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Catalytic Cu(II)−Amine Terminated Poly(amidoamine) Dendrimer Complexes for Aerobic Oxidative Polymerization To Form Poly(2,6-dimethyl-1,4-phenylene oxide) in Water

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Introduction. Aerobic oxidation catalyzed by copper complex is particularly fascinating because oxygen is an abundant and ecologically benign oxidant.[1,2] As an important example, copper-catalyzed oxidative polymerization of 2,6-dimethylphenol (DMP) produces poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by C−O coupling, an important engineering plastic, and an undesirable byproduct resulting from C−C coupling, i.e., 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (DPQ) (Scheme 1).[3−9] However, the mechanism for the C−O/C−C coupling selectivity in DMP polymerization has not been entirely elucidated.[10,11] Furthermore, both a solvent-recovery process and an antiexplosive reactor are required since the polymerization usually proceeds in an organic solvent under an oxygen atmosphere. From the view of green chemistry, the use of water as the solvent is the desired approach.[12,13] Nishide et al. recently reported the first oxidative polymerization of DMP to form PPO in water.[14,15] The catalysts used for the DMP polymerization in water were copper complexes with ligands containing N-donor which are usually small molecules, such as diethylamine and its derivatives, etc., which still require further improvement to enhance the catalytic activity.[16−18]

Recently, Yamamoto et al. reported oxidative polymerization of 2,6-difluorophenol under diluted catalytic conditions using a Cu(II)−dendritic phenylazomethines (DPAs) complex catalyst in an organic solvent, suggesting that the high activity of the new catalyst could be ascribed to the concentration effect of the dendrimer capsule.[19] Unfortunately, the Cu(II)−DPA complex cannot be used as the catalyst for polymerization of DMP in aqueous medium due to the poor solubility of DPA dendrimer in water. Polyamidoamines (PAMAMs),[20−23] a typical class of dendrimers, are expected to be suitable as the ligands for copper catalyst used in water since they are water-soluble hyperbranched macromolecules of monodispersed molecular weight with high density of nitrogens which can coordinate to copper ions. Furthermore, the structure and solubility of the PAMAM dendrimers and metallodendrimers could be tuned to locate of the catalytic sites. Cu(II)−PAMAM complexes have to date only been reported for structure studies,[24−30] water treatment,[31−33] and preparation of dendrimer-encapsulated Cu(0) nanoparticles.[26,27] In addition, PAMAMs have been used in catalysis so far by main two strategies. One approach is to attach a known catalytic unit to the PAMAM backbone, which already had applications in hydroformylation reactions of olefins with rhodium complex catalyst, carbonylation reactions of iodoarenes with palladium complex catalyst, etc.[34−38] The other one is the preparation of PAMAM encapsulated metal nanoparticles, which has been used as catalysts for the hydrogenation of alkenes, electrocatalytic reduction of O_2, etc.[39−42]

Here we report the first catalytic Cu(II)−PAMAM dendrimer (PAMAM, ethylenediamine core with amino terminal groups) complexes that catalyze aerobic oxidative polymerization of DMP in water with significantly high catalytic activity. The results are significant for three reasons as follows. First, it is the first example that Cu(II)−PAMAM dendrimer complexes are used as catalysts. Second, Cu(II)−PAMAM complexes catalyzed aerobic oxidative polymerization of DMP proceeds under mild conditions in water, resulting in a good yield of PPO and an extremely low content of DPQ. Third, the catalytic activity of Cu(II)−PAMAM complexes enhances greatly compared with the catalyst previously used.

Results and Discussion. The oxidative polymerizations of DMP in water were carried out in the presence of Cu(II)−ethylenediamine−*N*,*N*,*N*′,*N*′-tetraacetic acid tetrasodium salt (EDTA), Cu(II)−PAMAMG1, Cu(II)−PAMAMG3, and Cu(II)-PAMAMG5, and the results are summarized in Figure 1 and Table 1. The typical procedure is as follows (entry 10, Table 1). A $CuCl_2$ (0.43 mg, 2.5 μmol) aqueous solution was added to the aqueous solution containing PAMAMG3 (0.74 mg, 0.23 μmol, 1/11 molar amount based on the $CuCl_2$), and the resulting solution quickly changed its color to light blue. The oxidative polymerization of DMP (0.61 g, 5.0 mmol) in water was carried out by using Cu(II)−PAMAMG3 dendrimer complex as catalyst (1/2000 molar amount based on the DMP) under an oxygen atmosphere at 50 °C for 24 h. An off-white powder was obtained by filtration after salting out with sodium chloride and then extracted for 48 h to eliminate DPQ. The product was identified as PPO by ^{1}H NMR (see Figure S3 of the Supporting Information), and the molecular weight ($M_w = 5100$) was characterized by GPC. The content of DPQ was determined by a visible spectrophotometer. The low content of byproduct DPQ (Table 1) demonstrates that the novel Cu(II)−PAMAM complex catalysts are extremely selective to form PPO.

It was found that the major factors which influence the catalytic activity of the complexes in DMP polymerization in water are the generation of PAMAM dendrimers and the molar ratio of copper ions to the ligands. First, the generation number of PAMAM greatly affects the catalytic activity of Cu(II)−PAMAM complexes. When copper concentration reduces from 200 to 25 μmol/L, the PPO yields drop significantly with Cu(II)−PAMAMG1 complex, while the yields of PPO decrease gently by Cu(II)−PAMAMG3 complex and Cu(II)−PAMAMG5 complex, as shown in Figure 1a and Table 1. The yields of PPO by Cu(II)−PAMAMG5 complex are somewhat higher than those with Cu(II)−PAMAMG3 complex under the same condition. In addition, as shown in Table 1, the catalytic activity of the new Cu(II)−PAMAM complexes enhance greatly compared with that of the conventional Cu(II)−EDTA catalyst. Remarkably, by using Cu(II)−PAMAMG3 complex and Cu(II)−PAMAMG5 complex, the PPO yield still remains high (83% and 85%) at a copper concentration of 25 μmol/L, which is even higher than the result obtained through Cu(II)−EDTA complex at a much

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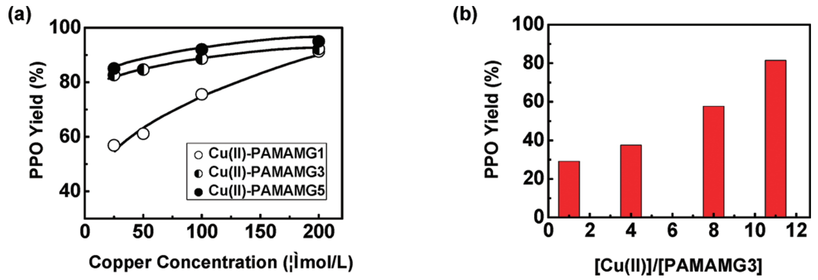


Figure 1. (a) Dependence of PPO yields on copper concentration. (b) Dependence of PPO yields on [Cu(II)]/[PAMAMG3] (the copper concentrations remained unchanged at 25 μmol L^{-1}). All the polymerizations were carried out in water (100 mL) under an oxygen atmosphere for 24 h at 50 °C: DMP 0.05 mol L^{-1}, sodium hydroxide 0.05 mol L^{-1}, and sodium *n*-dodecyl sulfate 0.005 mol L^{-1}.

Scheme 1. Oxidative Polymerization of DMP

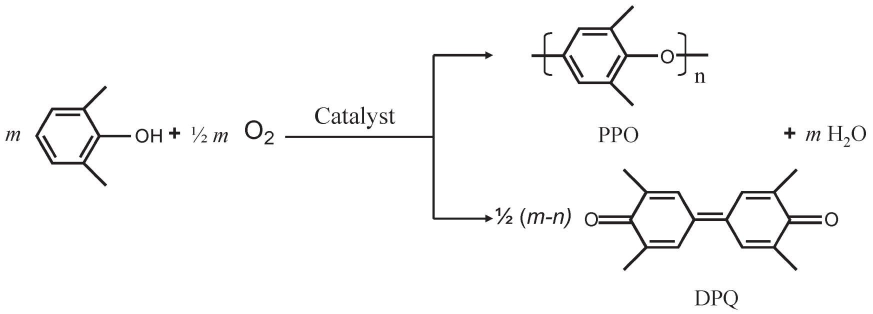
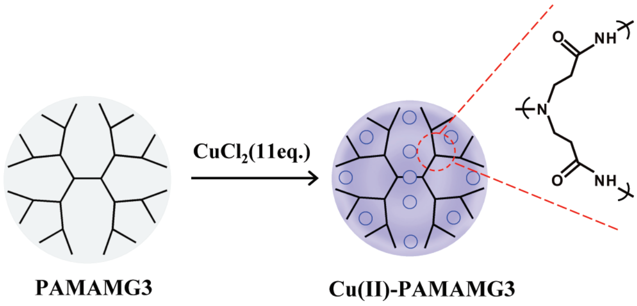


Table 1. Oxidative Polymerization of 2,6-Dimethylphenol (DMP) in Water[a]

entry	catalyst	[Cu(II)] (μmol L^{-1})	PPO yield (%)	PPO M_w (M_w/M_n)[b] ($\times 10^3$)	DPQ yield[c] (%)
1	Cu(II)−EDTA[d]	200	73	5.5 (2.0)	0.08
2	Cu(II)−EDTA[d]	100	45	5.2 (1.9)	0.12
3	Cu(II)−PAMAMG1[e]	200	91	8.3 (1.6)	0.10
4	Cu(II)−PAMAMG1[e]	100	76	6.3 (2.0)	0.08
5	Cu(II)−PAMAMG1[e]	50	61	4.6 (1.8)	0.08
6	Cu(II)−PAMAMG1[e]	25	57	4.3 (1.6)	0.08
7	Cu(II)−PAMAMG3[f]	200	92	8.9 (1.7)	0.12
8	Cu(II)−PAMAMG3[f]	100	89	6.1 (1.7)	0.12
9	Cu(II)−PAMAMG3[f]	50	85	5.8 (2.3)	0.08
10	Cu(II)−PAMAMG3[f]	25	83	5.1 (1.7)	0.10
11	Cu(II)−PAMAMG5[g]	200	95	8.6 (2.0)	0.09
12	Cu(II)−PAMAMG5[g]	100	92	7.4 (2.2)	0.10
13	Cu(II)−PAMAMG5[g]	25	85	5.7 (2.2)	0.09

[a] All the polymerizations were carried out in water (100 mL) under an oxygen atmosphere for 24 h at 50 °C: DMP 0.05 mol L^{-1}, sodium hydroxide 0.05 mol L^{-1}, and sodium *n*-dodecyl sulfate 0.005 mol L^{-1}. [b] Determined by gel permeation chromatography using polystyrene standard in toluene. [c] Determined by UV−vis spectroscopy at 421 nm. [d] [Cu]/[EDTA] = 1 from ref 6a. [e] [Cu]/[PAMAMG1] = 3. [f] [Cu]/[PAMAMG3] = 11. [g] [Cu]/[PAMAMG5] = 47.

Scheme 2. Preparation of the Catalyst by Coordination between PAMAMG3 and $CuCl_2$



higher copper concentration (200 μmol/L). This clearly illustrates a distinct advantage of Cu(II)−PAMAM complexes over the traditional Cu(II)−EDTA complex catalyst. The results are similar to those obtained by Yamamoto et al. with a Cu(II)−dendritic phenylazomethines (DPAG4) complex for oxidative polymerization of 2,6-difluorophenol in organic solvent, which suggested that Cu(II)−DPAG4 had a very high local concentration of copper complex. Thus, the high catalytic activity achieved by copper complexes with higher dendrimer generations might be ascribed to the concentration effect of copper complexes. Actually, the kinetic results also support the explanation. The initial oxidative polymerization rate of DMP in water is 5.06 × 10^{-2} mmol L^{-1} min^{-1} using the Cu(II)−PAMAMG3 complex (1/2000 molar amount based on the DMP) at 50 °C, which is faster than the rate by the Cu(II)−EDTA complex under the same condition (2.58 × 10^{-2} mmol L^{-1} min^{-1}).

Another important factor that influences the catalytic activity of the Cu(II)−PAMAM dendrimer complex is the molar ratio of copper ions to the ligands. As shown in Figure 1b, each polymerization was carried out at the same concentration of copper ions (25 μmol L^{-1}), and the

PPO yield increases with the increase of the [Cu(II)]/[PAMAMG3] molar ratio from 1 to 11. The low PPO yield at low [Cu(II)]/[PAMAMG3] molar ratio could be explained by the dispersed state of copper complexes and low concentration effect of the catalyst, which is unfavorable to the DMP polymerization. Moreover, the structure of Cu(II)−PAMAM complexes have been investigated by using UV−vis spectroscopy (UV−vis), electron paramagnetic resonance (EPR), extended X-ray absorption fine structure (EXAFS), and mass spectrometry (MS).[24−30] It was found that Cu(II) ions could chelate with PAMAM dendrimer at both external and internal layers,[29] and the major coordination sites for Cu(II) ions are terminal primary amines and internal tertiary amines.[25,31] Only two complexes are present at the outmost layer of PAMAM dendrimers: Cu−N_4 (Cu(II) ions coordinated with two terminal primary amines and two outmost layer tertiary amines) and Cu−N_2 (Cu(II) ions coordinated with two terminal primary amine groups and other weak coordination site such as amide groups or water).[25] When the molar ratio of Cu(II) to PAMAM is low, the Cu(II) ions tend to form Cu−N_4 complexes first. With the increase of the molar ratio of Cu(II) to PAMAM, the increased Cu(II) ions would form Cu−N_2 complexes after all the outmost layer tertiary amines have been occupied. For lower generation PAMAM dendrimer, the Cu(II) ion could bind with two internal tertiary amines.[30] Thus, based on the hypothesis that all coordination sites of PAMAM dendrimer involves in the complexation, a rough estimation suggested that PAMAMG3 could bind 11 Cu(II) ions. Therefore, the highest catalytic activity of the Cu(II)−PAMAMG3 complex with a full load of Cu(II) ions might be explained by a high local concentration of the Cu(II) complexes. The low PPO yield at low [Cu(II)]/[PAMAMG3] molar ratio might be due to inhibition of polymerization by uncoordinated sites of PAMAMG3 dendrimer. Indeed, we[18] and others[43−45] reported that the excess ligand would suppress the polymerization by competing with the substrate and the subsequent oligomers to coordinate with the copper ions. Hence, the results clearly demonstrate that the concentration state of the copper complexes in the PAMAMG3 dendrimer is indispensable for its high catalytic activity in the oxidative polymerization of DMP in water.

Conclusion. In summary, we have described the novel Cu(II)−PAMAM complex catalyst for aerobic oxidative polymerization of DMP in water. The catalysts exhibit excellent C−O/C−C coupling selectivity to form PPO. Furthermore, the catalytic activity of Cu(II)−PAMAM complexes enhances greatly compared with that of Cu(II)−EDTA complex. This work opens the door for Cu(II)−PAMAM complexes as the catalysts for oxidation reactions. Further structural characterization, kinetics, and mechanism studies of the oxidative polymerization using Cu(II)−PAMAM complexes are underway in our laboratory.

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Supporting Information Available: Synthesis and characterization of PAMAM dendrimers, general procedure for oxidative polymerization of DMP in water, and characterization of formed PPO and DPQ. This material is available free of charge via the Internet at http://pubs.acs.org.

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