Letter

"Radical-controlled" oxidative polymerization of 4-phenoxyphenol catalyzed by a dicopper complex of a dinucleating ligand

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Abstract

The oxidative polymerization of 4-phenoxyphenol (PPL) catalyzed by a dicopper complex with a dinucleating ligand, 1,2-bis[2-(bis(2-pyridyl)methyl)-6-pyridyl]ethane is described. The polymerization proceeded regioselectively to give crystalline unsubstituted poly(1,4-phenylene oxide) (PPO), in which μ-η^2:η^2-peroxo dicopper(II) species is probably involved as the active dioxygen intermediate. A copper complex with a mononucleating ligand of the similar structure, 1,1,1-tris(6-methylpyrid-2-yl)ethane, also catalyzed the oxidative coupling of PPL. The coupling selectivity for the dicopper/dinucleating ligand complex was close to that for the copper/mononucleating ligand complex. However, the initial reaction rate for the former was independent on the catalyst amount in a certain range, whereas that for the latter decreased with the decrease of the catalyst amount. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative polymerization; 4-Phenoxyphenol; Dicopper complex; Dinucleating ligand
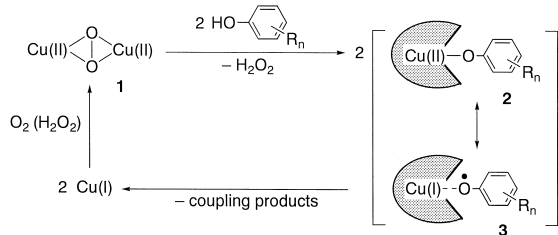
1. Introduction

Catalytic oxidative polymerization of 2,6-disubstituted phenols produced useful linear polymers

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[1–3], however for that of 2- and/or 6-unsubstituted phenols, it had been very difficult to control the regioselectivity of coupling of the phenoxy radicals [2,4,5]. Recently, we have achieved highly regioselective "radical-controlled" oxidative polymerization of 4-phenoxyphenol (PPL) [6–8], 2-methylphenol [9], 3-methylphenol [10], and 2,5-dimethylphenol [11] catalyzed by μ-η^2:η^2-peroxo dicopper(II) complex. By this polymerization of PPL, crystalline unsubstituted poly(1,4-phenylene oxide) (PPO) was synthesized for the first time via catalytic oxidative poly-

Scheme 1.

merization. The reaction mechanism is explained as follows (Scheme 1): a μ-η^2:η^2-peroxo dicopper(II) complex (**1**) reacts with phenols to give a phenoxo–copper(II) complex (**2**), equivalent to a phenoxy radical–copper(I) complex (**3**), which is not "free" radical but "controlled" radical. Hence, the regioselectivity in the subsequent coupling is regulated by the catalyst. In our previous papers, the key complex, the μ-η^2:η^2-peroxo dicopper(II) complex **1**, was formed in situ from the corresponding monocopper complex.

On the other hand, it has been reported that a dicopper(I) complex with a sterically hindered dinucleating ligand, 1,2-bis[2-(bis(6-methyl-2-pyridyl)-methy)-6-pyridyl]ethane, under dioxygen generated the most stable μ-η^2:η^2-peroxo dicopper(II) complex reported so far [12]. This finding encouraged us to use such a dicopper/dinucleating ligand complex as catalyst for "radical-controlled" oxidative polymerization and to investigate the effect of the dinucleating ligand complex catalyst on the coupling

selectivity and reaction rate. In the present work, the polymerizations of PPL catalyzed by a dicopper complex with the hindered dinucleating ligand (**4**) [12] and another dicopper complex with a less hindered one (**5**) [13,14] were performed (Scheme 2). A copper complex of a mononucleating ligand having a similar unit, 1,1,1-tris(6-methylpyrid-2-yl)ethane (**6**), was also employed as the catalyst.

2. Experimental

The dicopper/dinucleating ligand complexes **4** [12] and **5** [13] were prepared according to the reported papers. The copper/mononucleating ligand complex **6** was synthesized in a similar manner described previously [15]; the detail will be reported elsewhere. The preparation of oxidative coupling dimers of PPL (see below) was reported in the previous papers [4,7]. Acetonitrile was of anhydrous grade, other reagents and solvents were of reagent grade, and they were used without further purification. Size exclusion chromatography (SEC) was performed at 60°C with DMF containing 0.4 wt.% LiCl as eluent. Differential scanning calorimetry (DSC) was carried out under argon: the first heating was run from room temperature to 300°C at a rate of 10°C/min, and after cooling from 300°C to room temperature at a rate of 10°C/min, the second heating was done in a similar way as the first one.

R=Me, X=PF$_6$: **4**
R=H, X=CF$_3$SO$_3$: **5**

6

Scheme 2.
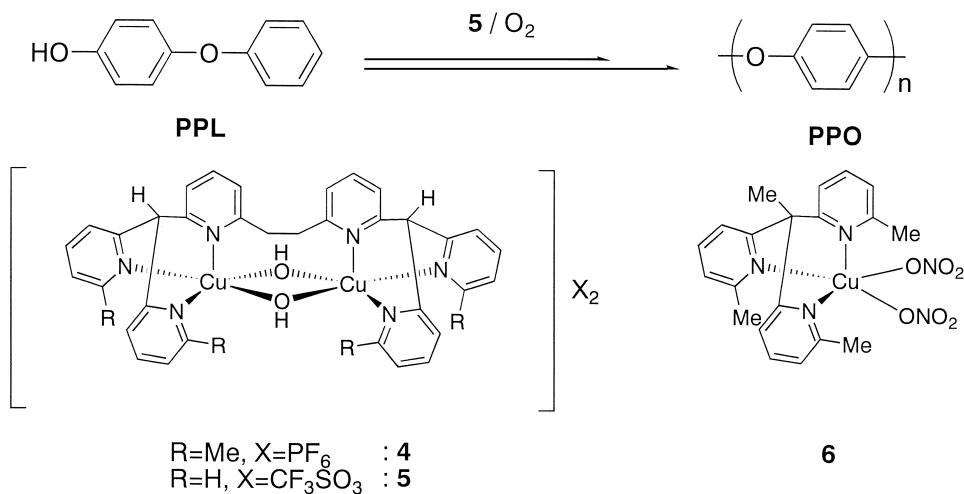
Under dioxygen (1 atm), a mixture of PPL (112 mg, 0.60 mmol), **5** (1.5 mg, 0.0015 mmol), 2,6-diphenylpyridine (6.9 mg, 0.030 mmol), and diphenyl ether (80 mg, internal standard) in toluene (1.2 g) and anhydrous acetonitrile (0.3 g) was kept at 40°C with vigorous stirring. At 0.2 h, a small portion (10 mg) of the reaction mixture was sampled, and then, the conversion of PPL (16%) and the total yield of dimers (11%) were determined by HPLC. After 98 h (conversion 96%), a few drops of conc. HCl aq. was added and a large amount of methanol was poured into the reaction mixture to precipitate the polymeric materials, which were collected by filtration, washed with methanol, and dried under vacuum to give 80 mg of the white polymer (yield 73%).

3. Results and discussion

The oxidative polymerization of PPL was carried out in the presence of the catalyst (0.5 mol% based on copper atom to PPL) in toluene/acetonitrile (4/1 w/w) under dioxygen (1 atm) at 40°C (Table 1). During the polymerization, a small portion of the reaction mixture was taken out for the determination of the amount of the residual PPL and the dimers, p-4, o-4, oo-22 and oo-13 (see the figure in Table 1) [6,7]. In the polymerization of PPL oxidized by an equimolar of 2,2′-azobisisobutyronitrile, a model system of free radical coupling, the dimer ratio of p-4, o-4, oo-22 and oo-13 was 82:4:2:12 at the PPL conversion of 27%. The formation of C–C coupling dimers, oo-22 and oo-13, was characteristic for the free radical coupling, however, the "radical-controlled" polymerization of PPL catalyzed by the μ-η^2:η^2-peroxo dicopper(II) complex did not give the C–C dimers.

In the case of the dicopper complex with the hindered dinucleating ligand **4**, the reaction did not proceed at all. The dicopper complex with less hindered dinucleating ligand **5** catalyzed the polymerization of PPL, and at 0.2 h, the conversion of

Table 1
Dimer ratio at initial stage of oxidative polymerization of PPL[a]

Catalyst	Time (h)	Conv.[b] (%)	Yield[c] (%)	Dimer ratio[d] (%)			
				p-4	o-4	oo-22	oo-13
4	17	0	0	–	–	–	–
5	0.2	16	11	89	10	0	1
6	16	11	7	87	11	1	1

[a] Polymerization of PPL (0.60 mmol) catalyzed by copper complex (0.0030 mmol based on copper atom) and 2,6-diphenylpyridine (0.030 mmol) in toluene (1.2 g) and acetonitrile (0.3 g) under dioxygen (1 atm) at 40°C.
[b] Conversion of PPL.
[c] Total yield of dimers.
[d] Four dimers shown below.

p-4

o-4

oo-22
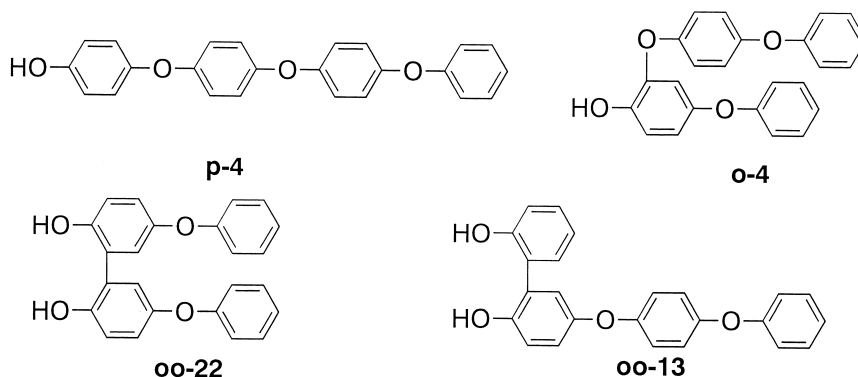
oo-13

PPL and total yield of dimers were 16% and 11%, respectively. Only 1% of oo-13 was detected, suggesting the coupling would be almost regioselectively controlled by the catalyst. The difference of catalytic activity between **4** and **5** seems to be due to that of steric hindrance around the copper atoms and/or that of counter ion (X). For the copper complex with the mononucleating ligand **6**, the reaction was very slow but the PPL conversion was 11% at 16 h, in which a little amount of C–C dimers was observed and the dimer ratio was almost the same as that for **5**.

The polymerization catalyzed by **5** and **6** was continued, until PPL was not consumed any more. For the catalyst **5**, the PPL conversion reached 96% at 98 h, and then, the white polymer was obtained as the methanol-insoluble part in 73% yield. From the IR analysis, the polymer mainly consisted of a 1,4-oxyphenylene unit [16], and the number- and weight-averaged molecular weight of the polymer were 2000 and 3500, respectively, estimated by SEC. A melting point was observed at 201°C in the second scan of DSC measurement of the polymer, showing the formation of crystalline PPO. In the polymerization by **6**, the PPL conversion did not reach to more than 16%, probably owing to the deactivation of the catalyst, and consequently, none of methanol-insoluble polymer was obtained.

The initial reaction rate toward the amount of catalyst was investigated for the dicopper/dinucleating ligand complex **5** and the copper/mononucleating ligand one **6** (Fig. 1). In the case of **5**, the initial reaction rate at the catalyst amount of 2 mol% (based on copper atom to PPL) was almost the same when using 0.5%. On the other hand, the initial reaction rate for **6** greatly increased with an increase in the amount. For the "radical-controlled" oxidative polymerization of PPL catalyzed by (1,4,7-triisopropyl-1,4,7-triazacyclononane)copper dichloride (**7**), a mononucleating ligand complex, the reaction rate strongly depended on the catalyst amount [8].

In the reaction of the dicopper/dinucleating ligand complex **5** with hydrogen peroxide, the μ-η^2:η^2-peroxo dicopper(II) complex was not detected [14], but the bis(μ-oxo) dicopper(III) complex was presumed to be generated [13]. In the formation of a bis(μ-oxo) complex, a μ-η^2:η^2-peroxo complex was assumed to be the precursor [17]. These data indi-
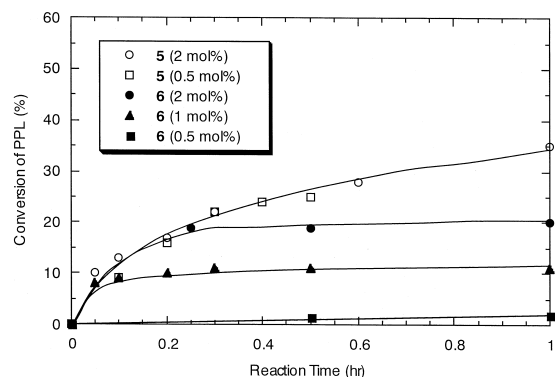

Fig. 1. Reaction rate at the initial stage of polymerization of PPL catalyzed by **5** and **6**.

cate, in the polymerization catalyzed by **5**, that μ-η^2:η^2-peroxo dicopper(II) complex could be also formed as an intermediate, and hence, the high regioselectivity for p-4 would be achieved via the "radical-controlled" mechanism. From the previous finding that a similar copper(I)/mononucleating ligand complex as **6** formed the μ-η^2:η^2-peroxo dicopper(II) complex under dioxygen [12], the polymerization by using **6** would also proceed in the "radical-controlled" manner.

The reaction rates in the oxidative polymerization catalyzed by the copper/mononucleating ligand complexes of **6** and **7** varied with the catalyst amounts. However, no change of the initial reaction rate in using 0.5 and 2 mol% of the catalyst amount of **5** is characteristic for the dicopper/dinucleating ligand complex. These differences in the behavior of reaction rate may be ascribed to the difference of the steric hindrance of the ligands, nature of counter ion, and/or ligand type between dinucleating and mononucleating.

4. Conclusion

The "radical-controlled" oxidative polymerization of PPL catalyzed by the dicopper complex of the dinucleating ligand **5** produced crystalline PPO. The coupling selectivity was almost the same as that of the copper complex of mononucleating ligand **6**. However, the behavior of reaction rate toward the catalyst amount; the initial reaction rate for **5** was

independent on the catalyst amount between 0.5 and 2 mol%, whereas the reaction rate decreased with a decrease in the amount of **6**. These data suggest that the catalyst amount can be reduced by the use of the dicopper/dinucleating ligand complex catalyst.

Acknowledgements

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