



Metal complexes catalyzed oxidative coupling of 2,6-dimethylphenol in micellar media

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ABSTRACT

The oxidative coupling reaction of 2,6-dimethylphenol (DMP) with H₂O₂ catalyzed by two copper(II) complexes (2,2'-dipyridylamine copper(II), L¹Cu and N,N'-bis(2-pyridinecarbonyl) ethylenediamine copper(II), L²Cu) in cationic surfactant cetyl trimethylammonium bromide (CTAB), gemini surfactants ethanediyl-1,2-bis(dodecyltrimethylammonium bromide) (12-2-12), dimethylene-1,2-bis(cetyltrimethylammonium bromide) (16-2-16), anionic surfactant sodium dodecyl benzene sulfonate (SDBS) and nonionic surfactant Triton X-100 (TX-100) micellar media were comparatively investigated at 25 °C. The kinetics of formation of 3,3',5,5'-tetramethyl-4,4'-diphenylquinone (DPQ) was studied. The kinetic parameters *k*₂ and *K*_m were obtained at pH 7.01. L¹Cu displayed better catalytic activity than L²Cu in mentioned above systems. For L¹Cu catalyzed systems, the cationic surfactant CTAB, 12-2-12 and 16-2-16 micellar media accelerated the oxidation of DMP. And the TX-100 and SDBS micelles showed little effect on reaction rate compared with the buffer solution. For the L²Cu catalyzed systems, these surfactants all inhibited the oxidation of DMP, and especially, the oxidation of DMP was not found in SDBS micellar solution in the catalyzed system at pH 7.01 and 25 °C. Micelles showed great influence on the yield of product and the selectivity of PPO. Under this work's conditions, DPQ was easily generated in aqueous solution, while PPO was remarkably promoted in micellar media, especially in SDBS micellar solution. As a green technology process, one outstanding advantage of this catalyzed system was that the products of polymer can be easily separated from the solution and the catalysts still remain in the micellar solution.

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1. Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPO) was widely used as a high-performance engineering plastic due to its good mechanical character, high glass transition temperature and the properties of chemical stability and self-extinguish [1–6]. PPO was generally prepared by the oxidative coupling of 2,6-dimethylphenol. In this reaction, PPO was formed by C–O coupling of phenolic moieties. The other product diphenylquinone (DPQ) generated from C–C coupling of two monomeric phenols, which was also recognized as an important material for electron transport [7].

Many copper(II) complexes were found as efficient catalysts in the catalysis process of oxidative coupling of DMP in organic solvents and water [8–12]. The use of water as the solvent for the oxidative polymerization was a green chemical process [12,13]. This reaction has been investigated extensively during the last

decades, however, no mechanism could be formulated yet that was able to solve all experimental findings. Up to now, several mechanistic proposals have been made accordingly which were thought to involve coupling of free phenoxy radicals, coupling of phenoxy radicals coordinated to catalyst, coupling of phenoxonium cation with phenol [14–17]. However the mechanism was yet not entirely clear.

Surfactant possesses hydrophilic and hydrophobic groups in their molecule. Surfactant and its micelle can alter reaction rate, mechanism and region- and stereochemistry [18–20]. Furthermore, the reactive intermediate could be inferred by the electrostatic effects of micelles [20]. In previous studies, we found that micelle and metallomicelle could efficiently increase the rate of hydrolysis and oxidation reactions [21–25]. In this work, we furtherly found that the distribution of products of the oxidation of DMP with H₂O₂ catalyzed by copper(II) complexes was also greatly changed by micelles. We were particularly interested in the property of the catalysis system in which the products of polymer could be easily separated from metallomicelle-catalyzed system under mild conditions.

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2. Experimental

2.1. Materials

CuCl₂·2H₂O, chloroform, absolute ethanol, 30% hydrogen peroxide, 2,2'-dipyridylamine, bromohexadecane, N,N,N',N'-tetramethyl ethylenediamine, sodium hydroxide, 1-dodecane bromide, 2,6-dimethylphenol (DMP), sodium dodecyl benzene sulfonate (SDBS), cetyl trimethylammonium bromide (CTAB), Triton X-100 (TX-100) were all analytical grade and were purchased from commercial sources. The 2,6-dimethylphenol (DMP) was purified by recrystallization. All other chemicals and solvents used were also analytical grade.

2.2. Synthesis of gemini surfactants and preparation of copper(II) complexes

2.2.1. Synthesis of gemini surfactant 16-2-16

The 16-2-16 was synthesized according to the literature [26]. The reaction was performed in absolute ethanol under reflux for 24 h in the presence of 1:3 proportion of N,N,N',N'-tetramethyl ethylenediamine and bromohexadecane. The solvent was removed by evaporation and the solid was recrystallized by ethyl acetate and ethanol to yield pure product. Anal. calcd. for C₃₈H₈₂N₂Br₂: C, 62.81; H, 11.29; N, 3.86%; found: C, 61.96; H, 11.02; N, 3.58%. ¹H NMR (300 MHz, CDCl₃), δ 0.9 (t, 6H, CH₂CH₃), 1.26 (m, 56H, CH₂), 1.83 (t, 4H, N-CH₂), 3.44–3.52 (s, 12H, N-CH₃), 3.73 (t, 4H, NCH₂CH₂N).

2.2.2. Synthesis of gemini surfactant 12-2-12

The 12-2-12 was also synthesized according to the literature [26]. By using the similar method as the synthesis of 16-2-16 in which 1-dodecane bromide was substituted for bromohexadecane. The crude products were recrystallized by acetone and ethanol. Anal. calcd. for C₃₀H₆₆N₂Br₂: C, 58.23; H, 10.75; N, 4.56%; found: C, 57.27; H, 10.23; N, 4.16%. ¹H NMR (300 MHz, CDCl₃), δ 0.89 (t, 6H, CH₂CH₃), 1.17 (m, 40H, CH₂), 1.81 (t, 4H, N-CH₂), 3.54 (s, 12H, N-CH₃), 3.68 (t, 4H, NCH₂CH₂N).

2.2.3. Preparation of L¹Cu

The L¹Cu was prepared according to the literature [27]. 2,2'-Dipyridylamine (1.71 g, 9.8 mmol) was added to hot trichloromethane (60 ml), and then to a hot CuCl₂·2H₂O (1.7 g, 10 mmol) in DMF (20 ml) solution under gentle stirring. Then, green precipitate was formed immediately. After some minutes it was filtered off, washed with trichloromethane and dried in vacuo. Anal. calcd. for C₁₀H₉N₃CuCl₂: C, 39.30; H, 2.95; N, 13.75; Cl, 23.22%; found: C, 39.38; H, 2.90; N, 13.45; Cl, 23.22%. The Cu loading was determined to be 3.17 mmol/g by ICP-AES.

2.2.4. Preparation of L²Cu

N,N'-bis (2-pyridinecarbonyl) ethylenediamine was prepared according to the literature [28]. Picolinate (2.46 g, 0.02 mol) in pyridine solution (8 ml) was added to ethylenediamine (0.01 mol, 0.68 ml) in pyridine (4 ml) under gentle stirring. Then triphenyl phosphate (5.21 ml, 0.0198 mol) was added slowly into the reaction mixture under reflux for 4 h in a water bath. Crystals formed overnight at room temperature and recrystallized by chloroform to yield the pure N,N'-bis (2-pyridinecarbonyl) ethylenediamine **1**. **1** (0.2 g) dissolved in hot ethanol was dropwise added into the CuCl₂·2H₂O (2.052 g, 0.012 mol) ethanol solution and the mixture was stirred for 2 h. Products were isolated by filtration, washed with cold ethanol and water. Anal. calcd. for C₁₄H₁₃N₄O₂CuCl: C, 45.66; H, 3.53; N, 15.22; Cl, 9.51%; found: C, 45.71; H, 3.45; N, 15.12; Cl, 9.57%. The Cu loading was determined to be 3.17 mmol/g

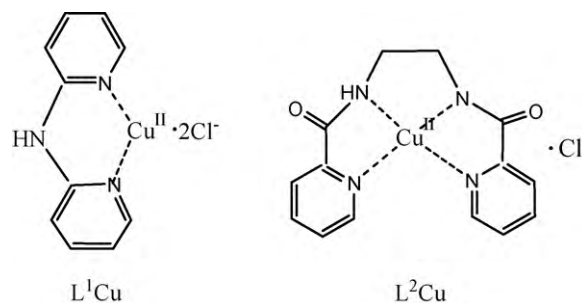


Fig. 1. Structure of two copper(II) complexes L¹Cu and L²Cu.

by ICP-AES. The two copper(II) complexes were outlined in Fig. 1.

2.3. Instruments and methods

Mass spectrometry was implemented with a Finnigan MAT 45001 mass spectrometer. Ultraviolet–visible absorbance measurements were performed with a TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with a thermostatic cell holder. Elemental analysis was implemented with a Carlo Erba 1106 instrument. The residual amount of DMP was implemented with FULI 9790 gas chromatograph.

0.01 M Tri (hydroxylmethyl) aminomethane (Tris) buffer solution was employed for all reactions. The concentration of H₂O₂ was determined by titrating a standardized ceric sulfate solution.

The typical reaction solution contained 5.0 × 10⁻⁵ M catalyst, 0.01 M hydrogen peroxide and desired concentration DMP. The reaction was carried out at 25 ± 0.2 °C. The initial DPO reaction rate R₀ was measured by monitoring the Formation of DPQ at 421 nm vs. time: R₀ = ΔA/(εlΔt). The unreacted amount of DMP was implemented with gas chromatograph.

In the enlarged experiment, the 5.0 × 10⁻³ M catalysts, 2.0 M hydrogen peroxide, and 1.0 × 10⁻¹ M DMP were mixed and the solution was kept at 25 ± 0.2 °C for 48 h. The insoluble solid product was filtered off from solution, dried and weighed.

3. Results and discussion

3.1. Effects of micelles on the rate of formation of DPQ

The oxidative coupling of DMP catalyzed by two copper(II) complexes were carried out in cationic CTAB, gemini 12-2-12 and 16-2-16, anion SDBS and nonionic TX-100 micelles, respectively. The initial reaction rates of formation of DPQ in aqueous solution and micellar media at pH 7.01 and 25 °C were calculated and shown in Table 1. From Table 1, it can be seen that L¹Cu displayed

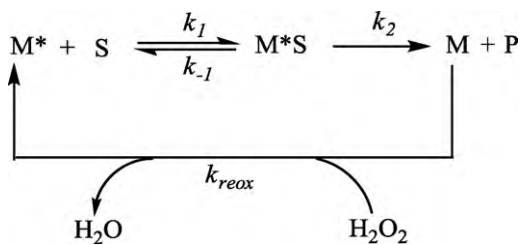
Table 1

The initial reaction rates R₀ of formation of DPQ in micellar media at pH 7.01 and 25 °C.

Systems	× 10 ⁹ R ₀ M s ⁻¹	
	L ¹ Cu	L ² Cu
Buffer	14.00	1.18
CTAB	26.10	0.69
12-2-12	26.00	1.05
16-2-16	32.61	1.08
Tx-100	14.92	0.52
SDBS	14.80	- ^a

Note: [LCu] = 5.0 × 10⁻⁵ M, [H₂O₂]₀ = 0.01 M, [DMP]₀ = 1.0 × 10⁻³ M, [CTAB] = 0.01 M, [TX-100] = 3.3 × 10⁻³ M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0 × 10⁻³ M.

^a Too small to be determined.



Scheme 1.

better catalytic activity than L²Cu. For L¹Cu catalyzed systems, these cationic micelles accelerated the reaction, while the non-ionic micelle TX-100 and anionic micelle showed a little effect on the reaction rate. For L²Cu, the initial formation rate of DPQ R_0 decreased in all of the micelles solution compared with the buffer solution, especially for SDBS, its reaction rate was too slow to be evaluated.

3.2. Kinetic analysis

It was found that the oxidative coupling reaction of DMP with H₂O₂ did not occur in the absence of catalysts, which showed that the copper(II) complexes displayed special catalytic characteristic for the oxidative coupling of DMP by H₂O₂ in aqueous solution and micellar media. As reported in previous studies [29,30], the copper(II) complexes with H₂O₂ may form an active oxygen species (M^{*}). In this work, we also thought the active oxygen species (M^{*}) as oxidant reacted with substrate DMP to produce DPQ. According to the experimental data, it can be found that the plots of R_0 vs. [DMP]₀ were all saturated curves, which had the character of Michaelis–Menten mechanism model. Thus the kinetic model, which was similar to Michaelis–Menten form, was proposed as Scheme 1.

In the first step, the active oxidant (M^{*}) could combine with substrate DMP (S) reversibly to form the intermediates (M^{*}S) with rate constants k_1 and k_{-1} . Then the intermolecular reaction of M^{*}S occurred, which was the rate-determining step with a rate constant k_2 . The process that catalyst M was oxidized to M^{*} again by H₂O₂ rapidly, and the rate constant k_{reox} was far larger than k_2 . In this work, the concentration of H₂O₂ was far excessive over copper(II) complex. So, almost all of M was oxidized to active state M^{*}. Thus based on Scheme 1, Eq. (1) could be obtained:

$$\frac{1}{R_0} = \frac{1}{k_2[M]_T} + \frac{K_m}{k_2[M]_T[S]_0} \quad (1)$$

where [M]_T was the total concentration of catalyst. [S]₀ was the initial concentration of DMP. K_m was the Michaelis constant.

$$K_m = \frac{k_{-1} + k_2}{k_1} \quad (2)$$

According to Eq. (1), the plot of $1/R_0$ vs. $1/[S]_0$ should be linear relationship. The experimental results indicated that $1/R_0$ vs. $1/[DMP]_0$ for the two copper(II) complexes catalyzed reactions displayed really good linear relationship (all the correlation coefficient $R > 0.99$) in the buffer solution and micellar media as shown in Figs. 2 and 3. The kinetic parameters k_2 and K_m could be obtained from the slope and intercept of the plot of $1/R_0$ vs. $1/[DMP]_0$, which were listed in Table 2.

In this oxidative coupling reaction, the DPQ generated from C–C coupling of two monomeric phenols. From Table 2 it can be found that for L¹Cu catalyzed systems, these cationic micelles (CTAB, 12-2-12, 16-2-16) all increased the formation rate of DPQ, while the nonionic micelle TX-100 and anionic micelle SDBS showed a little effect. This fact indicated that a reactive intermediate with negative charge may be formed in the process of generation of DPQ. So

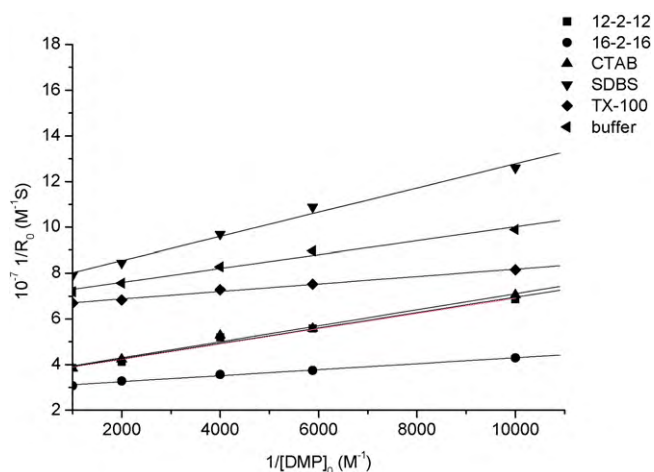


Fig. 2. Plot of $1/R_0$ vs. $1/[DMP]_0$ catalyzed by L¹Cu, at pH 7.01 and 25 °C. [L¹Cu] = 5×10^{-5} M, [H₂O₂]₀ = 0.01 M, [CTAB] = 0.01 M, [TX-100] = 3.3×10^{-3} M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0×10^{-3} M.

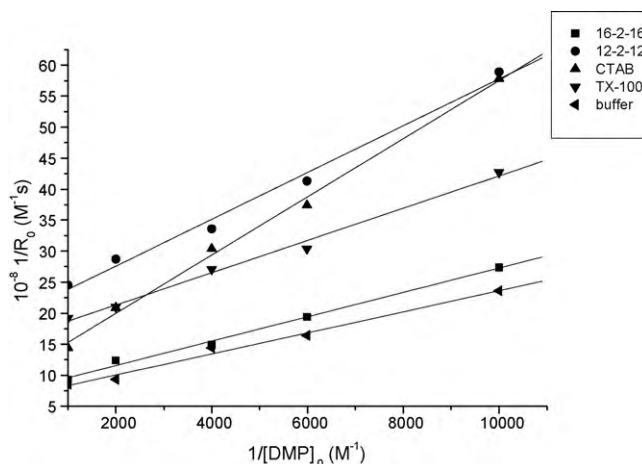


Fig. 3. Plot of $1/R_0$ vs. $1/[DMP]_0$ catalyzed by L²Cu, at pH 7.01 and 25 °C. [L²Cu] = 5×10^{-5} M, [H₂O₂]₀ = 0.01 M, [CTAB] = 0.01 M, [TX-100] = 3.3×10^{-3} M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0×10^{-3} M.

owing to the electrostatic effect, the cationic micelle could promote the reaction rate by attracting and steadying the electronegative intermediate. On the other hand, micelle could concentrate reaction substrate due to the hydrophobic effect and hence accelerate reaction rate. Thus neutral TX-100 showed somewhat increase in the reaction rate. And electronegative SDBS micelle showed somewhat decrease in rate owing to the electrostatic effect and the concentrated effect.

Table 2

Effects of micelles on the kinetic parameters k_2 and K_m at pH 7.01 and 25 °C.

Systems	L ¹ Cu		L ² Cu	
	$\times 10^4 k_2 \text{ s}^{-1}$	$\times 10^5 K_m \text{ M}$	$\times 10^5 k_2 \text{ s}^{-1}$	$\times 10^4 K_m \text{ M}$
Buffer	2.86	4.33	3.01	2.56
CTAB	5.57	9.78	1.88	4.42
12-2-12	5.59	9.42	1.00	1.88
16-2-16	6.69	4.39	2.62	2.57
TX-100	3.05	2.49	1.24	1.61
SDBS	2.67	7.06	– ^a	– ^a

Note: [LCu] = 5.0×10^{-5} M, [H₂O₂]₀ = 0.01 M, [CTAB] = 0.01 M, [TX-100] = 3.3×10^{-3} M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0×10^{-3} M.

^a Too small to be determined.

Table 3

The yields and ratios of products of reaction catalyzed by L¹Cu complex in aqueous solution and micellar media after 48 h at pH 7.01 and 25 °C.

Systems	Residua of DMP (%)	Yield of DPQ (%)	Yield of PPO (%)	W _{PPO} /W _{DPQ}
Buffer	0	56.14	43.86	0.78
TX-100	0	15.61	84.39	5.41
SDBS	0	10.88	89.12	8.19
CTAB	0	15.50	84.50	5.45
16-2-16	15.00	26.62	58.38	2.21
12-2-12	31.10	11.82	57.17	4.84

Note: [L¹Cu] = 5.0 × 10⁻⁵ M, [H₂O₂]₀ = 0.02 M, [DMP]₀ = 1.0 × 10⁻³ M, [CTAB] = 0.01 M, [TX-100] = 3.3 × 10⁻³ M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0 × 10⁻³ M.

Table 4

The yields and ratios of products of reaction catalyzed by L²Cu complex in aqueous solution and micellar media after 48 h at pH 7.01 and 25 °C.

Systems	Residua of DMP (%)	Yield of DPQ (%)	Yield of PPO (%)	W _{PPO} /W _{DPQ}
Buffer	10.20	52.00	37.80	0.73
TX-100	15.52	14.64	69.84	4.76
SDBS	33.91	6.12	59.97	9.78
CTAB	35.50	13.19	51.31	3.89
16-2-16	42.53	21.64	35.83	1.65
12-2-12	59.80	8.89	31.28	3.52

Note: [L²Cu] = 5.0 × 10⁻⁵ M, [H₂O₂]₀ = 0.02 M, [DMP]₀ = 1.0 × 10⁻³ M, [CTAB] = 0.01 M, [TX-100] = 3.3 × 10⁻³ M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0 × 10⁻³ M.

For L²Cu-catalyzed systems, L²Cu showed remarkable difference from L¹Cu in reaction activity and in sensitivity to microenvironment. It was possible that the four-coordinated copper(II) complex of L²Cu more difficult to associate with DMP owing to the steric hindrance and consequently resulted in the greater Michaelis constant *K_m* than L¹Cu (Table 2) and thus lead to the lower catalytic activity.

Compared with L¹Cu, L²Cu has better hydrophobic property and more poor solubility in water. Therefore, in micellar solution L²Cu may be solubilized in deeper inner of micelle (fence region), while L¹Cu could be solubilized on the surface of micelle (stern layer). Hence in micellar solution for L¹Cu and L²Cu catalyzed reaction, the catalysis reaction may take place in different region of micelle. In addition, most of substrate DMP molecule could be solubilized in stern layer of micelle (surface region) due to its good solubility in water and only a few could enter the inner of micelle, therefore for the L²Cu catalyzed system, the presence of micelle decreased the reaction rate.

4. The selectivity of PPO

In this oxidative coupling reaction, PPO was also formed by C–O coupling of phenolic moieties besides the DPQ generated from C–C coupling of two monomeric phenols. In order to analyze the amount of PPO generated in this reaction, the reactions were performed in different media at pH 7.01 and 25 °C for 48 h. Then the content of DMP in reaction solution was determined by gas chromatograph analysis. The reaction product was dissolve in acetone and the amount of DPQ was obtained by monitoring the absorbance at 421 nm by UV–vis analysis. Thus, the amount of PPO was evaluated by subtracting the weight of DPQ and of residual unreacted DMP from that of initial DMP. The results were listed in Tables 3 and 4. From Tables 3 and 4 it could be found that the micellar media caused great influence on the property of reaction. The micelle changed the reaction rate of formation of DPQ and that of PPO, which led to the variety of ratio of PPO to DPQ. From Table 3 it could be seen that the gemini surfactants has a significant inhibitory effect on the oxi-

Table 5

The yield and ratio of products of reaction catalyzed by LCu complexes at pH 7.01 and 25 °C.

Systems	L ¹ Cu		L ² Cu	
	Yield (%) ^a	W _{PPO} /W _{DPQ}	Yield (%) ^a	W _{PPO} /W _{DPQ}
Buffer	72.30	1.62	45.4	1.57
TX-100	73.22	4.91	43.2	4.40
SDBS	82.60	7.27	38.8	7.81
CTAB	71.91	5.20	36.8	4.78
16-2-16	62.91	2.98	40.2	3.08
12-2-12	48.70	2.04	22.3	4.86

Note: [LCu] = 5.0 × 10⁻³ M, [H₂O₂]₀ = 2.0 M, [DMP]₀ = 1.0 × 10⁻¹ M, [CTAB] = 0.01 M, [TX-100] = 3.3 × 10⁻³ M, [SDBS] = 0.012 M, [12-2-12] = 0.01 M, [16-2-16] = 1.0 × 10⁻³ M.

^a The yield of insoluble product.

dation of DMP, although the initial rate of formation of DPQ was accelerated (shown in Table 2). Since gemini has two hydrophobic long chain, its micelle has looser bulk than single chain surfactant. So it was possible that the products dissolved in gemini micelle were not easy to break away from the micelle and prevent the reagent DMP into the micelle, and therefore result in the decrease of the reaction rate with the reaction goes on. The anionic micelles with electronegative region can significantly improve the yield of PPO. The ratio of the PPO to DPQ increased from 0.79 in aqueous solution to 8.19 in SDDBS micellar media. This observation supported the mechanism that phenoxonium cation intermediate may form and favor the C–O coupling of oligomeric phenols [14,17]. From Table 4 we found that for L²Cu catalyzed system the micelles all inhibited the oxidation of DMP, a large amount of DMP remained in the reaction solution after 48 h and SDDBS micelle still showed the best selectivity of PPO. The construct of L²Cu complex was different from L¹Cu. The four coordinative Cu²⁺ in L²Cu complex were difficult to associate simultaneously with both H₂O₂ and DMP due to the effects of electron and steric hindrance.

In order to check the feasibility in industry application, reactions of 100-fold enlarged concentrations were carried out under similar experimental conditions. An interesting observation was found that the insoluble solid products formed and precipitated from the solution. The analysis results were listed in Table 5. From Table 5, it could be seen that there were relatively good product yields after 48 h reaction. Micellar medium significantly increased the ratio of PPO to DPQ. Especially in the SDDBS system, PPO had the highest yield. It was worth to note that a little number of –CH₃ group in benzene was furtherly oxidized into aldehyde or acid. Although some aspects need make further investigation, several advantages for the preparation of polymer in metallomicelle catalyzed system were obvious: water as green solvent, mild reaction conditions and products could be easily separate from the solution while catalysts remain in micellar media.

5. Conclusions

This study indicated that the oxidative coupling of DMP by H₂O₂ could take place in the buffer and micellar solution by using copper(II) complexes as catalysts at pH 7.01 and 25 °C. The micelles showed different influence on the oxidative coupling reaction. For L¹Cu catalyzed systems, the CTAB, 12-2-12 and 16-2-16 micellar media accelerated the oxidation of DMP. And the TX-100 and SDDBS micelles showed little effect on reaction rate compared with the buffer solution. For the L²Cu catalyzed systems, these surfactants all inhibited the oxidation of DMP. The micelles also showed great influence on the yield of product and the selectivity of PPO. DPQ was easily generated in aqueous solution, while PPO was remarkably promoted in micellar media, especially in SDDBS micellar solution. Gemini surfactants 12-2-12 and 16-2-16 did not display especial

property in catalysis. This study also supported the mechanism that phenoxonium cation intermediate may form and favor the C–O coupling of oligomeric phenols. This study showed that the metallomicelle exhibited excellent catalytic characteristic for the oxidative coupling of DMP and it may be a potential catalysis system for the preparation of other organic materials.

Acknowledgments

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