Mechanism of the Particle Formation During the Oxidative Polymerization of 2,6-Dimethylphenol in an Aqueous Medium

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ABSTRACT: The changes of the molecular weight and particle size with time during the oxidative polymerization of 2,6-dimethylphenol in an aqueous medium were studied. At the beginning of the oxidative polymerization, the oligomers with the hydrophilic phenoxy anion at the end of oligomer chains are formed rapidly in the aqueous medium. When the molecular weight of the oligomer reaches up to a critical value, the oligomer precipitates out from the water, resulting in the formation of the original particle (or domain). With the increase of the molecular weight, the concentration of the phenoxy anion and the surface charge density of the original particles decrease; therefore, the repulsion force between orig-inal particles weaken and the stability of particles in water decreases, resulting in the coagulation of the original particle and the formation of the primary particle. With the further progression of the polymerization, the primary particles coagulate and final particles are formed. A three-stage mechanism of the particle formation is proposed, that is, the particle nucleation, first coagulation, and second coagulation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3649–3653, 2007

Key words: 2,6-dimethylphenol (DMP); oxidative polymerization; particle formation; aqueous medium; poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)

INTRODUCTION

The oxidative polymerization of 2,6-dimethylphenol (DMP) developed by Hay and his GE group[1] provides a convenient method to prepare poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, Scheme 1(1)), an important engineering plastic. The reaction proceeds at room temperature with a certain amount of catalyst by eliminating an equimolar amount of water. Now the solution polymerization has been widely used in industrial PPO production.[2] However, the polymerization is carried out in organic solvents such as toluene and benzene under oxygen. Therefore, both a solvent-recovery process and an antiexplosive reactor are required.

On the view of green chemistry, the use of water as the reaction medium is environmentally friendly.[3] Furthermore, PPO can be separated from water easily because of its insolubility in water. Therefore, the oxidative polymerization of DMP to prepare PPO using water as the reaction medium would be of sig-nificance. Recently Nishide and coworkers[4] reported that the polymerization of DMP in water has been realized, and PPO with a number–average molecular weight of 1.3×10^4 was synthesized. In their study, DMP was dissolved in an alkaline aqueous solution to form the phenoxy anion, and the phenoxy anion was oxidized to the phenoxy radical. The C—O coupling of two phenoxy radicals gave the dimer, and then the oligomer and polymer. The formed oligomer and polymer were insoluble even in the alkaline aqueous solution, and precipitated out from water to form the polymer particle. However, there has been no report about the mechanism of the particle formation, although the particle formation is very important for the heterogeneous polymerization.

In this study, the changes of the molecular weight and particle size with the reaction time in an aqueous medium were studied, and the mechanism of the particle formation during the oxidative polymerization of DMP was proposed.
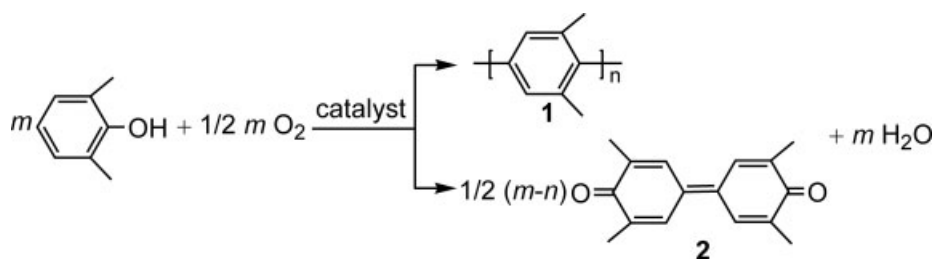
EXPERIMENTAL

Materials

DMP was obtained from Aldrich. Analytically pure sodium hydroxide (NaOH) and potassium ferricya-nide ($K_3Fe(CN)_6$) were supplied by Xiaoshan Chemistry and Wenzhou Chemistry, respectively. Sodium

Scheme 1 Oxidative polymerization of DMP.

dodecyl sulfate (SDS, chemical pure) was purchased from Shantou Chemistry.

Oxidative polymerization of DMP

The oxidative polymerization of DMP in aqueous medium was conducted according to the method described in the literature.[4] DMP (0.122 g, 1 mmol) was dissolved in water (100 mL) containing NaOH (2.00 g, 50 mmol) and SDS (29 mg, 0.1 mmol). $K_3Fe(CN)_6$ (0.658 g, 2 mmol) was added to the solution, and the mixture was vigorously stirred (300 rpm) under air at 50°C. During the process of the oxidative polymerization, the reaction was terminated by adding hydrochloric acid,[5] and a small quantity of the sample was taken out for the determination of the particle size. The precipitated product was separated as an off-white powder from the reaction mixture by simple filtration after salting out, and then the solid product was extracted by acetonitrile to eliminate 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienyli-dene)-2,6-dimethyl-2,5-cyclohexadienylidene (DPQ, Scheme 1[2]) for the measurement of the molecular weight of PPO.

Characterization

The solubility of DMP in water was measured by a UV/Visible spectrophotometer (UV751GW, Shanghai Xinyi Instrument) according to the method described in the literature.[6]

The molecular weight of PPO was determined by vapor pressure osmometer (VPO, Kanuer K-7000, Kanuer Instrument, Germany) and gel permeation chromatography (GPC, Waters 1525/2414, Waters Instrument).[7]

The total number of molecules including the monomer, oligomer, and polymer (N) during the oxidative polymerization was calculated according to eq. (1).

$$N = \frac{N_0 M_0}{M_n} \qquad (1)$$

where N_0 is the number of the initial DMP molecules, M_0 is the molecular weight of repeating unit

of PPO ($M_0 = 120$), and M_n is the number–average molecular weight of the product.

Zeta LS particle size analyzer (Zetasizer 3000HSA, Malvern Instrument) and Coulter LS particle size analyzer (Coulter LS-230, Coulter Instrument) were used to determine the size distribution of the polymer particle during the process of the oxidative polymerization. Before measurement, the sample was diluted and an excess of SDS was added to prevent the coagulation of particles. The particle number (n) formed in the aqueous solution was calculated according to eq. (2).[8]

$$n = \frac{6W}{\pi d^3 \rho} \qquad (2)$$

where W represents the weight of the polymer formed during the oxidative polymerization, d is the volume–average particle diameter, and ρ is the density of PPO (1.06 g/cm^3).

RESULTS AND DISCUSSION

### Formation of the polymer particle and evolution of the particle size with time

The solubility of DMP in water was measured by a UV/Vis spectrophotometer. It was found that temperature, SDS concentration, and pH influenced the solubility of DMP. The solubility of DMP in water was 0.3 g in 100 g of H_2O at 25°C and increased with the increase of temperature. The solubility of DMP was 6.1 g in 100 g of pH = 13.5 solution and was much larger than that in water because phenolic hydroxyl group in DMP reacted with hydroxyl in the alkaline solution to form the phenoxy anion.[4] The addition of the surfactant also increased the solubility of DMP in water. Therefore, DMP was dissolved in the alkaline solution under the reaction condition, and the oxidative polymerization started in a homogeneous aqueous medium. However, the reaction mixture became heterogeneous after the addition of the oxidant ($K_3Fe(CN)_6$) due to the insolubility of the formed oligomer and polymer in the same solution. This implies that at the action of $K_3Fe(CN)_6$, the oxidative polymerization of DMP in
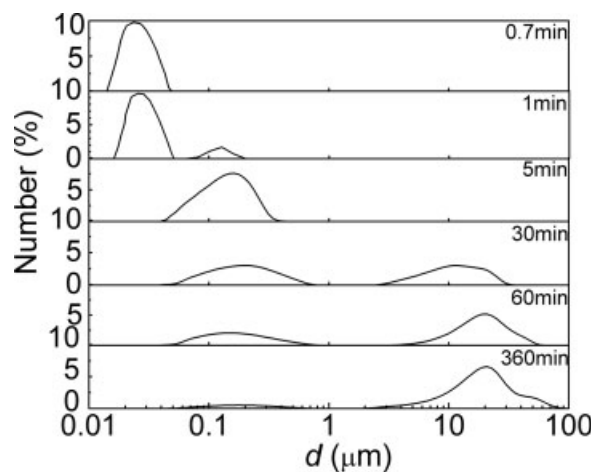
Figure 1 Evolution of the particle size distribution with time during the oxidative polymerization of DMP.

an aqueous medium must be very fast and belongs to the precipitation polymerization.

Figure 1 showed the evolution of the particle size distribution during the oxidative polymerization of DMP in an aqueous medium with time. As seen in Figure 1, the particle size increased with the development of the oxidative polymerization. At the beginning of the oxidative polymerization ($\sim$ 0.7 min), the particle size was about 20–50 nm. When the polymerization time was 1 min, a small peak with a particle size of 0.1-µm order appeared besides the peak with a particle size of 20–50 nm. At 5 min the peak with a particle size of 20–50 nm disappeared and the size of monodispersed particles was around 0.1-µm order. In comparison with the result obtained at 0.7 min, the particle size increased by one order of magnitude, indicating that the particle coagulation may happen. With the progression of the polymerization, a new peak with an average particle size of 10-µm order appeared and the particle size distribution curve became bimodal again at 30 min. With
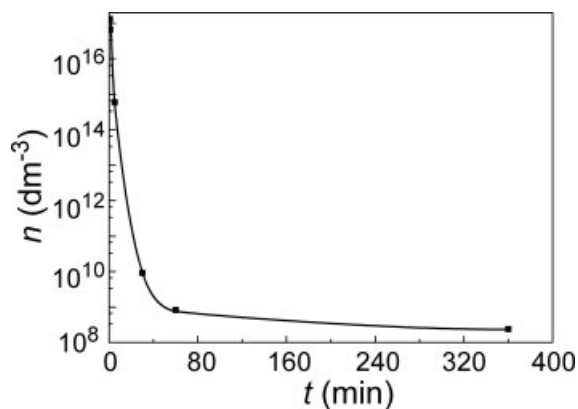
Figure 2 Change of the particle number (n) with the reaction time.
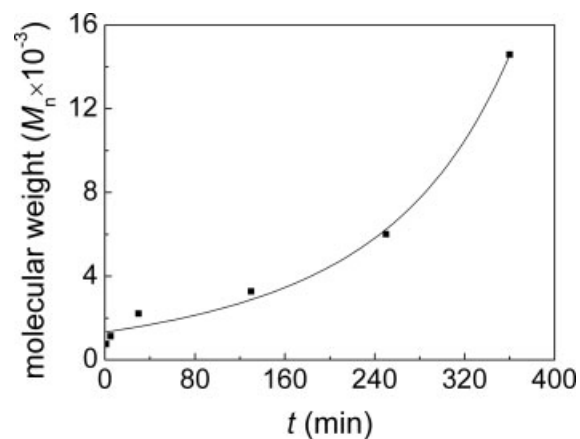
Figure 3 Change of the number–average molecular weight of PPO with time.

the increase of the reaction time, the particle number with a size of 0.1-µm order decreased and particles with a size of 10-µm order increased. At the end of the polymerization the particle size was mainly about 10-µm order.

Suppose the polymer particle is spherical and cannot be swelled by water, then the particle number (n) can be estimated according to eq. (2). Figure 2 clearly demonstrated that the value of n decreased rapidly with time, especially at the earlier stage of the reaction, which further indicated the coagulation of polymer particles during the oxidative polymerization of DMP.

Change of the molecular weight of PPO with time

The number–average molecular weight of PPO was determined by VPO and GPC (Fig. 3). As seen in Figure 3, during the process of oxidative polymerization of DMP, the molecular weight of PPO increased gradually at the earlier stage and rapidly at the later stage, which is in accordance with the traditional stepwise polymerization. Particularly, the number–average molecular weight of the oligomer at 0.7 min was determined to be 750, about six repeating units in an oligomer chain.

Mechanism of the particle formation during the oxidative polymerization of DMP

At the beginning of the oxidative polymerization of DMP, oligomers are formed rapidly in the aqueous medium. There are two parts in the oligomer, the hydrophobic part including benzene ring in the main chain and the hydrophilic one, that is, phenoxy anion at the end of the oligomer chain. The oligomer that has low molecular weight is dissolved in the alkaline solution due to the hydrophilicity of the phenoxy anion. When the oligomer reaches up to its
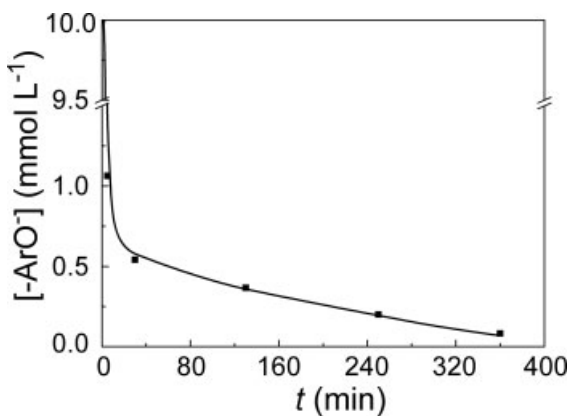
Figure 4 Change of the concentration of the phenoxy anion ([—ArO⁻]) with time during the oxidative polymerization of DMP.

critical molecular weight, the oligomer can not be dissolved in the alkaline solution and precipitates out from the aqueous solution, resulting in the formation of the original particle or domain with a size of 20 nm. According to the results of the molecular weight, we can conclude that the critical molecular weight and polymerization degree of the oligomer for the nucleation in the alkaline solution are about 750 and 6, respectively. In the particle, the hydrophobic part with benzene ring aggregates in the inside of the particle and the hydrophilic part with phenoxy anion points to the aqueous solution.

The key factor for the stability of the particle in the aqueous solution is the surface charge density of the particle. In addition to the SDS concentration, the concentration of the phenoxy anion on the surface of the particle is important for the stability of the particle. In a pH = 13.5 alkaline solution almost all of the phenolic hydroxyl groups in the monomer, oligomer, and polymer have been changed to phenoxy anions; therefore, the concentration of the phenoxy anion can be obtained according to eq.(1) and the results are shown in Figure 4. It was found that the concentration of the phenoxy anion ([—ArO⁻]) decreases significantly at the earlier stage of the oxidative polymerization, resulting in the decrease of the surface charge density of the original particles and the sta-

bility of particles in the aqueous solution. Therefore, the original particles with a size of 20–50 nm coagulates and primary particles with a size of 0.1-μm order forms (first coagulation). The coagulation results in the increase of the surface charge density and the stability of the particles. At this period of time the particle size distribution curve is bimodal with the coexistence of particles with a size of 20–50 nm and 0.1-μm order.

With the increase of the molecular weight of PPO, the surface charge density of the primary particles decreases gradually. The repulsion force between particles weakens and therefore the stability of particles in water decreases, resulting in further coagulation of the primary particles and the formation of the final particles with a size of 10-μm order. With the increase of the reaction time, the number of the primary particles gradually decreases, while that of the final particles with a size of 10-μm order increases, and at the end of the polymerization the particle size is mainly about 10-μm order.

Different from the radical polymerization, at the earlier stage of the oxidative polymerization DMP has been changed to the oligomer and the oligomer transfers from the aqueous solution into the particle phase. There is almost no monomer or oligomer in the aqueous solution; therefore, the increase of the particle size mainly depends on the coagulation during the oxidative polymerization of DMP, and the driving force of the particle coagulation is the decrease of the concentration of the hydrophilic phenoxy anion.

On the basis of the experimental results, a three-stage mechanism for the particle formation during the oxidative polymerization of DMP in an aqueous medium was proposed and the physical model is shown in Figure 5. At the earlier stage of polymerization, the oligomer is formed by the oxidative polymerization of DMP. When the oligomer reaches up to its critical molecular weight, the oligomer precipitates out from the water, resulting in the formation of original particles or domains. This stage is very short, about several minutes at the action of $K_3Fe(CN)_6$, and is called the particle nucleation.
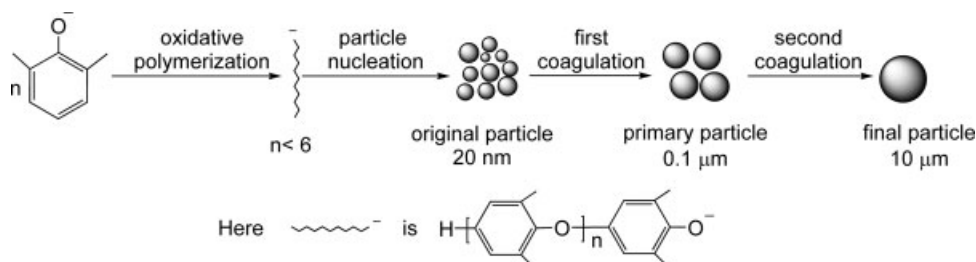
Figure 5 Proposed mechanism for the particle formation during the oxidative polymerization of DMP.

With the development of the oxidative polymerization, the molecular weight of the product increases and the concentration of the phenoxy anion decreases. Therefore, the surface charge density of the original particle decreases gradually, resulting in the first coagulation of original particles and the formation of primary particles.

With the further progression of the oxidative polymerization, the molecular weight of PPO increases and the second coagulation occurs.

In conclusion, the particle formation during the oxidative polymerization of DMP in an aqueous medium includes three stages, that is, the particle nucleation, the first coagulation, and the second coagulation.

CONCLUSIONS

At the action of $K_3Fe(CN)_6$, DMP is polymerized by oxidative coupling mechanism in aqueous medium to form the oligomer. When the oligomer reaches up to its critical molecular weight that could not dissolve in the aqueous medium, the oligomer precipitates out from the medium, resulting in the formation of the original particle. Therefore, the oxidative polymerization of DMP in an aqueous medium is the precipitation polymerization. According to the change of molecular weight and particle size with time, the particle formation during the oxidative polymerization of DMP in an aqueous medium can be divided into three-stages, that is, the particle nucleation, the first coagulation, and the second coagulation. Different from the radical polymerization, during the oxidative polymerization of DMP the increase of particle size mainly depends on the particle coagulation, and the driving force of the particle coagulation is the decrease of the concentration of the hydrophilic phenoxy anion with the polymerization time.

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