

# Aerobic Oxidative Polymerization of 2,6-Dimethylphenol in Water with a Highly Efficient Copper(II)–Poly(*N*-vinylimidazole) Complex Catalyst

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Received 19 April 2010; accepted 25 July 2010

DOI 10.1002/app.33088

Published online 11 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A Cu(II)–poly(*N*-vinylimidazole) (PVI) complex was prepared and used to catalyze the oxidative polymerization of 2,6-dimethylphenol (DMP) to form poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in water. The stoichiometric ratio between imidazole groups in PVI and copper ions was found to be 4 when continuous variation analysis was applied. Compared with a conventional Cu(II)–low-molecular-weight ligand complex, a high catalytic efficiency was observed in the polymerization of DMP catalyzed by the Cu(II)–PVI complex. The influence of the Cu(II)–PVI complex concentration and imidazole/Cu(II) molar ratio on the oxidative polymerization of

DMP was studied. Both the yield and molecular weight of PPO increased significantly with the catalyst concentration and decreased with the imidazole/Cu(II) molar ratio. The molecular weight of PVI also played an important role in the improvement of the catalytic efficiency. The high catalytic efficiency of the Cu(II)–PVI complex may have been due to the concentration effect of the catalyst and substrate. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 109–115, 2011

**Key words:** catalysts; metal–polymer complexes; poly(phenylene oxide)

## INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as an engineering plastic has been widely used in various areas, such as business equipment and the electrical and automotive industries. The oxidative polymerization of 2,6-dimethylphenol (DMP) to form PPO was first carried out by Hay and his GE group in 1959<sup>1</sup> with a copper–pyridine complex as a catalyst in a nitrobenzene solution. Along with the formation of PPO by C–O coupling, an undesirable byproduct, 3,3',5,5'-tertramethyl-4,4'-diphenoquinone (DPQ), was also produced by the C–C coupling of two monomeric phenols (Scheme 1). Although the oxidative polymerization of DMP in organic solvents has provided a convenient method for manufacturing PPO in industry, both a solvent-recovery process and an antiexplosive reactor are required in industrial PPO production.<sup>2</sup>

The use of water as reaction medium can realize a green chemical reaction. In 2004, Nishide et al.<sup>3</sup> first

used potassium ferricyanide as an oxidant to synthesize PPO in alkaline water. However, the use of potassium ferricyanide was also unacceptable from the view of green chemistry. Recently, Nishide et al.<sup>4</sup> selected copper–amine complexes with low-molecular-weight ligands, such as a Cu(II)–ethylenediamine *N,N,N',N'*-tetraacetic acid (EDTA) complex, as catalysts and oxygen as an oxidant to achieve the oxidative polymerization of DMP in alkaline water. This process was mild and environmentally benign; however, the catalytic efficiency was low and still needed to be improved.

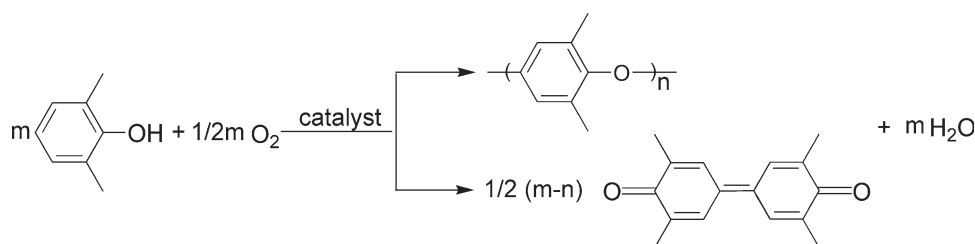
Copolymers of styrene and pyridine or imidazole derivatives were used as macromolecular ligands for copper ions in the oxidative polymerization of phenols in organic solvents by Challa and coworkers.<sup>5–9</sup> They found that copper–macromolecular ligand complexes were more active in oxidative coupling reactions than the corresponding low-molecular-weight analogue. Enlightened by this conclusion, poly(*N*-vinylimidazole) (PVI), a water-soluble and weakly basic linear polymer, was selected as the macromolecular ligand for copper ions, and the Cu(II)–PVI complex were expected to be highly efficient in the catalytic oxidative polymerization of DMP in water.

PVI has been used in catalysis so far with three strategies. First, PVI was used to catalyze the hydrolysis of esters and the addition of thiols to Michael acceptors in aqueous media.<sup>10,11</sup> In these reactions, the catalytic activity and selectivity of PVI were

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Contract grant sponsor: Natural Science Foundation of China; contract grant numbers: 20974100, 20674075.

Contract grant sponsor: Natural Science Foundation of Zhejiang Province; contract grant number: Y404299.



**Scheme 1** Oxidative polymerization of DMP.

comparable with those of the enzymes. Second, PVI was applied as a polymeric support for a known catalytic unit, which was used in the recovery and reusability of palladium catalysts and glucose oxidase.<sup>12,13</sup> Third, PVI coordinated with a number of different metal ions, such as Ag(I), Cu(II), Zn(II) and Co(II),<sup>14–17</sup> to form metal–PVI complexes, which have been widely applied in industrial effluent detoxification, the recovery of heavy metal ions, and catalytic reactions.<sup>18,19</sup> Although the catalytic properties of Cu(II)–polymeric imidazole complexes in organic solvents have been described extensively in the past 3 decades, few studies have been made dealing with the catalytic properties of these complexes in aqueous medium.<sup>5–9</sup>

In this study, a Cu(II)–PVI complex was used to catalyze the oxidative polymerization of DMP to synthesize PPO in water. The stoichiometric ratio between the imidazole groups in PVI and the copper ions was measured with an ultraviolet–visible (UV–vis) spectrophotometer. The influence of the Cu(II)–PVI complex concentration on the oxidative polymerization of DMP was studied, and the results were compared with those of the Cu(II)–EDTA complex. The high catalytic efficiency of the Cu(II)–PVI complex was observed, and possible explanations were proposed. In addition, the effects of the imidazole/Cu(II) molar ratio and the molecular weight of PVI on the oxidative polymerization of DMP were also studied.

## EXPERIMENTAL

### Materials

Analytically pure DMP and *N*-vinylimidazole were purchased from Aldrich (Shanghai, China). *N*-Vinylimidazole was purified by distillation under reduced pressure at 83°C/7 mmHg before use.<sup>19</sup> Chemically pure  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) and analytically pure benzene were provided by Sinopharm Chemical Reagent Co. (Shanghai, China). Analytically pure copper dichloride (CuCl<sub>2</sub>) and EDTA were obtained from Shanghai Zhenxing Chemistry Co. (Shanghai, China) and Sinopharm Chemical Reagent Co., respectively. Analytically pure sodium chloride (NaCl) and sodium hydroxide (NaOH) were supplied by Ningbo Chemistry Co. (Ningbo,

China) and Xiaoshan Chemistry Co. (Hangzhou, China), respectively. Chemically pure sodium *n*-dodecyl sulfate (SDS) was purchased from Shantou Chemistry Co. (Shantou, China).

### Synthesis of PVI

High-molecular-weight PVI samples were obtained by the polymerization of *N*-vinylimidazole (5 mL) in benzene (15 mL) in the presence of AIBN (0.05 g). The solution was stirred at 65°C for 5 h in an N<sub>2</sub> atmosphere (Scheme 2). PVI with different molecular weights were synthesized by variation of the molar ratio of the monomer to the initiator. Low-molecular-weight PVI was synthesized by the polymerization of a 20% solution of *N*-vinylimidazole in ethanol in the presence of 3% AIBN at 60°C for 16 h in an N<sub>2</sub> atmosphere.<sup>20</sup> The product was washed thoroughly with diethyl ether and dried in a vacuum oven at 50°C for 48 h.

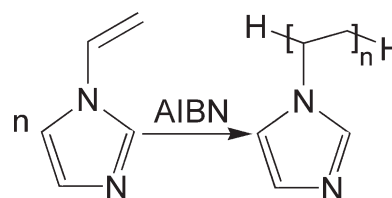
The viscosity-average molecular weights ( $M_{\eta}$ 's) of PVI used in this study were determined to be  $24.7 \times 10^4$ ,  $9.4 \times 10^4$ , and  $2.2 \times 10^4$  (the PVI sample names are shortened as PVI-24.7, PVI-9.4, and PVI-2.2, respectively).

### Preparation of the Cu(II)–PVI complex

CuCl<sub>2</sub> (0.43 mg, 2.5  $\mu$ mol) and PVI (0.94 mg, imidazole group = 10  $\mu$ mol) were dissolved in water (5 mL) to form a Cu(II)–PVI complex. Cu(II)–PVI complexes with different imidazole/Cu(II) molar ratios were also prepared in the same way.

### Oxidative polymerization of DMP in water catalyzed by the Cu(II)–PVI complex

A typical procedure for the oxidative polymerization of DMP in water catalyzed by the Cu(II)–PVI complex was as follows: DMP (0.610 g, 5.0 mmol),



**Scheme 2** Synthesis of PVI.

**TABLE I**  
Catalyzed Oxidative Polymerization of DMP in Water<sup>a</sup>

Entry	Catalyst	[Cu(II)] ( $\mu\text{mol/L}$ )	PPO yield (%)	DPQ yield (%) <sup>e</sup>	PPO $M_w$ ( $M_w/M_n$ ) $\times$ $10^3$ g/mol <sup>f</sup>
1	— <sup>b</sup>	0	35.7	0.25	2.4 (1.6)
2	Cu(II)-PVI-24.7 <sup>c</sup>	14.3	62.2	0.10	3.6 (2.0)
3	Cu(II)-PVI-24.7	16.7	82.7	0.11	4.4 (2.1)
4	Cu(II)-PVI-24.7	25	85.9	0.15	8.6 (2.1)
5	Cu(II)-PVI-24.7	50	93.8	0.16	9.6 (2.2)
6	Cu(II)-PVI-24.7	100	95.1	0.12	11.5 (2.3)
7	Cu(II)-EDTA <sup>d</sup>	25	39.3	0.10	2.7 (2.2)
8	Cu(II)-EDTA	50	48.6	0.07	3.1 (2.2)
9	Cu(II)-EDTA	200	85.4	0.07	5.4 (1.9)

<sup>a</sup> All of the polymerizations were carried out in water under oxygen at 50°C for 24 h with concentrations of 0.05 mol/L DMP, 0.005 mol/L SDS, and 0.05 mol/L NaOH.

<sup>b</sup> The polymerization was carried out without a catalyst.

<sup>c</sup> [Imidazole unit]/[Cu(II)] = 4.

<sup>d</sup> [EDTA]/[Cu(II)] = 1.

<sup>e</sup> Determined by UV-vis spectroscopy in toluene at 421 nm.

<sup>f</sup> Determined by GPC in toluene with polystyrene as a standard.  $M_n$  = number-average molecular weight.

NaOH (0.200 g, 5.0 mmol), and SDS (0.144 g, 0.5 mmol) were dissolved in water (95 mL). The previously prepared Cu(II)-PVI complex solution (5 mL) was added to the reactor. Oxygen was bubbled through the reaction mixture at a flow rate of 1.0 mL/min, and the pressure of oxygen above the reaction media was maintained at atmospheric pressure. The reaction mixture was vigorously stirred under oxygen at 50°C for 24 h. An off-white powder was obtained by filtration after salting out with NaCl and then extracted for 48 h to eliminate DPQ.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 2.09 (s, 6H, —CH<sub>3</sub>), 6.44 (s, 2H, aromatic C—H).

### Characterizations

The absorbance was measured with a UV751GW UV-vis spectrophotometer (Shanghai Xinyi Instrument Co., Shanghai, China). <sup>1</sup>H-NMR spectra was recorded by a GSX-270 spectrometer (JEOL Japan Electronics Co., Tokyo, Japan) in CDCl<sub>3</sub> with tetramethylsilane as an internal standard.

The intrinsic viscosity ( $[\eta]$ ; dL/g) of PVI was measured at 25°C with an Ubbelohde viscometer (Shanghai, China). The solvent was a 0.1 mol/L NaCl aqueous solution.  $M_n$  of PVI was calculated according to the Mark-Houwink equation [eq. (1)]:

$$[\eta] = KM_n^\alpha \quad (1)$$

where front factor ( $K$ ) is  $1.22 \times 10^5$  and exponent ( $\alpha$ ) is 0.51.<sup>21</sup>

The weight-average molecular weight ( $M_w$ ) and polydispersity of PPO were determined by gel per-

meation chromatography (GPC; Waters 1525/2414, Waters Instruments, Milford, Massachusetts) equipped with Waters Styragel HT4/HT3/HR1 columns and a refractive-index detector at 30°C. The mobile phase was toluene and was maintained at a flow rate of 1.0 mL/min. The molecular weight was calibrated with polystyrene standards. A typical GPC chromatogram (entry 5, Table I) is shown in Figure 1.

The content of DPQ was determined by a visible spectrophotometer. The polymerized product (15 mg) before extraction was dissolved in 25 mL of toluene, and the absorbance ( $A$ ) of the solution was measured by a visible spectrophotometer (Shanghai Xinyi Instrument Co., Shanghai, China) at 421 nm. The concentration of DPQ ( $c$ ) in toluene was calculated according to the Beer-Lambert law [eq. (2)]:

$$A = \lg(I_0/I) = \epsilon cl \quad (2)$$

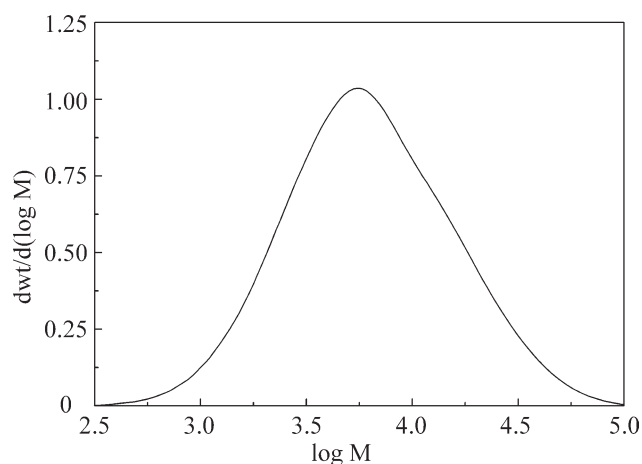
where  $I_0$  is the incident light intensity,  $I$  is the transmitted light intensity,  $l$  is the thickness of the colorimetric utensil, and  $\epsilon$  is the molar absorption coefficient of DPQ, which was determined to be  $6.5 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> by the Beer-Lambert law.

The residual copper yields in PPO without any copper removal were measured by atomic absorption spectroscopy (HITACHI 180-50, San Jose, California) by dissolution of the polymer in 40% phenyl sulfonic acid.

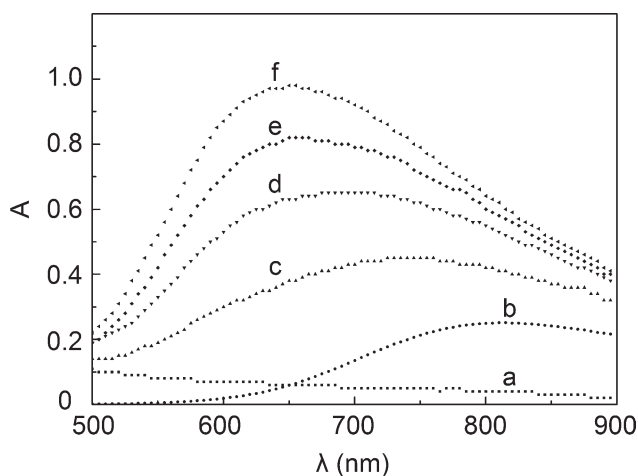
## RESULTS AND DISCUSSION

### Coordination number of the imidazole groups in PVI with Cu(II)

The absorption spectra of CuCl<sub>2</sub>, PVI, and Cu(II)-PVI complex solutions were recorded by a UV-vis spectrophotometer (Shanghai Xinyi Instrument Co., Shanghai, China), and the results are shown in



**Figure 1** GPC chromatogram (entry 5, Table I). wt = weight percent;  $M$  = weight-average molecular weight.



**Figure 2** Visible absorption spectra of PVI,  $\text{CuCl}_2$ , and  $\text{Cu(II)-PVI}$  complexes at pH 4.20: (a) PVI, [imidazole group] =  $2 \times 10^{-3}$  mol/L; (b)  $\text{CuCl}_2$ ,  $[\text{Cu(II)}] = 2 \times 10^{-3}$  mol/L; and (c,d,e,f)  $\text{Cu(II)-PVI}$  complexes, molar ratios of imidazole group in PVI to  $\text{Cu(II)} = 1, 2, 3,$  and  $4,$  respectively (the copper concentrations remained unchanged at  $2 \times 10^{-3}$  mol/L).  $\lambda$  = wavelength.

Figure 2. The  $\text{CuCl}_2$  solution showed a maximum absorption at 800 nm due to the d-d transition, whereas no absorbance peak was observed for PVI over the scan region. As PVI was added to the  $\text{CuCl}_2$  solution, the absorbance significantly increased, and the peak shifted to a shorter wavelength; this indicated the formation of the  $\text{Cu(II)-PVI}$  complex. When the molar ratio of imidazole groups in PVI to  $\text{Cu(II)}$  varied from 1 to 4, the absorbance of the  $\text{Cu(II)-PVI}$  complexes increased with little shift in the peak; this demonstrated that the formed complex concentration increased with the imidazole/ $\text{Cu(II)}$  molar ratio. When the molar ratio of imidazole groups in PVI to  $\text{Cu(II)}$  was 4, the maximum absorption wavelength of the  $\text{Cu(II)-PVI}$  complex appeared at 650 nm, which was consistent with the results obtained by Gold and Gregor.<sup>15</sup>

The method provided by Job<sup>22,23</sup> was used to spectrophotometrically determine the preferred coordination number of the imidazole groups in PVI with  $\text{Cu(II)}$ . The absorbance of the  $\text{Cu(II)-PVI}$  complexes with various imidazole/ $\text{Cu(II)}$  molar ratios [the total concentration of the imidazole groups in PVI and  $\text{Cu(II)}$  remained unchanged at 0.02 mol/L] at the maximum absorption wavelength were recorded and corrected according to a previous study.<sup>15</sup> The change in the absorbance with the  $\text{Cu(II)}$  molar fraction is shown in Figure 3.

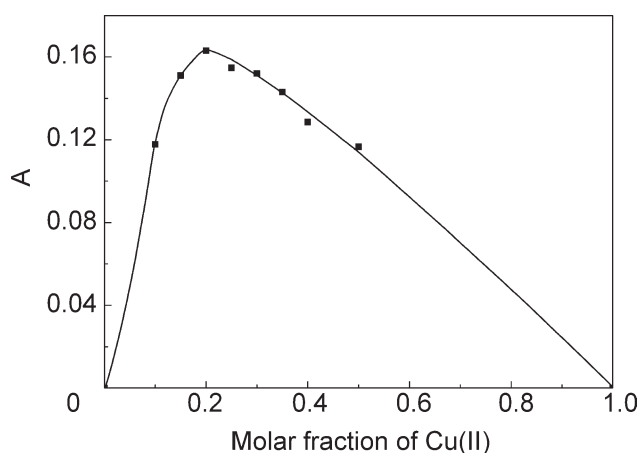
The absorbance of the  $\text{Cu(II)-PVI}$  complexes increased rapidly with  $\text{Cu(II)}$  molar fraction in the range 0–0.2 and then decreased with  $\text{Cu(II)}$  molar fraction in the range 0.2–1. A sharp maximum was observed when the  $\text{Cu(II)}$  molar fraction was 0.2; this indicated that the preferred coordination num-

ber of imidazole groups in PVI with  $\text{Cu(II)}$  under the experimental conditions was four, namely, one copper ion coordinated with four imidazole groups.

#### Effect of the $\text{Cu(II)-PVI}$ complex concentration on the oxidative polymerization of DMP

The  $\text{Cu(II)-PVI}$  complex prepared from  $\text{Cu(II)}$  and PVI-24.7 [ $\text{Cu(II)-PVI-24.7}$ ] was applied in the oxidative polymerization of DMP in water, and the results are summarized in Table I (entries 2–6). The oxidative polymerization of DMP in water proceeded slowly without any catalyst, and 35.7% PPO was obtained with an  $M_w$  of  $2.4 \times 10^3$  (entry 1). When the  $\text{Cu(II)-PVI-24.7}$  complex was used as a catalyst, both the yield and molecular weight of PPO increased significantly with the  $\text{Cu(II)-PVI-24.7}$  complex concentration. The DPQ yields in all entries catalyzed by the  $\text{Cu(II)-PVI-24.7}$  complex were lower than 0.2%; this demonstrated that the C–O/C–C coupling selectivity of the  $\text{Cu(II)-PVI}$  complex catalyst was good enough to predominantly form PPO. When the concentration of the  $\text{Cu(II)-PVI-24.7}$  complex increased from 14.3 to 100  $\mu\text{mol/L}$ , the PPO yield increased from 62.2 to 95.1%, and the molecular weight of PPO increased from  $3.6 \times 10^3$  to  $11.5 \times 10^3$ , respectively.

To compare the influence of ligands on the oxidative polymerization of DMP in water, polymerizations with the  $\text{Cu(II)-EDTA}$  complex as the catalyst were also conducted under the same experimental conditions (entries 7–9). As shown by a comparison of entries 4 and 5 with entries 7 and 8, at the same  $\text{Cu(II)}$  concentration, the yield and molecular weight of PPO catalyzed by the  $\text{Cu(II)-PVI-24.7}$  complex were much higher than those of PPO catalyzed by the  $\text{Cu(II)-EDTA}$  complex. The PPO yield was still as high as 82.7% (entry 3) when the  $\text{Cu(II)-PVI-24.7}$  complex concentration dropped to 16.7  $\mu\text{mol/L}$  (1/



**Figure 3** Continuous variations analysis of the  $\text{Cu(II)-PVI}$  complex.

**TABLE II**  
Effect of the [Imidazole unit]/[Cu(II)] Molar Ratio on the Polymerization of DMP in Water<sup>a</sup>

Entry	Imidazole/ Cu(II) molar ratio	PPO yield (%)	DPQ yield (%)	PPO $M_w$ ( $M_w/M_n$ ) $\times$ $10^3$ g/mol
3	4	82.7	0.11	4.4 (2.1)
10	6	59.8	0.11	4.3 (2.4)
11	10	39.3	0.11	3.2 (2.2)
12	20	27.0	0.14	2.7 (1.9)

<sup>a</sup> All of the polymerizations were carried out in water under oxygen at 50°C for 24 h with concentrations of 16.7  $\mu\text{mol/L}$  Cu(II), 0.05 mol/L DMP, 0.005 mol/L SDS, and 0.05 mol/L NaOH.

3000 of the DMP concentration), which was comparable with the result obtained with the Cu(II)–EDTA complex at a concentration of 200  $\mu\text{mol/L}$  (1/250 of the DMP concentration; entry 9). These results suggest that only a very low concentration of the Cu(II)–PVI-24.7 complex was required to retain the relatively high PPO yield, and the catalytic efficiency of the Cu(II)–PVI-24.7 complex was nearly 10 times higher than that of the Cu(II)–EDTA complex. The significant enhancement in the catalytic efficiency may have been due to the concentration effect mentioned by Yamamoto et al.,<sup>24</sup> which is discussed in detail later.

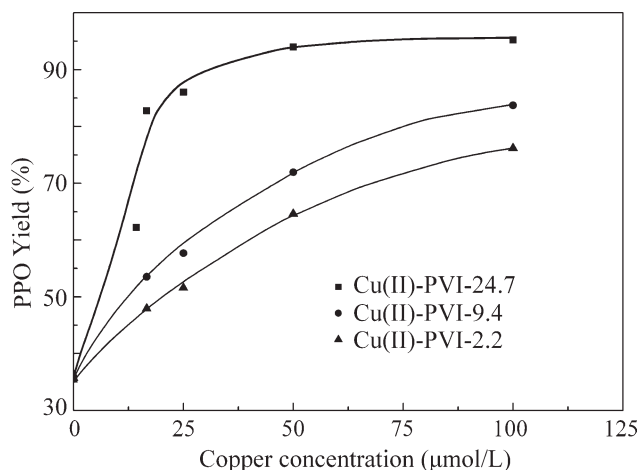
The residual copper ion concentrations in PPO catalyzed by Cu(II)–PVI-24.7 (entry 4, Table I) and Cu(II)–EDTA (entry 7, Table I) were determined to be 2.7 and 2.2 ppm, respectively, which were lower than the previous results.<sup>4</sup> The results showed that the catalyst was not trapped in the formed PPO. The water-soluble catalyst preferred to remain in water.

#### Effect of the molar ratio of the imidazole groups in PVI to Cu(II) on the oxidative polymerization of DMP

Another important factor that affected the oxidative polymerization of DMP was the molar ratio of copper ions to ligand. Hay et al.<sup>25</sup> found that C–O/C–C coupling selectivity and the oxygen absorption rate in *o*-dichlorobenzene were profoundly influenced by the molar ratio of copper ions to ligand. Increasing the pyridine/Cu(II) molar ratio favored C–O coupling for the formation of PPO and led to a maximum oxygen absorption rate at a molar ratio of 100. The effects of imidazole groups in the PVI/Cu(II) molar ratio on the oxidative polymerization of DMP in water [at a fixed Cu(II) concentration of 16.7  $\mu\text{mol/L}$ ] are summarized in Table II.

Both the PPO yield and its molecular weight decreased with increasing imidazole/Cu(II) molar ratio. When the imidazole/Cu(II) molar ratio increased from 4 to 20, the PPO yield dropped from 82.7 to

27.0%, whereas the molecular weight of PPO decreased from  $4.4 \times 10^3$  to  $2.7 \times 10^3$ . Two possible explanations were considered. First, the preferred coordination number of the imidazole groups in PVI with Cu(II) under the experimental conditions was 4. Thus, when the imidazole/Cu(II) molar ratio was greater than 4, an excessive amount of imidazole ligand existed in the complex; this could compete against the substrates for the coordination sites of the copper ions and resulted in the inhibition of the oxidative polymerization. This explanation was consistent with that mentioned by Lim et al.<sup>26</sup> in the biphasic synthesis of PPO.<sup>26</sup> They found that there existed an optimum ligand-to-catalyst ratio, beyond which the excess ligand behaved as an inhibitor. Second, a high ligand concentration was undesirable because it resulted in the dispersed state of copper ions in the complex and a weakening concentration effect of the catalyst. Each entry in Table II was carried out with the same concentration of copper ions (16.7  $\mu\text{mol/L}$ ), and the imidazole/Cu(II) molar ratios were 4, 6, 10, and 20, respectively. When the imidazole/Cu(II) molar ratio was 4, every imidazole unit in PVI coordinated with Cu(II). The local concentration of Cu(II) in each PVI random coil reached a maximum with a full load of Cu(II). With increasing imidazole/Cu(II) molar ratio, the number of imidazole units increased; this resulted in the existence of the uncoordinated imidazole unit at a fixed concentration of Cu(II). For example, when the imidazole/Cu(II) molar ratio was 20, only one-fifth of the imidazole units in each PVI coil coordinated with the copper ions. The number of Cu(II) ions in each PVI coil decreased with imidazole/Cu(II) molar ratio, which resulted in the dispersed state of Cu(II) in the complex, and the local concentration of Cu(II) in the PVI coil decreased significantly. Therefore, the concentration effect of the catalyst was greatly weakened with increasing imidazole/



**Figure 4** Dependence of the PPO yield on the copper concentration [imidazole groups in PVI/Cu(II) = 4].

Cu(II) molar ratio; this was unfavorable for the formation of PPO.

### Effect of the molecular weight of PVI on the oxidative polymerization of DMP in water

To clarify the influence of the molecular weight of PVI, the oxidative polymerizations of DMP in water were carried out in the presence of Cu(II)–PVI-24.7, Cu(II)–PVI-9.4, and Cu(II)–PVI-2.2 complexes, respectively, and the results are shown in Figure 4. When the Cu(II)–PVI-24.7 complex was used as the catalyst, the PPO yield increased rapidly with catalyst concentration in the low-concentration region. In the high-concentration region, the PPO yield was independent of the catalyst concentration. In comparison with the Cu(II)–PVI-24.7 complex, the PPO yield increased much more gently with the catalyst concentration in the range 0–100  $\mu\text{mol/L}$  for the Cu(II)–PVI-9.4 and Cu(II)–PVI-2.2 complexes. Remarkably, the PPO yield catalyzed by the Cu(II)–PVI-24.7 complex at a concentration of 25  $\mu\text{mol/L}$  was even higher than that catalyzed by the Cu(II)–PVI-9.4 complex at a concentration of 100  $\mu\text{mol/L}$ . These results clearly illustrate that the molecular weight of the polymer ligand played an important role in the enhancement of the catalytic efficiency. When the molecular weight of the polymer ligand increased, the catalytic efficiency was significantly enhanced; this was ascribed to the higher concentration effect of the catalyst.

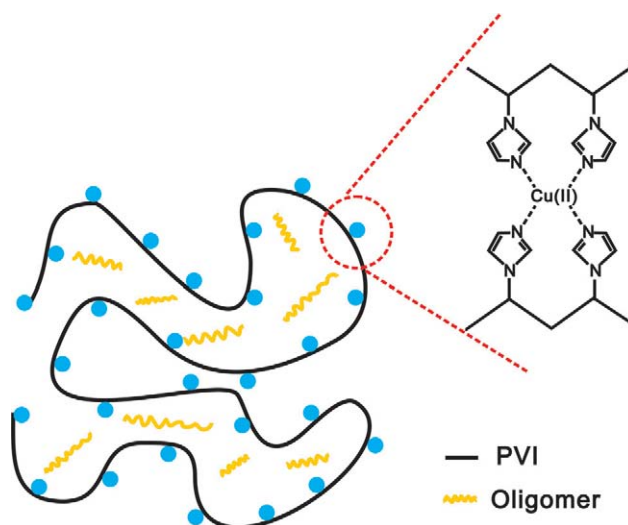
Cu(II)–low-molecular-weight ligand complexes, such as the Cu(II)–EDTA complex, are evenly distributed in aqueous media. On the contrary, PVI formed a microheterogeneous region occupied by a polymer chain with a definite volume; this resulted in uneven distribution in aqueous media. The unperturbed dimension of PVI was estimated by linear extrapolation according to the Stockmayer–Fixman equation [eq. (3)]:<sup>21</sup>

$$[\eta]/M_{\eta}^{1/2} = K_0 + 0.51 \Phi_0 B M_{\eta}^{1/2} \quad (3)$$

where  $B$  is related to the second virial coefficient and is assumed to be constant for all molecular weights and  $K_0$  is the intercept for the plot of  $[\eta]/M_{\eta}^{1/2}$  against  $M_{\eta}^{1/2}$ , which is  $1.4 \times 10^3$  for PVI in a 0.1 mol/L NaCl solution according to ref. 21. The unperturbed end-to-end distance ( $\langle r_0^2 \rangle^{1/2}$ ) is related to  $K_0$  by eq. (4):

$$\langle r_0^2 \rangle = (K_0/\Phi_0)^{2/3} M_{\eta} \quad (4)$$

where  $\Phi_0$  is the Flory universal constant ( $2.6 \times 10^{21}$  dL/g for  $[\eta]$ ). With  $M_{\eta}$  of PVI,  $\langle r_0^2 \rangle^{1/2}$  for PVI-24.7 was calculated to be 40.4 nm. The copper ions coordinated with imidazole groups were confined in the



**Scheme 3** Concentration effect of the catalyst and substrates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nanoscale area occupied by the PVI random coil; therefore, the catalyst was unevenly distributed in the reaction medium, and its local concentration increased significantly; this resulted in the concentration effect of the catalyst.

PVI is an amphiphilic polymer. The hydrophobic C–C backbone forms a hydrophobic domain, whereas the hydrophilic imidazole group coordinates with copper ions. The oxidative polymerization of DMP in water belonged to the precipitation polymerization.<sup>27</sup> Oligomer, including the hydrophobic benzene ring in the main chain and the hydrophilic phenoxy anion at the end of the chain, precipitated from the water. The precipitated oligomer was apt to concentrate in the hydrophobic domain occupied by the PVI random coil. Therefore, a microreactor (Scheme 3) formed, where both the Cu(II)–PVI complex and oligomer concentrated. In the microreactor, the probability of collision between the catalyst and substrates largely increased, which favored the further oxidative polymerization of the oligomer. In summary, the concentration effect of the catalyst and substrates may have been responsible for the enhancement of the catalytic efficiency of the Cu(II)–PVI complex. With increasing molecular weight of PVI, the concentration effect was increased, and the catalytic efficiency was further improved.

## CONCLUSIONS

A Cu(II)–PVI complex was prepared and was used as a catalyst in the oxidative polymerization of DMP in water. The stoichiometric ratio between the imidazole groups in PVI and copper ions was found to be 4 by UV–vis spectroscopy. The yield and

molecular weight of PPO increased dramatically with the catalyst concentration but decreased with the imidazole/Cu(II) molar ratio because of the existence of the excessive ligand. With increasing molecular weight of PVI, the catalytic efficiency of the Cu(II)-PVI complex was further improved.

Compared with the conventional catalyst, the novel Cu(II)-PVI complex catalyst showed an enhancement in the catalytic efficiency, which was nearly 10 times higher than that of the Cu(II)-EDTA complex. This phenomenon may have been due to the concentration effect of the catalyst and substrates. Further mechanism studies on the oxidative polymerization with Cu(II)-PVI complex catalyst are still underway in our laboratory.

The authors thank G. R. Shan for his great help with the experiments. They also express sincere gratitude to L. Zhou and Y. L. Guo for the great help with the experiments and for their discussions.

## References

1. Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. *J Am Chem Soc* 1959, 81, 6335.
2. Saito, K.; Masuyama, T.; Nishide, H. *Green Chem* 2003, 5, 535.
3. Saito, K.; Tago, T.; Masuyama, T.; Nishide, H. *Angew Chem Int Ed* 2004, 43, 730.
4. Saito, K.; Kuwashiro, N.; Nishide, H. *Polymer* 2006, 47, 6581.
5. Challa, G.; Schouten, A. J.; Brinke, G. T.; Meinders, H. C. *Modification of Polymers*; Carraher, C. E.; Tsuda, M., Eds., 1980, Chap. 2.
6. Verlaan, J. P. J.; Bootsma, J. P. C.; Challa, G. *J Mol Catal* 1982, 14, 211.
7. Verlaan, J. P. J.; Bootsma, J. P. C.; Koning, C. E.; Challa, G. *J Mol Catal* 1983, 18, 159.
8. Verlaan, J. P. J.; Zwiers, R.; Challa, G. *J Mol Catal* 1983, 19, 223.
9. Challa, G. *J Mol Catal* 1983, 21, 1.
10. Letsinger, R. L.; Klaus, I. S. *J Am Chem Soc* 1965, 87, 3380.
11. Beletskaya, I. P.; Tarasenko, E. A.; Khokhlov, A. R.; Tyurin, V. S. *Russ J Org Chem* 2007, 43, 1733.
12. Beletskaya, I. P.; Khokhlov, A. R.; Tarasenko, E. A.; Tyurin, V. S. *J Organomet Chem* 2007, 692, 4402.
13. Pekel, N.; Salih, B.; Güven, O. *J Mol Catal B* 2003, 21, 273.
14. Gold, D. H.; Gregor, H. P. *J Phys Chem* 1960, 64, 1461.
15. Gold, D. H.; Gregor, H. P. *J Phys Chem* 1960, 64, 1464.
16. Liu, K. J.; Gregor, H. P. *J Phys Chem* 1965, 69, 1252.
17. Pekel, N.; Güven, O. *Polym Bull* 2004, 51, 307.
18. Molina, M. J.; Gómez-Antón, M. R.; Rivas, B. L.; Maturana, H. A.; Piérola, I. F. *J Appl Polym Sci* 2001, 79, 1467.
19. Takafuji, M.; Ide, S.; Ihara, H.; Xu, Z. *Chem Mater* 2004, 16, 1977.
20. Annenkov, V. V.; Danilovtseva, E. N.; Likhoshway, Y. V.; Patwardhan, S. V.; Perry, C. C. *J Mater Chem* 2008, 18, 553.
21. Tan, J. S.; Sochor, A. R. *Macromolecules* 1981, 14, 1700.
22. Job, P. *Ann Chim* 1928, 9, 113.
23. Job, P. *Ann Chim* 1936, 6, 97.
24. Yamamoto, K.; Kawana, Y.; Tsuji, M.; Hayashi, M.; Imaoka, T. *J Am Chem Soc* 2007, 129, 9256.
25. Endres, G. F.; Hay, A. S.; Eustance, J. W. *J Org Chem* 1963, 28, 1300.
26. Dautenhahn, P. C.; Lim, P. K. *Ind Eng Chem Res* 1992, 31, 463.
27. Liu, Q.; Shentu, B. Q.; Zhu, J. H.; Weng, Z. X. *J Appl Polym Sci* 2007, 104, 3649.