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Acid-Promoted Electron Transfer to Facilitate Oxidative Polymerization of Diaryl Disulfides

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A catalytic amount of Lewis acids ([Lewis acid]/[Disulfide]=1/200) facilitated electron transfer from diaryl disulfides to a stoichiometric amount of another oxidizing agent by which linear poly[thio(1,4-arylene)] was produced. Such Lewis acids as $SbCl_5$ and $FeCl_3$ facilitated oxidation of diphenyl disulfide by quinones more efficiently than protic acids such as CF_3COOH, where the Lewis acid showed more than 200-fold more activity than the protic acid. Oxovanadium complex-catalyzed oxygen-oxidation of disulfides was also facilitated by these Lewis acids. The catalysis of these Lewis acids includes not only the activation of quinones or the oxovanadium complex, but also the lowering of the oxidation potential of the monomers.

Oxidative polymerization of aromatic compounds provides structure-defined polymers. These are often used as engineering plastics taking advantage of such properties as thermal stability and chemical resistance due to the aromatic chains. Indeed, oxidative polymerization of 2,6-dimethylphenol is employed as a successful commercial process to provide poly[oxy(2,6-dimethyl-1,4-phenylene)] (PPO) resin which is used as a typical engineering plastic.[1)]

Dioxygen is a typical and most convenient oxidant. Autoxidation systems catalyzed by metal complexes, e.g., O_2-oxidation of thiophenols catalyzed by phthalocyanine,[2)] attract much attention as convenient synthetic methods where a well-defined catalytic mechanism is often essential to improve the reaction.

Our studies on the oxidative polymerization of disulfides have revealed that linear poly[thio(1,4-phenylene)] (PPS) of high purity is produced through the oxidation of diphenyl disulfide by a stoichiometric amount of quinones[3)] and that oxovanadium complexes catalyze the autoxidation of disulfides. This may provide a desirable clean process for the mass production of PPS resin at room temperature.[4)] However, the oxidative polymerization of disulfides has a serious drawback in that a large amount of strong protic acid such as CF_3COOH or CF_3SO_3H is essential for the polymerization not only to suppress the nucleophilic side reaction to the active species, phenylbis(phenylthio)sulfonium cation, but also to activate quinones or oxovanadium complexes because of the high oxidation potential of disulfides.[5)]

We report here the oxidative polymerization of diphenyl disulfide in the presence of Lewis acids. The effect of Lewis acids on the catalysis was systematically investigated. The addition of a catalytic amount of Lewis acid facilitates electron transfer under mild conditions which effectively improved the polymerization with quinones or dioxygen as oxidants.

Experimental

General Procedures. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was obtained from Merck Co. Reagent-grade Lewis acids as $SbCl_5$, $SnCl_4$, $FeCl_3$, $BF_3\cdot O(C_2H_5)_2$, $TiCl_4$, $ZnCl_2$, and $AlCl_3$ were obtained from Kanto Chem. Co. and were used without further purification. Dichloromethane was distilled from CaH_2 immediately prior to use. Diphenyl disulfide (DPS) was purified by recrystallization from ethanol, dried in vacuo for 1 d at 30 °C, and recovered as white needles (mp 59 °C). 3,5-Dimethylbenzenethiol was prepared by Leuckart's method from the corresponding alkyl-substituted anilines as starting materials.[6)] Bis(3,5-dimethylphenyl) disulfide was prepared by the oxidation of the corresponding thiophenol with iodine in ethanol, and purified by distillation. The structures of the monomers were confirmed by spectroscopic measurements before the polymerization. The purities of the disulfides were >99.8% as measured by gas chromatography. Other reagents were obtained from commercial sources. Oxobis(2,4-pentanedionato)vanadium(IV) $[VO(acac)_2]$ was prepared from 2,4-pentanedione and vanadium(IV) oxide sulfate, and recrystallized from benzene. An electrochemical-grade $[n\text{-}Bu_4N]BF_4$ was recrystallized from dichloromethane-diethyl ether and dried under vacuum.

^1H and ^{13}C NMR spectra were recorded on either a JEOL GSX-400 or JEOL FX-90Q spectrometer. The IR spectra of the polymer were measured by using a JAS IR-810 spectrometer. The melting point of the polymer was determined by differential scanning calorimetry (DSC) using a Seiko DSC/220C with a heating rate of 20 °C min^{-1}. The molecular weight of the polymer was determined by GPC using a Shimadzu LC-9A system and Asahipac (GS 510H and 310H) columns. *N*-Methyl-2-pyrrolidone (NMP) was used as an eluent at 25 °C with a flow rate of 1.0 $cm^3\,min^{-1}$. The detector was a UV-vis spectrophotometer (Shimadzu SPD-6A, 265 nm). The GPC was calibrated by polystyrene standards. Electrochemical measurements were carried out in a two-compartment cell kept under nitrogen atmosphere. Platinum disk (0.126 cm^2), platinum wire, and Ag/AgCl electrodes were used as working, auxiliary, and reference electrodes, respectively. The potential was controlled by a Nikko Keisoku DPG-3 dual potentiogalvanostat and a Nikko Keisoku DPC-3 function generator. The electrolyte solution contained 0.1 $mol\,dm^{-3}$ tetrabutylammonium tetrafluoro-

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borate. Mass spectra were obtained using a JEOL Model JMS-DX300 spectrometer with an ionization energy of 20 eV.

Polymerization Procedure. Oxidative polymerizations of disulfides were carried out at 20 °C. A typical procedure was as follows. Monomer, bis(3,5-dimethylphenyl) disulfide (10 mmol, 2.74 g), was dissolved in 50 cm^3 of dichloromethane. The solution was poured into a mixture containing 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (10 mmol, 2.27 g) in 50 cm^3 of dichloromethane in a closed vessel to which was added $SbCl_5$ (1 mmol, 0.229 g). The vessel was kept airtight. The reaction mixture was stirred under a nitrogen atmosphere for 20 h. After the polymerization, the mixture was poured into 500 cm^3 of hydrochloric acid–methanol (5 vol%) to precipitate the polymer. The white powder was collected by filtration and washed with methanol and an aqueous solution of potassium hydroxide (5 wt%) several times. After neutralization and washing with methanol, the product was dried in vacuo at 70 °C for 1 d. The polymerization of unsubstituted diphenyl disulfide was carried out under the same conditions.

Oxovanadium complex-catalyzed oxygen-oxidative polymerization in the presence of a Lewis acid was carried out as follows. $VO(acac)_2$ (10 $mmol\,dm^{-3}$, 0.265 g), $FeCl_3$ (20 $mmol\,dm^{-3}$, 0.324 g), and acetic anhydride (0.2 $mol\,dm^{-3}$, 4.2 g) were dissolved in oxygen-saturated dichloromethane (100 cm^3) to which was added the monomer, bis(3,5-dimethylphenyl) disulfide (0.1 $mol\,dm^{-3}$, 2.74 g). The mixture was stirred for 20 h. The solution turned dark blue after a few hours. The product was isolated as a white powder by pouring the reaction mixture into hydrochloric acid–methanol. Polymer yield: 80 wt%. The polymerization with catalytic amounts of other Lewis acids was carried out under similar conditions.

O_2 Uptake Measurements. The amount of oxygen consumed was determined by modified Warburg's apparatus as follows. Oxobis(2,4-pentanedionato)vanadium(IV) (0.5 mmol, 0.132 g) and $FeCl_3$ (1 mmol, 0.162 g) were dissolved in 1,1,2,2-tetrachloroethane (40 cm^3) in a closed vessel maintained at 20 °C. The mixture was stirred under a dry argon atmosphere for ca. 30 min until a steady state was reached. A similar vessel equipped with a manometer and a buret was connected to the vessel with a pressure tube. The atmosphere in the vessel was replaced by oxygen and the whole instrument was kept airtight. A solution of diphenyl disulfide (50 mmol, 1.09 g) in 1,1,2,2-tetrachloroethane (10 cm^3) was added to an acidic solution of $VO(acac)_2$. 1,1,2,2-Tetrachloroethane was carefully added from the buret to the second vessel to keep the pressure at 1 atm. Oxygen consumption was measured from the net amount of 1,1,2,2-tetrachloroethane thus added during the reaction.

Spectroscopic Data. **Poly[thio(1,4-phenylene)].** Elemental analysis. Calcd for (C_6H_4S): C, 66.63; H, 3.73; S, 29.64%. Found: C, 66.50; H, 3.80; S, 29.51%. IR (KBr, cm^{-1}) 3025 (ν_{C-H}), 1395, 1480, 1580 ($\nu_{C=C}$), and 820 (δ_{C-H}). CP-MAS ^{13}C NMR δ=129.1 and 131.5 (phenyl C). MS *m/z* 756, 648, 540, 434, 326, 218, and 110. Melting point=200°C.

Poly[thio(2,6-dimethyl-1,4-phenylene)]. Elemental analysis. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54%. Found: C, 69.36; H, 5.80; S, 24.80%. IR (KBr, cm^{-1}) 2850, 2920, 2950, 2975, 3040 (ν_{C-H}), 1370, 1450, 1570 ($\nu_{C=C}$), 870, and 853 (δ_{C-H}). ^1H NMR ($CDCl_3$) δ=2.3 (methyl 6H) and 6.7 (phenyl 2H). ^{13}C NMR ($CDCl_3$) δ=22 (methyl C), 125, 127, 140, and 144 (phenyl C). The molecular weight of the polymer obtained from the oxidation with quinones as an oxidant and $SbCl_5$ as a catalyst was determined to be M_w=6000.

Results and Discussion

Acid-Catalyzed Polymerization of Diaryl Disulfides with DDQ. Oxidative polymerization of bis(3,5-dimethylphenyl) disulfide with DDQ as oxidant was examined in the presence of Lewis acids. Polymerization of the monomer was performed in dichloromethane at room temperature for 20 h with an equimolar amount of DDQ. Addition of Lewis acids was effective in facilitating the polymerization to produce poly[thio(2,6-dimethyl-1,4-phenylene)]. During the polymerization, 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH) precipitated in the reaction mixture as a white powder, which suggests a polymerization mechanism through oxidation of the disulfide (Eq. 1).

$$n/2\ \text{Ar–S–S–Ar} + n/2\ \text{DDQ} \xrightarrow{\text{Lewis acid}} \text{+Ar–S+}_n + n/2\ \text{DDH}. \tag{1}$$

The polymer was obtained as a white powder that was soluble in common organic solvents such as dichloromethane. The linear structure of the polymer was confirmed by its IR spectrum. The absorptions at 870 and 853 cm^{-1} which have been attributed to the isolated C–H out-of-plane vibration of benzene[7] were observed in the IR spectrum of poly[thio(2,6-dimethyl-1,4-phenylene)]. The absorption band at 820 cm^{-1} attributed to the C–H out-of-plane vibration of 1,4-substituted benzene was observed in the IR spectrum of poly[thio(1,4-phenylene)], but no absorptions at 840 and 880 cm^{-1} ascribed to tri- and tetrasubstituted benzene were observed.

Since diaryl disulfide exhibits a high oxidation potential (1.5—1.7 V vs. Ag/AgCl), strong oxidants such as DDQ are required for the oxidative polymerization of the disulfide. The polymerization of bis(3,5-dimethylphenyl) disulfide proceeds in the presence of an equimolar amount of $SbCl_5$ though the polymer yield was $<60\%$. Other Lewis acids were not effective as oxidants. These results suggest that these Lewis acids act as acid catalysts in the polymerization.

The effect of the concentration of these Lewis acids was examined. A lesser amount of Lewis acid was required for the polymerization than the protic acids such as CF_3COOH or CF_3SO_3H (Table 1). A catalytic amount of Lewis acids ([Lewis acid]/[monomer]= 1/10—1/200) was enough for the polymerization (Fig. 1). The use of a strong Lewis acid such as $SbCl_5$ resulted in efficient formation of the polymer, which is consistent with the polymerization of disulfides with an equimolar amount of Lewis acid as oxidant.[8] The

Table 1. Oxidative Polymerization of Bis(3,5-dimethylphenyl) Disulfide with DDQ

Acid	Concn $\mathrm{mol\,dm^{-3}}$	[Acid]/[Monomer]	Polymer yield wt %
$SbCl_5$	0.01	1/10	92
$SnCl_4$	0.01	1/10	90
$FeCl_3$	0.01	1/10	88
$BF_3O(C_2H_5)_2$	0.01	1/10	35
$TiCl_4$	0.01	1/10	22
$ZnCl_2$	0.01	1/10	1
$MgCl_2$	0.01	1/10	0
$AlCl_3$	0.01	1/10	0
CF_3SO_3H	0.01	1/10	63
CF_3COOH	1	10	90
CCl_3COOH	1	10	86
CH_3COOH	1	10	0

[Monomer]=0.1, [DDQ]=0.1 ($\mathrm{mol\,dm^{-3}}$). Solvent=CH_2Cl_2, r.t., 20 h.

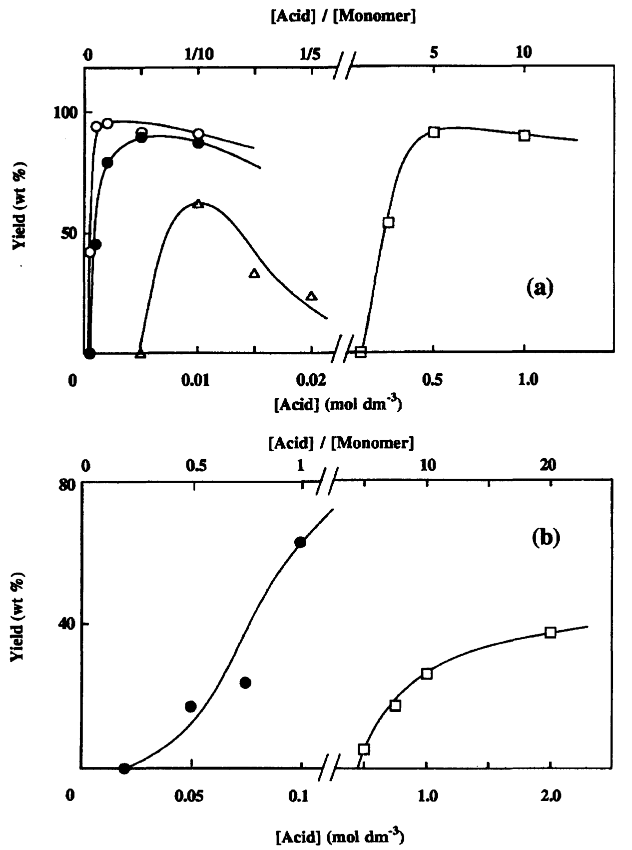

Fig. 1. Plots of polymer yield vs. acid concentration in the oxidative polymerization of diaryl disulfides in dichloromethane (20 h) in the presence of 0.2 $\mathrm{mol\,dm^{-3}}$ $(CF_3CO)_2O$. Monomer: (a) 0.1 $\mathrm{mol\,dm^{-3}}$ bis(3,5-dimethylphenyl) disulfide, (b) 0.1 $\mathrm{mol\,dm^{-3}}$ diphenyl disulfide. Acid: $SbCl_5$ (○), $FeCl_3$ (●), CF_3SO_3H (△), CF_3COOH (□).

polymerization of unsubstituted diphenyl disulfide with DDQ was also facilitated by $FeCl_3$ more efficiently than protic acids. However, a larger amount was required than with the polymerization of bis(3,5-dimethylphenyl) disulfide.

The effect of the Lewis acid in the catalysis of the polymerization was also examined. The cyclic voltammogram of DDQ (1 $\mathrm{mmol\,dm^{-3}}$) exhibited two quasireversible reduction processes at E_1=0.6 V and E_2=−0.2 V vs. Ag/AgCl in nitrobenzene. Addition of $FeCl_3$ decreased the peak at E_2 and a single irreversible reduction peak was observed at 0.75 V vs. Ag/AgCl in the presence of 20 $\mathrm{mmol\,dm^{-3}}$ $FeCl_3$ (Fig. 2). The reduction of $FeCl_3$ proceeded at potentials more negative than 0.5 V vs. Ag/AgCl. The reduction peak current at 0.75 V was twice as large as that of the respective current originally measured at E_1 and E_2 in the absence of $FeCl_3$. These results suggest that the reduction potential of DDQ shifts to the positive side in the presence of $FeCl_3$. A CT-complex of hydroquinone and $FeCl_3$ has been reported[9] by which the complex formation of DDQ and $FeCl_3$ is reasonably predicted.

In addition, the oxidation peak potential of bis(3,5-dimethylphenyl) disulfide shifted to the negative side by ca. 50 mV on addition of $FeCl_3$.[10] The roles of $FeCl_3$ may include not only the enhancement of the oxidizing ability of DDQ more effectively than protic acids, but also the lowering of the oxidation peak potential of diphenyl disulfide to facilitate electron transfer in the polymerization.

Some metal oxides are known to act as solid acids. Such heterogeneous acids are expected to provide clean processes for oxidative polymerization under mild conditions, and in addition, solid acids such as V_2O_5 and MoO_5 have been found to be effective as oxidizing agents for the oxidative polymerization of bis(3,5-dimethylphenyl) disulfide. The polymerization of alkyl-substituted diphenyl disulfides with a stoichiometric amount of V_2O_5 gave the corresponding polymer in a >90 wt % yield. However, DDQ was not activated by these solid acids, and oxidative polymerization of bis-

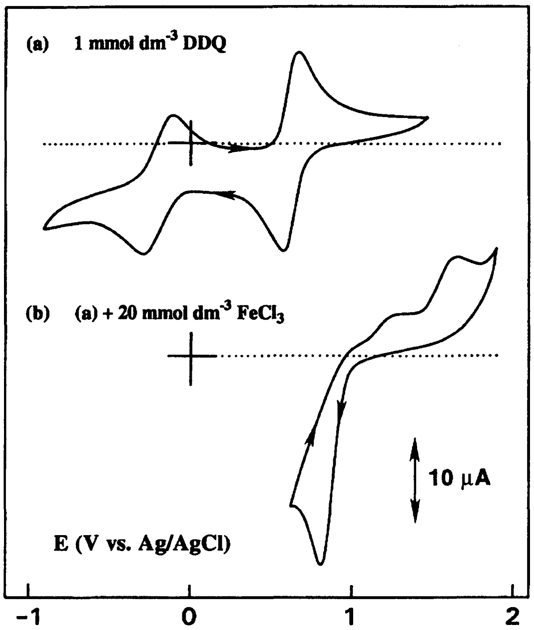

Fig. 2. Steady-state cyclic voltammograms of DDQ in anaerobic nitrobenzene containing 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate. Scan rate= 0.1 V s^{-1}.

(3,5-dimethylphenyl) disulfide with DDQ in the presence of a catalytic amount of these solid acids did not give polymer, which may be due to the heterogeneous process of these solid acids. These results also indicate that the electrophilicity of the Lewis acids as well as their acidity is effective to facilitate the electron transfer in the oxidative polymerization of disulfide with DDQ.

Oxygen-Oxidative Polymerization of Disulfide in the Presence of Lewis Acids. The catalysis of Lewis acids as electron mediators between disulfide and oxygen was examined. A catalytic amount of the Lewis acids $FeCl_3$, $AlCl_3$, $SbCl_5$, $TaCl_5$, WCl_6, $SnCl_4$, $TiCl_4$, $ZnCl_2$, $VOCl_2$, $MoCl_5$, and $NbCl_5$ was added respectively to solutions containing the monomer, CF_3SO_3H, and $(CF_3CO)_2O$ in O_2-saturated dichloromethane. Only $MoCl_5$ proved to be effective as a catalyst, though the polymer yield was <60 wt %.

In contrast, oxygen-oxidative polymerization of bis(3,5-dimethylphenyl) disulfide in the presence of a catalytic amount of both Lewis acid and oxovanadium catalyst produced the polymer. The polymer was efficiently produced when $FeCl_3$ was used. The polymer was confirmed to be a linear poly[thio(2,6-dimethyl-1,4-phenylene)]. The IR spectrum of the polymer was in agreement with that of the polymer previously obtained.

The unsubstituted monomer (DPS) also produced the corresponding polymer in an ca. 50% yield but a larger amount of $FeCl_3$ was required compared to the polymerization of bis(3,5-dimethylphenyl)disulfide.

The presence of dehydrating agent is essential in avoiding the deactivation of the oxovanadium catalyst by the reduced forms of O_2 such as H_2O_2 or H_2O. In the presence of protic acids, trifluoroacetic anhydride is required for the efficient formation of the polymer, and the use of trichloroacetic anhydride or acetic anhydride lowers the polymer yield. However, in the presence of $FeCl_3$, acetic anhydride gave the polymer in a good yield (Table 2), which suggests that $VO(acac)_2$ is more efficiently activated by $FeCl_3$ than protic acids.[11)]

Stoichiometric oxygen absorption was observed in the polymerization (Fig. 3). The polymerization did not proceed in the absence of oxygen. These results suggest that the polymerization proceeds through the oxygen oxidation of disulfide which is a mechanism similar to that proposed for the polymerization with protic acids.

The polymerization was carried out with various amounts of $FeCl_3$ added (Fig. 4). The molecular weight of the polymer increased with the concentration of $FeCl_3$. However, the polymer yield reached a maximum value near $[FeCl_3]/[monomer]=0.5$, which indicates that $FeCl_3$ acts as a co-catalyst in the polymerization rather than as an oxidizing agent. The increase in the yield and the molecular weight above $[FeCl_3]/[monomer]=0.5$ may be attributed to dehydration by $FeCl_3$.

The catalysis of $FeCl_3$ in the oxovanadium-mediated O_2-oxidation of disulfide was examined. $FeCl_3$ has been used as an oxidant in the oxidation of thiols to disulfide.[12)] $FeCl_3$ has also been adopted as a catalyst for the oxygen oxidation of thiols in which Fe(II) is reoxidized by dioxygen to Fe(III).[13)] In addition, $FeCl_3$ has the ability to oxidize disulfide to produce the polymer, though the yield is not good. In the absence of $VO(acac)_2$, polymerization with a catalytic amount of $FeCl_3$ ($[FeCl_3]/[Disulfide]=0.2$) did not produce the polymer efficiently (yield <15 wt%). The addition of trifluoroacetic anhydride or trichloroacetic anhydride

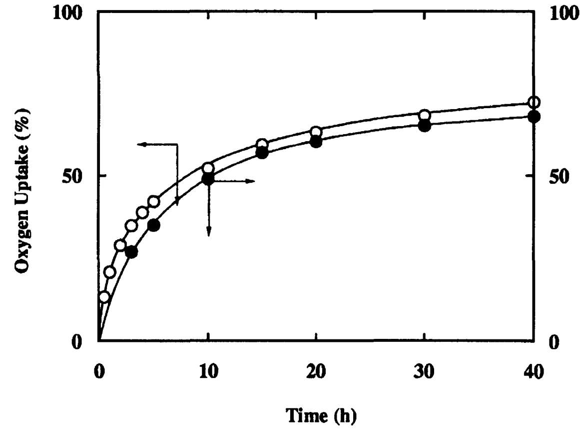

Fig. 3. $VO(acac)_2$-catalyzed O_2-oxidative polymerization of bis(3,5-dimethylphenyl) disulfide at 20 °C in 1,1,2,2-tetrachloroethane (1 atm of O_2 pressure, solvent: 50 ml). $[VO(acac)_2]=0.01$, $[FeCl_3]=0.02$, $[monomer]=0.1$ (mol dm^{-3}). O_2 uptake and the yield of the polymer are expressed as fraction parts of the value measured.

Table 2. $VO(acac)_2$-Catalyzed O_2-Oxidative Polymerization of Bis(3,5-dimethylphenyl) Disulfide

Acid	Concn mol dm^{-3}	Dehydrating agent	Polymer yield wt %
$FeCl_3$	0.02	$(CF_3CO)_2O$	80
$FeCl_3$	0.02	$(CCl_3CO)_2O$	87
$FeCl_3$	0.02	$(CH_3CO)_2O$	86
$FeCl_3$	0.02	—	58
$SbCl_5$	0.02	—	0
$SnCl_4$	0.02	—	0
$AlCl_3$	0.02	—	0
CF_3COOH	1	$(CF_3CO)_2O$	93
CF_3COOH	1	$(CCl_3CO)_2O$	0
CF_3COOH	1	$(CH_3CO)_2O$	0
CF_3COOH	1	—	0

[Monomer] = 0.1, [$VO(acac)_2$] = 0.01, [Dehydrating Agent] = 0.2 (mol dm^{-3}). Solvent = O_2-saturated CH_2Cl_2, r.t., 20 h.

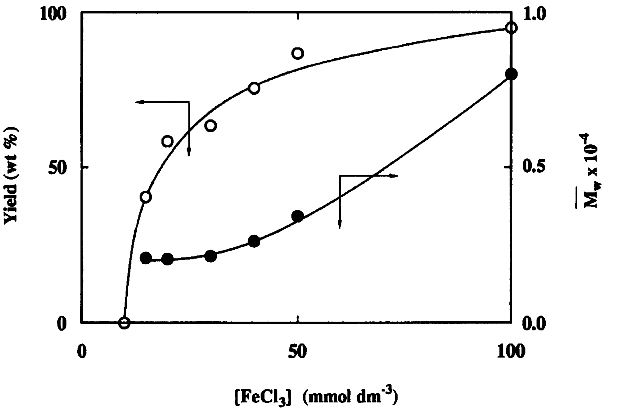

Fig. 4. Effect of $FeCl_3$ concentration on $VO(acac)_2$-catalyzed O_2-oxidative polymerization of bis(3,5-dimethylphenyl) disulfide in CH_2Cl_2. [$VO(acac)_2$] = 0.01, [monomer] = 0.1 (mol dm^{-3}). Polymerization was performed under oxygen atmosphere for 20 h (r.t.).

did not improve the polymerization. Thus, $FeCl_3$ does not act as a mediator to facilitate the electron transfer from disulfide to oxygen.

The blue solution of $VO(acac)_2$ in dichloromethane exhibited weak absorption in the visible spectrum due to the d–d transition of vanadium(IV). After addition of acetic anhydride and $FeCl_3$, the color of the solution changed to dark brown, and the resulting solution did not exhibit the ESR signal of vanadium(IV). The intense absorption of the solution in the visible spectrum is attributed to the CT-absorption between the disproportionated vanadium(III) and vanadium(V).[14] This mechanism is also supported by the fact that triphenylmethyl tetrafluoroborate, a typical Lewis acid, induces dimerization of VO(salen) to form a μ-oxo dinuclear complex (Eq. 2) which produces vanadium(III) and vanadium(V) via disproportionation.[15]

$$[\text{VO}] + \text{Lewis acid} \longrightarrow [\text{VOV}] \qquad (2)$$

$$n/2\ \text{Ar–S–S–Ar} \xrightarrow{[\text{VOV}],\ O_2} \left(\text{Ar–S}\right)_n \qquad (3)$$

Thus, the first step of the interaction may be the complex formation between $FeCl_3$ and $VO(acac)_2$ by the electrophilic reaction of $FeCl_3$ to the oxygen atom of the VO unit through which the μ-oxo dimer is produced, as is observed in the reaction of VO(salen) and triphenylmethyl cation. Other Lewis acids such as $SbCl_5$, $SnCl_4$, and $AlCl_3$ were not effective in activating the oxovanadium complex in the oxidative polymerization of disulfide (Table 2). $FeCl_3$ proved to be effective for the activation of the oxovanadium catalyst to produce vanadium(V) as an oxidant of disulfide and vanadium(III) which can be reoxidized by oxygen.

Thus, the efficient O_2-oxidative polymerization of bis(3,5-dimethylphenyl) disulfide without using trifluoroacetic anhydride was accomplished by the use of a Lewis-acid catalyst which promoted electron transfer in the presence of an oxovanadium catalyst.

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11) The effect of acid anhydride includes dehydration of the reaction mixture to allow activation of the oxovanadium catalyst by acid to produce a μ-oxo dimer that can act as an electron mediator in the polymerization. Even in the absence of dehydrating reagents, polymerization proceeded by the addition of a strong acid such as CF_3SO_3H and $FeCl_3$. However, polymerization with a weaker acid such as CF_3COOH required a strong dehydrating reagent such as $(CF_3CO)_2O$ (Table 2) which is considered to assist the dimer formation ($2[VO]+2H^+=[VOV]+H_2O$) by dehydration.

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