CHEMISTRY LETTERS, pp. 1101-1104, 1993.

Photo-Oxidative Polymerization of Bis(3,5-dimethylphenyl) Disulfide for Synthesis of Poly(thioarylene)

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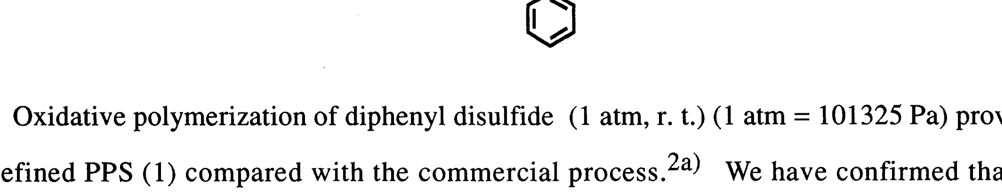
Bis(3,5-dimethylphenyl) disulfide was subject to photo-oxidation in the presence of 2,3-dicyanonaphthalene as a sensitizer. The photo-redox system enabled efficient formation of poly(thio-2,6-dimethyl-1,4-phenylene) non-contaminated with metal salt at room temperature through the electrophilic reaction of the sulfonium cation produced by the photo-oxidation.

Poly(thio-1,4-phenylene) (PPS) is known as engineering plastic having excellent performances such as thermal stability and good electrical characteristics.1) Commercial PPS is produced by polycondensation of p-dichlorobenzene with sodium sulfide in N-methylpyrrolidone under high temperature and pressure. Lenz and co-workers have reported the preparation of PPS by the polycondensation of p-halothiophenoxy metal salts. These polycondensation reactions proceed with the stoichiometric formation of metal halides. The salt contamination degrades the electric performance and moldability, which restricts the use as insulating material. It is difficult to remove the formed salts to provide pure PPS.



(1)

Oxidative polymerization of diphenyl disulfide (1 atm, r. t.) (1 atm = 101325 Pa) provides pure structure-defined PPS (1) compared with the commercial process.2a) We have confirmed that oxovanadium complexes are available as catalysts for oxygen-oxidative polymerization of disulfides.[2b] However, the redox system which catalyze the oxidative polymerization is restricted because of the high oxidation potential of disulfides. Photo-induced electron transfer enables redox processes which are even uphill in the ground state.[3] Photo-catalyzed oxidative polymerization has sometimes been applied to the synthesis of aromatic polymers because of its advantages for the fine fabrication of designed patterns.[4] We now describe the photo-redox system which catalyzes the oxidative polymerization of a disulfide for the synthesis of a PPS derivative with high purity.

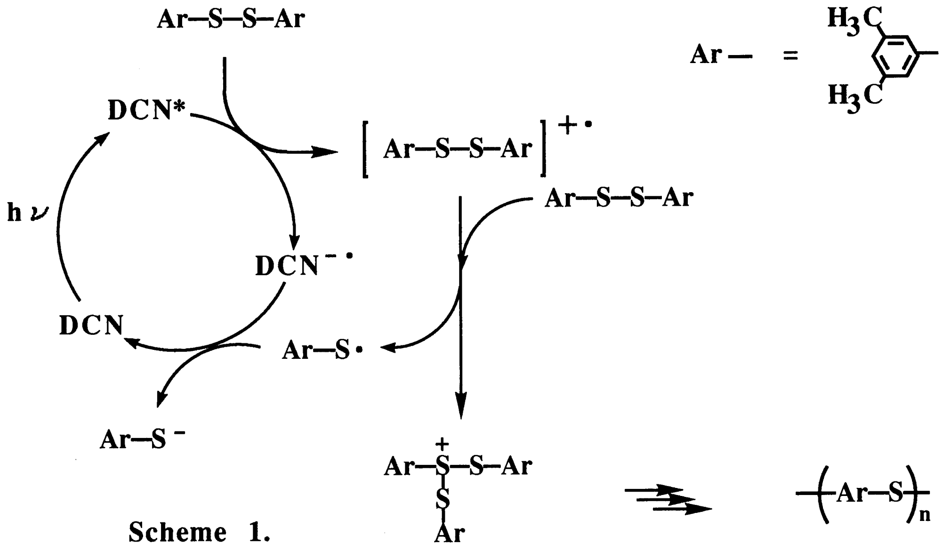
Aromatic nitriles were examined as photo-redox catalysts. The solution of bis(3,5-dimethylphenyl) disulfide (DPS; 50 mM (1M = 1 mol dm^{-3})) with the aromatic nitrile (5 mM) in acetonitrile (20 cm^{3}) was placed in a quartz glass tube and irradiated for 20 h with wavelength longer than 300 nm by using a high-pressure mercury lamp and the filter (HOYA B410).[5] By pouring the reaction mixture to hydrochloric methanol, the product was isolated as white powder. 2,3-Dicyanonaphthalene (DCN) acted as a catalyst to give the polymer in good yield, which was identified to be poly(thio-2,6-dimethyl-1,4-phenylene) non-contaminated with metal salt (Na, K, Cu < 1ppm) by IR, NMR, and elemental analysis.[6]

Table 1. Photo-Oxidative Polymerization of Bis(3,5-dimethylphenyl) Disulfide[a] in the Presence of Aromatic Nitriles as Catalysts

Catalyst[b]	CF_3COOH / mol dm^{-3}	Polymer yield / wt %
1,3-Dicyanobenzene	0	2
1,4-Dicyanobenzene	0	3
2,3-Dicyanonaphthalene	0	23
	1.0	62
9-Cyanoanthracene	0	0
9,10-Dicyanoanthracene	0	0

a) 50 mmol dm^{-3} in acetonitrile, 20 h. b) 5 mmol dm^{-3}.

The photopolymerization of the disulfide did not proceed in the absence of DCN. The turnover number of DCN was >60, which indicates that DCN acts as an efficient electron mediator. The polymer yield could be controlled by the irradiation time. 3,5-Dimethyl thiophenol was detected in the reaction mixture after the irradiation. The catalytic cycle is estimated as follows. DPS is oxidized by the photo-activated DCN* to produce



Scheme 1.

the sulfonium cation and the thiophenoxy radical. The reduced catalyst is regenerated by the oxidation by the radical since the radical anion of 1,4-dicyanonaphthalene is oxidized by selenophenoxy radical.[7] It has been already concluded that the sulfonium cation electrophilically react to form phenylene sulfide bond.[8] The photo-sensitized polymerization proceeds through the electron transfer process shown in Scheme 1.

The oxidation potential of DPS is ca. 1.5 V vs Ag/AgCl. Since the reduction of DCN proceeds at much more negative potential (ca. -1.3 V) in the ground state, the direct uphill electron transfer from DPS to DCN does not proceed. However, the reduction of the photo-activated DCN* proceeds at more positive potential (ca. 2 V). In this system, the oxidation of DPS by DCN takes place because the large potential gap in the ground state is compensated with photo-energy. 9-Cyanoanthracene or 9,10-dicyanoanthracene does not act efficiently because the reduction potential in the excited state is not enough to oxidize DPS. 1,3- or 1,4-Dicyanobenzene is not an efficient catalyst because the absorption band is overlapped with that of the disulfide.

The polymerization does not proceed efficiently in nonpolar solvent as dichloromethane or 1,1,2,2-tetrachloroethane. In acetonitrile, the presence of acid improved the polymerization because the nucleophilic side reaction to the sulfonium cation is suppressed. The maximum yield of the polymer should be 50% according to the stoichiometry of the polymerization (Scheme 1). However, in the presence of trifluoroacetic acid (1.0 M), the polymer yield increased up to 62%. This shows the possibility of the regeneration of the catalyst as a side reaction by the electron transfer to an acceptor (e.g. H^+ or O_2) other than the thiophenoxy radical.

The present photo-oxidative electron transfer is applicable to the oxidative polymerization of disulfide which provides poly(thio-2,6-dimethylphenylene) with high purity.

This work was supported by the Grant-in-Aid for Scientific Research (Nos. 04750707, 040850) and Developmental Scientific Research (No. 04555223) from the Ministry of Education, Science and Culture, Japan, and The Asahi Glass Foundation.

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5) Longest wavelength absorption of DCN is at 342 nm. DPS and poly(2,6-dimethyl-1,4-phenylene) do not have strong absorption at this wavelength.

6) Poly(thio-2,6-dimethyl-1,4-phenylene), C_8H_8S requires C, 70.54; H, 5.92; S, 23.54, found: C, 69.9; H, 6.1; S, 24.8, Na, 0 ppm; Cl < 10 ppm, Another metals, 0 ppm, IR (KBr, /cm^{-1}) 2850, 2920, 2975, 3040 ($\nu_{C\text{-}H}$); 1370, 1450, 1570 ($\nu_{C=C}$); 875 ($\delta_{C\text{-}H}$); ^{1}H-NMR (90MHz; solvent $CDCl_3$ /ppm) δ 2.3 (methyl 6H); δ 6.7 (phenyl 2H); ^{13}C-NMR (90MHz; solvent $CDCl_3$ /ppm) δ 125, 127, 140, 144 (phenyl C) δ 22 (methyl C). $T_{d10\%}$ (temperature for 10% weight loss of polymer) 420 °C. The weight averaged molecular weight of the polymer is ca. 3000.

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(Received March 15, 1993)