

# Immobilization of Copper(II)-Poly(*N*-vinylimidazole) Complex on Magnetic Nanoparticles and Its Catalysis of Oxidative Polymerization of 2,6-Dimethylphenol in Water

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**ABSTRACT:** Poly(*N*-vinylimidazole) (PVI) was grafted onto magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles through siloxane bonds to produce PVI-grafted Fe<sub>3</sub>O<sub>4</sub> nanoparticles (shortened as Fe<sub>3</sub>O<sub>4</sub>-g-PVI). The amount of imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI was estimated to be 1.16 mmol/g by elemental analysis and thermal gravimetric analysis. The Fe<sub>3</sub>O<sub>4</sub>-g-PVI coordinated with Cu(II) to form the immobilized Cu(II)-PVI complex. The stoichiometric ratio between imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI and Cu(II) was found to be 4 and the complex formation constant (*K*) was calculated to be  $5.6 \times 10^{14} \text{ mol}^{-4} \text{ L}^4$ . The immobilized Cu(II)-PVI complex was employed to catalyze the oxidative polymerization of 2,6-dimethylphenol (DMP) in water

and showed excellent C—O/C—C selectivity to form PPO. After polymerization, the immobilized Cu(II)-PVI complex catalyst was collected by an external magnetic field and reused in the next run with additional immobilized catalyst and copper ions. After three runs of oxidative polymerization of DMP, the recovery rate of the immobilized Cu(II)-PVI catalyst was above 95% and the yield of PPO maintained as high as 79.2% with the addition of supplementary catalysts. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** immobilized Cu(II)-PVI complex catalyst; 2,6-dimethylphenol; oxidative polymerization; water

## INTRODUCTION

Nishide and coworkers first carried out the oxidative polymerization of 2,6-dimethylphenol (DMP) in water and poly(2,6-dimethyl-1,4-phenylene) (PPO) was obtained. However, the molar ratio between catalyst and monomer was up to 1/10, and the catalytic efficiency was low.<sup>1–3</sup> Compared with the conventional Cu(II)-low molecular weight ligand catalysts, the novel Cu(II)-polymer ligand catalysts, such as Cu(II)-poly(*N*-vinylimidazole) (Cu(II)-PVI) complex, showed an enhancement in the catalytic efficiency.<sup>4</sup> However, there are still other unresolved issues in the synthesis of PPO in water, for example, the recycle and reuse of catalysts.

Immobilization of soluble catalysts on an inert support and collection through filtration after reaction is a common technique to recycle catalysts. For example, Challa and Verlaan et al. immobilized pyridine and imidazole derivatives on silica or polystyrene to

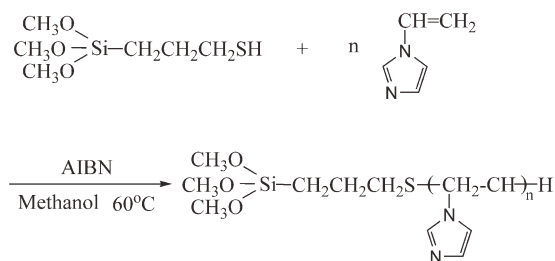
coordinate with Cu(II) and employed these immobilized complexes to catalyze the oxidative polymerization of phenols in organic solutions.<sup>5–8</sup> This method combined the advantages of both homogeneous and heterogeneous catalysts. The immobilized catalysts can not only maintain the high efficiency and high selectivity as homogeneous catalysts, but also be easily separated from the reaction system as heterogeneous catalysts. However, this method is not suitable for the recovery and recycle of catalysts used in the oxidative polymerization of DMP in water. The oxidative polymerization of DMP in water belongs to the precipitation polymerization.<sup>9</sup> The formed polymer and oligomer with a critical molecular weight also precipitated from the water, which are difficult to separate from the immobilized catalysts. Therefore, new methods should be proposed to solve this problem.

The use of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles as the support is an effective method to solve this problem. After reaction, the immobilized catalysts can be separated by an external magnetic field from a complicated multiphase system. Furthermore, there are a lot of advantages when the size of support decreases to the nanometer scale: sufficient surface area which was desirable for grafting, negligible residual magnetization in the absence of an external magnetic field which is beneficial to dispersion, sufficient

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**Figure 1** Synthesis of PVI-containing silicane coupling agent.

contacts of catalysts, and substrates which can maintain high catalytic efficiency.<sup>10</sup> In the present article, PVI was grafted onto  $\text{Fe}_3\text{O}_4$  nanoparticles through siloxane bonds and then coordinated with Cu(II) to form the immobilized Cu(II)-PVI complex. The immobilized Cu(II)-PVI complex was employed to catalyze the oxidative polymerization of DMP in water. After polymerization, the immobilized Cu(II)-PVI complex catalyst was collected by an external magnetic field and reused in the next run with an additional PVI-grafted  $\text{Fe}_3\text{O}_4$  nanoparticles (shortened as  $\text{Fe}_3\text{O}_4$ -g-PVI) and copper ions. The recovery and reuse of Cu(II)-PVI complex catalyst in the oxidative polymerization of DMP in water was realized.

## EXPERIMENTAL

### Materials

Analytically pure 2,6-DMP, 3-mercaptopropyltrimethoxysilane (MPS), and *N*-vinylimidazole were purchased from Aldrich. *N*-vinylimidazole was purified by distillation under reduced pressure at  $83^\circ\text{C}/7$  mmHg before use. Analytically pure copper dichloride ( $\text{CuCl}_2$ ) and sodium hydroxide ( $\text{NaOH}$ ) were obtained from Shanghai Zhenxing Chemistry Co. and Xiaoshan Chemistry Co., respectively. Chemically pure  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) and sodium *n*-dodecyl sulfate (SDS) were provided by Sinopharm Chemical Reagent Co. and Shantou Chemistry Co., respectively. Analytically pure hydrochloric acid was purchased from Hangzhou Chemistry Co.. Analytically pure iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) were provided by Sinopharm Chemical Reagent Co..

### Preparation of magnetic $\text{Fe}_3\text{O}_4$ nanoparticles

Magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared using coprecipitation as reported before.<sup>11</sup> A total of 22.5 mL of 1 mol/L  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.4 mol/L HCl, and 0.5 mol/L  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was prepared as a source of iron. A total of 250 mL of 0.5 mol/L NaOH was added to a reactor and preheated to  $80^\circ\text{C}$ . The prepared iron

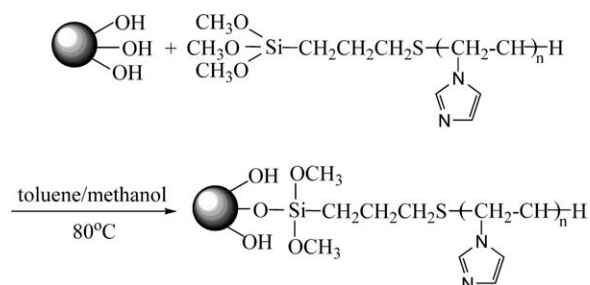
solution was slowly dropped into the reactor under high-speed mechanical stirring (1200 rpm) in an  $\text{N}_2$  atmosphere. After 30 min, black powder was collected by an external magnetic field, washed with methanol and water for three times, and dried in vacuum oven at  $30^\circ\text{C}$  for 24 h. IR (KBr):  $573\text{ cm}^{-1}$  ( $\text{Fe}-\text{O}-\text{H}$ ).

### Synthesis of PVI-containing silicane coupling agent

PVI-containing silicane coupling agent was prepared as reported by Takafuji et al. (Fig. 1).<sup>10</sup> A total of 2.72 mL *N*-vinylimidazole (30 mmol) and 0.3-mL MPS (1.5 mmol) were dissolved in 30-mL methanol and added into a reactor with a  $\text{N}_2$  inlet, followed by the addition of 56.4-mg AIBN. The solution was stirred at  $60^\circ\text{C}$  for 48 h in a  $\text{N}_2$  atmosphere. After the reaction, diethyl ether was added into the solution at  $-20^\circ\text{C}$  and white powder precipitated. The product was washed thoroughly with diethyl ether and dried in vacuum oven at  $30^\circ\text{C}$  for 48 h. IR (KBr):  $1499\text{ cm}^{-1}$  ( $\text{C}=\text{N}$ ),  $1413\text{ cm}^{-1}$  ( $-\text{CH}_2-$ ),  $1229\text{ cm}^{-1}$  ( $-\text{C}-\text{N}-$ ),  $2946\text{ cm}^{-1}$  ( $-\text{OCH}_3$ ),  $1089\text{ cm}^{-1}$  ( $\text{Si}-\text{O}$ ),  $824\text{ cm}^{-1}$  ( $\text{Si}-\text{C}$ ),  $745\text{ cm}^{-1}$ ,  $661\text{ cm}^{-1}$  ( $\text{S}-\text{C}$ ).  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , ppm):  $\delta$  6.78–7.46 ( $-\text{CH}=\text{N}-\text{CH}=\text{CH}-\text{N}-$ ), 3.64–2.63 ( $-\text{CH}-$ ), 2.39–1.72 ( $-\text{CH}_2-$ ,  $\text{OCH}_3$ ), 0.60 ( $\text{SiCH}_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ , ppm):  $\delta$  137.5 ( $\text{N}-\text{C}=\text{N}$ ), 129.8, 117.6 ( $-\text{N}-\text{C}=\text{C}-\text{N}=\text{C}$ ), 53.2 ( $-\text{CH}-\text{N}-$ ), 50.5 ( $\text{OCH}_3$ ), 41.9 ( $-\text{CH}_2-$ ), 24.6 ( $-\text{CH}_2-\text{CH}_2-\text{S}-$ ), 14.6 ( $\text{Si}-\text{CH}_2-$ ).

### Preparation of $\text{Fe}_3\text{O}_4$ -g-PVI

PVI-containing silicane coupling agent was grafted onto  $\text{Fe}_3\text{O}_4$  nanoparticles as follows (Fig. 2): 1.9 g  $\text{Fe}_3\text{O}_4$  nanoparticles and 1.7 g PVI-containing silicane coupling agent dispersed in 100-mL toluene/methanol (80:20 volume ratio) solution. The reaction mixture was stirred (900 rpm) at  $80^\circ\text{C}$  for 48 h. After the reaction, the nanoparticles were washed repeatedly with methanol, collected by an external magnetic field, and dried in vacuum oven at  $50^\circ\text{C}$  for 24 h. IR (KBr):  $1499\text{ cm}^{-1}$  ( $\text{C}=\text{N}$ ),  $1413\text{ cm}^{-1}$  ( $-\text{CH}_2-$ ),  $1229\text{ cm}^{-1}$  ( $-\text{C}-\text{N}-$ ),  $2946\text{ cm}^{-1}$  ( $-\text{OCH}_3$ ),  $1089\text{ cm}^{-1}$



**Figure 2** Preparation of  $\text{Fe}_3\text{O}_4$ -g-PVI.

(Si—O), 824 cm<sup>-1</sup> (Si—C), 745 cm<sup>-1</sup>, 661 cm<sup>-1</sup> (S—C), 573 cm<sup>-1</sup> (Fe—O—H).

### Preparation of the immobilized Cu(II)-PVI complex

A total of 0.2068 g Fe<sub>3</sub>O<sub>4</sub>-g-PVI ([imidazole group] = 2.4 × 10<sup>-4</sup> mol) coordinated with 0.0102 g CuCl<sub>2</sub>·2H<sub>2</sub>O (6 × 10<sup>-5</sup> mol) in 10-mL water to form the immobilized Cu(II)-PVI complex.

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

A typical procedure for the oxidative polymerization of DMP in water catalyzed by the immobilized Cu(II)-PVI complex is as follows: DMP (0.366 g, 3.0 mmol), NaOH (0.120 g, 3.0 mmol), and SDS (0.086 g, 0.3 mmol) were dissolved in 50-mL water. The previously prepared immobilized Cu(II)-PVI complex solution was added to the reactor. Oxygen is bubbled through the reaction mixture at a flow rate of 1.0 mL/min and the pressure of oxygen above the reaction media maintains at atmospheric pressure. The reaction mixture was vigorously stirred (600 rpm) under oxygen at 50°C for 24 h. After the polymerization, the immobilized Cu(II)-PVI complex catalyst was separated from the reaction solution by an external magnetic field, washed with water, dried in vacuum oven at 30°C for 24 h and reused in the next run of polymerization. The pH of the reaction solution was adjusted to 7 by HCl. An off-white powder was obtained by filtration after salting out with sodium chloride and then extracted for 48 h to eliminate DPQ.

### Characterizations

The content of DPQ was determined by a UV751GW UV-vis spectrophotometer (Shanghai Xinyi Instrument). Fifteen micrograms of the polymerized product before extraction was dissolved in 25-mL toluene and the absorbance (*A*) of the solution was measured by UV-vis spectrophotometer at 421 nm. The concentration of DPQ (*C*) in toluene was calculated according to Beer-Lambert's law [eq. (1)].

$$A = \lg(I_0/I) = \epsilon cl \quad (1)$$

where *I*<sub>0</sub> is the incident light intensity, *I* is the transmitted light intensity, *l* is the thickness of the colorimetric utensil,  $\epsilon$  is the molar absorption coefficient of DPQ, which was determined to be 6.5 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> by Beer-Lambert's law.

The weight-average molecular weight and polydispersity of PPO were determined by gel permeation chromatography (GPC, Waters 1525/2414,

Waters Instrument) equipped with Waters Styragel HT4/HT3/HR1 columns and a refractive index detector at 30°C. The mobile phase was toluene and maintained at a flow rate of 1.0 mL/min. The molecular weight was calibrated with polystyrene standards.

A drop of the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles and Fe<sub>3</sub>O<sub>4</sub>-g-PVI were respectively placed on carbon-coated copper grids and dried under ambient conditions. The morphology of Fe<sub>3</sub>O<sub>4</sub>-g-PVI was recorded using a 1200EX transmission electron microscope (TEM) (JEOL Corporation, Japan). The amounts of C, N, and H in the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles and Fe<sub>3</sub>O<sub>4</sub>-g-PVI were determined by elemental analysis (EA) using a Flash EA 1112 analyzer (ThermoFingnigan, Italy). Infrared spectra of the prepared Fe<sub>3</sub>O<sub>4</sub> nanoparticles and Fe<sub>3</sub>O<sub>4</sub>-g-PVI were obtained with a NICOLET 5700 spectrometer (Thermo Electron Corporation, USA). A sample of finely crushed KBr was used as the background. The amount of PVI grafted on the magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles was estimated by Pyris 1 thermal gravimetric analyzer (Perkin-Elmer Corporation, USA) in an N<sub>2</sub> atmosphere. The sample was heated from 100 to 600°C at a rate of 10°C/min.

The average degree of polymerization of PVI-containing silicane coupling agent was determined by DMX-500 <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy (Bruker, Switzerland). In methanol-*d*<sub>4</sub> (CD<sub>3</sub>OD), the integral values of peaks around  $\delta = 6.78$ –7.46 ppm and  $\delta = 0.60$  ppm were used to calculate the degree of polymerization.<sup>10</sup>

The complexing amount of Cu(II) with the imidazole group in Fe<sub>3</sub>O<sub>4</sub>-g-PVI was determined by 180–50 atomic absorption spectroscopy (AAS; Hitachi, Japan). A total of 0.01 g Fe<sub>3</sub>O<sub>4</sub>-g-PVI was dispersed in 10-mL Cu(II) solution ranged from 0 to 0.4 mmol/L by ultrasonication. After 1 h, the mixture was centrifuged at 15,000 rpm for 30 min. The supernatant was used to analyze the concentration of Cu(II).

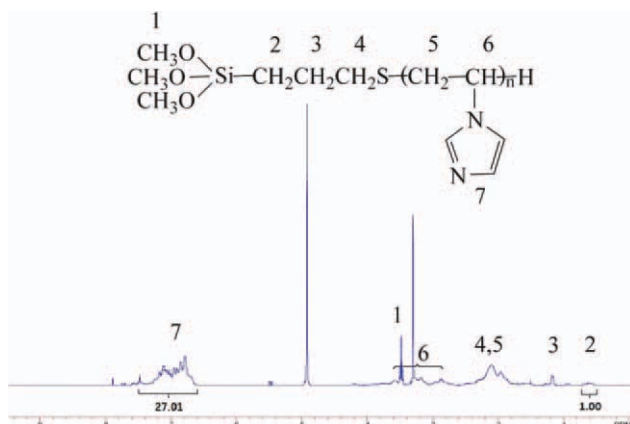
The amount of Cu(II) in the recycled Cu(II)-PVI complex catalyst was also determined by 180–50 AAS. A total of 0.02 g of the recycled Cu(II)-PVI complex catalyst was mixed with 0.4 mL 0.5 mol/L HCl and dispersed under ultrasonication for 30 min. The mixture was centrifuged at 15,000 rpm for 30 min and the supernatant was used to analyze the concentration of Cu(II).

## RESULTS AND DISCUSSION

### Preparation of Fe<sub>3</sub>O<sub>4</sub>-g-PVI

PVI-containing silicane coupling agent was prepared by polymerization of *N*-vinylimidazole with MPS. According to the reference, the peak at  $\delta = 0.60$  ppm (peak 2) was ascribed to two protons of SiCH<sub>2</sub>, and



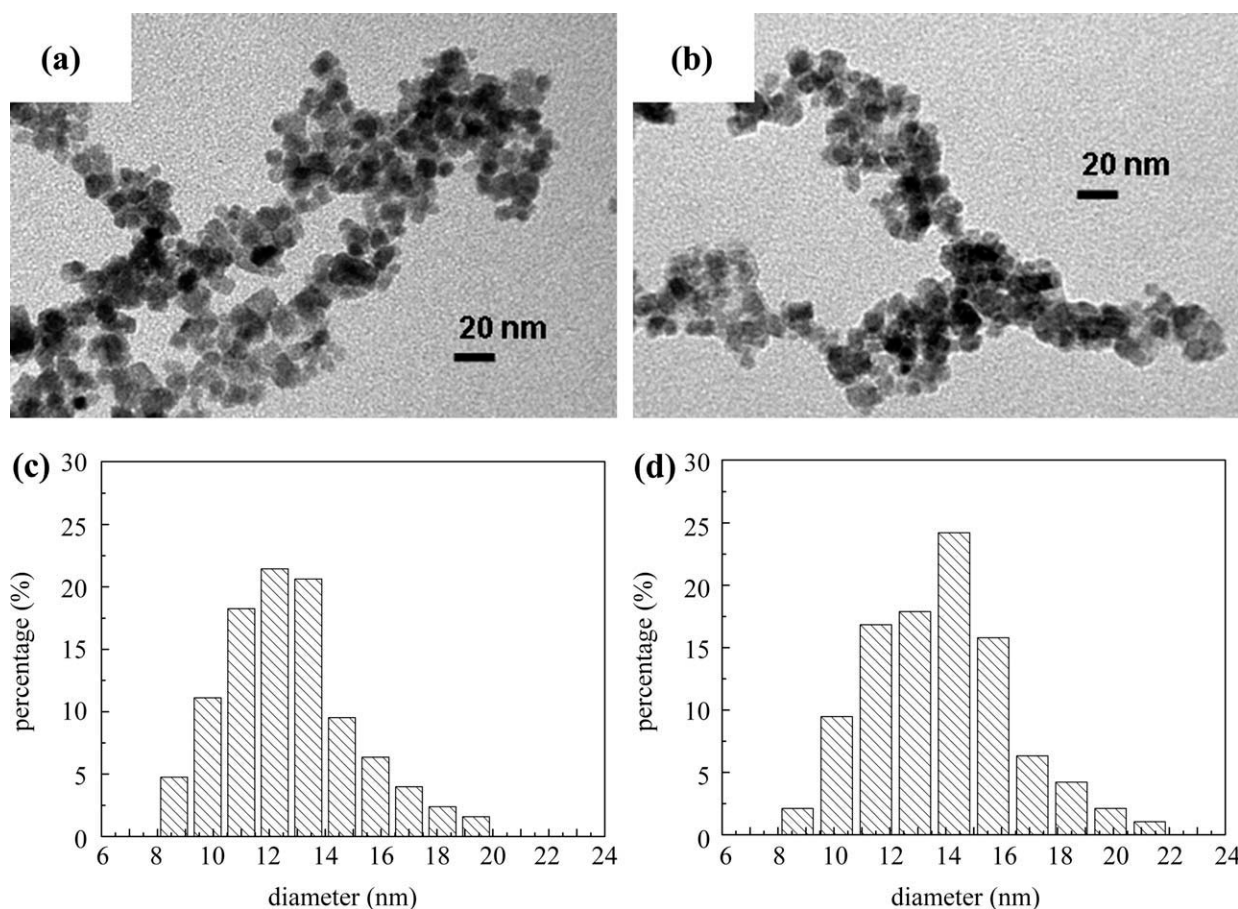


**Figure 3**  $^1\text{H-NMR}$  of PVI with alkoxyisilane in one end. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

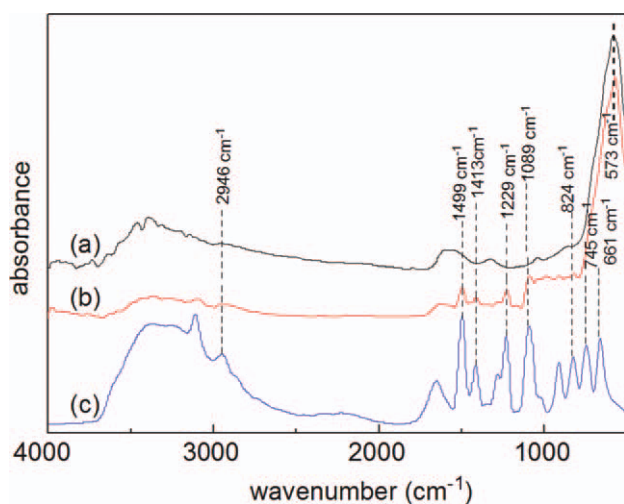
the peak around  $\delta = 6.78\text{--}7.46$  ppm (peak 7) was assigned to three protons of imidazolyl ring.<sup>10</sup> Since the ratio of integral values of peaks 7 and 2 is about 27, the average polymerization degree of PVI was calculated to be 18. Other peaks and their corresponding protons were showed in Figure 3.<sup>12</sup>

The morphologies of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-g-PVI}$  nanoparticles were shown in Figure 4(a,b).  $\text{Fe}_3\text{O}_4$  nanoparticles were dispersive in water due to the hydroxyl groups on their surface. Particle diameters were analyzed by Nano Measurer according to the TEM images and the size distribution were plotted [Fig. 4(c,d)]. Statistical analysis of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-g-PVI}$  particles gave a mean diameter of 12.27 nm and 13.74 nm, respectively. In comparison with  $\text{Fe}_3\text{O}_4$  the diameter of  $\text{Fe}_3\text{O}_4\text{-g-PVI}$  nanoparticles increased due to the existence of the thin polymer coating.

Figure 5 was the IR spectra of  $\text{Fe}_3\text{O}_4$  nanoparticles,  $\text{Fe}_3\text{O}_4\text{-g-PVI}$  and PVI-containing silicane coupling agent. The IR peak at  $573\text{ cm}^{-1}$  in  $\text{Fe}_3\text{O}_4$  nanoparticles (spectrum a) was ascribed to the vibration of  $\text{Fe-O-H}$ . The IR peaks at  $1499\text{ cm}^{-1}$ ,  $1413\text{ cm}^{-1}$ , and  $1229\text{ cm}^{-1}$  in PVI (spectrum c) were assigned to the vibration of  $\text{C=N}$ ,  $-\text{CH}_2-$ , and  $-\text{C-N-}$ , respectively. Peaks at  $2946\text{ cm}^{-1}$ ,  $1089\text{ cm}^{-1}$ , and  $824\text{ cm}^{-1}$  were ascribed to  $-\text{OCH}_3$ ,  $\text{Si-O}$ , and  $\text{Si-C}$  in silicane coupling agent, respectively. Furthermore, peaks at  $745\text{ cm}^{-1}$  and  $661\text{ cm}^{-1}$  were assigned to the vibration of  $\text{S-C}$ , indicating that PVI-containing



**Figure 4** TEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles (a) and  $\text{Fe}_3\text{O}_4\text{-g-PVI}$  (b) and diameter distributions of  $\text{Fe}_3\text{O}_4$  nanoparticles (c) and  $\text{Fe}_3\text{O}_4\text{-g-PVI}$  (d).



**Figure 5** FTIR spectra of  $\text{Fe}_3\text{O}_4$  nanoparticles (a),  $\text{Fe}_3\text{O}_4$ -g-PVI (b), and PVI-containing silicane coupling agent (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

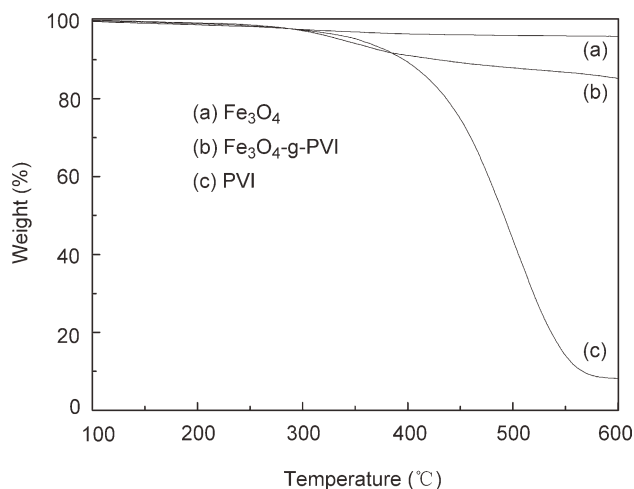
silicane coupling agent was successfully synthesized. Before characterization,  $\text{Fe}_3\text{O}_4$ -g-PVI was extracted by water to remove PVI which had not been grafted onto  $\text{Fe}_3\text{O}_4$  nanoparticles. As shown in Figure 5, the features of both  $\text{Fe}_3\text{O}_4$  nanoparticles and PVI-containing silicane coupling agent were observed in  $\text{Fe}_3\text{O}_4$ -g-PVI, which confirmed that PVI had been successfully grafted onto  $\text{Fe}_3\text{O}_4$  nanoparticles.

The EA results of  $\text{Fe}_3\text{O}_4$  nanoparticles,  $\text{Fe}_3\text{O}_4$ -g-PVI, and PVI were showed in Table I. A small quantity of H (0.5%) presented in  $\text{Fe}_3\text{O}_4$  nanoparticles before grafting PVI, which may come from the residual hydroxyl on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles. The N content of  $\text{Fe}_3\text{O}_4$ -g-PVI was determined to be 3.3%. According to the N content, the amount of imidazolyl groups and PVI on  $\text{Fe}_3\text{O}_4$  nanoparticles were calculated to be 1.16 mmol/g and 10.9%, respectively.

Figure 6 was the results of thermal gravimetric analysis (TGA) of  $\text{Fe}_3\text{O}_4$  nanoparticles (a),  $\text{Fe}_3\text{O}_4$ -g-PVI (b) and pure PVI (c). PVI began to lose weight at 350°C and the total weight loss was 91.8% at 480°C. From curve a, we found that the weight of  $\text{Fe}_3\text{O}_4$  nanoparticles did not change much from 100 to 600°C. The total weight loss was only 4.0% at 600°C. The thermal response of curve b was quite different from curve a. The weight of  $\text{Fe}_3\text{O}_4$ -g-PVI began to

**TABLE I**  
EA Results of  $\text{Fe}_3\text{O}_4$  Nanoparticles,  $\text{Fe}_3\text{O}_4$ -g-PVI, and PVI

	C/%	H/%	N/%	C/N
$\text{Fe}_3\text{O}_4$	0	0.5	0	
$\text{Fe}_3\text{O}_4$ -g-PVI	8.8	1.2	3.3	2.7
PVI	57.5	7.1	24.2	2.4



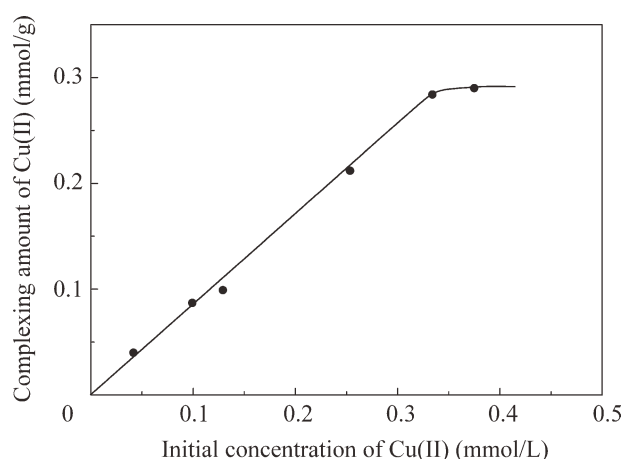
**Figure 6** TGA curves of  $\text{Fe}_3\text{O}_4$  nanoparticles (a),  $\text{Fe}_3\text{O}_4$ -g-PVI (b), and PVI (c).

decrease at 300°C and the total weight loss was up to 14.8% at 600°C. The amount of PVI grafted onto  $\text{Fe}_3\text{O}_4$  nanoparticles was calculated to be 10.9% from the weight loss of PVI and the difference of the weight loss between curves a and b, which was consistent with the result obtained by EA.

The amount of the ungrafted PVI-containing silicane coupling agent could be collected by evaporating the solvent and the value was determined to be 1.41 g. Therefore, the amount of PVI grafted on  $\text{Fe}_3\text{O}_4$  nanoparticles was calculated to be 10.8%, which was consistent with the results obtained by EA and TGA.

### Coordination of $\text{Fe}_3\text{O}_4$ -g-PVI with Cu(II)

PVI have been studied extensively due to their coordinated capacity with metal ions such as Ni(II), Co(II), Cu(II), and Zn(II), which can be used for the removal



**Figure 7** The complexing amount of  $\text{Fe}_3\text{O}_4$ -g-PVI for Cu(II) under different initial concentration of Cu(II) (initial pH of solution = 5.3).

**TABLE II**  
Complexing Amount of Fe<sub>3</sub>O<sub>4</sub>-g-PVI for Cu(II) Under Different Initial Concentration of Cu(II)<sup>a</sup>

Entry	Initial concentration of Cu(II) in solution (mmol/L)	Remained concentration of Cu(II) in solution (mmol/L)	Complexing amount of Cu(II) (mmol/g)
1	0.0417	0.0014	0.040
2	0.0992	0.0120	0.087
3	0.1291	0.0274	0.099
4	0.2535	0.0409	0.212
5	0.3339	0.0441	0.284
6	0.3748	0.0724	0.290

<sup>a</sup> Initial pH of solution = 5.3.

of heavy metals from industrial effluents.<sup>13,14</sup> Figure 7 showed the complexing amount of Fe<sub>3</sub>O<sub>4</sub>-g-PVI for Cu(II) under different initial Cu(II) concentrations.

A total of 0.01 g Fe<sub>3</sub>O<sub>4</sub>-g-PVI was dispersed in 10 mL Cu(II) solution ranged from 0 to 0.4 mmol/L and Cu(II) coordinated with the imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI. After 1 h, the particles were collected by an external magnetic field and the concentration of Cu(II) in supernatant was determined by AAS. The complexing amount of Fe<sub>3</sub>O<sub>4</sub>-g-PVI for Cu(II) could be calculated according to AAS results. As shown in Figure 7, the complexing amount of Fe<sub>3</sub>O<sub>4</sub>-g-PVI for Cu(II) increased with the initial concentration of Cu(II) and then remained constant, which suggested that the complexing was saturated. The saturated complexing amount of Fe<sub>3</sub>O<sub>4</sub>-g-PVI for Cu(II) was 0.29 mmol/g. Because the amount of imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI was determined to be 1.16 mmol/g, the coordinated number between imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI and Cu(II) was calculated to be 4, which was the same as the situation in unimmobilized PVI.<sup>15,16</sup> These results confirmed that almost all the imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI were accessible and can be coordinated with Cu(II) in water.

The complex formation constant of Fe<sub>3</sub>O<sub>4</sub>-g-PVI with Cu(II) can be calculated from Table II. The complex formation constant (*K*) was expressed as eq. (2).

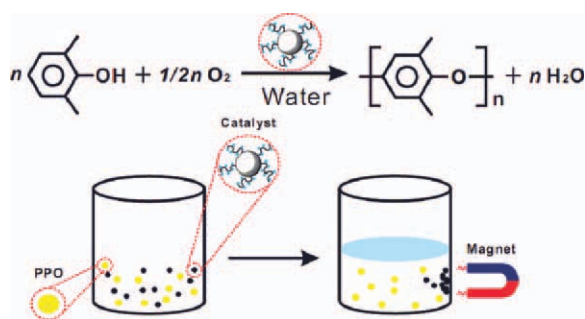
$$\text{Cu(II)} + \text{Im}_4 \leftrightarrow \text{Cu(II)-Im}_4$$

$$K = \frac{[\text{Cu(II)-Im}_4]}{[\text{Cu(II)}][\text{Im}]^4} \quad (2)$$

Take entry 4 as an example. The concentration of Cu(II) changed from the initial 0.2535 to 0.0409 mmol/L, therefore the concentration of Cu(II)-Im<sub>4</sub> complex was 0.2126 mmol/L. The concentration of imidazolyl groups ([Im]) in the solution after coordination was 0.3096 mmol/L. The value of *K* was calculated to be  $5.6 \times 10^{14} \text{ mol}^{-4} \text{ L}^4$ . The equilibrium constant of free PVI coordinated with Cu(II) was reported to be  $10^{11}$  to  $10^{15} \text{ mol}^{-4} \text{ L}^4$  by Gold et al.<sup>15</sup> The *K* value obtained in our experiments was insistent with the reference.

### The oxidative polymerization of DMP in water catalyzed by the immobilized Cu(II)-PVI complex catalyst

The immobilized Cu(II)-PVI complex was used to catalyze the oxidative polymerization of DMP in water (Scheme 1) and the results were summarized in Table III. As shown in Table III, the immobilized Cu(II)-PVI complex can effectively catalyze the oxidative polymerization of DMP in water, with desirable selectivity to form PPO. High yield of PPO (86.1%) was obtained with the weight-average molecular weight of  $6.8 \times 10^3$  in the first run. However,



**Scheme 1** The oxidative polymerization of DMP in water catalyzed by the immobilized Cu(II)-PVI complex catalyst. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE III**  
Oxidative Polymerization of DMP in Water with the Immobilized Cu(II)-PVI Complex Catalyst<sup>a</sup>

Run	PPO yield (%)	DPQ yield (%)	PPO <i>M<sub>w</sub></i> ( <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> ) ( $\times 10^3$ g/mol)
1	88.3%	0.3%	6.8 (1.9)
2	57.4%	0.4%	3.6 (2.4)
3	40.7%	0.2%	2.6 (2.1)

<sup>a</sup> All the polymerizations were carried out in water under oxygen at 50°C for 24 h ([Cu(II)] = 1 mmol/L, [DMP] = 0.05 mol/L, [SDS] = 0.005 mol/L, and [NaOH] = 0.05 mol/L).



**TABLE IV**  
**Oxidative Polymerization of DMP in Water Catalyzed by the Immobilized Cu(II)-PVI Catalyst with Additional Fe<sub>3</sub>O<sub>4</sub>-g-PVI and Copper Chloride<sup>a</sup>**

Run	PPO yield (%)	DPQ yield (%)	PPO $M_{w}$ ( $M_{w}/M_{n}$ ) ( $\times 10^3$ g/mol)	Recovery rate of catalyst (%)
1	86.1	0.3%	6.8 (1.9)	95.8%
2	83.0	0.2%	7.3 (2.0)	97.4%
3	79.2	0.1%	6.8 (2.7)	96.6%

<sup>a</sup> All the polymerizations were carried out in water under oxygen at 50°C for 24 h ([Cu(II)] = 1 mmol/L, [DMP] = 0.05 mol/L, [SDS] = 0.005 mol/L, and [NaOH] = 0.05 mol/L).

when the recovered immobilized catalyst was directly reused in the oxidative polymerization for the second and third run, the yield and molecular weight of PPO decreased dramatically.

The amount of the PVI-g-Fe<sub>3</sub>O<sub>4</sub> recovered from the first run was determined to be 94.2% by EA and TGA. The recovery rate of Cu(II) was determined to be 78.5% by AAS. Two possible explanations were considered for the loss of Cu(II). First, the immobilized Cu(II)-PVI could not be totally recovered. Second, when the immobilized Cu(II)-PVI complex was recovered after the polymerization and washed with water, the dissociation of Cu(II) with imidazolyl groups in PVI occurred. The effective concentration of catalyst decreased due to the loss of immobilized catalyst and Cu(II), which resulted in the decrease of the yield and molecular weight of PPO.

To maintain the concentration of catalyst, fresh immobilized PVI-g-Fe<sub>3</sub>O<sub>4</sub> and copper chloride (0.0120 g PVI-g-Fe<sub>3</sub>O<sub>4</sub> and 0.0022 g CuCl<sub>2</sub> · 2H<sub>2</sub>O for run 2, and 0.0120 g PVI-g-Fe<sub>3</sub>O<sub>4</sub> and 0.0021 g CuCl<sub>2</sub> · 2H<sub>2</sub>O for run 3, respectively.) were added to the recovered catalyst according to the results of EA and AAS and reused for the next run. The results were showed in Table IV.

With additional immobilized catalyst and copper chloride, the PPO yield in the second and third run were 83.0% and 79.2% with the weight-average molecular weight of  $7.3 \times 10^3$  g/mol and  $6.8 \times 10^3$  g/mol, respectively. Compared with the result obtained in the first run of polymerization, the yield and weight-average molecular weight of PPO almost remained. The recovery rate of the immobilized Cu(II)-PVI complex catalyst in three runs of polymerization was over 95%. These results confirmed that the immobilized Cu(II)-PVI complex catalyst

used in the oxidative polymerization of DMP in water has been successfully recovered and reused.

## CONCLUSIONS

Fe<sub>3</sub>O<sub>4</sub>-g-PVI has been synthesized and characterized. The amount of imidazolyl group in Fe<sub>3</sub>O<sub>4</sub>-g-PVI was estimated to be 1.16 mmol/g by EA and TGA. Fe<sub>3</sub>O<sub>4</sub>-g-PVI coordinated with Cu(II) to form the immobilized Cu(II)-PVI complex. The stoichiometric ratio between imidazolyl groups in Fe<sub>3</sub>O<sub>4</sub>-g-PVI and Cu(II) was found to be 4 and the complex formation constant (*K*) was calculated to be  $5.6 \times 10^{14}$  mol<sup>-4</sup> L<sup>4</sup>. The immobilized Cu(II)-PVI complex was employed to catalyze the oxidative polymerization of DMP in water and showed excellent C—O/C—C selectivity to form PPO. After polymerization, the immobilized Cu(II)-PVI complex catalyst was collected by an external magnetic field and reused in the next run with additional immobilized catalyst and copper ions. After three runs of oxidative polymerization of DMP, the recovery rate of immobilized Cu(II)-PVI catalyst was above 95% and the yield of PPO maintained as high as 79.2% with the addition of supplementary catalysts.

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