Depolymerization of Poly(2,6-dimethyl-1,4-phenylene oxide) under Oxidative Conditions

Kei Saito, Toru Masuyama, Kenichi Oyaizu, and Hiroyuki Nishide*[a]

Abstract: Depolymerization of an engineering plastic, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), was accomplished by using 2,6-dimethylphenol (DMP) under oxidative conditions. The addition of an excess amount of DMP to a solution of PPO in the presence of a CuCl/pyridine catalyst yielded oligomeric products. When PPO ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$) was allowed to react with a sufficient amount of DMP, the molecular weight of the product decreased to $M_n = 4.9 \times 10^2$ ($M_w/M_n = 1.5$). By a prolonged reaction with the oxidant, the oligomeric product was repolymerized to produce PPO essentially identical to the starting material, making the oligomer useful as a reusable resource. During the depolymerization reaction, an intermediate phenoxyl radical was observed by ESR spectroscopy. Kinetic analysis showed that the rate of the oxidation of PPO was about 10 times higher than that of DMP. These results show that a monomeric phenoxyl radical attacks the polymeric phenoxyl to induce the redistribution via a quinone ketal intermediate, leading to the substantial decrease in the molecular weight of PPO, which is much faster than the chain growth.

Keywords: depolymerization · green chemistry · polymerization · polyphenyleneoxide · reaction mechanisms

Introduction

Oxidative polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper–amine complexes, discovered in 1959 by A. S. Hay,[1–3] provides a convenient method to synthesize poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The other product of this reaction is formed by C–C coupling of two monomeric phenols, 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone (DPQ) which degrades the polymer upon further processing at high temperature. The reaction conditions are mild, and the by-product is only H_2O by the suppression of the formation of DPQ. Oxidative polymerization is an atom economical reaction that does not require any leaving groups and removal of the by-product from the resulting polymer. Because of the increasing importance of low waste and reusable polymers in green chemistry, oxidative polymerization of DMP is one of the ideal polymerization processes. However, in spite of this the synthesis and properties of PPO have focused on its use as an engineering plastic.[4] In particular, the unraveling of the reaction mechanism for the extension of the monomer has long been a target.[2, 5–8] Recently, the oxidative polymerization of 2,6-unsubstituted phenols was accomplished by suppressing the coupling reaction at the 2,6-positions by means of a steric crowding effect by employing tyrosinase model complexes as catalysts.[9] On the other hand, copper complexes with enhanced oxidizing ability have been found to catalyze the oxygen-oxidative polymerization of phenols 2,6-disubstituted with electron-withdrawing groups. This has led to the first synthesis and characterization of high molecular weight poly(2,6-difluoro-1,4-phenylene oxide).[10, 11] It should be pointed out that the polymerization mechanism is still not fully resolved. The reaction is considered to involve the carbon–oxygen coupling of aryloxy radicals, but the polymerization does not occur simply by the coupling of polymeric aryloxy radicals and monomer radicals. Based on several experimental results, it was concluded that the most likely pathway involves the formation of a quinone ketal intermediate.[12–17] This mechanism can be divided into rearrangement and redistribution steps. The rearrangement is a concerted Claisen-type rearrangement, which is a special case of a sigmatropic rearrangement proposed by Ionescu et al.[16] This rearrangement results in the quinone group being shifted over the backbone of the oligomeric species, until eventually the end is reached. According to this mechanism, two dimeric phenols could give a tetramer as the primary product. The other mechanism, the redistribution, follows a pathway in which the newly formed C–O bond in the quinone ketal intermediate may dissociate to reform two dimeric species, or the other ether bond may be cleaved to form a monomeric

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and a trimeric species from the two dimeric phenols (Scheme 1).

There are a few studies that have focused on the mechanism of the redistribution.[18–22] White et al. reported the equilibration reaction of PPO with phenolic compounds by the redistribution mechanism, in which DPQ, *tert*-butyl perbenzoate, and benzoyl peroxide acted as active initiators. In the presence of the initiator, PPO reacts with phenolic compounds to form a mixture of low molecular weight hydroxyl arylene ethers,[18] and a bifunctional polymer is formed when low molecular weight PPO is allowed to react with DPQ.[19] Based on the reversibility of the redistribution mechanism, one can consider that the reaction of PPO with a large number of phenolic compounds will induce the depolymerization of PPO. Recently, the redistribution reactions have been exploited for the tail end functionalization of PPO. When using a *para*-functionalized phenol, the reaction yields a tail-functionalized PPO.[23] In this reaction, DPQ, CuCl/4-(dimethylamino)pyridine, and $Cu(NO_3)_2$/*N*-methylimidazole were used as the catalyst, depending on the phenolic compound, the desired reaction time, and the product purity. The redistribution reaction using PPO and DMP was attempted, but 1–3 weeks were needed to depolymerize PPO substantially. On the other hand, the phase-transfer-catalyzed depolymerization of PPO in the presence of either 2,4,6-trimethylphenol or 4-*tert*-butyl-2,6-dimethylphenol have also been reported,[24] for which a radical-anion mechanism was presented.

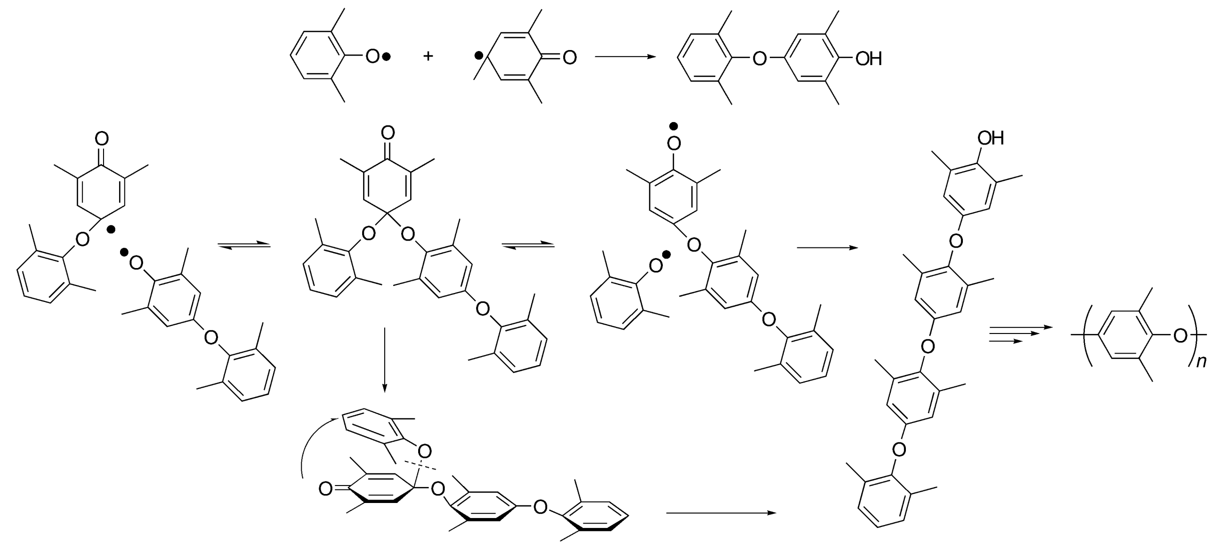
It should be noted that previous studies on the depolymerization of PPO did not focus on their potential utility from the viewpoint of green chemistry, and had the drawback that the products were not reusable resources due to the lack of reactivity with respect to repolymerization. Depolymerization of PPO to a repolymerizable oligomer should have great advantages as a sustainable technology in the development of green chemistry.

Herein, we focus on the depolymerization and repolymerization of PPO in the development of oxidative polymerization of DMP as a green chemistry polymerization process. We chose DMP as the phenolic compound to induce the depolymerization of PPO. With the addition of DMP to PPO, the depolymerization of PPO occurs and yields oligomeric products. The oligomeric products are identical to those produced during the polymerization of DMP, and thus the repolymerization can subsequently take place. The reaction time and the ratio of DMP to PPO were varied to adjust the molecular weight of the oligomeric products. The molecular weight decreases were determined by gel permeation chromatography (GPC). Throughout this study, CuCl/pyridine was used as the catalyst. The time course of the decrease in molecular weight, the effect of the oxidizing agent, the detection of an intermediate radical, and the depolymerization rate constant were determined. The kinetics of the depolymerization are discussed in the context of determining the driving force that governs the equilibrated system.

Results and Discussion

Depolymerization of PPO with DMP using a CuCl/pyridine catalyst: Depolymerization of PPO ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$) with DMP in toluene was examined in the presence of a catalyst (CuCl/pyridine = 1:100). The reactions were carried out under air at room temperature and at several different PPO and DMP concentrations. The molecular weight of PPO was significantly decreased to produce an oligomeric product ($M_n = 1.6 \times 10^3$, $M_w/M_n = 2.3$) at a reaction time of 1 min, as a consequence of the depolymerization of PPO by DMP at initial concentrations of 0.25 unit mol L^{-1} and 0.025 mol L^{-1}, respectively. The molecular weight changes during the course of the depolymerization are shown in Figure 1. The molecular weight of PPO readily decreased to a M_n of 550 ($M_w/M_n = 1.6$) at a reaction time of 10 min when the initial concentrations of PPO and DMP were 0.25 unit mol L^{-1} and 0.25 mol L^{-1}, respectively.

The molecular weight remained at this low value for several minutes, but gradually began to increase as the reaction time increased. This result indicates that the low molecular weight state is a transient state during the ongoing redistribution and



Scheme 1. Redistribution mechanism.

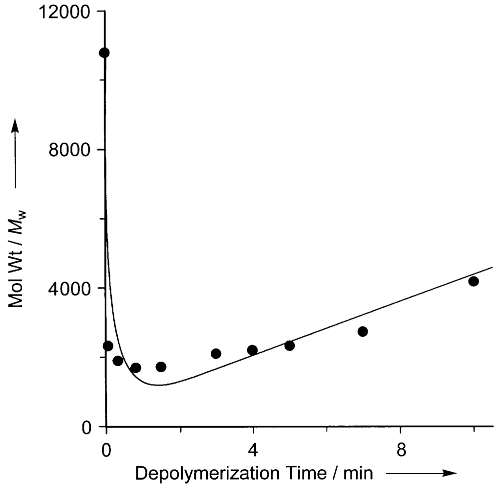


Figure 1. Time course of the molecular weight of PPO ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$, 0.25 unit mol L^{-1}) during the reaction with DMP (0.025 mol L^{-1}) in the presence of the CuCl/pyridine catalyst (CuCl/pyridine 1:100) in toluene under air at room temperature.

rearrangement process. The ratio of pyridine to copper was selected (CuCl/pyridine = 1:100) in this reaction to suppress formation of DPQ ($\leq 1\%$; based on UV/Vis spectroscopy ($\lambda_{max} = 421$ nm) of the reaction solution as reported by Driessen and Reedijk et al[8]).[3] In addition, Reedjik et al. reported that the formation of DPQ could be reduced in the oxidative polymerization by starting from mixtures of DMP and PPO oligomers.[25] This result does not conflict with the suppression of DPQ formation in our reaction.

GPC traces obtained with solutions during the depolymerization (Figure 2) clearly show that the original two peaks of PPO and DMP are merged into a one peak, which supports the overall decrease in the molecular weight of PPO.

The depolymerization of PPO is based on the rapid distribution of phenoxyl radicals (vide infra). The subsequent slow increase in the molecular weight indicates the concomitant rearrangement of the resulting oligomers. The transient state at the lowest molecular weight would correspond to the transition state at which these two processes are balanced. If DMP is added when the molecular weight is at the lowest value, a further depolymerization is expected to occur to give even lower molecular weight products. Based on this consideration, the stepwise depolymerization of PPO ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$) with DMP in toluene was examined in the presence of the catalyst. Thus, PPO and DMP (0.1 mol per PPO unit mol) were allowed to react in the first step. Then, 0.1 mol of DMP per PPO unit mol was added to the solution at the minimum point of the molecular weight of PPO. This procedure was repeated 10 times such that the same amount of DMP was finally added to the same mol amount of PPO. The molecular weight of PPO efficiently decreased to produce an oligomeric product ($M_n = 4.9 \times 10^2$, $M_w/M_n = 1.5$) without yielding the rearranged polymers (Figure 3).

According to the redistribution reaction, if all the DMP added to the solution attacked PPO, the degree of polymerization, n', of the resulting oligomer could be calculated by Equation (1), when x mol of PPO with the degree of polymerization of n is allowed to react with y mol of DMP.

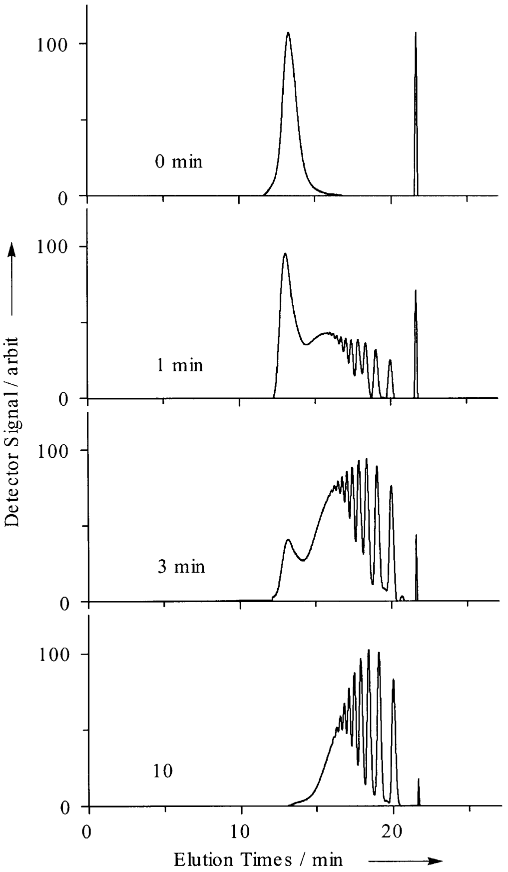


Figure 2. GPC traces obtained from the reaction mixture of PPO and DMP with the time passage of 0, 1, 3, and 10 min. In the presence of the CuCl/pyridine catalyst in toluene under air at room temperature. PPO = 0.25 unit mol L^{-1}, DMP = 0.25 mol L^{-1}

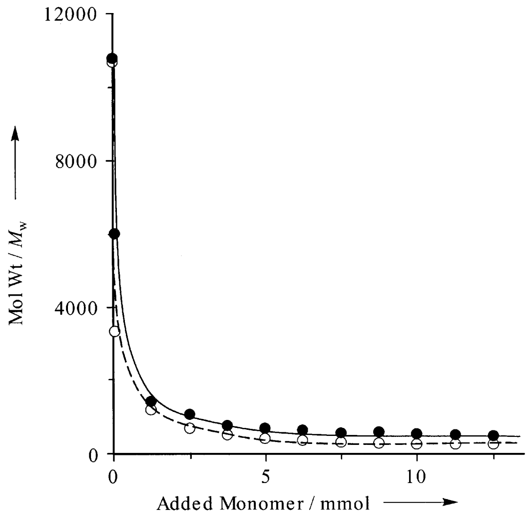


Figure 3. Molecular weight changes of PPO during the stepwise depolymerizations with DMP (See text for experimental details). ● = determined value, ○ = calculated value

$$n' = \frac{nx + y}{x + y} \tag{1}$$

Figure 3 also shows that the determined molecular weights are quite close to the calculated values, which means that the molecular weight can be modulated due to the quantitative progress of the reaction. An important aspect with regard to the nature of the polymerization is derived from the result: the quantitative redistribution of the phenoxyl radical indicates the lack of concomitant rearrangement during the reaction which would increase the molecular weight from that calculated according to Equation (1). It seems that the rearrangement is initiated only when an apparent steady-state of the redistribution is accomplished with statistical distribution of the molecular weights of the oligomer.

Repolymerization of the oligomeric product using the CuCl/pyridine catalyst: Repolymerization of the oligomeric product of the depolymerization was attempted. An admixture of the oligomeric product and a small amount of the catalyst in toluene afforded PPO after stirring under O_2. The polymer was obtained as an off-white powder after precipitation from methanol. While the polymerization of DMP under the same conditions yields PPO with a molecular weight of $M_n = 3.0 \times 10^2$ ($M_w/M_n = 1.4$), the molecular weight of the product from the oligomer was significantly higher ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.6$). Based on this result, oligomeric products are reusable resources and indeed more reactive for the oxidative polymerization.

ESR spectrum of the depolymerized PPO: Although the depolymerization of PPO with DMP has been established, it can be considered that the coupling of the polymeric phenoxyl radical and the monomeric phenoxyl radical is not kinetically favored due to the low concentration of the terminal polymeric phenoxyl radical. Percec et al. reported a radical anion mechanism for the depolymerization.[24] They thought that the redistribution reaction of the depolymerization occurred by the coupling of a polymeric phenolate and a monomeric phenoxyl radical. However, the experimental evidence for this interpretation seems to be lacking. To elucidate the depolymerization mechanism, the ESR spectrum of the solution was recorded during the depolymerization. The solution of PPO and DMP in toluene in the presence of the catalyst was used as the sample solution. The ESR spectrum of the phenoxyl radical gave a sharp signal at $g = 2.0044$, which showed a hyperfine structure caused by the interaction with six protons of the methyl group (Figure 4).

The ESR spectrum of PPO in toluene in the presence of the catalyst showed a similar signal, but there was no ESR signal from the solution of DMP under the same conditions. The ESR absorption ascribed to a divalent copper ion was recorded in every case. These results suggest that the phenoxyl radical observed from the solution during the depolymerization is ascribed to the polymeric phenoxyl radical. A similar ESR spectrum of the independently prepared 2,6-dimethylphenoxy radical has been reported.[26] These results show that the major mechanism of depolymerization involves the radical–radical coupling of the polymeric phenoxyl radical and the monomeric phenoxyl radical. The radical concentration of the polymer terminal groups was determined to be 20% under the depolymerization conditions.

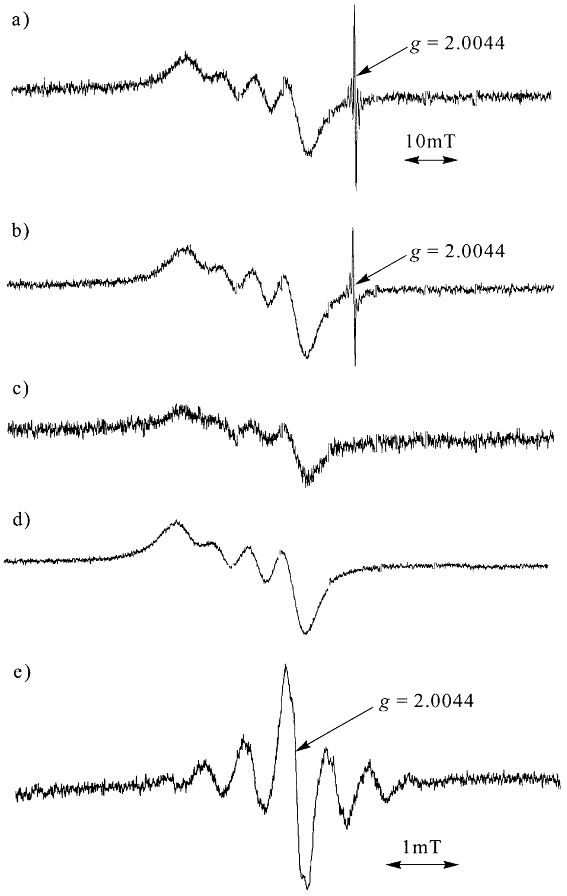


Figure 4. a) ESR spectrum of the depolymerization toluene solution. CuCl = 0.01 mol L^{-1}, CuCl/pyridine 1:100, PPO = 0.25 unit mol L^{-1}, DMP = 0.025 mol L^{-1}. b) ESR spectrum of the toluene solution of PPO in the presence of the catalyst. CuCl = 0.01 mol L^{-1}, CuCl/pyridine 1:100, PPO = 0.25 unit mol L^{-1}. c) ESR spectrum of the toluene solution of DMP in the presence of the catalyst. CuCl = 0.01 mol L^{-1}, CuCl/pyridine 1:100, DMP = 0.025 mol L^{-1}. d) ESR spectrum of the toluene solution of divalent copper. CuCl = 0.01 mol L^{-1}, CuCl/pyridine 1:100. e) Part of the ESR spectrum of depolymerization toluene solution near $g = 2.0$. CuCl = 0.01 mol L^{-1}, CuCl/pyridine 1:100, PPO = 0.25 unit mol L^{-1}, DMP = 0.025 mol L^{-1}.

Kinetic analysis by UV/Vis spectra: Having established that the depolymerization mechanism of PPO is a radical–radical coupling, one may consider that the polymerization of the monomer could prevail over the depolymerization due to the low concentration of the terminal polymeric phenoxy radical. In the first step of the catalytic cycle of the polymerization, the substrate (i.e., the phenolate ion) coordinates to the copper complex and one electron is transferred from the substrate to the copper(II) ion. The activated substrate dissociates from the catalyst and the reduced copper(I) catalyst is oxidized to the original copper(II) complex by oxygen. UV/Vis spectroscopy revealed that a steep rise in the absorbance of the d–d transition occurred when DMP was added to the solution of the CuCl/pyridine catalyst solution.[27] This change in the absorbance was caused by the change in the molar optical density of the d–d transition due to the coordination of DMP to the Cu catalyst and could be measured by UV/Vis spectroscopy. The absorbance due to the d–d transition provides the amount of the copper(II) ion during the reaction, that is, the rate of electron transfer from the substrate to the copper ion, which gives the rate constant k for the formation of the phenoxy radical (Figure 5).

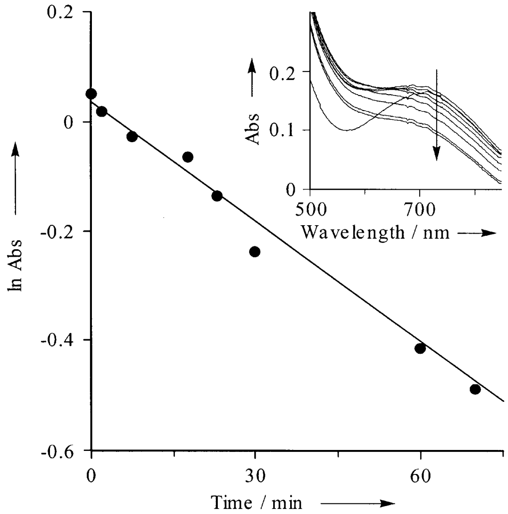


Figure 5. Kinetic plots for the decrease of the d–d absorption. CuCl = 0.01 molL^{-1}, CuCl/pyridine 1:100, PPO = 0.2 unit molL^{-1} toluene solution, under air at room temperature. Inset: Visible spectral changes for the reaction solution recorded at $t = 0$, 0.25, 2, 8, 20, 25, 30, 60, and 70 min.

The rate constant indicates that the polymeric phenoxyl radical ($k = 0.53\ s^{-1}$) is produced 10 times faster than the monomeric radical ($k = 0.034\ s^{-1}$). Therefore, it was clearly shown that PPO tends to be oxidized about 10 times faster than DMP. This result indicates that the slowly generated monomeric phenoxyl radical, once formed, reacts readily with the abundant polymeric radical in the solution, resulting in the depolymerization of the polymeric radical rather than the polymerization of the monomeric radical. Added support for this interpretation was provided by the consideration of oxidation potentials (vide infra).

Oxidation potential from electrochemistry: One can expect that the oxidation potential of the phenoxyl radicals would become lower as the molecular weight increases. The potentials for the oxidation of PPO, DMP and 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (dimer) were measured by cyclic voltammetry. Cyclic voltammograms of DMP, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol and PPO in CH_2Cl_2 showed irreversible oxidation peaks at room temperature (Figure 6).

At a constant sweep rate, the oxidation peak potentials (versus Ag/AgCl) were observed at 1.67, 1.34, and 1.20 V for DMP, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (dimer), and PPO, respectively. The oxidation peak potential became lower as the molecular weight increased. This result also clearly shows that PPO is more reactive than DMP and the oligomer.[25]

Depolymerization mechanism: Based on the above results, we propose the depolymerization mechanism given in Scheme 2.

The high concentration of the terminal phenoxyl radical may be balanced by the slowly generated DMP which is present in excess. Because PPO is 10 times more reactive than DMP, the polymeric phenoxyl radical and the monomeric phenoxyl radical are both generated in the solution. The monomeric phenoxyl radical attacks the *para* position of the terminal group of PPO with the n degree of polymerization to induce the redistribution via the quinone ketal intermediate. After the formation of the quinone ketal intermediate, the redistribution could take place to yield the $n-1$ polymeric phenoxyl radical and dimer phenoxyl radical. The dimeric phenoxyl radical can attack the $n-1$ polymeric phenoxyl radical again. By repeating this redistribution, the depolymerization occurs and the molecular weight reduces. It should be added that only tace amounts of DPQ were formed in this depolymerization reaction. This result could be also explained based the fact that PPO is 10 times more reactive than DMP. The formation of DPQ is caused by the coupling of the two monomeric phenoxyl radicals. But in this depolymerization reaction, the monomeric phenoxyl radical is reacts readily with the abundant polymeric radical and does not react with the other monomeric phenoxyl radical. By way of this mechanism, DPQ formation was efficiently suppressed in the depolymerization.

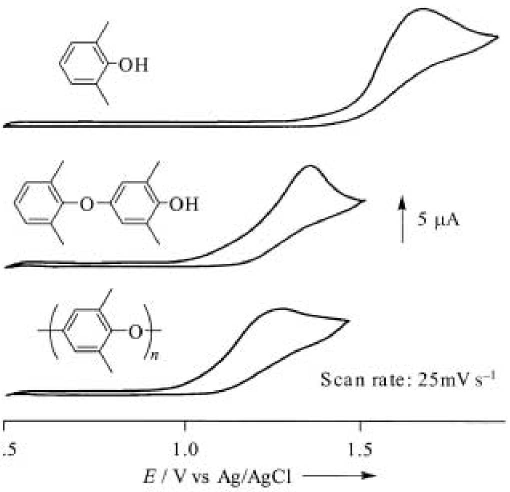
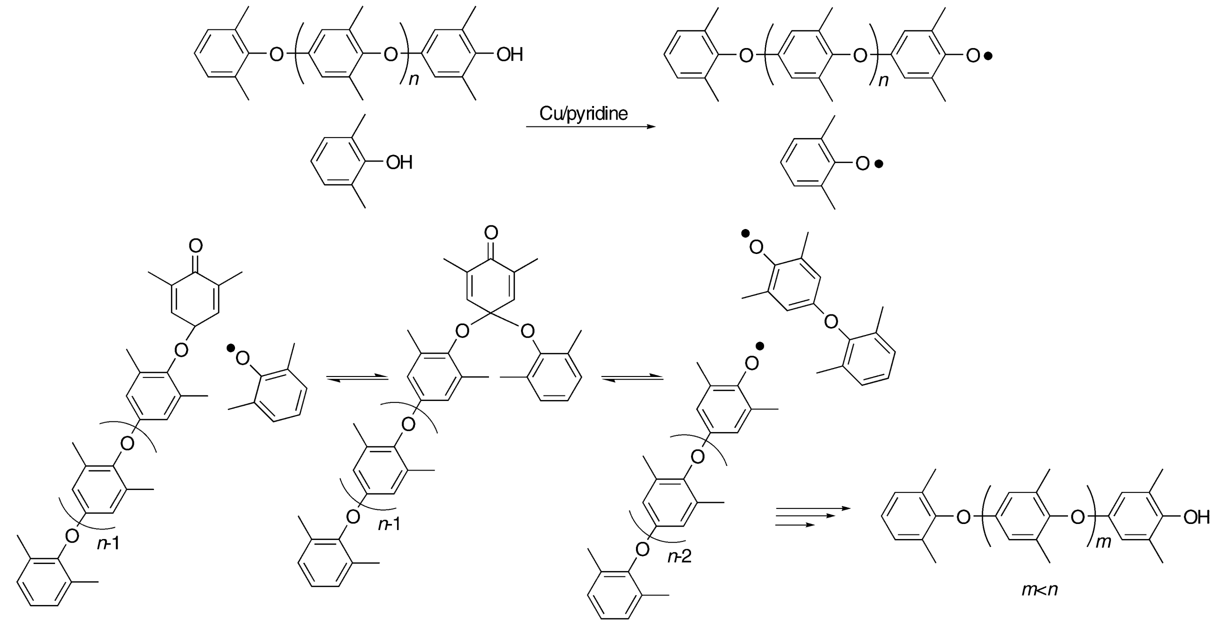


Figure 6. Cyclic voltammograms of the CH_2Cl_2 solutions in the presence of the 1 mmolL^{-1} of the monomer, the oligomer, and the polymer with 0.1 molL^{-1} $(C_4H_9)_4NBF_4$ and 1 mmolL^{-1} 2,6-diphenylpyridine. Scan rate: 25 mVs^{-1}.

Interestingly, the depolymerization can only occur according to the redistribution mechanism. When PPO and DMP are mixed under the oxidization conditions, first the redistribution occurs exclusively. After the redistribution has occurred and the molecular weight has reached a minimum, the molecular weight then abruptly increases according to the rearrangement. If additional DMP is added when the molecular weight is at a minimum, the subsequent increase in the molecular weight is effectively suppressed. Therefore, when DMP is gradually added, the molecular weight is effectively reduced.

Conclusion

Based on the reversibility of the redistribution reaction, the depolymerization of PPO with DMP using the CuCl/pyridine catalyst was accomplished to yield an oligomeric product. The



Scheme 2. Depolymerization mechanism.

depolymerization proceeds almost quantitatively by the redistribution of the phenoxyl group, and the final molecular weight can be modulated. The oligomeric products obtained from the depolymerization are reusable and are also more reactive compounds for the synthesis of PPO. The polymeric phenoxyl radical and the monomeric phenoxyl radical are both generated under the proposed oxidation conditions. The monomeric phenoxyl radical attacks the phenoxyl radical of PPO and thereby induces the redistribution via a quinone ketal intermediate. Repetition of this redistribution is concluded as the depolymerization mechanism.

Experimental Section

Materials: Methanol, toluene, pyridine, copper(I) chloride, and DMP were obtained from the Kanto Chemical Co. Chloroform was of GPC quality from Merck. Solvents were purified by distillation prior to use. DMP was purified by repeated recrystallization from *n*-hexane.

Measurements: The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-LA500 (500 MHz and 125 MHz for ^{1}H and ^{13}C, respectively) spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. All spectra were obtained in $CDCl_3$ at room temperature. Molecular weights were determined by gel permeation chromatography (GPC) using a Tosoh highly sensitive GPC system HLC-8220GPC equipped with a UV-8220 at a detection absorbance set at 254 nm. The measurements were made at 40 °C using the UV detector. Tosoh TSK GEL SuperHZ2000 × 2, SuperHZ3000 × 1, and SuperHZM-M × 1 with chloroform as the solvent (0.35 mL min^{-1}) were used to analyze the PPO and depolymerized products, in which the calibration curves were obtained by using polystyrene standards.

Depolymerization of PPO with DMP using a CuCl/pyridine catalyst: Depolymerization experiments were performed with different PPO and DMP concentrations. Typical experimental conditions for the reaction of PPO (0.25 unit mol L^{-1}) and DMP (0.25 mol L^{-1}) are as follows. PPO (1.5 g, $M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$, 12.5 unit mmol) and DMP (1.5 g, 12.5 mmol) were dissolved in toluene (40 mL). A mixture of CuCl (0.124 g, 1.25 mmol) and pyridine (10 mL, 1.25 mmol) was added to the solution which was constantly stirred (300 rpm) for 6 h. The reaction was performed under air at room temperature. A 0.2 mL sample was taken at different reaction times, which was then neutralized with cold 2.5 N HCl and diluted with chloroform. The toluene/chloroform layer was collected, and the solvent was evaporated. An oligomeric product was obtained as an off-white powder. The same reaction are performed again and stopped after 10 min. An oligomeric product (3.00 g, yield: 100 %) was obtained as an off-white powder after the same treatment. Products were dissolved in chloroform to determine the molecular weight by GPC. ^{1}H NMR: (500 MHz, $CDCl_3$, TMS): $\delta = 6.44$ (s, 2H; aromatic C-H), 6.36 (m; aromatic C-H head end group), 7.09 (m; aromatic tail end group), 4.22 (m; -OH), 2.09 ppm (s, 6H; -CH_3); $M_n = 5.5 \times 10^2$, $M_w/M_n = 1.6$.

Stepwise depolymerization of PPO: PPO (1.5 g, $M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$, 12.5 unit mmol) and DMP (0.15 g, 1.25 mmol) were dissolved in toluene (40 mL). A mixture of CuCl (0.124 g, 1.25 mmol) and pyridine (10 mL, 1.25 mmol) was added to the solution which was constantly stirred (300 rpm). An oligomeric product was obtained as mentioned above (yield: 100 %). The molecular weight of the product was determined by GPC and the minimum point of the molecular weight of PPO was determined. Subsequently, DMP (0.15 g, 1.25 mmol) was added to the solution at the minimum point of the molecular weight. The next minimum point of the molecular weight and its molecular weight were then established. This operation was repeated 10 times in total (DMP: 12.5 mmol).

UV/Vis spectral detection of DPQ: PPO (1.5 g, $M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$, 12.5 unit mmol) and DMP (0.15 g, 1.25 mmol) were dissolved in toluene (40 mL). A mixture of CuCl (0.124 g, 1.25 mmol) and pyridine (10 mL, 1.25 mmol) was added to the solution which was constantly stirred (300 rpm). A 1 mL sample was taken at different reaction times (0.5, 5, 10, 20, and 30 min) and diluted to 10 mL with toluene. This diluted solution gave a UV/Vis absorption with a maximum at 421 nm, which was ascribed to DPQ (see Supporting Information). The molar extinction coefficient ε was determined to be 38000 mol^{-1} dm^3 cm^{-1} in toluene/pyridine (49:1, v/v) by using the pure DPQ. The amount of DPQ formed in the depolymerization reaction solution was estimated to be 0.9 ± 0.1 % versus the amount of DMP added, or 0.09 ± 0.01 % versus the obtained oligomeric product. The amount of DPQ was almost constant during the whole reaction. The same depolymerization reaction was performed with PPO (0.25 unit mol L^{-1}) and DMP (0.25 mol L^{-1}): Amount of DPQ formed was 0.9 ± 0.1 % versus the amount of DMP added, or 0.45 ± 0.05 % vs. the obtained oligomeric product.

Repolymerization of the oligomeric product using the CuCl/pyridine catalyst: A mixture of CuCl (0.124 g, 1.25 mmol) and pyridine (10 mL, 1.25 mol) was added to a solution of the oligomeric product (1.5 g, $M_n = 4.9 \times 10^2$, $M_w/M_n = 1.5$, 12.5 unit mmol) in toluene (50 mL). The reaction was performed under air at room temperature. After 10 min, the reaction mixture was poured into methanol to precipitate the product. The polymer was obtained as an off-white powder (yield: 100 %). ^{1}H NMR: (500 MHz,

$CDCl_3$, TMS): δ 6.44 (s, 2H; aromatic C-H), 2.09 ppm (s, 6H; -CH_3); $M_n = 1.0 \times 10^4$, $M_w/M_n = 1.6$.

Detection of radical species by ESR spectra: The ESR spectra were recorded of the toluene solution of PPO ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$, 0.25 unit mol L^{-1}) and DMP (0.025 mol L^{-1}) in the presence of the catalyst (CuCl/pyridine 1:100), the toluene solution of PPO (0.25 unit mol L^{-1}) in the presence of the catalyst, the toluene solution of DMP (0.025 mol L^{-1}) in the presence of the catalyst, and the toluene solution of the copper catalyst (CuCl = 0.01 mol L^{-1}, CuCl/pyridine 1:100). The ESR spectra were determined by using a JEOL JES-TE200 ESR spectrometer with 100 kHz field modulation under air at room temperature. The radical concentration in the sample solution was determined by a careful integration of the ESR signal standardized with that of a TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) solution.

Kinetic analysis: The kinetics of the depolymerization was based on the UV/Vis spectra of the toluene solution of PPO ($M_n = 1.0 \times 10^4$, $M_w/M_n = 1.2$, 0.25 unit mol L^{-1}), the catalyst (CuCl/pyridine 1:100), and DMP (2.5 mmol L^{-1}) under the same conditions obtained with the Shimadzu UV-2100 spectrometer under air at room temperature. The depolymerization was monitored by the spectra recorded at different reaction times.

Electrochemical measurements: Cyclic voltammetry was carried out in a conventional two-compartment cell. A glassy carbon disk-platinum ring was used as the working electrode and polished before each experiment with 0.05 μm alumina paste. The auxiliary electrode, a coiled platinum wire, was separated from the working solution by a fine-porosity frit. The reference electrode was a commercial Ag/AgCl electrode immersed in a salt brige consisting of 0.1 mol L^{-1} tetrabutylammonium tetrfluoroborate ((n-$C_4H_9)_4NBF_4$), which was placed in the main cell compartment. The formal potential of the ferrocene/ferrocenium couple in dichloromethane was 0.34 V s^{-1} versus this reference electrode. The voltammetric investigation was carried out in CH_2Cl_2 in the presence of a sample (1 mmol L^{-1}), (n-$C_4H_9)_4NBF_4$ (0.1 mol L^{-1}) and 2,6-diphenylpyridine (1 mmol L^{-1}), and all potentials were quoted with respect to this Ag/AgCl refernce electrode at a scan rate 25 mV. A Nikko Keisoku DPGS-1 dual potentiogavanostat and a Nikko Keisoku NFG-3 universal programmer were employed with a Graphtec WX2400 X-Y recorder to obtain the voltammograms.

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