A Heterogeneous Kinetic Model of the Oxidative Polymerization of 2,6-Dimethylphenol with a Copper-EDTA Complex in Water

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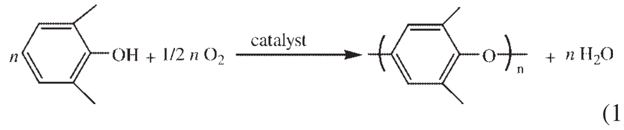
The heterogeneous oxidative polymerization kinetics of 2,6-dimethylphenol (DMP) catalyzed by a copper(II)-EDTA complex in water was studied. During the oxidative polymerization of DMP in water the oxygen uptake rate increases with an increase in DMP concentration and an increase in temperature. The Michaelis–Menten kinetic model as applied to the polymerization of DMP in organic solvents is not appropriate for the description of the full course of DMP polymerization in water. A new heterogeneous kinetic model is proposed to describe the catalyst deactivation during the oxidative polymerization as well as the difference in reactivity between the monomer, water-soluble oligomer and water-insoluble oligomer. The polymerization rate estimated by the new model is consistent with the measured data. © 2009 American Institute of Chemical Engineers *AIChE J*, 55: 2716–2724, 2009

Keywords: 2,6-dimethylphenol, oxidative polymerization, a copper-EDTA complex, kinetic model, water

Introduction

The oxidative polymerization of 2,6-dimethylphenol (DMP) catalyzed by a copper-amine complex in an organic solvent under oxygen as developed by Hay and his GE group provides a convenient method to prepare poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), an important engineering plastic (Eq. 1).[1,2] Now PPO is widely used in the electrical, appliance, and automotive industries, owing to its excellent impact and dielectric properties, as well as high modulus.



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Tsuchida et al. studied the change in oxygen uptake with time during the oxidative polymerization of DMP catalyzed by a copper-alkyl amine complex in *o*-dichlorobenzene, and proposed using the Michaelis–Menten model, which was well known in enzyme catalysis, to describe the oxidative polymerization kinetics of DMP in organic solvents.[3,4] Mobley et al. reported that catalyst deactivation occurred during the polymerization of DMP and the oligomer showed higher reactivity than the monomer.[5] The Michaelis-Menten model was thus modified to take catalyst deactivation into account as well as the difference in reactivity between the monomer and the oligomer.

The oxidative polymerization of DMP in organic solvents has been well studied and is widely used in industrial PPO production. However, both a solvent recovery process and an antiexplosive reactor are required. For green chemistry, the use of water as a reaction medium is considered environmentally friendly[6,7] and PPO can easily be separated from water due to its insolubility in water.[8,9] In 2004, Nishide et al. firstly reported the polymerization of DMP in water

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using potassium ferricyanide as an oxidant to synthesize PPO.[10] The use of potassium ferricyanide was, however, not acceptable from a green chemistry point of view. The oxidative polymerization of DMP in water was achieved by Nishide et al. by using the copper-amine complex as a catalyst in 2006.[11]

We recently reported that the oxidative polymerization of DMP in water was a heterogeneous reaction due to the insolubility of oligomers and polymers in water.[12] The heterogeneous polymerization kinetics of DMP in water was different from the homogeneous polymerization kinetics of DMP in organic solvents. The oxidative polymerization kinetics of DMP in water had not been carried out previously, as it was a newly developed synthetic method for preparing PPO.

In this article, the influence of DMP concentration and reaction temperature on the oxidative polymerization rate was studied and a new kinetic model was proposed taking catalyst deactivation into account as well as the difference in reactivity between the monomer, the water-soluble oligomer and the water-insoluble oligomer. The kinetic parameters were also estimated by nonlinear multiple regression analysis.

Experimental

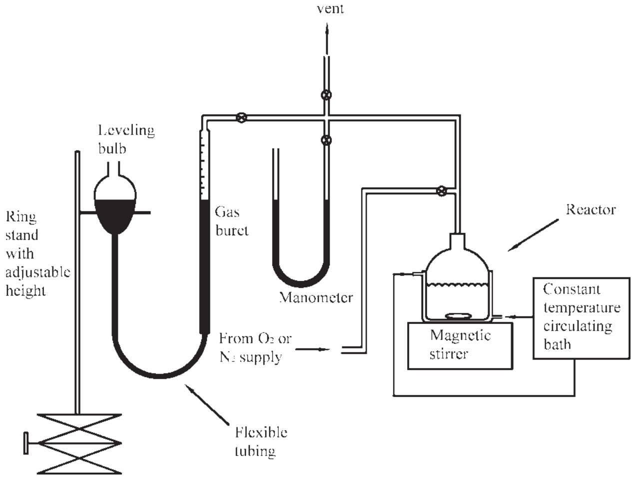
Materials

Analytically pure DMP was obtained from Aldrich. Analytically pure copper dichloride ($CuCl_2$) and ethylene diamine tetraacetic acid (EDTA) were obtained from Shanghai Zhenxing Chemistry and Sinopharm Chemical Reagent, respectively. Analytically pure sodium chloride (NaCl) and sodium hydroxide (NaOH) were supplied by Ningbo Chemistry and Xiaoshan Chemistry, respectively. Chemically pure sodium *n*-dodecyl sulfate (SDS) was purchased from Shantou Chemistry.

The oxidative polymerization of DMP

The oxidative polymerization of DMP in water was followed by monitoring oxygen uptake in a closed batch reactor system (Scheme 1) maintained at atmospheric pressure and at constant temperature. The following was a typical procedure for the polymerization.

A magnetically stirred flask (100 mL) was charged with water (45 mL), DMP (2.5 mmol), sodium *n*-dodecyl sulfate (SDS, 2.5 mmol) and sodium hydroxide (NaOH, 25 mmol) under nitrogen. $CuCl_2$ (0.25 mmol) and EDTA (0.25 mmol) were dissolved in 5 mL water to prepare the Cu-EDTA complex. The prepared aqueous solution containing DMP, SDS, and NaOH was added to the reactor, which was a 100 mL one-necked flask equipped with a constant temperature water bath. Stirring in the reactor was done by a magnetic stir bar which drew gas from the surface into the liquid and created a good gas/liquid mixture. The reactor was connected to a manometer and a gas buret (see Scheme 1). The fluid in the leveling bulb and manometer was colored by butyl phthalate. After filling the gas buret with oxygen the reactor system was closed. The reactor was brought to the desired temperature and the leveling bulb was used to adjust the system to atmospheric pressure as read on the manometer.



Scheme 1. The experimental apparatus.

To initiate the reaction 5 mL of the previously prepared Cu-EDTA complex was injected into the reactor with a syringe through the serum stopper under vigorous stirring. The temperature was kept constant throughout the reaction by the water bath. As oxygen was consumed the leveling bulb was raised as necessary to maintain atmospheric pressure.

During the oxidative polymerization of DMP the volume of oxygen uptake from the gas buret was recorded as a function of time. When the reaction stopped consuming oxygen, the reaction mixture was neutralized with hydrochloric acid. The precipitated product was separated as an off-white powder from the reaction mixture by simple filtration after salting out and was dried in vacuo. The product was extracted for 48 h with acetonitrile to eliminate 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone (DPQ), the by-product of C—C coupling of DMP. The viscosity of PPO in toluene at 25°C was determined with an Ubbelohde viscometer.

Results and Discussion

The oxidative polymerization kinetics of DMP in water

To determine the oxidative polymerization kinetics of DMP in water the relationship between oxygen uptake and time was studied and the result is shown in Figure 1 and Table 1. The oxygen uptake rate increases with DMP concentration due to an increase in collision probability between substrates. The oxygen uptake rate also increases with temperature due to an increase in substrate mobility at high temperature. At the same DMP concentration the total oxygen uptake (n_{O_2}, mmol) during the oxidative polymerization and the inherent viscosity of PPO synthesized in water ($[\eta]_{inh}$, dL/g) decreases with an increase in temperature. The decrease of the inherent viscosity indicates that the molecular weight of PPO decreases with an increase in temperature, which might ascribe to the increase of the side reaction of C—C coupling of DMP to form DPQ and the depolymerization of PPO at high temperature.

According to Eq. 1 the molar ratio of DMP to oxygen is 2:1 during the oxidative polymerization of DMP and DMP must be activated to the phenolate anion in order to undergo oxidative polymerization. All the phenolic proton of DMP is

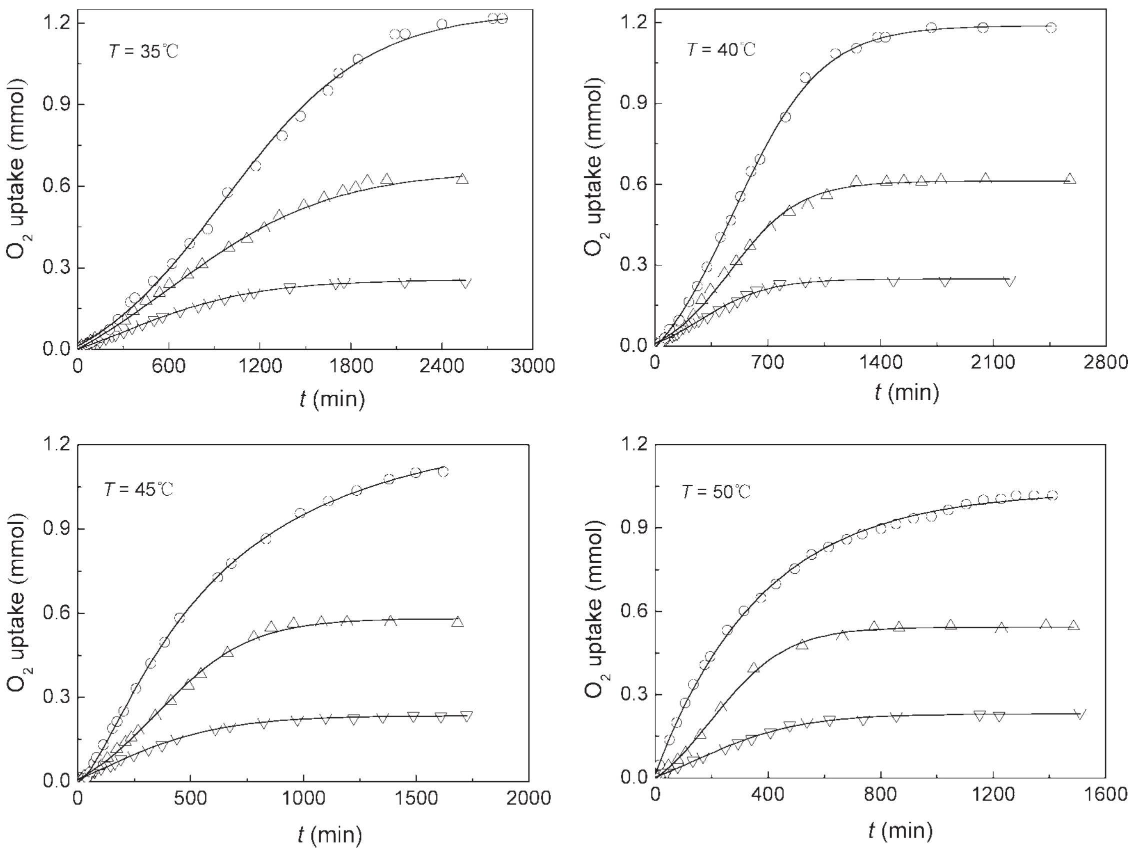
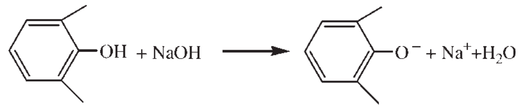


Figure 1. The change in oxygen uptake with time at various DMP concentrations and temperatures (▽: [DMP] = 10 mmol/L, △: [DMP] = 25 mmol/L, ○: [DMP] = 50 mmol/L, the smooth lines were the spline fit of the experimental data.).

removed quickly to form the phenolate anion by NaOH in water (Eq. 2), and thus all DMP is in the phenolate anion form ($[\text{DMP}]_0 = [\text{XO}^-]_0$).[13] The change of the concentration of phenolate anion ($[\text{XO}^-]$) during the oxidative polymerization can thus be calculated according to Eq. 3.



(2)

$$[\text{XO}^-] = \frac{[\text{XO}^-]_0 V - 2n_{\text{O}_2}}{V} \tag{3}$$

where V represents the volume of the reaction mixture.

During the polymerization of DMP, the reaction extent of phenolate anion (P) can be calculated according to Eq. 4 and the number average molecular weight of PPO (M_n) is estimated based on the reaction extent of phenolate anion (Eq. 5). The change of the number average molecular weight of PPO calculated by Eq. 5 with time is shown in Figure 2. The results indicates that during oxidative polymerization of DMP the molecular weight of PPO initially has a gradual increase and then a rapid final increase, which is consistent with the traditional stepwise polymerization.

$$P = \frac{[\text{XO}^-]_0 - [\text{XO}^-]}{[\text{XO}^-]_0} \tag{4}$$

$$M_n = \frac{M_0}{1 - P} \tag{5}$$

where M_0 is the molecular weight of the repeating unit of PPO ($M_0 = 120$).

The polymerization rate of DMP [R, mmol/(L min)] can be determined by Eq. 6 and the result is shown in Figure 3.

Table 1. Polymerization Conditions and Results

$[\text{DMP}]_0$ (mmol/L)	T (°C)	n_{O_2} (mmol)	$[\eta]_{\text{inh}}$ (dL/g)*
10.00	35.00	0.25	0.28
25.00	35.00	0.62	0.26
50.00	35.00	1.22	0.25
10.00	40.00	0.25	0.27
25.00	40.00	0.62	0.26
50.00	40.00	1.18	0.24
10.00	45.00	0.24	0.22
25.00	45.00	0.57	0.21
50.00	45.00	1.10	0.19
10.00	50.00	0.24	0.19
25.00	50.00	0.55	0.17
50.00	50.00	1.02	0.14

*Determined with an Ubbelohde viscometer.

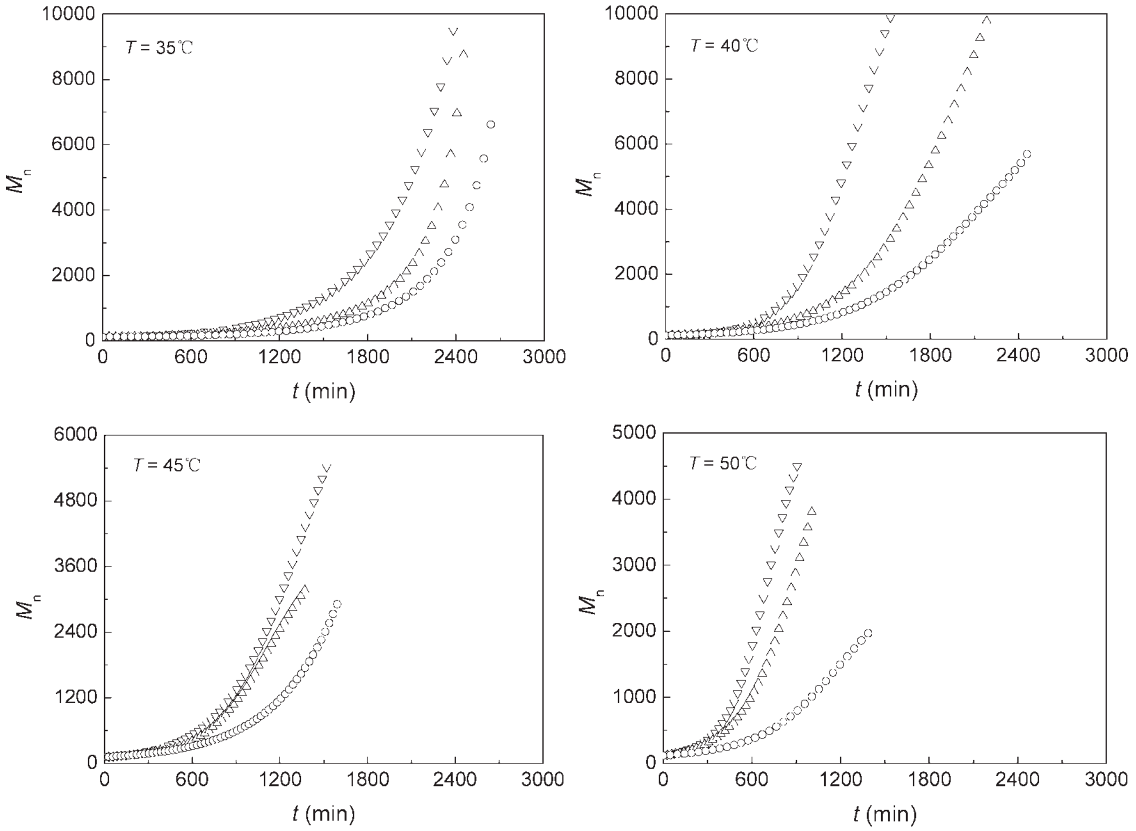


Figure 2. The change of the number average molecular weight of PPO calculated by Eq. 5 with time (▽: [DMP] = 10 mmol/L, △: [DMP] = 25 mmol/L, ○: [DMP] = 50 mmol/L).

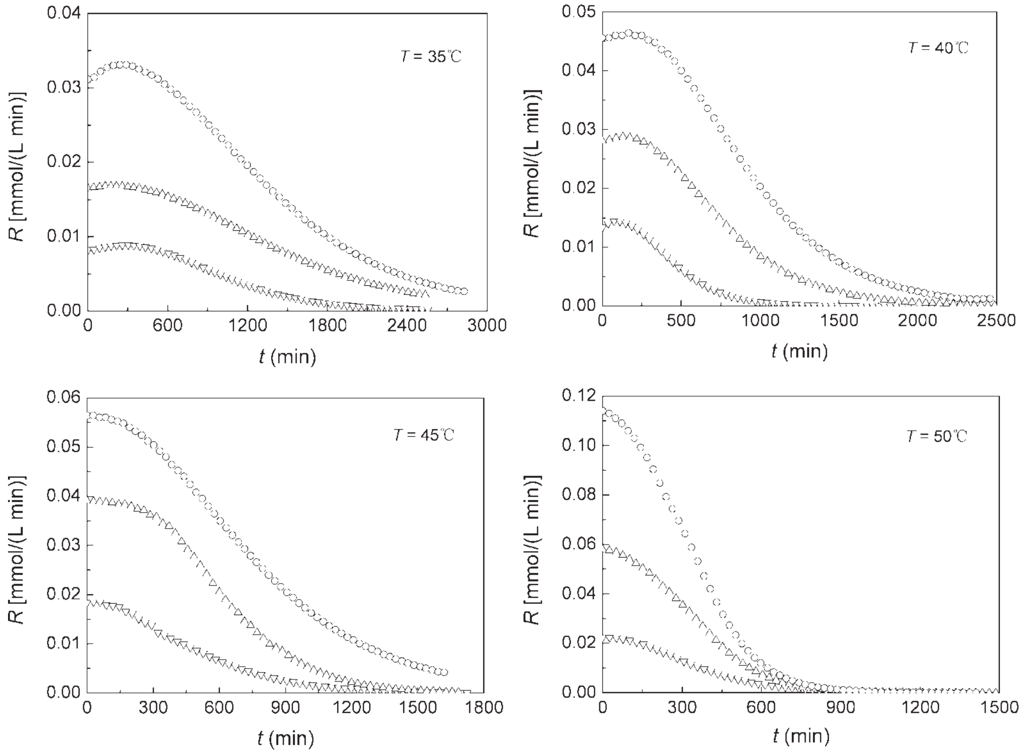


Figure 3. The change of the oxidative polymerization rate of DMP with time (▽: [DMP] = 10 mmol/L, △: [DMP] = 25 mmol/L, ○: [DMP] = 50 mmol/L).

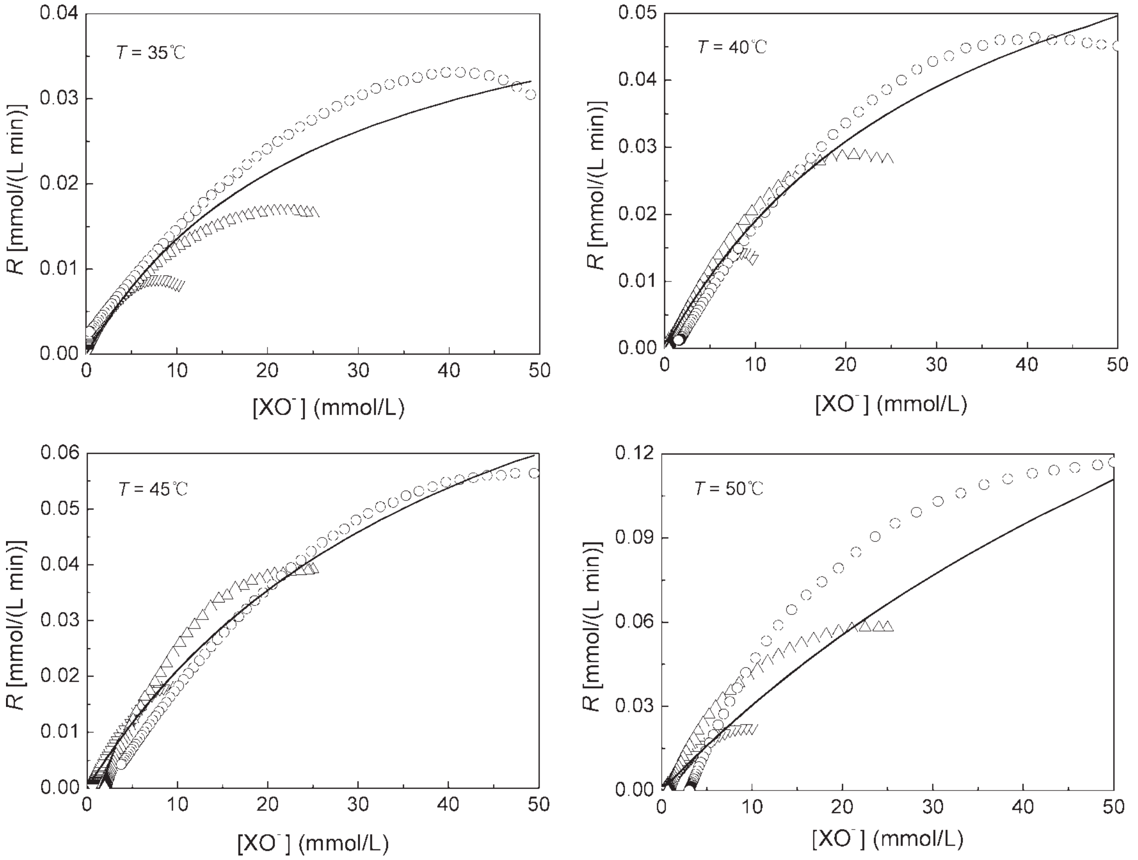


Figure 4. Relationship between the polymerization rate of DMP and the concentration of phenolate anion at various temperatures (▽: [DMP] = 10 mmol/L, △: [DMP] = 25 mmol/L, ○: [DMP] = 50 mmol/L, —: Fitted by Eq. 7).

$$R = -\frac{d[\mathrm{XO}^-]}{dt} = \frac{2}{V}\frac{dn_{\mathrm{O}_2}}{dt} \tag{6}$$

At the lower temperatures, the polymerization rate of DMP initially increases with time and then decreases; whereas at the high temperatures, the polymerization rate of DMP consistently decreases with time. Nakaoka reported that in comparison with DMP, compounds with electron donor groups at the para position, such as 2,4,6-trimethylphenol or 2,6-dimethyl-4-methoxyphenol, had a higher oxidation rate.[14] Mobley et al. proposed that the oligomer showed higher reactivity than the monomer due to the electron donating ether group para to the hydroxyl group in the oligomer.[5] The initial polymerization rate of DMP thus increases with time due to formation of the oligomer with high reactivity and the further decrease of the oxidative polymerization rate is due to a decrease in the phenolate anion concentration. At the higher temperatures the reactive monomer rapidly converts to the oligomer and the polymerization rate of DMP thus consistently decreases with time.

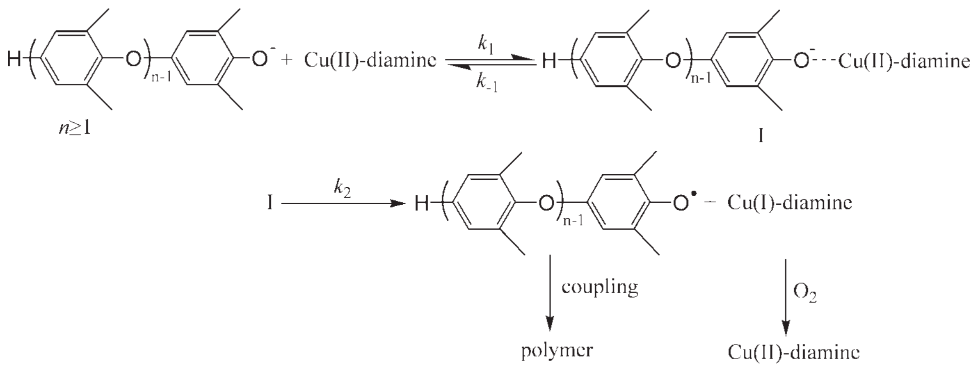
Figure 4 shows the relationship between the polymerization rate of DMP and the concentration of phenolate anion calculated using Eq. 3. The polymerization rate of DMP increases initially and then decreases as the concentration of phenolate anion decreases at 35°C and 40°C, while the polymerization rate of DMP at 45°C and 50°C consistently decreases with a decrease in the concentration of phenolate anion.

Tsuchida et al. found that the polymerization mechanism of DMP catalyzed by a copper-amine complex in an organic solvent was similar to that of a Michaelis–Menten type reaction (Scheme 2).[3] During the oxidative polymerization of DMP, the phenolic proton of DMP is removed by alkali to form the phenolate anion. In the reversible first step the copper-amine catalyst forms an intermediate complex with the phenolate anion. The rate-determining k_2 reaction is the dissociation of the intermediate complex to form a reactive phenoxyl radical and the reduced form of the catalyst. The C—O coupling of phenoxyl radicals gives the dimer, oligomer, and polymer. The polymer-building reaction of the phenoxyl radical and the regeneration of catalyst to the oxidized form are considered to be rapid. For every two cycles in Scheme 2 a new ether link is formed, thus building the polymer in stepwise fashion.

Tsuchida et al. indicated that the oxidative polymerization rate of DMP in organic solvents could be calculated according to Eq. 7.[15]

$$R = \frac{k_2[\mathrm{C}][\mathrm{XO}^-]}{K_\mathrm{m} + [\mathrm{XO}^-]} \tag{7}$$

where [C] represents the concentration of a catalyst (mmol/L), k_2 is the dissociation rate constant of the intermediate complex that forms a reactive phenoxyl radical and the reduced form of the catalyst (min^{-1}), K_m is Michaelis–Menten



Scheme 2. The oxidative polymerization mechanism of DMP in organic solvents.

constant (mol/L) and $K_m = (k_{-1} + k_2)/k_1$. Because $k_1 \gg k_2$ and $k_{-1} \gg k_2$ Tsuchida et al. assumes that $K_m \approx k_{-1}/k_1$. K_m reflects the affinity between the catalyst and the phenolate anion. Tsuchida et al. supposed that the catalyst concentration did not change with polymerization time.[15]

The relationship between the oxidative polymerization rate of DMP and the concentration of phenolate anion was curve-fitted using Eq. 7 and the result is shown in Figure 4 (line). The fit does not capture the observed maximum at lower temperatures and there is the great deviation between the experimental data and the fitted line at the high concentration of phenolate anion, indicating that the homogeneous polymerization kinetic model is not suitable for the polymerization of DMP in water.

Establishment of the heterogeneous kinetic model for the polymerization of DMP in water

Mobley et al. reported that the oligomer had a high reactivity compared with the monomer due to the electron donating ether group para to the hydroxyl group in the oligomers.[5] We found that the oxidative polymerization of DMP in water was a heterogeneous process.[12] The oligomer with a polymerization degree (n) of 6 is insoluble even in alkaline water and precipitates from water to form polymeric particles. The reaction mixture thus becomes heterogeneous and under these circumstances some of the reactive functional groups may be buried within the formed particle, resulting in a decrease in apparent reactivity of the water-insoluble oligomers. There are thus three types of phenolate anion in the reaction system, i.e., monomeric ($n = 1$) phenolate anions, water-soluble oligomeric ($1 < n < 6$) phenolate anions and water-insoluble oligomeric ($n \geq 6$) phenolate anions. The species of phenolate anions during the heterogeneous polymerization of DMP in water are shown in Scheme 3. The oxidative polymerization mechanism of DMP in water is thus illustrated in Scheme 4.

The total dissociation rate constant of the intermediate complex (k_2) can be estimated by Eq. 8.

$$k_2 = k_{21}\alpha + k_{25}\beta + k_{2n}\gamma \tag{8}$$

where α, β, and γ are the molar fractions of the monomer, water-soluble oligomer and water-insoluble oligomer, respectively. $\alpha + \beta + \gamma = 1$. k_{21}, k_{25}, and k_{2n} are dissociation rate constants of the intermediate complexes that produce the reduced catalysts and the phenoxyl radicals in the monomer, water-soluble oligomer and water-insoluble oligomer, respectively.

According to Flory's statistical theory, α, β, and γ are functions of the reaction extent of phenolate anion (P),[16] so then

$$\alpha = 1 - P \tag{9}$$

$$\beta = P - P^5 \tag{10}$$

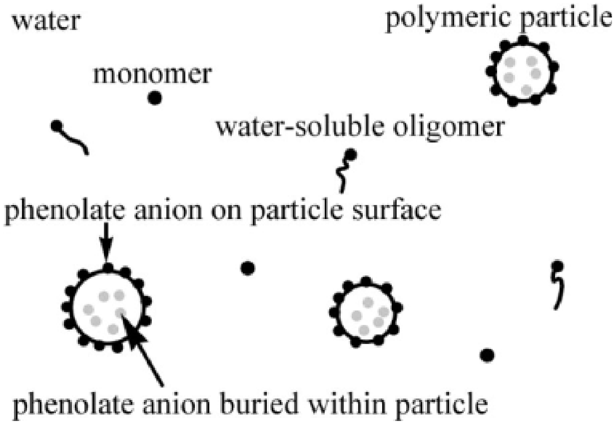
$$\gamma = P^5 \tag{11}$$

From Eq. 4 we obtain Eqs. 12–14.

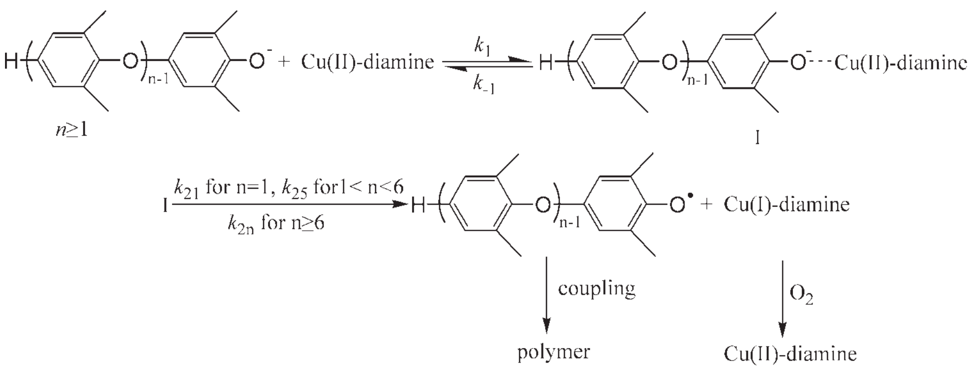
$$\alpha = \frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0} \tag{12}$$

$$\beta = 1 - \frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0} - \left(1 - \frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0}\right)^5 \tag{13}$$

$$\chi = \left(1 - \frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0}\right)^5 \tag{14}$$



Scheme 3. The species of phenolate anions during the heterogeneous polymerization of DMP in water.



Scheme 4. The oxidative polymerization mechanism of DMP in water.

The total dissociation rate constant of the intermediate complex (k_2) is thus:

$$k_2 = k_{25} - (k_{25} - k_{21})\frac{[\mathrm{XO^-}]}{[\mathrm{DMP}]_0} - (k_{25} - k_{2n})\left(1 - \frac{[\mathrm{XO^-}]}{[\mathrm{DMP}]_0}\right)^5 \tag{15}$$

The oxidative polymerization rate of DMP in water can be derived as in Eq. 16 by inserting Eq. 15 into Eq. 7.

$$R = \left[k_{25} - (k_{25} - k_{21})\frac{[\mathrm{XO^-}]}{[\mathrm{DMP}]_0} - (k_{25} - k_{2n})\left(1 - \frac{[\mathrm{XO^-}]}{[\mathrm{DMP}]_0}\right)^5\right]\frac{[\mathrm{C}][\mathrm{XO^-}]}{K'_\mathrm{m} + [\mathrm{XO^-}]} \tag{16}$$

Mobley reported that catalyst deactivation occurred during the polymerization of DMP and assumed that the catalyst deactivation step was first order with regard to catalyst

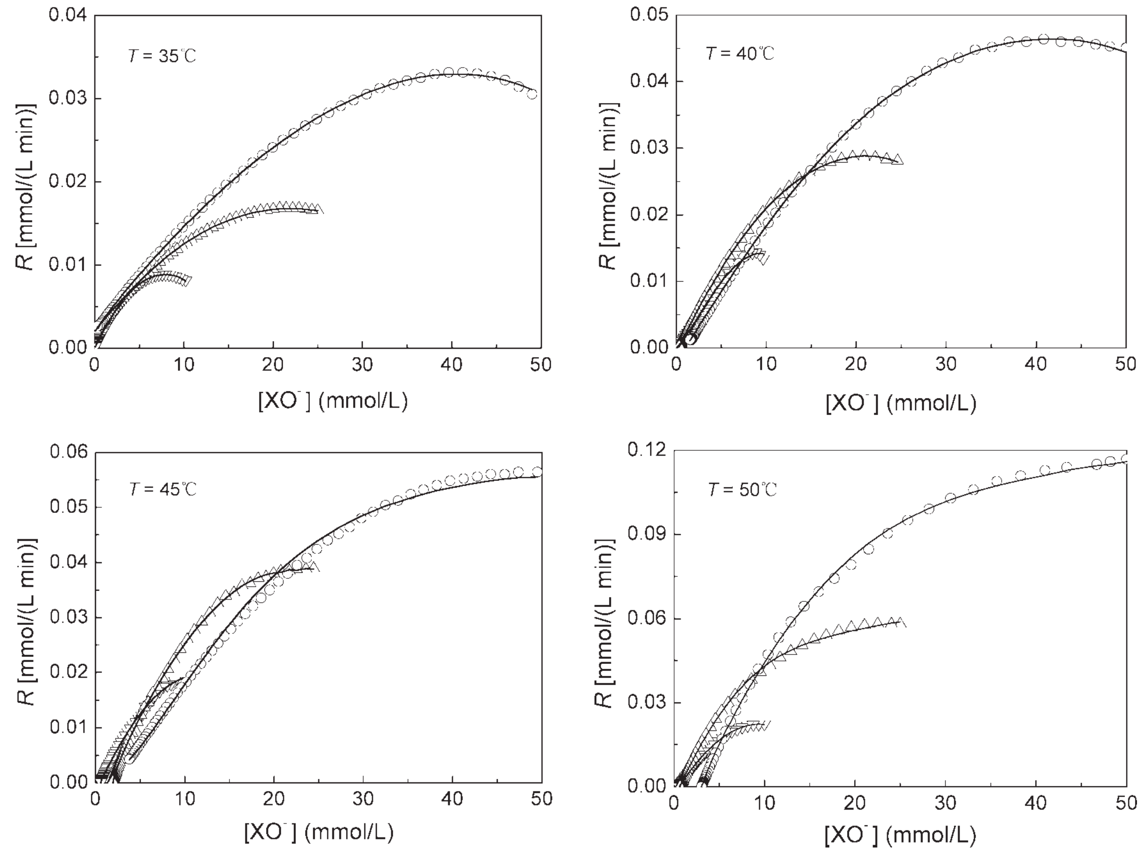


Figure 5. Relationship between the polymerization rate of DMP and the concentration of phenolate anion curve-fitted by the established model at various temperatures (▽: [DMP] = 10 mmol/L, △: [DMP] = 25 mmol/L, ○: [DMP] = 50 mmol/L, —: Fitted by Eq. 19).

Table 2. Kinetic Parameters Estimated by Nonlinear Multiple Regression Analysis

T (°C)	35	40	45	50	ΔH (kJ/mol)	ΔS (J/mol K)	E_a (kJ/mol)	A (min^{-1})
K'_m (mmol/L)	20.89	37.11	84.26	138.69	–	–	–	–
$1/K'_m$ (L/mol)	47.87	26.95	11.87	7.21	−107.63	−316.95	–	–
k_{21} (10^3 min^{-1})	3.20	5.72	11.51	26.81	–	–	117.01	2.03×10^{17}
k_{25} (10^3 min^{-1})	9.53	17.95	29.88	64.96	–	–	103.69	3.51×10^{15}
k_{2n} (10^3 min^{-1})	1.64	3.74	5.19	10.15	–	–	96.04	3.35×10^{13}
k_3 (10^4 min^{-1})	3.75	5.56	9.26	16.13	–	–	80.82	1.79×10^{10}

concentration (Eq. 17).[5] Although the order of deactivation kinetics has not been independently confirmed, the assumption of first order deactivation is chemically reasonable.

$$[\mathrm{C}] = [\mathrm{C}]_0 e^{-k_3 t} \tag{17}$$

where k_3 is the deactivation rate constant of the catalyst.

The determination of oxidative polymerization kinetics of DMP in water is thus based on the first order deactivation mechanism (Eq. 18).

$$R = \left[k_{25} - (k_{25} - k_{21})\frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0} - (k_{25} - k_{2n})\left(1 - \frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0}\right)^5\right] \times \frac{[\mathrm{C}]_0 e^{-k_3 t}[\mathrm{XO}^-]}{K'_m + [\mathrm{XO}^-]} \tag{18}$$

Assuming $A = k_{25} - k_{21}$ and $B = k_{25} - k_{2n}$, Eq. 18 is rewritten as follows:

$$R = \left[k_{25} - A\frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0} - B\left(1 - \frac{[\mathrm{XO}^-]}{[\mathrm{DMP}]_0}\right)^5\right]\frac{[\mathrm{C}]_0 e^{-k_3 t}[\mathrm{XO}^-]}{K'_m + [\mathrm{XO}^-]} \tag{19}$$

Equation 19 is thus the established heterogeneous kinetic model of DMP oxidative polymerization in water.

The verification of the heterogeneous kinetic model

The relationship between the oxidative polymerization rate of DMP and phenolate anion concentration was curve-fitted using Eq. 19 and the result (line) is shown in Figure 5. The lines fit the experimental data very well. The established kinetic model is thus useful for fitting the relationship between the oxidative polymerization rate of DMP and the concentration of the phenolate anion during the oxidative polymerization of DMP in water.

Values of these parameters in Eq. 19 were estimated by nonlinear multiple regression analysis and the results are listed in Table 2. K'_m increases with temperature, indicating that intermediate complex formation is difficult at high temperature.[17] The dissociation rate of the intermediate complex (k_{21}, k_{25}, and k_{2n}) increases with an increase in temperature. The catalyst deactivation rate constant (k_3) also increases with temperature, which is reasonable for catalyst deactivation.

From Table 2, k_{21} is seen to be lower than k_{25} due to low monomer reactivity compared with the water-soluble oligomers. k_{2n} is lower than k_{25}, which indicates that the reactive functional group is partially buried within the polymer particle, resulting in the decreased apparent reactivity of the water-insoluble oligomer.[12]

The relationship between ln$k$ (ln$k$ represented lnk_{21}, lnk_{25}, lnk_{2n}, and lnk_3, respectively) and $1/T$ is shown in Figure 6. lnk_{21}, lnk_{25}, lnk_{2n}, and lnk_3 change linearly with regards to $1/T$, which suggests that the relationship between ln$k$ and $1/T$ obeys the Arrhenius equation (Eq. 20). The apparent activation energy (E_a) and pre-exponential factor (A) were calculated and listed in Table 2.

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{20}$$

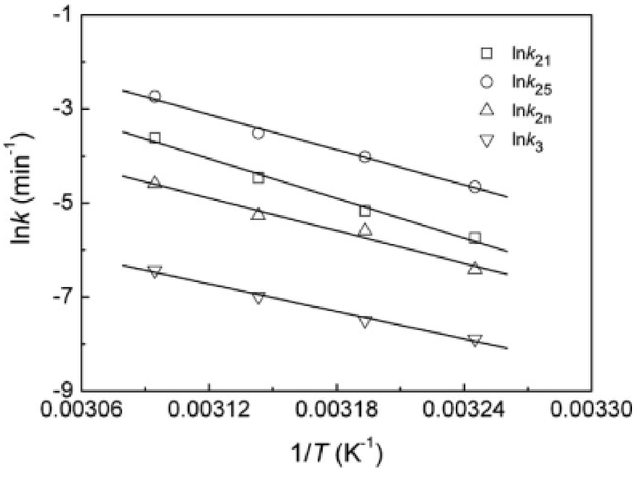


Figure 6. Relationship between ln*k* (lnk_{21}, lnk_{25}, lnk_{2n}, lnk_3) and 1/*T*.

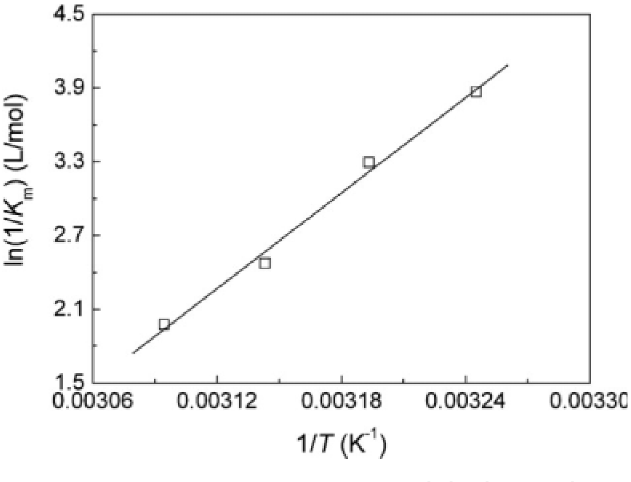


Figure 7. Relationship between ln(1/K_m) and 1/*T*.

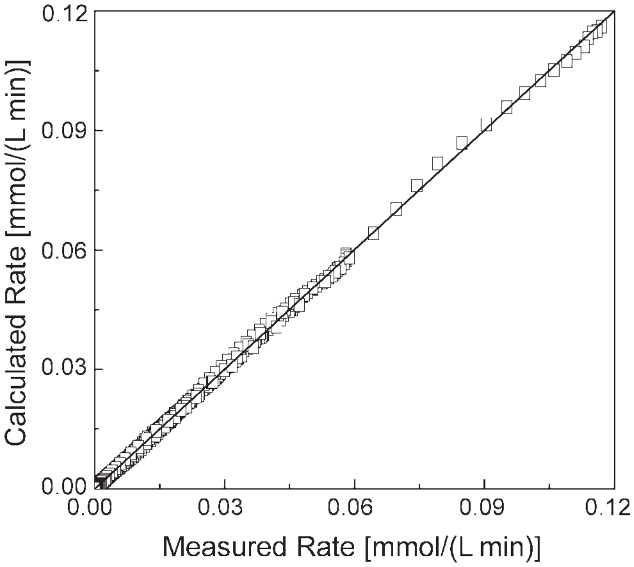


Figure 8. The polymerization rate estimated by Eq. 19 vs. that measured by oxygen uptake.

The relationship between $\ln(1/K'_{\mathrm{m}})$ and $1/T$ is shown in Figure 7. $\ln(1/K'_{\mathrm{m}})$ changes linearly with $1/T$, which suggests that the relationship between $\ln(1/K'_{\mathrm{m}})$ and $1/T$ obeys the Van't Hoff equation (Eq. 21). The enthalpy (ΔH) and entropy (ΔS) were thus calculated and the values of ΔH and ΔS are also listed in Table 2.

$$\ln\left(\frac{1}{K_{\mathrm{m}}}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{21}$$

The polymerization rate estimated by Eq. 19 was compared with the rate measured by the oxygen uptake and the result is shown in Figure 8. The average deviation between the polymerization rate estimated by Eq. 19 and the rate measured by oxygen uptake is 3.88%, indicating that the kinetic model expressed by Eq. 19 fits the experimental data well.

Conclusions

The oxidative polymerization rate of DMP in water increases with an increase in DMP concentration and an increase in temperature. At the same DMP concentration, the total oxygen uptake and the inherent viscosity of PPO synthesized in water decreases with an increase in temperature. A previously proposed Michaelis-Menten kinetic model is inadequate for the description of the full course of DMP polymerization in water. By considering a first order catalyst deactivation and the difference in reactivity of the monomer, the water-soluble oligomer and the water-insoluble oligomer, a new heterogeneous kinetic model is proposed. The new kinetic model fits the experimental data well. Values of kinetic parameters are also obtained using nonlinear multiple regression analysis.

Acknowledgments

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