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OXIDATIVE POLYMERIZATION BEHAVIOR OF 2,6-DIMETHYLPHENOL IN AQUEOUS MEDIA WITH POTASSIUM FERRICYANIDE*

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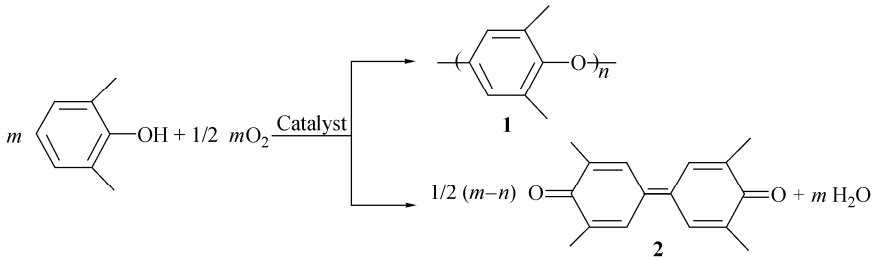
Abstract The effects of potassium ferricyanide, sodium *n*-dodecyl sulfate, sodium hydroxide and temperature on the molecular weight and the yield of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) synthesized in an aqueous medium were studied. It was found that oxygen in air had little influence on the oxidative polymerization of 2,6-dimethylphenol (DMP) in the aqueous medium, and potassium ferricyanide was only an oxidant during the oxidative polymerization of DMP. Sodium *n*-dodecyl sulfate could stabilize polymer particles and facilitate the oxidative polymerization of DMP on the surface of polymer particles, which resulted in the increase of the molecular weight of PPO. The yield and molecular weight of PPO increased significantly with NaOH concentration at first and then decreased with NaOH concentration. The high molecular weight PPO with high yield was obtained at 50°C, but both the yield and molecular weight of PPO decreased with the further increase of temperature.

Keywords: 2,6-Dimethylphenol (DMP); Oxidative polymerization; Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO); Aqueous medium.

INTRODUCTION

Under the catalysis of copper-amine complex the oxidative polymerization of 2,6-dimethylphenol (DMP) to form poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, Scheme 1 (**1**)) in organic solvent was first established by Hay and his GE group[1]. Besides PPO, a small quantity of by-product, 3,3′,5,5′-tertramethyl-4,4′-diphenoquinone (DPQ, Scheme 1 (**2**)), was also obtained by C－C coupling of DMP. Now the solution polymerization has been widely used in the industrial PPO production. However, both a solvent recovery process and an antiexplosive reactor are required.



Scheme 1 The oxidative polymerization of DMP

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On the view of green chemistry, the use of water as the reaction medium is environmentally friendly[2]. Furthermore, PPO can be separated easily due to its insolubility in water. However, copper-amine complex is easy to hydrolyze in water to form the inactive copper hydroxide that can not catalyze the oxidative polymerization[3, 4], which inhibited the further study on the oxidative polymerization of DMP in water .

Haynes[5] reported that phenol can be oxidized to phenoxy radical under the action of potassium ferricyanide, meanwhile potassium ferricyanide was reduced to potassium ferrocyanide. Recently Nishide[6] reported that the oxidative polymerization of DMP in water has been realized under the action of potassium ferricyanide. However, the number-average molecular weight of PPO synthesized in water is only up to 1.3×10^4 and insufficient for an engineering plastic. Furthermore, the formation of DPQ results in the decrease of the yield and thermal stability of PPO[7].

It is believed that a further study of the dependence of the molecular weight and yield of PPO synthesized in water on various factors is necessary for the future industrial application of this newly developed synthetic method for preparing PPO. In this paper, the effects of potassium ferricyanide ($K_3Fe(CN)_6$), sodium *n*-dodecyl sulfate (SDS), sodium hydroxide (NaOH) and temperature on the molecular weight of PPO and the yields of PPO and DPQ synthesized in aqueous media were studied.

EXPERIMENTAL

Materials

Analytical grade DMP was obtained from Aldrich. Analytical grade sodium hydroxide (NaOH) and chemical grade sodium *n*-dodecyl sulfate (SDS) were purchased from Xiaoshan Chemical Co. and Shantou Chemical Co., respectively. Potassium ferricyanide ($K_3Fe(CN)_6$) and potassium ferrocyanide ($K_4Fe(CN)_6$) were supplied by Wenzhou Chemical Co.

Oxidative Polymerization of DMP

The oxidative polymerization of DMP in aqueous media was carried out according to the method described in the literature[6]. A typical procedure for the oxidative polymerization of DMP is as follows: DMP (0.244 g, 2 mmol) was dissolved in water (100 mL) containing NaOH (2.00 g, 50 mmol) and SDS (57.6 mg, 0.2 mmol). $K_3Fe(CN)_6$ (1.316 g, 4 mmol) was added to the solution, and the mixture was vigorously stirred (300 r/min) under air at 50°C for 6 h. The precipitated product was separated as an off-white powder from the reaction mixture by a simple filtration after being salted out, and then the solid product was extracted by acetonitrile to eliminate 3,3′,5,5′-tertramethyl-4,4′-diphenoquinone (DPQ) for the measurement of the yield and molecular weight of PPO.

Apparatus and Measurements

The molecular weight of PPO was determined by gel permeation chromatography (GPC, Waters 1525/2414, Waters Instrument Co., USA). Monodispersed polystyrene was used as a standard substance.

The content of DPQ was determined by a visible spectrophotometer (721, Shanghai Xinyi Instrument Co.). The maximal absorption peak of pure DPQ in toluene solution was observed at 421 nm, and the molar absorption coefficient (ε) of DPQ was determined to be 6.5×10^4 L mol^{-1}cm^{-1} according to Beer-Lambert's law. The obtained product was dissolved in toluene and the absorbance at 421 nm (A) was measured by visible spectrophotometer. The concentration of DPQ (c) in the solution was calculated according to Beer-Lambert's law (Eq. 1).

$$A = \lg (I_0/I) = \varepsilon c l \quad (1)$$

Where I_0 is the incident intensity, I is the transmitted intensity, and l is the thickness of the colorimetric utensil.

The weight of DPQ synthesized (m_{DPQ}) was estimated based on the calculated c, and DPQ yield (y_{DPQ}) was calculated according to Eq. (2).

$$y_{DPQ} = \frac{m_{DPQ}}{m_0} \times \frac{2 \times 122}{240} \times 100\% \quad (2)$$

Where, m_0 is the weight of DMP monomer, 240 is the molecular weight of DPQ and 122 is the molecular weight of DMP.

PPO yield (y_{PPO}) was calculated according to Eq. (3).

$$y_{PPO} = \frac{m_{PPO}}{m_0} \times \frac{122}{120} \times 100\% \quad (3)$$

Where m_{PPO} is the weight of PPO synthesized and 120 is the molecular weight of the repeating unit of PPO.

A Coulter LS particle size analyzer (Coulter LS-230, Coulter Instrument) was used to determine the size distribution of polymer particles. Before measurements, the sample was diluted, and an excess of SDS was added to prevent the coagulation of polymer particles.

RESULTS AND DISCUSSION

The Role of Potassium Ferricyanide during the Oxidative Polymerization of DMP

In the homogeneous solution polymerization, DMP first deprotonated to form phenoxy anion (phenolate), and phenoxy anion was oxidized to phenoxy radical by copper(II)-amine complex. The C—O coupling of phenoxy radical gave the dimer, and then the oligomer and polymer. During the oxidative polymerization of DMP copper(II)-amine complex was reduced to copper(I)-amine complex simultaneously, while copper(I)-amine complex was oxidized by oxygen in the atmosphere to copper(II)-amine complex again. Therefore, copper-amine complex acts as a catalyst during the oxidative polymerization of DMP[8, 9].

In order to clarify the role of $K_3Fe(CN)_6$ during the oxidative polymerization of DMP, the polymerization of DMP was conducted under the atmosphere of nitrogen or air. The molecular weight of PPO and yields of PPO and DPQ were summarized in Table 1. The yield and the weigh-average molecular weight (M_w) of PPO under nitrogen were 92.37% and 5.3×10^4, respectively, which were consistent with the results obtained under air (88.38% and 4.6×10^4) at the same concentrations of DMP and $K_3Fe(CN)_6$, indicating that oxygen in air had little influence on the oxidative polymerization of DMP, and oxygen was not an oxidant during the oxidative polymerization of DMP. In addition, DPQ yield under air (0.25%) was almost the same with the result (0.24%) obtained under nitrogen.

Table 1. Effect of atmosphere on the yields of PPO and DPQ and the molecular weight of PPO

Condition	Yield (%)		$M_w \times 10^{-4}$
	y_{PPO}	y_{DPQ}	
N_2	92.37	0.24	5.3
Air	88.38	0.25	4.6

During the oxidative polymerization of DMP potassium ferricyanide was reduced to potassium ferrocyanide. Therefore, the polymerization of DMP was also carried out under the action of potassium ferrocyanide. It was found that there was no PPO formed after 6 h at 50°C under air atmosphere, which indicated that potassium ferrocyanide can not be reoxidized to potassium ferricyanide by oxygen under experimental conditions and potassium ferricyanide only acted as an oxidant, instead of a catalyst.

The effect of potassium ferricyanide concentration on PPO yield was also examined, and the result is shown in Fig. 1. It was found that PPO yield increased linearly with the increase of the molar ratio of potassium ferricyanide to DMP first. When the molar ratio of potassium ferricyanide to DMP was 2, PPO yield was 90%. When the molar ratio of potassium ferricyanide to DMP was over 2, PPO yield no longer changed with the further increase of the molar ratio.

Figure 2 showed the effect of the molar ratio of potassium ferricyanide to DMP on the molecular weight of PPO. It was demonstrated that with the increase of the molar ratio of potassium ferricyanide to DMP at first the

molecular weight of PPO increased gradually and then increased significantly. The reason for this trend was that the oxidative polymerization of DMP was a stepwise polymerization[10], and potassium ferricyanide was an oxidant.

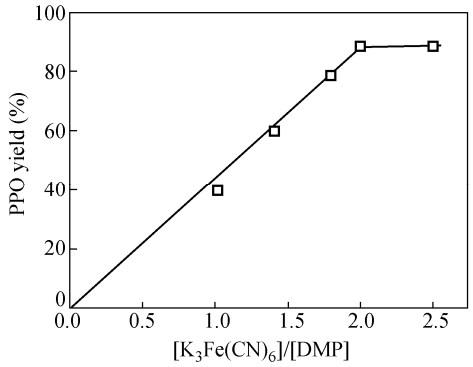

Fig. 1 Effect of the molar ratio of potassium ferricyanide to DMP on PPO yield
[DMP] = 0.02 mol·L^{-1}, [NaOH] = 0.5 mol·L^{-1}, [SDS] = 0.002 mol·L^{-1}, 50°C, 6 h, in air

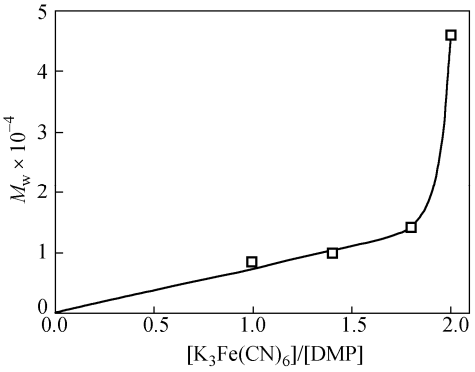

Fig. 2 Effect of the molar ratio of potassium ferricyanide to DMP on the molecular weight of PPO
[DMP] = 0.02 mol·L^{-1}, [NaOH] = 0.5 mol·L^{-1}, [SDS] = 0.002 mol·L^{-1}, 50°C, 6 h, in air

Effect of potassium ferricyanide concentration on DPQ yield is presented in Fig. 3. It was found that in the aqueous medium DPQ yield increased with potassium ferricyanide concentration, and DPQ yield was 0.24% when the molar ratio of potassium ferricyanide to DMP was 2.

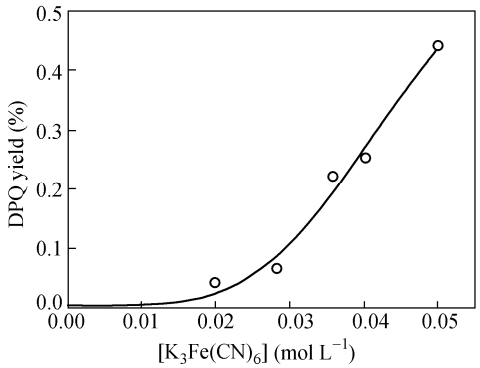

Fig. 3 Effect of potassium ferricyanide concentration on DPQ yield
[DMP] = 0.02 mol·L^{-1}, [NaOH] = 0.5 mol·L^{-1}, [SDS] = 0.002 mol·L^{-1}, 50°C, 6 h, in air

Effect of SDS on the Oxidative Polymerization of DMP

During the oxidative polymerization of DMP the formed oligomer and polymer became insoluble even in alkaline water, and precipitated out from water to form the polymer particle[6]. Therefore, the oxidative polymerization at the later stage mainly took place on the surface or within the polymer particles. For the stepwise polymerization, the polymerization at the later stage was very important to the molecular weight of polymer. However, the coagulation of polymer particles due to the instability in water resulted in the decrease of the particle surface area, which was not in favor of the further oxidative polymerization on the particle surface[11]. The surfactant may stabilize polymer particles during the oxidative polymerization of DMP in water. Therefore, the effect of SDS on the oxidative polymerization of DMP was examined, and the results are listed in Table 2. It was found that after the introduction of SDS both the yield and molecular weight of PPO were high in comparison with the results obtained without SDS.

Table 2. Effect of SDS on the polymerization of DMP

SDS ($mol \cdot L^{-1}$)	Yield (%)		$M_w \times 10^{-4}$
	y_{PPO}	y_{DPQ}	
0	63.61	0.43	0.60
0.002	88.38	0.25	4.6

Figure 4 shows the particle size distribution of the final PPO particles. It can be seen that after the addition of SDS the number-average particle diameter of the final PPO particles was 99 nm, which was much smaller than that without SDS (241 nm). These results indicated that SDS could stabilize polymer particles and inhibit the particle coagulation, and consequently facilitate the oxidative polymerization of DMP on the surface of polymer particles at the later stage, which resulted in the increase of the molecular weight of PPO.

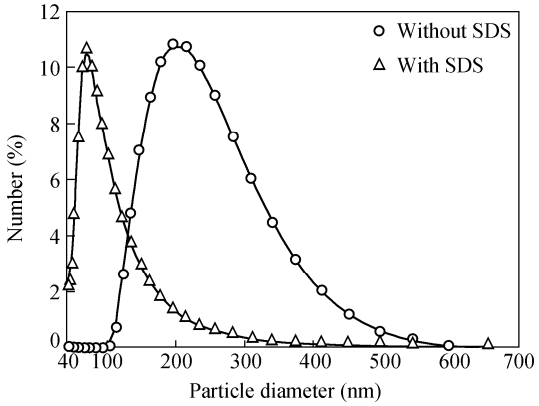

Fig. 4 Particle size distribution of the final PPO particles after the addition of SDS ($0.002\ mol \cdot L^{-1}$) or without SDS
[DMP] = $0.02\ mol \cdot L^{-1}$, [NaOH] = $0.5\ mol \cdot L^{-1}$, [$K_3Fe(CN)_6$] = $0.04\ mol \cdot L^{-1}$, 50°C, 6 h, in air

Effect of NaOH Concentration on the Oxidative Polymerization of DMP

The oxidative polymerization of DMP can not proceed without the addition of NaOH due to its high oxidation potential[6]. After introducing NaOH the oxidative polymerization of DMP has been realized. Therefore, the effect of NaOH concentration on the yield and molecular weight of PPO was examined. Figure 5 shows that both PPO yield and the weight-average molecular weight of PPO increase with NaOH concentration first and then decrease with the increase of NaOH concentration. When NaOH concentration was $0.5\ mol \cdot L^{-1}$, the molecular weight of PPO reached its maximum, and its weight-average molecular weight was 4.6×10^4.

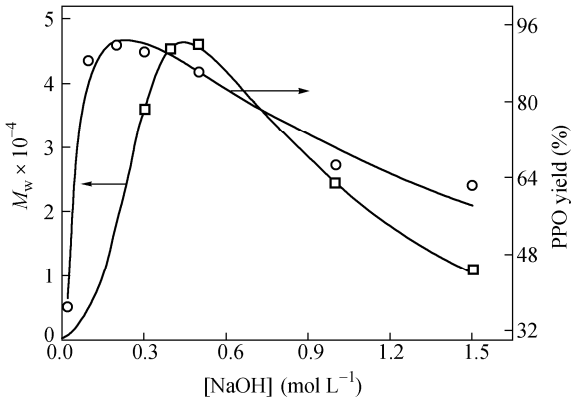

Fig. 5 Effect of NaOH concentration on the yield and weight-average molecular weight of PPO
[DMP] = $0.02\ mol \cdot L^{-1}$, [$K_3Fe(CN)_6$] = $0.04\ mol \cdot L^{-1}$, [SDS] = $0.002\ mol \cdot L^{-1}$, 50°C, 6 h, in air

In order to clarify the dependence of the molecular weight of PPO on NaOH concentration, the change of the oxidation potential of DMP with NaOH concentration was studied, and the results are shown in Fig. 6. It was found that the oxidation potential of DMP significantly decreased with NaOH concentration, while the reduction potential of $K_3Fe(CN)_6$ did not change with NaOH concentration[12]. The increase in the difference between the reduction potential of $K_3Fe(CN)_6$ and the oxidation potential of DMP with NaOH concentration facilitated the oxidative polymerization of DMP, which resulted in the increase of the yield and molecular weight of PPO. The decrease of the molecular weight of PPO at the high NaOH concentration may be explained by the high ionic strength, which reduced the colloidal stability.

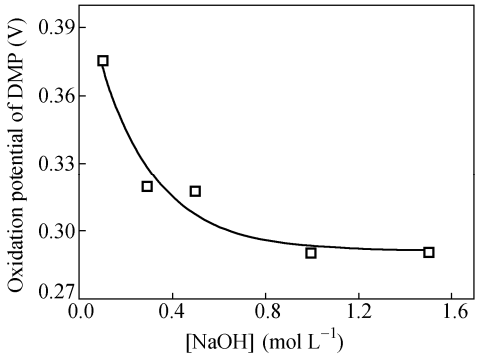

Fig. 6 The influence of NaOH concentration on the oxidation potential of DMP
[DMP] = 0.02 mol·L^{-1}

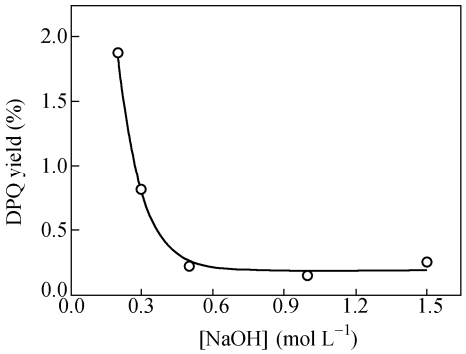

Fig. 7 Effect of NaOH concentration on DPQ yield
[DMP] = 0.02 mol·L^{-1}, [$K_3Fe(CN)_6$] = 0.04 mol·L^{-1}, [SDS] = 0.002 mol·L^{-1}, 50°C, 6 h, in air

The effect of NaOH concentration on DPQ yield is presented in Fig. 7. It was found that DPQ yield decreased with the increase of NaOH concentration. When NaOH concentration was 0.5 mol·L^{-1}, DPQ yield was 0.24%. DPQ yield did not change significantly with NaOH concentration when NaOH concentration was higher than 0.5 mol·L^{-1}. Camus[13] also reported that NaOH can inhibit the formation of DPQ in the study on the oxidative polymerization of DMP with a copper-amine complex as the catalyst.

Effect of Temperature on the Polymerization of DMP

The effect of temperature on the polymerization of DMP was examined, and the result is listed in Table 3. At low temperatures the polymerization rate was so slow that affected the progress of the polymerization. At 50°C the high molecular weight PPO with the high yield was obtained, however, both the yield and molecular weight of PPO decreased with the further increase of temperature. The decrease of PPO yield with the increase of temperature may be ascribed to the easy formation of DPQ by C—C coupling at higher temperatures[14]. In addition, PPO may depolymerize by redistribution in the existence of DPQ at higher polymerization temperature[15, 16]. Therefore the molecular weight of PPO obtained at higher temperatures, was relatively low, which was consistent with that obtained by Hay in the study of oxidative polymerization of DMP in the organic solvent[17].

Table 3. Effect of temperature on the polymerization of DMP

Temperature (°C)	Yield (%)		$M_w \times 10^{-4}$
	y_{PPO}	y_{DPQ}	
50	88.38	0.25	4.6
60	76.82	0.28	2.3
70	72.75	0.30	1.3

CONCLUSIONS

Potassium ferricyanide, SDS, NaOH and temperature had a significant effect on the oxidative polymerization of DMP in aqueous media. Potassium ferricyanide can only act as an oxidant for the oxidative polymerization of DMP in the aqueous medium. Both the yield and molecular weight of PPO increased after introducing SDS, which indicated that SDS can stabilize polymer particles and facilitate the oxidative polymerization of DMP. The molecular weight of PPO increased with the increase of NaOH concentration at first due to the decrease of the oxidation potential of DMP. The decrease of the molecular weight of PPO at the high NaOH concentrations may be explained by the high ionic strength, which reduced the colloidal stability. The high molecular weight PPO with the high yield was obtained at 50°C, but both the yield and molecular weight of PPO decreased with the further increase of temperature.

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