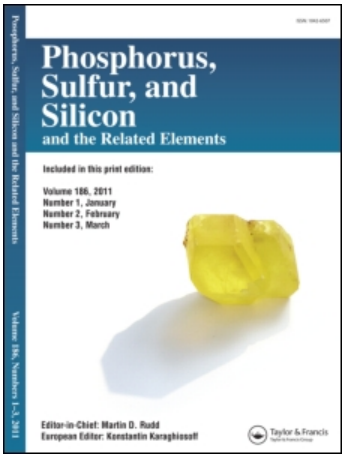

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Oxidation of Disulfides by 4-Electron Transfer to O_2: A $Ru(bpy)_3^{2+}$-Catalyzed Photo-Oxidation System for Selective Formation of Polythioethers

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Tris(2,2'-bipyridine)ruthenium(II) chloride catalyzed the photo-oxidative polymerization of diaryl disulfides by O_2, by which poly(thioarylene)s were efficiently produced. The polymerization proceeded through the electrophilic reaction of the sulfonium cation which was produced selectively by the photo-redox system.

INTRODUCTION

Sulfonium cation is an excellent electrophile to react with aromatic compounds, which provides a simple and selective method for the formation of thioether bond. A typical example has been provided by the oxidation of diphenyl disulfide in acidic media yielding phenylbis(phenylthio)sulfonium cation, which polymerizes to produce poly(thio-1,4-phenylene).[1] When O_2 is used as an oxidant under acidic conditions, 4-electron reduction system of O_2 to H_2O offer a desirable catalysis to circumvent the partially reduced oxygens such as peroxides which readily produces side products such as sulfoxides and sulfones. Indeed, the catalysis of oxovanadium complexes such as $VO(acac)_2$ in the O_2-oxidative polymerization of diphenyl disulfide has been confirmed to involve a homogeneous 4-electron reduction of O_2 to H_2O.[2] We report here a simple photo-catalytic system of a ruthenium(II) complex for the polymerization of disulfides, which provided an additional example of the O_2-oxidation system for the selective formation of thioether bonds.

PHOTO-OXIDATIVE POLYMERIZATION OF DIPHENYL DISULFIDE

A catalytic amount of $Ru(bpy)_3^{2+}$ acted as an electron mediator form the disulfide to O_2. Irradiation of a solution containing $Ru(bpy)_3^{2+}$, bis(3,5-dimethylphenyl) disulfide, trifluoroacetic acid and trifluoroacetic anhydride in dichloromethane using a high pressure mercury lamp with a filter (λ>350 nm) resulted in the formation of poly(thio-

2,6-dimethyl-1,4-phenylene) in high yield (Table 1). The catalytic efficiency of $Ru(bpy)_3^{2+}$ (ca. 1700%) was higher than the previously reported value for the catalysis by 2,3-dicyanonaphthalene in the photo-oxidative polymerization of bis(3,5-dimethylphenyl) disulfide.[3] Moreover, the ruthenium(II) complex provided the first photo-catalytic system for the polymerization of diphenyl disulfide. The linear structure of the obtained polymers were confirmed.

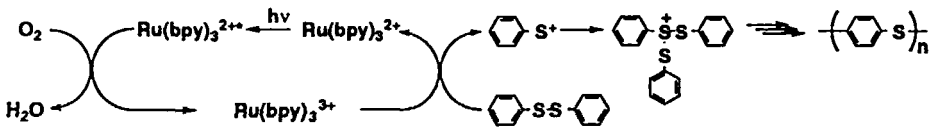
TABLE 1
Results of Polymerization.[a)]

Monomer	Catalyst	CF_3COOH (mol/L)	Polymer Yield (wt%)	T_m (°C)
3,5-DMDPS[b)]	$Ru(bpy)_3^{2+}$ [d)]	0.1	79	-
3,5-DMDPS	$Ru(bpy)_3^{2+}$	0.5	83	-
3,5-DMDPS	$Ru(bpy)_3^{2+}$	2.0	87	-
DPS[c)]	$Ru(bpy)_3^{2+}$	0.5	32	187
DPS	$Ru(phen)_3^{2+}$ [e)]	0.5	14	-

[a)] Reaction conditions: Solvent = CH_2Cl_2, [Monomer] = 0.1 mol/L, [Catalyst] = 5 mmol/L, $[(CF_3CO)_2O]$ = 0.1 mol/L, 20 hr, high pressure Hg lamp with HOYA B410 filter (λ>350 nm). [b)] Bis(3,5-dimethylphenyl) disulfide. [c)] Diphenyl disulfide. [d)] Tris(2,2'-bipyridine)ruthenium(II) chloride. [e)] Tris(1,10-phenanthroline)ruthenium(II) chloride.

CATALYTIC MECHANISM

The active species for the oxidation of disulfide is a ruthenium(III) complex produced by the photoactivation of ruthenium(II) followed by the electron transfer to O_2. The O_2 uptake measurement revealed a stoichiometry based on 4-electron reduction of O_2 yielding H_2O at the reduction side. Thus no sulfoxide or sulfone bond was detected. The selective photoexcitation of $Ru(bpy)_3^{2+}$ (λ_{max} = 440 nm) resulted in the catalysis as shown in Scheme 1.



Scheme 1

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