of oxygen in the polymerization of diphenyl disulfide (0.05 mol/L). The dependence of V_0 on the O_2 pressure over the range of 0–0.5 atm is shown in Figure 3. First-order disulfide substrate kinetics were observed at O_2 pressures above 0.6 atm. Zero order was found below 0.5 atm. V_0 became constant above 0.5 atm and is proportional to the oxygen partial pressure below 0.5 atm. These results support the belief that the rate-determining step in this catalytic cycle under atmospheric pressure is the oxidation process in which diphenyl disulfide is oxidized by the high-valence species of the vanadyl complex. The observed zero-order [O_2] dependence is consistent with this since the activated vanadyl species is a much better oxidant than O_2. This is also consistent with the fact that a 2-electron transfer occurs in the catalytic system as indicated by the electrochemical measurements.

One intriguing aspect of these VO-catalyzed oxidations was the observed effect of substituents in a series of methyl-substituted diphenyl disulfides on the observed rate of the reaction. The VO-catalyzed oxidation of bis(3,5-dimethylphenyl) disulfide displays zero-order substrate kinetics. Not only a linear plot of oxygen partial pressures obtained over the range of 0.33-1 atm but also the initial rate agrees with that of diphenyl disulfide at the low partial

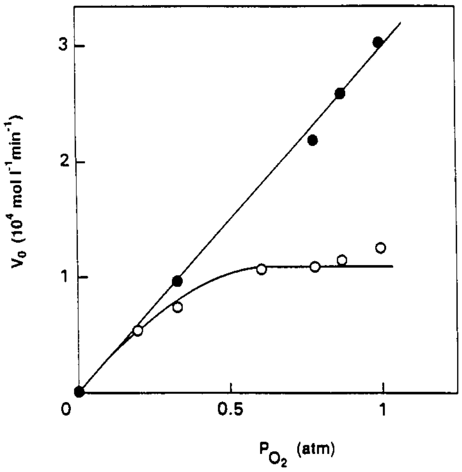


Figure 3. Effect of oxygen partial pressure (P_{O_2}) on oxygen uptake rate (V_0) in the VO-catalyzed polymerization of 0.1 mol/L diphenyl disulfide (○) and bis(3,5-dimethylphenyl) disulfide (●) at 20 °C in 1,1,2,2-tetrachloroethane in the presence of CF_3SO_3H ($C_2H_2Cl_4$ (50 mL) with [disulfide] = 0.1 mol/L, [acid] = 0.01 mol/L, and sub/cat. = 40).

Table II. O_2 Oxidative Polymerization of Diphenyl Disulfide with Catalyst

catalyst	[cat.]/[monomer]	$E_{1/2}$ (V vs Ag/AgCl)	OPS yield (wt %)
DDQ[a]	0.1	1.2[b] (Q/OH)	0
$Pb(CH_3COO)_4$	0.1	1.5[b] (3+/4+)	0
$Cu(acac)_2$	0.1	−0.3 (1+/2+)	0
$Fe(acac)_3$	0.1	−0.65 (2+/3+)	0
VO(salen)	0.1	0.5 (4+/5+)	0
$VO(Bzac)_2$	0.1	1.1 (4+/5+)	95
$VO(acac)_2$	0.1	1.1 (4+/5+)	92
$VO(acac)_2$	0.01	1.1 (4+/5+)	68
VOTPP[c]	0.01	1.5 (4+/5+)	95
$V(acac)_3$	0.1	0.8 (3+/4+)	85
V_2O_5[d]	2.0	*e*	97

[a] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. [b] Oxidation peak potential. [c] Reaction time 120 h. [d] 5 valence, under N_2 atmosphere. [e] Insoluble.

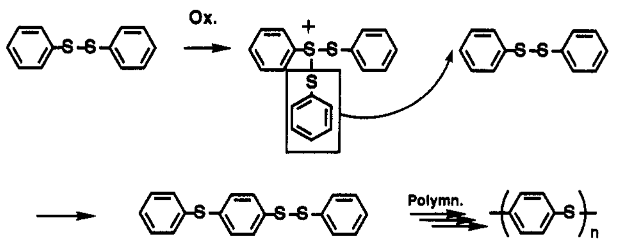
pressure (0.33 atm). These results do not exclude the possibility that the rate-determining step is the reoxidation of the lower valence VO species (3 valence) formed by the disproportionation with oxygen.

Bis(3,5-dimethylphenyl) disulfide is oxidized in this system 3 times more rapidly than the nonsubstituted diphenyl disulfide system. While this may be due at least in part to the fact that bis(3,5-dimethylphenyl) disulfide is about 0.2 V easier to oxidize than the diphenyl disulfide, it is not clear at this point if other factors (*e.g.*, steric) affecting the interaction with high-valence VO species may be operative.

A variety of other metal complexes were utilized under the same conditions. However, all of them are not effective as a catalyst for the oxygen oxidative polymerization of diphenyl disulfide (Table II). Even though an equimolar amount of 2,3-dichloro-5,6-*p*-benzoquinone (DDQ) and lead tetraacetate can oxidize disulfide to yield OPS due to the high oxidizing ability, the oxidants do not act as a catalyst for the efficient formation of OPS. The reduced species of the oxidant is not reoxidized with oxygen. The other complexes such as $Cu(acac)_2$, $Fe(acac)_2$, and VO-(salen) cannot oxidize disulfide due to this lower redox potential.

In contrast $VO(Bzac)_2$ with the same redox potential as $VO(acac)_2$ is effective as a catalyst in the polymerization. Even in the presence of 0.2% VO(TPP) complex as a catalyst the polymerization proceeds quantitatively for 120 h accompanied by oxygen uptake, though the polymerization rate is slow.

Scheme I



Equimolar vanadium(V) pentaoxide reacts with diphenyl disulfide to yield PPS (>90%) even under an oxygen-free atmosphere. $V(acac)_3$ (trivalent species) is easily oxidized to $VO(acac)_2$ with oxygen. The redox potentials of $VO(acac)_2$ and $V(acac)_3$ are 0.9 and 1.1 V (vs Ag/AgCl), respectively. The activated $VO(acac)_2$ in the presence of acid exhibits the properties of both vanadium(III) and vanadium(V) species in the catalytic system.

The OPS yield also depends on the acidity of the mixture. The oxidative polymerization does not proceed in the absence of acids. Strong acids such as trifluoromethanesulfonic acid and trifluoroacetic acid are effective in the VO-catalyzed polymerization (Table I). A 100 times smaller amount of trifluoromethanesulfonic acid is sufficient to form PPSs efficiently in comparison with trifluoroacetic acid (TFA), because the acidity of trifluoromethanesulfonic acid is more than 100 times greater than that of trifluoroacetic acid.[27] The oxidative polymerization of diphenyl disulfides is facilitated by the high oxidizing ability of the activate $VO(acac)_2$ produced by the acid. Diphenyl disulfides are not oxidized with only oxygen or only an equimolar amount of $VO(acac)_2$ in the absence of acid due to the high oxidation peak potential (1.6 V vs Ag/AgCl) of diphenyl disulfide.[28] The VO catalyst is estimated to an excellent electron mediator through activation by acid to promote electron transfer between diphenyl disulfide and molecular oxygen.

The intermediate species formed from diphenyl disulfide in the oxidations of this type have been studied using nonpolymerizable dimethyl disulfide as a model compound. Methylbis(methylthio)sulfonium cation salt has been isolated quantitatively by the oxidation of dimethyl disulfide. The detailed structure has been confirmed by ^1H NMR spectra and elemental analysis.[19,29,30] It is believed that the phenylbis(phenylthio)sulfonium cation is an active species in this polymerization, and the polymerization mechanism (Scheme I) has been discussed previously.[19,31,32] Diphenyl disulfide is oxidized to yield the phenylbis(phenylthio)sulfonium cation by the activated vanadium species through electron transfer. The electrophilic attack of the sulfonium cation proceeds on the benzene ring of the monomer or oligomer. The oxidation and the electrophilic reaction are continuously repeated to form PPS.

Catalytic Mechanism. The typical blue color of VO-$(acac)_2$ solution (λ_{max} = 596, 676 nm ascribed to the d–d transition of the vanadium(IV) complex) changed immediately to dark blue (λ_{max} = 647 nm) in the presence of acid (Figure 4). The optical density increases ca. 50 times more than that of d–d absorption, and the half-wave width is *ca.* 200 nm.

The color of the solution fades to light blue after bubbling oxygen. The resulting solution shows ^{51}V NMR signals at −440 and −570 ppm ascribed to 5-valence vanadium species. These results suggested that a vanadium(III) species was oxidized to a vanadium(V) species with molecular oxygen,

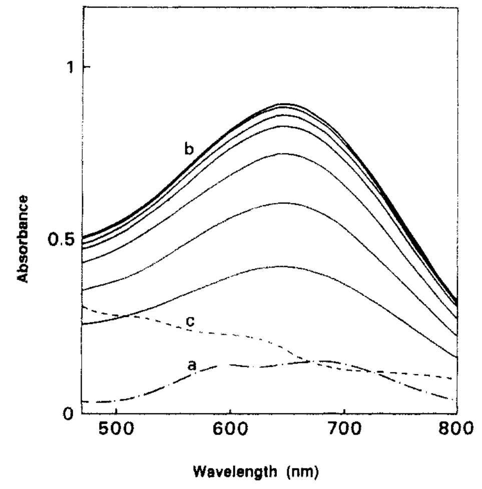


Figure 4. Electronic absorption spectra of 2.5 mmol/L VO(acac)$_2$ (a), spectral change of VO(acac)$_2$ at an interval of 20 min at 20 °C in dichloromethane under anaerobic conditions after adding 0.01 mol/L CF_3SO_3H and 0.2 mol/L $(CF_3CO)_2O$ (b), and VO(acac)$_2$ at 20 °C in dichloromethane in the presence of 0.01 mol/L CF_3SO_3H and 0.2 mol/L $(CF_3CO)_2O$ after adding 0.1 mol/L diphenyl disulfide under anaerobic conditions (c).

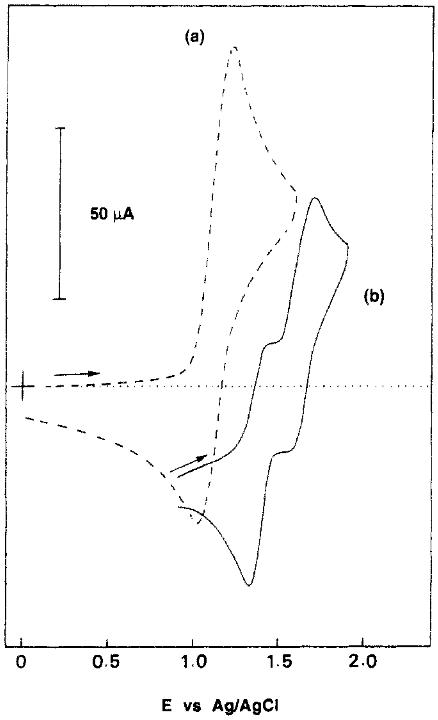


Figure 5. Cyclic voltammograms of VO(acac)$_2$ at 20 °C in dichloromethane under anaerobic conditions (a) and in an acidic environment (b) ([VO(acac)$_2$] = 2.5 mmol/L, [CF_3SO_3H] = 0.01 mol/L, and [$(CF_3CO)_2$] = 0.2 mol/L; scanning rate 50 mV/s).

just as the V(III)(acac)$_3$ is easily oxidized to VO(acac)$_2$ with oxygen. When diphenyl disulfide is added, the dark blue solution instantly turns light brown under anaerobic conditions. Weak d–d absorptions at approximately 500 and 600 nm are observed and are attributed to the vanadium(III) species (Figure 4).

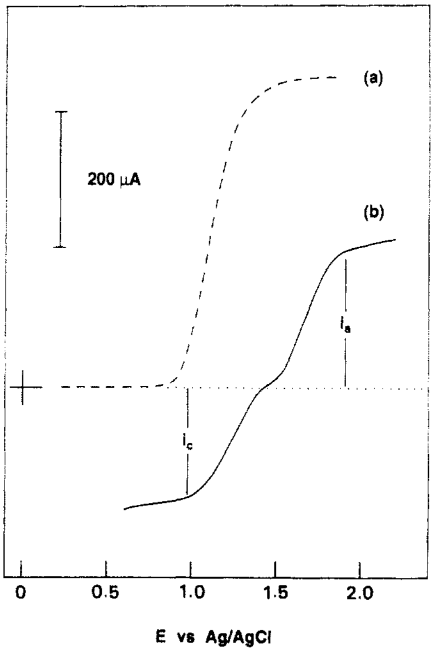


Figure 6. Rotating disk voltammograms of VO(acac)$_2$ at 20 °C in dichloromethane under anaerobic conditions (a) and in an acidic environment (b) ([VO(acac)$_2$] = 2.5 mmol/L, [CF_3SO_3H] = 0.01 mol/L, and [$(CF_3CO)_2$] = 0.2 mol/L; rotating rate 1000 rpm).

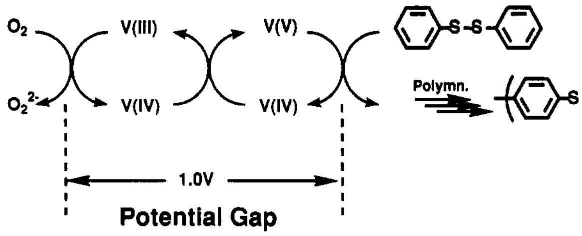
The redox potential ($E_{1/2}$) of VO(acac)$_2$ is at 1.1 V in dichloromethane solution (Figure 5). The oxidation current ascribed to the oxidation of V(IV) to V(V) is observed over 1.1 V in rotating disk voltammetry (RDV) (Figure 6). The number of electrons transfered was determined to be 1 by chronopotentiometry. After the addition of degassed trifluoromethanesulfonic acid and trifluoroacetic anhydride to an anaerobic dichloromethane solution of VO(acac)$_2$, the RDV reveals that the redox potential is 1.5 V in the neutral solution, but the reduction current was observed below 1.5 V (Figure 6). The reduction current reaches a maximum after 2 equiv is added.

In the acidic environment, two redox waves were observed at very close potentials in cyclic voltammetry (Figure 5). Quantification of the number of electrons transfered was accomplished by chronopotentiometry.[33] The number of electrons transfered was determined to be 1.8. Thus, two-step electron transfer occurs at 1.5 V through two redox couples. These results support the observation that i_c and i_a are ascribed to the reduction of the vanadium(V) species and the oxidation of the vanadium(III) species, respectively (Figure 6). That is, the redox potential of the V(III)/V(IV) couple approximately agrees with that of V(IV)/V(V). This result is also confirmed by CV in an acidic medium (Figure 5). The redox couples ascribed to V(III)/V(IV) and V(IV)/V(V) were observed to be close in redox potential. The electron transfer from diphenyl disulfide to oxygen occurs through the two redox couples to bridge the large potential gap. The limiting oxidation current of the V(III) species, i_a, decreases on bubbling oxygen through the solution, and the i_c decreases upon the addition of diphenyl disulfide. Monitoring the resulting solutions by RDV also reveals the formation of vanadium(V) and vanadium(III) species in the acidic solution of VO(acac)$_2$.

Conclusions

VO-catalyzed O_2 oxidative polymerization of diphenyl disulfides is demonstrated to yield quantitatively pure PPSs. The catalytic mechanism involves the disproportionation of the VO complex to the vanadium(III) and vanadium(V) species in the acidic environments of this experiment (Scheme II). The vanadium(V) species reacts with diphenyl disulfide to form the active species of the polymerization. The vanadium(III) species is reoxidized with molecular oxygen. VO(acac)$_2$ acts as an excellent electron mediator through a 2-electron transfer to molecular oxygen from diphenyl disulfide. The resulting two redox systems of VO complexes bridge the large potential

Scheme II



gap between reduction of oxygen and oxidation of monomer. This polymerization represents the first example of a VO-catalyzed oxygen oxidative polymerization of diphenyl disulfide through electron transfer.

Acknowledgment. We thank Prof. Dr. Fred C. Anson at the California Institute of Technology for helpful discussion. This work was partially supported by a Grant-in-Aid for Development Scientific Research (No. 04555223) and Scientific Research (Nos. 04750707, 0869, and 040850) from the Ministry of Education, Science and Culture, Japan, and The Asahi Glass Foundation.

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