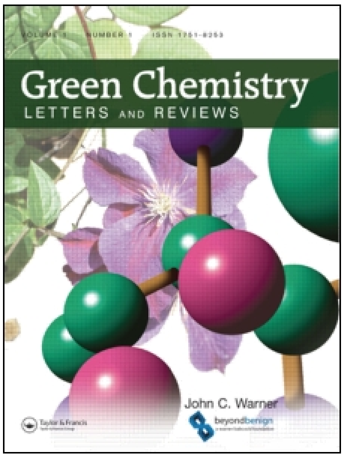

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ORIGINAL ARTICLE

Green synthesis of soluble polyphenol: oxidative polymerization of phenol in water

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The simple stirring of phenol with an oxidant in water provided a novel green way to synthesize soluble polyphenol. The soluble polyphenol obtained had a high poly(phenylene oxide) unit ratio, poly(phenyleneoxide)/poly(phenylene) = ca. 80/20. Additionally, the insoluble fraction was identified as a poly(phenyleneoxide), which has a crosslinking point for every 5.5×10^3 molecular weight. These results suggest that oxidative polymerization in water can be run in a manner to control the coupling selectivity of phenol. Both the soluble polyphenol and the insoluble fraction showed a high thermal stability. Oxidative polymerization in water provides the potential for a formaldehyde-free and regioselected soluble poly(phenyleneoxide) from phenol.

Keywords: Oxidative polymerization; polyphenyleneoxide; phenol; phenolic resin; water solvent

Introduction

The most interesting simple phenolic polymer in industry is a formaldehyde-free and soluble polyphenol. Phenolic resin, such as phenol formaldehyde resin, has high insulation properties and heat and flame resistance, and has been favored in a wide range of applications, from commodity-molded materials to aerospace industries (*1*). However, low environmental impact, e.g. formaldehyde-free and low petroleum dependency, is expected in phenolic resin production due to the desired approach of the green chemical process (*1*,*2*). Oxidative polymerization of a variety of phenols is a green chemical process that provides a convenient and industrially useful method to prepare phenolic polymers with a high thermal stability, and it could be an alternative process for the preparation of phenolic resin without using formaldehyde, an extra monomer for production (*3*). Oxidative polymerization of ortho protected 2,6-dimethylphenol is well known to form linear *p*-coupled poly(2,6-dimethyl-1,4-phenyleneoxide) with a copper-amine catalyst (*3–9*). Poly (2,6-dimethyl-1,4-phenyleneoxide), a phenolic polymer with high thermal stability, is widely used as a high-performance engineering plastic (*4*). On the other hand, oxidative polymerization of phenol is known to form an insoluble polymerized product with uncontrolled crosslinking because both the *p*- and *o*-position of the monomer phenol are open and available for coupling (*3*,*5*). The synthesis of a soluble polyphenol from the oxidative polymerization of phenol is the simplest, environmentally benign, and least expensive phenolic polymer synthesis, and it is one of the active targets in the field of polymer synthesis (*10–15*).

The control of coupling selectivity is especially important in the formation of soluble polyphenol from phenol. When the coupling proceeds only at the *p*-position, the resulting polymer is the linear poly(1,4-phenyleneoxide). Coupling at the *o*-position gives an insoluble polymer consisting of a mixture of phenylene unit and 1,4- and 1,6-phenyleneoxide units. The more 1,4-phenyleneoxide units present in the polymer, the better the solubility. There are existing studies that focused on the control of the coupling selectivity in phenol polymerization. The highly regioselective oxidative polymerization of 4-phenoxylphenol (phenol dimer) and phenol derivatives have been accomplished by suppressing the coupling reaction at the *o*-position based on the steric crowding effect of using the tyrosinase model complexes as catalysts (*10*). Recently, regioselective enzymatic synthesis of polyphenols by template oxidative polymerization of phenol has been reported (*14*,*15*). Templates, such as poly(ethylene glycol) and poly(ethylene glycol) monododecyl ether, interacted with the monomer during the enzymatic oxidative polymerization and controlled the coupling selectivity. However, the polymers obtained in this effort were still a mixture of phenylene and 1,4- and

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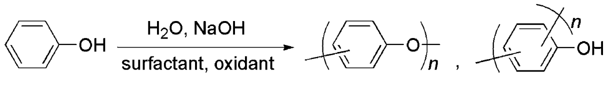
1,6-phenyleneoxide units, and their molecular weights were low ($<10^4$). No successful regioselective oxidative polymerization of phenol to form the soluble liner poly(1,4-phenyleneoxide) has been reported.

We have developed a system using water at high pH as a reaction solvent for the oxidative polymerization of 2,6-dimethylphenol to form poly(2,6-dimethyl-1,4-phenyleneoxide) with an oxidant or with an alkaline-resistant copper catalyst (*16–19*). This oxidative polymerization procedure in water provides a green chemical process to produce engineering plastics.

Studies of this aqueous system suggest that the polymerization mechanism is different from that of the polymerization in organic solvents. The oxidation potential of phenols is significantly decreased in water at high pH, and the phenoxyl radicals are redistributed to a high molecular weight polymer despite the fact that the polymer precipitated from the water as it was formed. Our hypothesis is that this unique proposed redistribution mechanism can effect coupling selectivity and could yield soluble poly(phenyleneoxide).

In this paper, we report on the oxidative polymerization of phenol to form soluble polyphenol in aqueous conditions. In this study, the oxidative polymerization of phenol in alkaline water using oxidant with a surfactant was carried out, and the structure and properties of the obtained polymers were studied. The potential of the reaction from a green chemical process approach is also discussed (Scheme 1).



Scheme 1.

Results and discussion

The oxidative polymerization of phenol was carried out in an aqueous environment. This reaction uses only water as a solvent, and the reaction proceeded under ambient conditions. The formed product can be precipitated out and separated from a reaction mixture by simple filtration after the reaction.

A mixture of phenol and potassium ferricyanide in water (pH >13.5) was vigorously stirred under air with a surfactant. Polymerization results are given in Table 1. Sodium *n*-dodecyl sulfate (SDS), dodecylpyridinium chloride (DPC), and polyethylene glycol monostearate (PGM) ($n=10$, 25, 40) were used as surfactants. The reaction mixture became a latex and the color of the mixture changed from black to brown during the reaction. After the reaction, the resulting slightly brownish powder could be separated by simple filtration after it was precipitated by salting out. The brownish powder obtained could be partially dissolved in organic solvents, either DMF or dimethylsulfoxide (DMSO). The brownish powder obtained was extracted with DMF to separate the polymer into two parts – DMF soluble and DMF insoluble.

The added amount of surfactant affected the nature of the polymer obtained, i.e. increased the yield and the molecular weight of the soluble polyphenol. Reaction without surfactant gave a highly DMF insoluble product. Reaction with an anionic (SDS) and a cationic (DPC) surfactant yielded a small amount of DMF soluble product, but most of the solids were insoluble. A highly DMF soluble product ($>90\%$ DMF soluble) was quantitatively obtained by the addition of a non-ionic surfactant (PGM) in the same manner as the previously reported enzymatic polymerization (*15*). The molecular weight of the product was $>10^4$ (entry 4, Table 1).

^{1}H-NMR of the DMF soluble portion of the product from entry 4 of Table 1 is shown in Figure 1. Kobayashi et al. reported the ^{1}H-NMR of a polyphenol, which is a mixture of phenylene and 1,4- and 1,6-phenyleneoxide units, in the study of enzymatic oxidative polymerization of phenol with a non-ionic polymer surfactant (^{1}H-NMR(DMSO-*d6*), $6.6-7.7$ (br, Ar), $9.2-9.7$ (br, ArOH)) (*15*). The ^{1}H-NMR of the DMF soluble polymer we obtained is extremely similar to this reported ^{1}H-NMR of polyphenol. The differences were: (a) the aromatic absorption in our material at ~ 7 ppm appears as one broad peak (the peak at ~ 7 ppm in the reported NMR is shown as a broad multiplet), (b) the $-$OH phenoxy around 9 ppm disappeared, and (c) we observed a peak at ~ 12 ppm. Currently, it is unclear why the phenoxyl peak shifted, but we believe that the peak at ~ 12 ppm is the phenoxy $-$OH which shifted from ~ 9 ppm in the previously reported materials. It may well be that this shift is a result of hydrogen–bonding interaction between the phenoxy groups. Based on the ^{1}H-NMR and IR spectra of the DMF soluble polymer obtained (entry 4, Table 1), we identified this as polyphenol in which the unit ratio of the poly(phenyleneoxide)/poly(phenylene) is *ca.* 80/20. We believe that this very high ratio of the poly(phenyleneoxide) in the polyphenol from the oxidative polymerization of phenol is a result of selective coupling at the *p*-position. The more phenyleneoxide units present, the better the solubility of the polymer. Due to this high regioselectivity, the polyphenol obtained is DMF soluble despite its high molecular weight of $>10^4$.

We attempted to characterize the structure of the DMF insoluble portion of the product by CP-MAS ^{13}C-NMR and viscoelasticity measurements. The CP-MAS ^{13}C-NMR obtained is shown in Figure 2.

Table 1. Oxidative polymerization of phenol in water*.

Surfactant	Entry	Surfactant (mmol/l)	Yield (%)	Soluble** (%)	Insoluble** (%)	$(3M_nM_w/M_n)$† ($\times 10^3$) (–)
1	–	–	42	10	90	0.8 (1.2)
2	SDS	10	50	40	60	1.4 (2.7)
3	DPC	10	80	63	47	4.8 (1.2)
4	PGM (*n*-45)	5	91	91	9	12 (3.7)
5	PGM (*n*-45)	10	92	92	8	14 (2.0)
6	PGM (*n*-25)	5	90	90	10	12 (2.5)
7	PGM (*n*-10)	5	80	70	30	9.4 (3.2)

*All polymerizations were carried out in water under oxygen at 50°C; reaction time of 24 h. Phenol 0.1 mol/l, sodium hydroxide 0.5 mol/l, potassium ferricyanide 0.2 mol/l. **DMF soluble and DMF insoluble portion of the polyphenol. †Molecular weight of DMF soluble portion of polyphenol determined by gel permeation chromatography relative to polystyrene standards in DMF.

Phenol tetramer, 4-[4-(4-phenoxy-phenoxy)phenoxy]phenol (TP), a model for poly(1,4-phenyleneoxide) was synthesized for comparison of the CP-MAS ^{13}C-NMR spectra. Phenol dimer, 4-phenoxylphenol was synthesized from the Ullmann reaction of phenols, and the TP was synthesized from the same reaction of the dimers. The DMF insoluble fraction obtained (entry 4, Table 1) and TP showed similar peaks in CP-MAS ^{13}C-NMR spectra. It must be pointed out that it is difficult to detect a difference between poly(phenyleneoxide) spectra and poly(phenylene) spectra from CP-MAS ^{13}C-NMR spectra, especially in determining the unit ratio of the poly(phenyleneoxide)/poly(phenylene). The spectra did suggest that the DMF soluble fraction of the product is polyphenol and that most of the units are poly(phenyleneoxide). To investigate the amount of crosslinking (phenylene unit) in the polymer, viscoelasticity of the DMF insoluble fraction of the polyphenol obtained was measured (entry 4, Table 1; Figure 3).

Both *G*' (storage modules) and *G*'' (loss modules) of the DMF insoluble fraction of the polymer were constant even under low angle rate area compared to the commercial poly(2,6-dimethyl-1,4-phenylene oxide) in which *G*' and *G*'' decreased. This result indicates that the DMF insoluble fraction of our polymer product is stiff, and that it is difficult to carry out a melt molding. Crosslinking density (M_c) could be measured by the following equation: $M_c = (\rho RT)/G$, (ρ = density, R = gas constant, T = absolute temperature, G = equilibrium elasticity). M_c of the DMF insoluble fraction was 5.5×10^3. This result demonstrates that the DMF insoluble portion is poly(phenylene oxide) with a crosslinking point (phenylene unit) at every unit of 5.5×10^3 molecular weight.

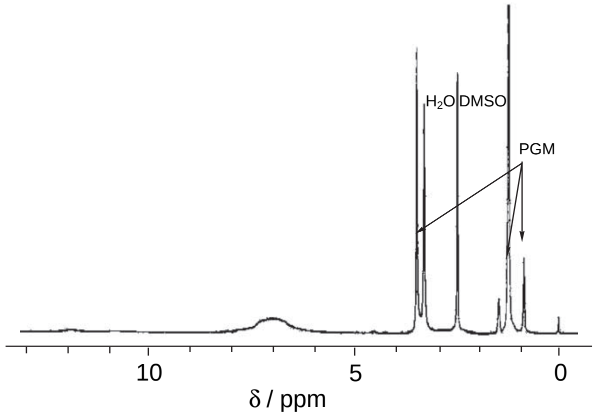


Figure 1. ^{1}H-NMR spectrum of the DMF soluble polyphenol (entry 4 in Table 1) from oxidative polymerization of phenol in water.

These results suggest that even the DMF insoluble fraction has a high ratio of the poly(phenyleneoxide) in the polymer, and the oxidative polymerization of phenol in water can control the coupling selectivity of phenol.

The DMF soluble polyphenol and the insoluble polyphenol were analyzed by thermogravimetry (TG) and differential scanning calorimetry (DSC), and both polymers showed a high thermal stability. The 10%-thermal degradation temperature ($T_{d10\%}$) and the glass transition temperature (T_g) of the DMF soluble and insoluble polyphenols were determined as $T_{d10\%} = 192°C$, $T_g = 86°C$ and $T_{d10\%} = 439°C$, $T_g = 177°C$, respectively (Figure 4). These high thermal stabilities of the polyphenols obtained show that the oxidative polymerization of phenol in water has the potential to provide an alternative process for the preparation of phenolic polymer, without using formaldehyde and an extra monomer, for production in a novel green way.

Experimental section

Oxidative polymerization of phenol in water

The following is a typical procedure for the polymerization. Phenol (0.94 g, 10 mmol) was dissolved in water (100 ml) containing sodium hydroxide (2.00 g, 50 mmol) and surfactant (molar range from 0 to

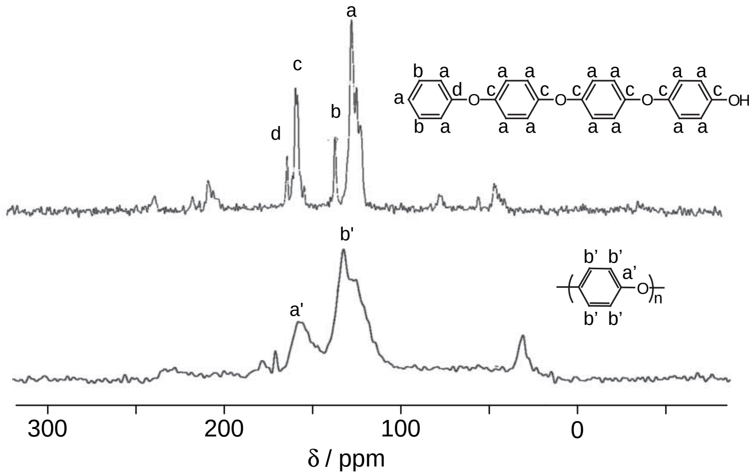


Figure 2. CP-MAS ^{13}C-NMR spectrum of the DMF insoluble polyphenol (entry 4 in Table 1) from the oxidative polymerization of phenol in water.

1 mmol). Potassium ferricyanide (6.58 g, 20 mmol) was added to the solution, and the mixture was vigorously stirred in air at 50°C for 24 h. The reaction mixture turned brownish and the polymer was obtained as a slightly brownish powder by filtration after salting out with the addition of sodium chloride and by washing with water. The obtained polymer was dried under vacuum and extracted with *N*,*N*-dimethylformamide (DMF) to separate the DMF soluble portion. DMF soluble portion: ^{1}H-NMR: (500 MHz, DMSO-d6, TMS) δ 6.5 − 7.9 (br, Ar), 11.8–12.2 (br, ArOH)), IR (KBr): $\nu_{\text{C–O–C}} = 1213\ \text{cm}^{-1}$.

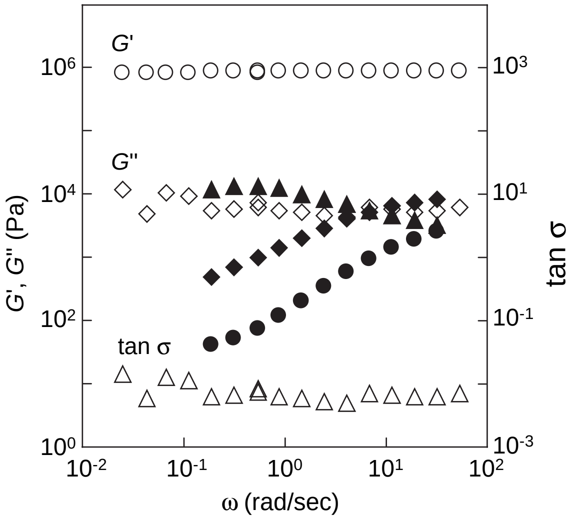


Figure 3. Viscoelasticity of the DMF insoluble polyphenol (entry 4 in Table 1). Obtained polyphenol DMF insoluble polyphenol ○ (*G*'), ◇ (*G*''), Δ (tan σ), poly(2,6-dimethyl-1,4-phenylene oxide) ● (*G*'), ◆ (G''), ▲ (tan σ).

4-[4-(4-Phenoxy-phenoxy)-phenoxy]phenol (TP) synthesis

4-Phenoxyphenol and 4-phenoxyanisole were synthesized according to the previously report (*20*,*21*). The Ullmann reaction of 4-(4-bromophenoxy)anisole with 4-phenoxyanisole was carried out as follows. 4-(4-Bromophenoxy)anisole (93.0 g, 0.5 mol) and 4-phenoxyanisole (47.1 g, 0.5 mol) were heated at 150°C in the presence of copper powder (5.0 g), cupric acetate (5.0 g), and potassium *tert*-butoxide (56.1 g, 0.5 mol). When the calculated amount of *tert*-butanol was removed, the reaction mixture was heated to 200°C for 12 h. The crude product was recrystallized from hexane, yielding 111 g (yield 58%) of 4-[4-(4-phenoxy-phenoxy)-phenoxy]anisole. 4-[4-(4-Phenoxy-phenoxy)-phenoxy]anisole (76.8 g, 0.2 mol) was treated with hydroiodic acid (120 ml) in refluxing glacial acetic acid (240 ml) for 12 h. Recrystallization from hexane gave 4-[4-(4-phenoxy-phenoxy)-phenoxy]phenol in 73 g, 99% yield. ^{1}H-NMR: (500 MHz, CDCl$_3$, TMS) δ 7.32 (2H, t, Ar), 7.07 (H, t, Ar), 6.99 (2H, s, Ar), 6.97 (2H, t, Ar), 6.91 (H, t, Ar), 6.79 (2H, s, Ar), 4.71 (s, 1H, −OH), ^{13}C-NMR: (125 MHz, CDCl$_3$, TMS) δ 157.8, 153.8, 150.8, 129.7, 122.9, 120.4, 119.9, 119.6, 116.3, IR (KBr): $\nu_{\text{C–O–C}} = 1240\ \text{cm}^{-1}$, mass: m/z 370 (found), 370.1 (calcd).

Measurements

^{1}H and ^{13}C-NMR spectra were recorded on a JEOL JNM-LA500. CP-MAS ^{13}C-NMR spectra were recorded on a JEOL CMX400. Molecular weights of PPO were determined by gel permeation chromatography (GPC) using Tosoh TSK GEL α-4000 × 1 and α-2500 × 1 as the columns with DMF as the eluent, in

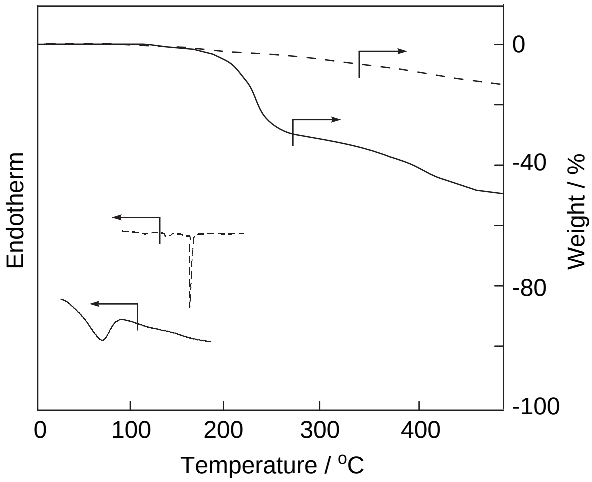


Figure 4. TG and DSC thermograms of the obtained polyphenol. Dotted line: DMF insoluble portion, solid line: DMF soluble portion.

which the calibration curve was obtained using polystyrene standards. Viscoelasticity analysis of the polymer was performed with a UBM Rheogel-E4000. Thermal analyses of the polymer were performed over a temperature range from 0 to 450°C for the TG and from –100 to 250°C for the DSC with a Seiko DSC 5200 thermal analyzer at a heating rate of 10°C/min under nitrogen. DSC data refers to the second heating cycle of annealing.

Conclusion

We have succeeded in oxidatively polymerizing phenol to form a soluble polyphenol in aqueous conditions. This reaction uses only water as a solvent, the reaction proceeds in an ambient condition, and the formed product can be precipitated out and separated from a reaction mixture by simple filtration after the reaction. The soluble polyphenol obtained had a high poly(phenylene oxide) unit ratio, poly(phenyleneoxide)/poly(phenylene) = ca. 80/20. Additionally, the insoluble fraction was identified as a poly(phenyleneoxide), which has a crosslinking point for every 5.5×10^3 molecular weight. These results suggest that oxidative polymerization in water can be run in a manner to control the coupling selectivity of phenol. The soluble polyphenol and the insoluble fraction both showed high thermal stability. This oxidative polymerization of phenol in water provides the potential of a green chemical process for a formaldehyde-free and regioselected soluble poly(phenyleneoxide) production.

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