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Preparation of Poly(thio-1,4-phenylene)s by Oxygen-Oxidative Polymerization of Diaryl Disulfides

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Oxygen-oxidative polymerization of diphenyl disulfides with vanadyl acetylacetonate ($VO(acac)_2$) was studied by the kinetics based on oxygen uptake. Lineweaver–Burk plots reveal that the oxidation of diphenyl disulfide is a rate-determining step for the VO-catalyzed oxidative polymerization of diphenyl disulfide. K_m (Michaelis constant) and V_{max} were determined to be 1.6×10^{-2} mol dm^{-3} and 1.5×10^{-4} mol dm^{-3} min^{-1}, respectively. The polymerization rate is influenced by the oxidation potential of disulfides. The reoxidation step of the catalyst by oxygen is the rate determining step in case of the polymerization of alkyl-substituted disulfides such as bis(3-methylphenyl)disulfide, bis(2,5-dimethylphenyl)disulfide, and bis(3,5-dimethylphenyl)disulfide because the oxidation step of the disulfides is facilitated due to their lower oxidation potentials.

Oxidative polymerization is an important and convenient method for the synthesis of aromatic polymers. Poly(oxy-2,6-dimethyl-1,4-phenylene) (POP) is efficiently prepared through oxygen oxidation in the presence of catalytic amount of Cu–amine complexes where the polymerization mechanism and kinetics have been investigated.[1—5] However, 2,6-dimethylthiophenol, which is an analogous compound of 2,6-dimethylphenol, is not polymerized by the copper catalyst.

We have recently reported that poly(thio-1,4-phenylene) (PTP) is prepared through the oxygen oxidative polymerization of diphenyl disulfide at room temperature in the presence of vanadyl(IV) complex.[6—8] The oxidative polymerization provides highly pure PTP in contrast to the polycondensation process which needs a high temperature and a high pressure.[9—11] The quantitative oxygen uptake is observed during the polymerization. This paper describes the polymerization of alkyl-substituted diphenyl disulfides and their kinetic studies based on the oxygen uptake during the oxygen oxidative polymerization. V_{max} and K_m (Michaelis constant) were calculated from the Lineweaver–Burk plots, as have been described for poly(oxy-2,6-dimethyl-1,4-phenylene).[5]

Experimental

Materials. Diphenyl disulfide was purified by recrystallization from ethanol and dried in vacuo for 1 d at 30 °C, and was recovered as white needles (mp 59 °C). Substituted diphenyl disulfides (bis(2-methylphenyl)disulfide, bis(3-methylphenyl)disulfide, and bis(2,5-dimethylphenyl)disulfide) were prepared by the oxidation of the corresponding thiophenols. Bis(2,6-dimethylphenyl)disulfide and bis(3,5-dimethylphenyl) disulfide were prepared by the Leuckart's method from the corresponding anilines as starting materials.[12] Dichloromethane and 1,1,2,2-tetrachloroethane were purified by distillation. A reagent-grade trifluoroacetic acid and trifluoromethanesulfonic acid (Kantoh Chemical Co., >99.5%) were used without further purification. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (Merck, >98%), vanadyl acetylacetonate ($VO(acac)_2$) (Tokyo Kasei, >95%), V_2O_5 (Kantoh Chemical Co., >99%), and $VOCl_3$ (Kantoh Chemical Co.) were also used without further purification. Benzoquinone and naphthoquinone were purified by recrystallization from ethanol and dried in vacuo for 1 d at 30 °C.

Polymerization Method. The typical experiment is as follows. Diphenyl disulfide (10 mmol, 2.18 g) was dissolved in 50 cm^3 of tetrachloroethane. The solution was rapidly poured into the mixture containing $VO(acac)_2$ (0.25 mmol, 0.066 g), trifluoromethanesulfonic acid (1 mmol, 0.15 g), and trifluoroacetic anhydride (50 mmol, 10.5 g) in 50 cm^3 of tetrachloroethane. The reaction mixture was stirred at 20 °C under oxygen atmosphere for 40 h. After the polymerization, the mixture was poured into 500 cm^3 of hydrochloric acid–methanol (5 vol%) to precipitate the polymer. White powder was collected by filtration and washed with methanol and with an aqueous solution of potassium hydroxide (5 wt%) for several times. After neutralization and washing with methanol, the product was dried in vacuo at 70 °C for 1 d.

Measurements. ^{1}H and ^{13}C NMR spectra were measured on a JEOL GSX-400 spectrometer. The IR spectrum of the polymer was measured by using a JAS IR-810 spectrometer. Differential scanning calorimetry (DSC) was carried out with a heating rate of 20 °C min^{-1} on a Seiko DSC/220C. 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. The oxygen uptake during the polymerization was determined by using modified Warburg's manometer. Reaction temperature during the polymerization was kept at 20 °C. Oxidation and reduction potentials of diphenyl disulfides were measured by cyclic voltammetry which was carried out in a two-compartment cell kept under nitrogen atmosphere. Platinum disk (0.126 cm^2), platinum wire, and Ag/AgCl were used as a working, an auxiliary, and a reference electrode, respectively. The

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potential was controlled by a Nikko Keisoku DPG-3 dual potentiogarvanostat and a Nikko Keisoku DPC-3 function generator with a scanning rate of 100 m V s^{-1}.

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, 66.51; H, 3.85; S, 29.55%. IR (KBr, cm^{-1}) 3025 (ν_{C-H}), 1395, 1480, 1580 ($\nu_{C=C}$), 820 (δ_{C-H}). CP-MAS ^{13}C NMR $\delta=129.1$, 131.5 (phenyl C). X-Ray diffraction pattern (Cu $K\alpha$) $2\theta=19$, 21. MS m/z 756, 648, 540, 434, 326, 218, 110. $M_w=5450$, $M_n=1050$.

Poly(thio-2-methyl-1,4-phenylene). Elemental analysis. Calcd for (C_7H_6S): C, 68.81; H, 4.95; S, 26.24%. Found: C, 68.50; H, 4.77; S, 25.92%. IR (KBr, cm^{-1}) 2920, 2950, 2980, 3050 (ν_{C-H}), 1440, 1460, 1580, ($\nu_{C=C}$), 820, 880 (δ_{C-H}). ^{1}H NMR ($CDCl_3$) $\delta=2.3$ (methyl 3H), 7.1 (phenyl 3H). ^{13}C NMR ($CDCl_3$) $\delta=21$ (methyl C); 127, 130, 131, 134, 136, 141 (phenyl C). NMR signals of methylene proton and carbon were not detected at $\delta=3.6$ and 60, respectively.

Poly(thio-3-methyl-1,4-phenylene). Elemental analysis. Calcd for (C_7H_6S): C, 68.81; H, 4.95; S, 26.24%. Found: C, 68.61; H, 4.79; S, 26.02% IR (KBr, cm^{-1}) 2920, 2950, 2980, 3050 (ν_{C-H}), 1440, 1460, 1580 ($\nu_{C=C}$), 820, 880 (δ_{C-H}). ^{1}H NMR ($CDCl_3$) $\delta=2.3$ (methyl 3H), 7.1 (phenyl 3H). ^{13}C NMR ($CDCl_3$) $\delta=21$ (methyl C); 127, 130, 131, 134, 136, 141 (phenyl C).

Poly(thio-2,5-dimethyl-1,4-phenylene). Elemental analysis. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54%. Found: C, 69.40; H, 5.49; S, 25.01%. IR (KBr, cm^{-1}) 2850, 2910, 2960 (ν_{C-H}), 1450, 1470, 1590 ($\nu_{C=C}$), 880 (δ_{C-H}). CP-Mass ^{13}C NMR $\delta=20$ (methyl C), 124, 132, 141 (phenyl C).

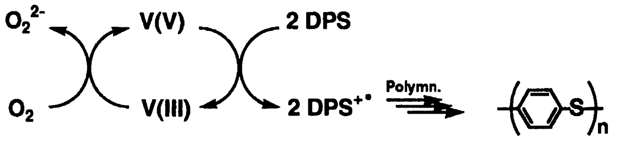
Poly(thio-2,6-dimethyl-1,4-phenylene). Elemental analysis. Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54%. Found: C, 69.26; H, 5.69; S, 24.30%. IR (KBr, cm^{-1}) 2850, 2930, 2950 (ν_{C-H}), 1380, 1450, 1560 ($\nu_{C=C}$), 860, 880 (δ_{C-H}). ^{1}H NMR ($CDCl_3$) $\delta=2.3$ (methyl 6H), 7.0 (phenyl 2H). ^{13}C NMR ($CDCl_3$) $\delta=22$ (methyl C), 124, 129, 136, 140, 141, 144 (phenyl C).

Poly(thio-3,5-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, 5.76; S, 24.85%. IR (KBr, cm^{-1}) 2850, 2920, 2950, 2975, 3040 (ν_{C-H}), 1370, 1450, 1570 ($\nu_{C=C}$), 875 (δ_{C-H}). ^{1}H NMR ($CDCl_3$) $\delta=2.3$ (methyl 6H), 6.7 (phenyl 2H). ^{13}C NMR ($CDCl_3$) $\delta=22$ (methyl C), 125, 127, 140, 144 (phenyl C).

Results and Discussion

Oxidative polymerization of diphenyl disulfide (DPS) proceeds efficiently at room temperature under oxygen atmosphere in the presence of catalytic amount of VO(acac)$_2$. The oxygen uptake is observed continuously during the polymerization. Oxygen acts as an electron acceptor for the polymerization. In the absence of VO-complex, the polymerization does not proceed due to the low oxidizing ability of dioxygen ($O_2+2e+2H^+=H_2O_2$, $E_{1/2}=0.5$ V vs. Ag/AgCl). We have already found that the strong oxidizing agents such as DDQ are essential for the oxidative polymerization of diphenyl disulfide because of its high oxidation potential (1.7 V vs. Ag/AgCl).[13]

VO(acac)$_2$ acts as an excellent electron mediator to bridge the potential gap of 1.0 V between the oxidation potential of disulfide and the reduction potential of oxygen. In order to elucidate the active species of the catalyst, the polymerization with vanadium(V) species was carried out under oxygen and nitrogen atmosphere. Pentavalent vanadium species, such as V_2O_5 and $VOCl_3$ which have a stong oxidizing ability, are effective for the oxidative polymerization of DPS (Fig. 1). The polymer was efficiently produced even under nitrogen atmosphere in the presence of an equimolar amount of V_2O_5. The polymerization with vanadium(IV) species such as VO(acac)$_2$ does not provide PTP under nitrogen atmosphere. These indicate that vanadium(V) species oxidize diphenyl disulfide directly to yield PTP. In case of vanadium(IV), we have already reported that vanadyl(IV) complex disproportionates to tri- and pentavalent species in the acidic solution.[8] Therefore, the geared cycle through tri-, tetra-, and pentavalent vanadium species is formed in the electron transfer system between disulfide and oxygen (Eq. 1).



(1)

The oxygen-oxidative polymerization of DPS with VO(acac)$_2$ consists of four elementary reaction steps as follows: (1) Disproportionation of VO(acac)$_2$; (2) oxidation of DPS; (3) reoxidation of vanadium(III) species

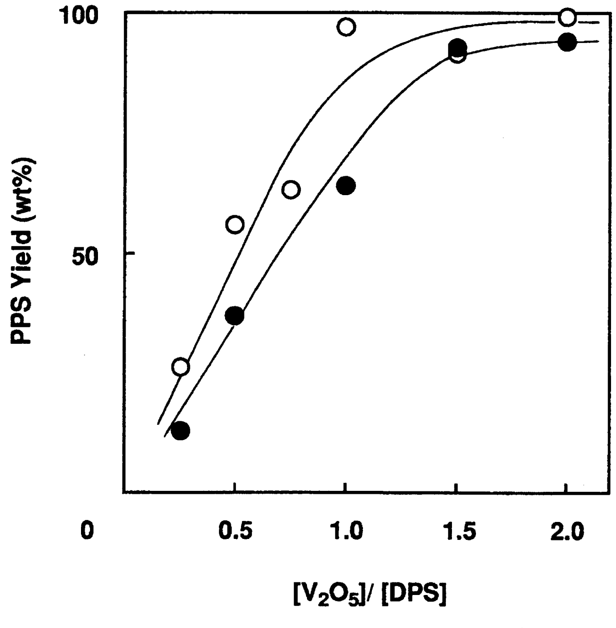


Fig. 1. Polymerization of DPS (0.1 mol dm^{-3}) with V_2O_5: (○) under oxygen; (●) under nitrogen. Solvent: CH_2Cl_2 containing CF_3SO_3H (0.01 mol dm^{-3}) and $(CF_3CO)_2O$ (0.2 mol dm^{-3}). Reaction time: 40 h (r.t.).

by oxygen; (4) electrophilic substitution of sulfonium cation as an active species. It has been already concluded that the oxidative polymerization of DPSs proceeds rapidly through cationic mechanism.[14,15]

The kinetics in the catalytic system of the polymerization was examined by the use of the initial rate of the oxygen uptake. Vanadyl complexes disproportionate to yield tri- and pentavalent species of vanadium in acidic solution.[7] We have already concluded that the oxidation proceeds through two electron transfer geared by V^{3+}/V^{5+} redox couple. The acidification of $V^{IV}O$ complex results in the formation of vanadium(III) and vamadium (V) species via disproportionation. The disproportionation efficiency increases with the concentration of acid. However, the initial rates of polymerization determined by the oxygen uptake are not affected by the concentration of trifluoromethanesulfonic acid (Fig. 2). This result means that the disproportionation is not a rate-determining step.

The initial polymerization rate (V_0) can be measured by oxygen uptake in the polymerization of a large excess of diphenyl disulfide with 2.5 mmol dm^{-3} of $VO(acac)_2$. V_0 tends to be a limiting value when the diphenyl disulfide concentration increases (Fig. 3b). Thus, the polymerization proceeds according to a Michaelis–Menten type reaction, the steady state being maintained.

Lineweaver–Burk plots (L–B plots) of the reaction were shown in Fig. 3a. The reciprocal of the initial rate of O_2 uptake vs. [diphenyl disulfide]$^{-1}$ is linear at 1 atm (=101325 Pa) of oxygen. The polymerization rate is influenced by the partial pressure of oxygen. The same L–B plots were observed at oxygen pressure above 0.6 atm. However, V_0 is constant vs. diphenyl disulfide concentration at 0.33 atm of oxygen pressure.

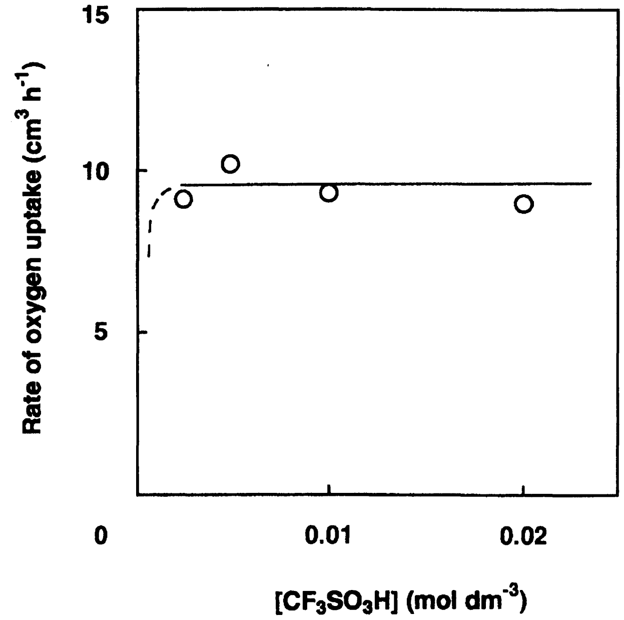


Fig. 2. Effect of the acid concentration on the polymerization of DPS under oxygen (1 atm). $VO(acac)_2$: 2.5 mmol dm^{-3}, DPS: 0.1 mol dm^{-3}, $(CF_3CO)_2O$: 0.5 mol dm^{-3}. Solvent: $(CHCl_2)_2$ (50 cm^3), 20 °C.

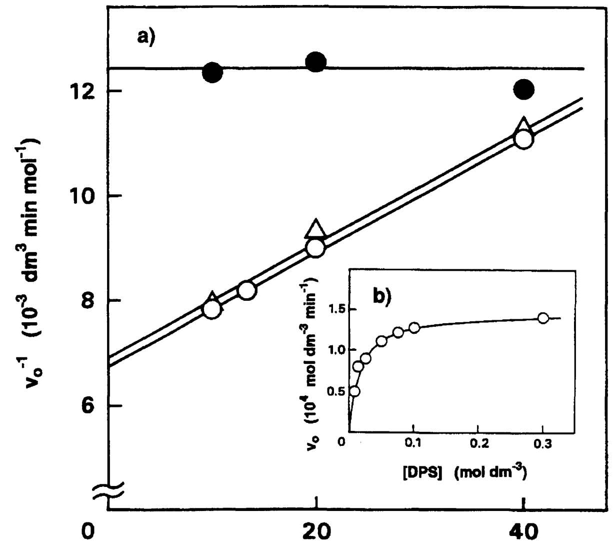


Fig. 3. (a) Lineweaver–Burk plots for the polymerization of DPS with (○) 1.0 atm; (△) 0.78 atm; (●) 0.33 atm of partial pressure of oxygen. $VO(acac)_2$: 2.5 mmol dm^{-3}, CF_3SO_3H: 0.01 mol dm^{-3}, $(CF_3CO)_2O$: 0.5 mol dm^{-3}. Solvent: $(CHCl_2)_2$ (50 cm^3), 20 °C. (b) Effect of the monomer concentration on the initial rate of the polymerization.

V_{max} and K_m were calculated from L–B plots (Table 1). V_{max} for DPS is small in comparison with that for the polymerization of 2,6-dimethylphenol with Cu-amine complex. While K_m is consistent with each other, k_2 for DPS is much smaller than that for 2,6-dimethylphenol.

$$\mathrm{E} + \mathrm{S} \overset{k_1}{\rightleftharpoons} \mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P} \tag{2}$$

It is caused by the fact diphenyl disulfide shows higher oxidation potential (1.7 V vs. Ag/AgCl) than that of 2,6-dimethylphenol (0.45 V vs. Ag/AgCl in methanol). The oxidative polymerization of 3,5-dimethyl DPS with lower oxidation potential (1.4 V vs. Ag/AgCl) shows higher polymerization rate than that of DPS, which is mentioned in the following section.

Figure 3 involves the effect of oxygen pressure on the polymerization. The rate-determining step for the polymerization of DPS changes with partial pressure of oxygen. The L–B plots for 0.33 atm of oxygen pressure is parallel to X-axis. That is, the polymerization rate is constant in the region of low partial oxygen pressure regardless of the monomer concentration. It is clear that the lower oxygen pressure makes the rate of the reoxidation of catalyst slow in the oxidation of DPS.

V_0 was measured at various partial pressure of oxygen in the polymerization of diphenyl disulfide. The dependence of the oxygen uptake rate on O_2 pressure

Table 1. Kinetic Constants for the Oxygen-Oxidative Polymerization of Diphenyl Disulfide and 2,6-Dimethylphenol

Catalyst	$10^4\ V_{max}$	$10^2\ K_m$	$10^{-1}\ K_1$[a]	$10k_2$[b]
	mol dm^{-3} min^{-1}	mol dm^{-3}	dm^3 mol^{-1}	min^{-1}
VO(acac)$_2$[c]	1.5	1.6	6.3	0.6
Cu–Pyridine[d]	73	2.5	4.0	15

a) $K_1=1/K_m$, b) $k_2=V_{max}/[E_0]$, $[E_0]=2.5\times10^{-3}$ (mol dm^{-3}), c) For diphenyl disulfide, d) For 2,6-dimethylphenol.

Table 2. Oxidative Polymerization of Diaryl Disulfides[a]

Substituent	Polymer yield	$10^3\ M_w$[b]	E[c]	$10^2\ K_m$[d]	$10^4 V_{max}$[d]
	wt%		V	mol dm^{-3}	mol dm^{-3} min^{-1}
Non	76	—	1.7	1.6	1.5
2-Methyl	85	2.6	1.6	—	—
3-Methyl	97	4.6	1.6	—	—
2,5-Dimethyl	100	—	1.5	—	—
3,5-Dimethyl	93	9.2	1.5	—	—
2,6-Dimethyl	73	1.6	1.7	7.4	1.3

a) [DPS]=0.1, [VO(acac)$_2$]=0.005, [CF$_3$COOH]=1.0, [(CF$_3$CO)$_2$O]=0.2 (mol dm^{-3}), b) Measured by GPC, c) Oxidation peak potential of disulfides (vs. Ag/AgCl), d) Calculated by Lineweaver–Burk plots.

over the range of 0—0.5 atm was observed. V_0 became constant above 0.5 atm and was proportional to the partial pressure of oxygen below 0.5 atm. These results also support the idea that the rate-determining step is the oxidation process in which diphenyl disulfide is oxidized by the high-valent species of vanadyl complex in the catalytic cycle under oxygen atmosphere.

The VO-catalyzed oxidative polymerization can be applicable for substituted DPSs. The oxidative polymerization of alkyl-substituted diphenyl disulfides, such as bis(2-methylphenyl)disulfide, bis(3-methylphenyl)disulfide, bis(2,5-dimethylphenyl)disulfide, bis(2,6-dimethylphenyl)disulfide, or bis(3,5-dimethylphenyl)disulfide, was carried out in the same conditions (Table 2). Each polymerization proceeds accompanied with the oxygen uptake, and the corresponding PTPs are formed in high yield. V_{max} and K_m were calculated by using the L–B plots. The kinetics showed linear L–B plots for the each monomer (Fig. 4). V_{max} and K_m for bis(2,6-dimethylphenyl)disulfide were determined to be 1.3×10^{-4} mol dm^{-3} min^{-1} and 7.4×10^{-2} mol dm^{-3}, respectively from the L–B plots. K_m for bis(2,6-dimethylphenyl)disulfide is larger than that for DPS (Table 2). It suggests that the steric hindrance in case of bis(2,6-dimethylphenyl)disulfide reflects the stability of the intermediate complex (Michaelis complex) which results in the larger K_m.

K_m values for bis(3-methylphenyl)disulfide, and bis(2,5-dimethylphenyl)disulfide were not determined because their VO-catalyzed oxidation displays zero-order substrate kinetics. The results imply two possibilities that K_m is close to zero, or that the reaction rate is independent of the monomer concentration. Bis(3-methylphenyl)disulfide, bis(2,5-dimethylphenyl)disulfide, and bis(3,5-dimethylphenyl)disulfide show low oxidation potential in comparison with that of DPS or bis(2,6-dimethylphenyl)disulfide (Table 2), which results in ca. 10 times larger oxidation rate of disulfide. The polymerization rate for bis(3,5-dimethylphenyl)disulfide increases with the increase of partial pressure of oxygen. That is, the rate-determining step is estimated to be the reoxidation of the catalyst by oxygen in these cases,

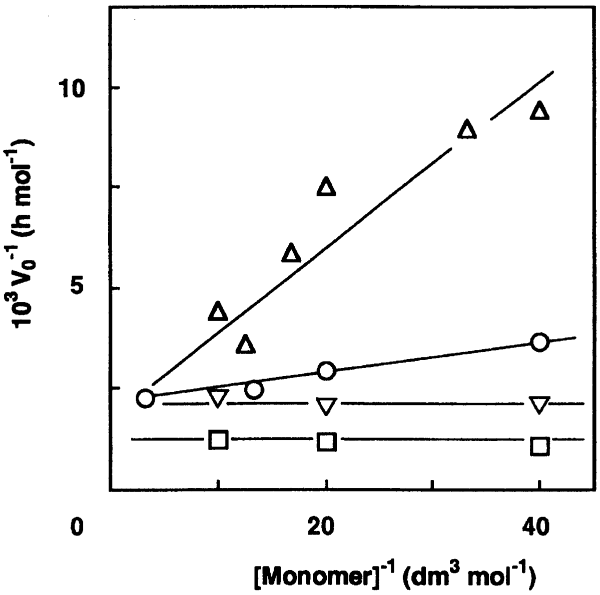
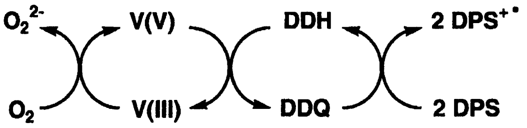


Fig. 4. Lineweaver–Burk plots for subsituted DPS: (○) DPA; (△) bis(2,6-dimethylphenyl)disulfide; (▽) bis(3-methylphenyl)disulfide; (□) bis(2,5-dimethylphenyl)disulfide. VO(acac)$_2$: 2.5 mmol dm^{-3}, CF$_3$SO$_3$H: 0.01 mol dm^{-3}, (CF$_3$CO)$_2$O: 0.5 mol dm^{-3}. Solvent: (CHCl$_2$)$_2$ (50 cm^3), 20 °C.

which is similar to the case for the polymerization of DPS under low partial pressure of oxygen.

Oxidative polymerization of DPS with stoichiometric amount of DDQ provides PTP formation rapidly in comparison with that by VO-catalyzed oxygen oxidation. Thus, the control experiments to improve the rate determining step were carried out using small amount of DDQ ([DDQ]/[DPS]=0.1).

The polymerization of DPS with oxygen proceeds in the presence of a catalytic amount of VO(acac)$_2$ and DDQ. The VO-catalyzed polymerization is promoted by DDQ (Fig. 5). This suggests that DPS is oxidized directly by DDQ, which shows the higher oxidation ability than VO(acac)$_2$. Although an equimolar amount of DDQ provides PTP in high yield, the polymerization does not proceed in the presence of a catalytic amount of DDQ. Therefore, 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDH) which is formed as a reduced species of DDQ, is reoxidized by vanadium(V). That is, a new geared cycle of DDH/DDQ is generated between DPS and oxygen in the electron transfer system (Eq. 3) which facilitate the polymerization because of the efficient oxidation of DDH with vanadium(V).



(3)

Polymerization of bis(3,5-dimethylphenyl)disulfide with oxygen was carried out in the presence of a catalytic amount of VO(acac)$_2$ and quinones such as benzoquinone or naphthoquinone. The polymerization was facilitated by the quinones (Fig. 6). Since DPS can not be oxidized by benzoquinone or naphthoquinone because of their low oxidation potentials, the quinones acts as an efficient oxidant for the oxidation of vanadium(III) species. The hydroquinones formed as reduced species are reoxidized by oxygen. In case of bis(3,5-dimethylphenyl)disulfide, new geared cycle of HQ/Q improves the rate determining step (reoxidation of the vanadium(III) species).

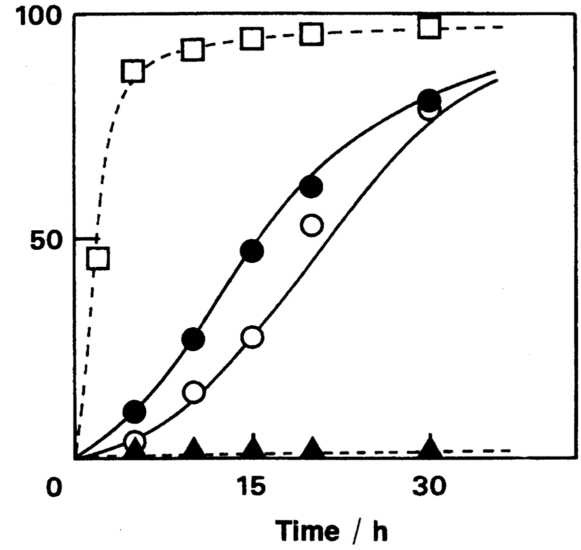


Fig. 5. Oxygen oxidative polymerization of DPS (0.1 mol dm^{-3}): (●) with VO(acac)$_2$ (5 mmol dm^{-3}) and DDQ (5 mmol dm^{-3}); (○) with VO(acac)$_2$ (5 mmol dm^{-3}); (▲) with DDQ (5 mmol dm^{-3}); (□) with DDQ (0.1 mol dm^{-3}). Solvent: CH_2Cl_2 containing CF_3COOH (1 mol dm^{-3}) and $(CF_3CO)_2O$ (0.2 mol dm^{-3}) at 20 °C.

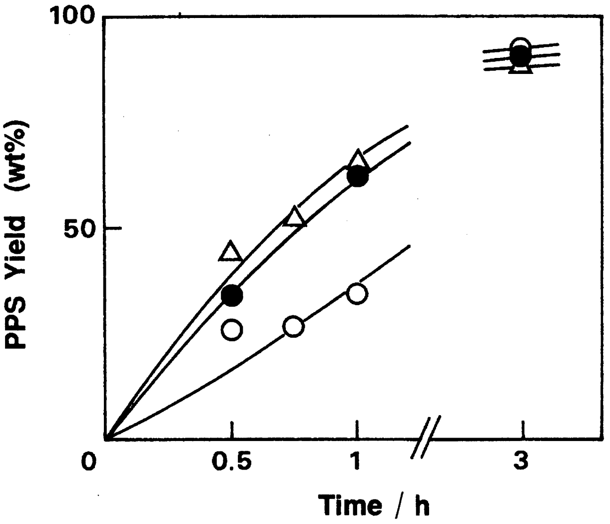


Fig. 6. Oxygen oxidative polymerization of bis(3,5-dimethylphenyl)disulfide (0.05 mol dm^{-3}): (△) with VO(acac)$_2$ (5 mmol dm^{-3}) and *p*-benzoquinone (5 mmol dm^{-3}); (●) with VO(acac)$_2$ (5 mmol dm^{-3}) and 1,4-naphthoquinone (5 mmol dm^{-3}); (○) with VO(acac)$_2$ (5 mmol dm^{-3}). Solvent: CH_2Cl_2 containing CF_3SO_3H (0.01 mol dm^{-3}) and $(CF_3CO)_2O$ (0.2 mol dm^{-3}) at 20 °C.

In conclusion, the rate of the oxygen-oxidative polymerization of disulfides are controlled by combining a new geared cycle. The quinones act as excellent electron mediators for the polymerization of diphenyl disulfides.

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