

Oxidative Polymerization of 2,6-Dimethylphenol To Form Poly(2,6-dimethyl-1,4-phenyleneoxide) in Water**

Kei Saito, Takahiro Tago, Toru Masuyama, and
Hiroyuki Nishide*

One of the critical factors in realizing a green chemical reaction process involves the choice of water as the reaction solvent,^[1] particularly for polymer production on a large scale. The oxidative polymerization of 2,6-dimethylphenol (**1**; DMP), reported in 1959 by A. S. Hay and his GE group,^[2] provides a convenient and industrial method to prepare poly(2,6-dimethyl-1,4-phenyleneoxide) (**2**; PPO), an important plastic in engineering. This polymerization proceeds at room temperature and is an ideal atom-economical reaction that does not require any leaving groups (Scheme 1). 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 needed for the industrial production. Herein we report the first oxidative polymerization of DMP to form PPO in water as a green chemical process.

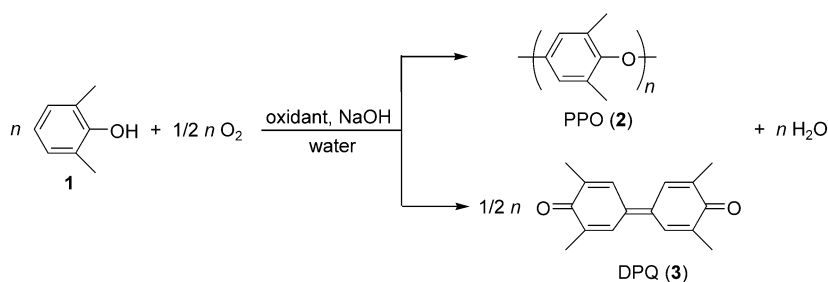
Although the preparation of PPO has been studied in detail,^[3–5] there has been no report in which water was used as the polymerization solvent, except for a few studies in aqueous–organic biphasic solvents.^[6,7] The oxidation of DMP in water is well-known to give predominantly DPQ (**3**), which is formed by the C–C coupling of two monomeric phenols (Scheme 1).^[6,8] There is another unsolved problem associated with polymerization in water: The dimer of DMP is insoluble, even in an alkaline aqueous solution, and the molecular weight of the formed PPO remains very low. We have now succeeded in oxidatively polymerizing DMP to form high-molecular-weight PPO in water. DMP was vigorously stirred in an alkaline aqueous solution with an oxidant in air. In this reaction, the DMP monomer was insoluble in water but it dissolved in water when an equimolar amount of base (NaOH) was added.^[9] The formed dimer and the following oligomers and polymers were insoluble in the alkaline aqueous solution, and the reaction mixture became heterogeneous immediately after the addition of the oxidant (see a photograph of the polymerization in water in the Supporting Information). The precipitated product could be

[*] K. Saito, T. Tago, T. Masuyama, Prof. Dr. H. Nishide
Department of Applied Chemistry, Waseda University
Tokyo 169-8555 (Japan)
Fax: (+813) 3209-5522
E-mail: nishide@waseda.jp

[**] This work was partially supported by Grants-in-Aid for Scientific Research (No. 13450384) and for the 21COE Research “Practical Nano-Chemistry” from MEXT, Japan. We thank Dr. Kenichi Oyaizu for productive discussions.



Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



Scheme 1. Oxidative polymerization of 2,6-dimethylphenol in water.

separated as an off-white powder from the reaction mixture by simple filtration after the polymerization, and the recovered alkaline aqueous solution could be used repeatedly for the polymerization. The product was identified as PPO by ^1H -, ^{13}C NMR, and IR spectroscopy. The 10%-thermal-degradation temperature ($T_{\text{d}10\%}$) and glass-transition temperature (T_g) were determined to be 401 °C and 208 °C, respectively,^[10] by TG and DSC and were found to be comparable with those of the commercial values.^[11]

Some examples of the polymerization are given in Table 1. The control reaction (Table 1, entry 1) showed that the oxidation of DMP did not proceed without the addition of base. Another control reaction (Table 1, entry 2) revealed that the oxidation of DMP with an equal amount of base and potassium ferricyanide in water predominantly gave DPQ and a small amount of the phenyleneoxide oligomer ($M_n = 4.0 \times 10^2$, $M_w/M_n = 1.5$) as previously reported.^[6,8] We found that the oxidation of DMP resulted in polymerization at an optimal temperature of 50 °C in the presence of excess base (relative to the monomer) (Table 1, entry 5),^[12] significantly, DPQ formation was suppressed to less than 0.4%.^[13] The addition of a surfactant as an emulsifier was effective: High-molecular-weight PPO ($M_n > 10^4$) was obtained almost quantitatively (98 %) by the addition of sodium *n*-dodecyl sulfate (Table 1, entry 6). Upon addition of the surfactant, the reaction mixture became a latex, but the polymer could also be separated by a simple filtration after being salted out.

The use of potassium ferricyanide as an oxidant is not adequate from the point of view of a green process. However, DMP was also oxidatively polymerized to give PPO in the

presence of a copper catalyst (e.g. [Cu(tmeda)]⁺; Table 1, entry 7) and oxygen or an excess of a metal oxide (e.g., MnO_2 ; Table 1, entry 8) without the formation of DPQ in the same alkaline medium at 50 °C. The former catalytic reaction could be improved by tuning the conditions.

Phenol derivatives such as 2,6-diphenylphenol were also polymerizable in the basic solution to form the corresponding PPO derivatives such as poly(2,6-diphenyl-1,4-phenyleneoxide) (Table 1, entry 9).

One of the reasons for using alkaline water as the solvent is a significant decrease in the oxidation potential of phenols. The pH value of the aqueous phase of the reaction mixture was 13.5 ($[\text{NaOH}] = 0.5 \text{ M}$). Cyclic voltammograms in the alkaline aqueous solution (Figure 1, inset) showed irreversible oxidation peaks of the phenol groups of DMP and 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (dimer), and their oxidative potentials were estimated to be 0.26 and 0.12 V

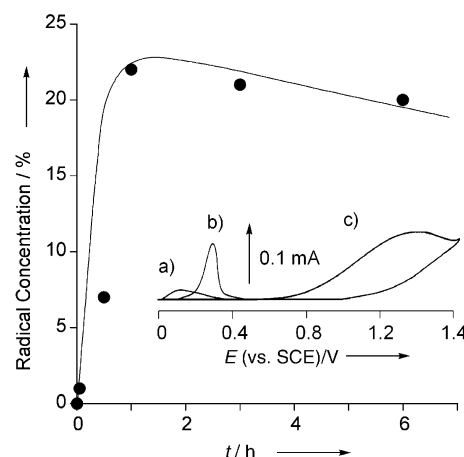


Figure 1. Radical concentration determined by SQUID. Inset: Cyclic voltammograms a) DMP in water with sodium hydroxide (0.5 M), b) dimer of DMP in water with sodium hydroxide (0.5 M), and c) DMP in CH_2Cl_2 with pyridine (3.0 M). Phenol concentration: 0.01 M; scan rate: 25 mVs^{-1} .

Table 1: Oxidative polymerization of 2,6-dimethylphenol in water.^[a]

Entry	ArOH [mmol] ^[b]	Oxidant or catalyst [mmol]	NaOH [mmol]	SDS [mmol] ^[c]	T [°C]	Yield [%]		PPO	
						DPQ ^[d]	PPO	M_n [10^3]	M_w/M_n ^[e]
1	50	$\text{K}_3[\text{Fe}(\text{CN})_6]$	100	0	0	RT	0.1	0	
2	50	$\text{K}_3[\text{Fe}(\text{CN})_6]$	100	50	0	RT	74	23	0.4
3	50	$\text{K}_3[\text{Fe}(\text{CN})_6]$	100	250	0	RT	66	32	1.6
4	1.0	$\text{K}_3[\text{Fe}(\text{CN})_6]$	2.0	50	0	RT	24	74	3.9
5	1.0	$\text{K}_3[\text{Fe}(\text{CN})_6]$	2.0	50	0	50	0.4	76	3.5 ^[g]
6	1.0	$\text{K}_3[\text{Fe}(\text{CN})_6]$	2.0	50	0.1	50	0.4	98	13
7	50	$[\text{Cu}(\text{tmeda})]\text{Cl}_2$ ^[f]	5.0	50	5.0	50	0.2	67	2.9
8	1.0	MnO_2	10	50	0	50	0	24	5.0
9	0.5	$\text{K}_3[\text{Fe}(\text{CN})_6]$	1.0	50	0.5	70	0.9	96	6.9

[a] All the polymerizations were carried out in water (100 mL) under air (except entry 7, which was carried out under oxygen), 6 h. [b] DMP, except entry 9, which was studied with 2,6-diphenylphenol. [c] Sodium *n*-dodecyl sulfate. [d] Determined by UV/Vis absorption at $\lambda_{\text{max}} = 421 \text{ nm}$. [e] Determined by gel-permeation chromatography relative to polystyrene standards in chloroform. [f] tmeda = *N,N,N',N'*-tetramethylethylenediamine. [g] The molecular weight was determined to be 3.4×10 by NMR spectroscopic analysis (terminal phenolic group content).

(vs. SCE), respectively. The former value is much lower than that of DMP (1.31 V) in a basic organic solvent such as dichloromethane involving pyridine as the base. The oxidative potential for the dimer was lower than that of the DMP monomer, suggesting that the oxidation potential of the terminal phenolic group becomes lower as the polymerization progresses.

The ESR spectrum of the polymerization mixture was recorded: The signal at $g = 2.0044$ was ascribed to the organic phenoxyl radical. After filtering the powder product from the mixture and quickly washing with alkaline water, it was transferred to the capsule of a SQUID magnetometer to determine the radical concentration of the powder product.^[14] The radical concentration in the polymerization reaction (Figure 1) was maintained at approximately 20% per polymer molecule or per polymer terminal phenolic group.^[15] The polymerization mechanism of DMP in the water is described below.

DMP is dissolved in the basic aqueous phase to form the phenolate anion, and is oxidized to the phenoxyl radical. The C–O coupling of two phenoxyl radicals gives the dimer. The formed dimer and oligomer are insoluble in the alkaline aqueous solution, and the reaction mixture becomes heterogeneous. However, the terminal phenolic groups located at the water interface are oxidized to give the polymeric phenoxyl radicals, which are redistributed to the high-molecular-weight polymer in the solid that precipitates from the water.

In summary, we have described the polymerization of DMP to form PPO in water. The oxidative polymerization of phenols in alkaline water has the potential to become a convenient green polymerization procedure.

Experimental Section

Oxidative polymerization of DMP in water with $K_3[Fe(CN)_6]$ (Table 1, entry 6): DMP (0.122 g, 1 mmol) was dissolved in water (100 mL) containing sodium hydroxide (2.00 g, 50 mmol) and sodium *n*-dodecyl sulfate (29 mg, 0.1 mmol). Potassium ferricyanide (0.658 g, 2 mmol) was added to the solution, and the mixture was vigorously stirred (3000 rpm) under air at 50 °C for 6 h. The polymer was obtained as an off-white powder (98%) by filtration after salting out by the addition of sodium chloride (5.84 g, 0.25 mol) and by washing with water. 1H NMR: (500 MHz, $CDCl_3$, TMS): $\delta = 6.44$ (2H, s; H_{Ar}), 2.09 ppm (s, 6H; CH_3); ^{13}C NMR: (125 MHz, $CDCl_3$, TMS): $\delta = 16.8$, 114.5, 132.5, 145.4, 154.7 ppm; IR (KBr): $\tilde{\nu}_{C-O-C} = 1186\text{ cm}^{-1}$. The reactions described in Table 1, entries 1–5, 8, and 9 were carried out analogously.

Oxidative polymerization of DMP in water with $[Cu(tmeda)]$ (Table 1, entry 7): A solution $[Cu(tmeda)]$ (0.250 g, 5 mmol) in water (10 mL) was added to a solution of DMP (6.10 g, 50 mmol), sodium hydroxide (2.00 g, 50 mmol), and sodium *n*-dodecyl sulfate (1.45 g, 5 mmol) in water (90 mL). The mixture was then vigorously stirred (3000 rpm) in oxygen at 50 °C for 6 h. After salting out with sodium chloride (29.2 g, 1 mol), the product was obtained by filtration. The reprecipitation from chloroform to methanol gave an off-white polymer (67%). The 1H , ^{13}C NMR, and IR spectra were similar to those described above.

UV/Vis spectral detection of DPO: A sample of the filtered product (1.2 mg) was removed and dissolved in toluene (10 mL). This solution gave a UV/Vis absorption with the maximum at 421 nm, which was ascribed to DPO. The molar extinction coefficient ϵ was

determined to be $54000\text{ M}^{-1}\text{ cm}^{-1}$ in toluene using pure DPO. The amount of formed DPO is given as a percentage of the feed amount of DMP.

SQUID magnetic measurement: The magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer. Powder samples for the measurement were prepared as follows: The polymerizations of DMP with potassium ferricyanide were carried out as described above for 0.05, 0.5, 1, 3, and 6 h. After these reaction times, the powder product was filtered, quickly washed with alkaline water, and transferred to the capsule of the SQUID magnetometer. The magnetization was measured from 0.5 to 7 T at 1.8, 2, 2.5, 3, 5, 20, and 200 K. The static magnetic susceptibility was measured from 1.8 to 200 K in a field of 0.5 T.

Received: September 2, 2003 [Z52764]

Keywords: green chemistry · oxidation · polymerization · radicals · water chemistry

- a) C.-J. Li, T.-H. Chan, *Organic Reactions in Aqueous Media*, Wiley, New York, **1997**; b) P. Tundo, P. Anastas, D. S. Black, J. Breen, T. Collins, S. Memoli, J. Miyamoto, M. Polyakoff, W. Tumas, *Pure Appl. Chem.* **2000**, *72*, 1207–1228; c) J. M. Desimone, *Science* **2002**, *297*, 799–803.
- a) A. S. Hay, H. S. Blanchard, G. F. Endres, J. W. Eustance, *J. Am. Chem. Soc.* **1959**, *81*, 6335–6336; b) A. S. Hay, *J. Polym. Sci.* **1962**, *58*, 581–591; c) A. S. Hay, *Macromolecules* **1969**, *2*, 107–108; d) A. S. Hay, *J. Polym. Sci. Part A* **1998**, *36*, 505–517.
- a) E. Tsuchida, M. Kaneko, H. Nishide, *Makromol. Chem.* **1972**, *151*, 221–234; b) E. Tsuchida, H. Nishide, *Makromol. Chem.* **1975**, *176*, 1349–1358; c) E. Tsuchida, H. Nishide, *Adv. Polym. Sci.* **1977**, *24*, 1–87; d) K. Oyaizu, Y. Kumaki, K. Saito, E. Tsuchida, *Macromolecules* **2000**, *33*, 5766–5769.
- D. Aycok, V. Abolins, D. M. White, *Encyclopedia of Polymer Science and Engineering*, Vol. 13, 2nd ed., Wiley, New York, **1986**, pp. 1–30.
- a) W. Koch, W. Risse, W. Heitz, *Makromol. Chem. Suppl.* **1985**, *12*, 105–123; b) E. Tsuchida, F. Suzuki, E. Shouji, K. Yamamoto, *Macromolecules* **1994**, *27*, 1057–1060; c) P. J. Baesjou, W. L. Driessen, G. Challa, J. Reedijk, *J. Am. Chem. Soc.* **1997**, *119*, 12590–12594; d) H. A. M. van Aert, M. H. P. van Gendersen, G. J. M. L. van Steenpaal, L. Nelissen, E. W. Meijer, *Macromolecules* **1997**, *30*, 6056–6066; e) H. Higashimura, K. Fujisawa, Y. Moro-oka, M. Kubota, A. Shiga, A. Terahara, H. Uyama, S. Kobayashi, *J. Am. Chem. Soc.* **1998**, *120*, 8529–8530.
- a) G. D. Staffin, C. C. Price, *J. Am. Chem. Soc.* **1960**, *82*, 3632–3634; b) C. C. Price, N. S. Chu, *J. Polym. Sci.* **1962**, *61*, 135–141.
- a) H. Komoto, K. Ohmura, *Makromol. Chem.* **1973**, *166*, 57–68; b) V. Percec, T. D. Shaffer, *J. Polym. Sci. Polym. Lett. Ed.* **1986**, *24*, 439–446; c) K. Mühlbach, V. Percec, *J. Polym. Sci. Polym. Chem. Ed.* **1987**, *25*, 2605–2627; d) R. Ikeda, J. Sugihara, H. Uyama, S. Kobayashi, *Macromolecules* **1996**, *29*, 8702–8705; e) H. Yonami, H. Uyama, S. Kobayashi, *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *36*, 719–730; f) Y. M. Chung, W. S. Ahn, P. K. Lim, *J. Mol. Catal. A* **1999**, *148*, 117–126.
- C. G. Haynes, A. H. Turner, W. A. Waters, *J. Chem. Soc.* **1956**, 2823–2831.
- The solubility of DMP in aqueous NaOH (0.5 M) is $< 61\text{ g L}^{-1}$.
- $T_{d10\%}$ and T_g were for the polymer described in Table 1, entry 6.
- F. E. Karasz, H. E. Bair, J. M. O'Reilly, *J. Polym. Sci. Part A-2* **1968**, *6*, 1141–1148.
- The formation of DPO in water was hardly affected by temperature, in contrast to the case in organic solvents. G. F. Endres, A. S. Hay, J. W. Eustance, *J. Org. Chem.* **1963**, *28*, 1300–1305.

- [13] The yield of DPQ was determined by the UV/Vis absorption at $\lambda_{\text{max}} = 421$ nm. The formation of DPQ was suppressed dramatically. By comparison, conventional polymerization methods (e.g., catalyzed by a copper–amine complex in toluene at room temperature) give DPQ in 3–5% yield. a) F. J. Viersen, G. Challa, *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 97–102; b) F. J. Viersen, J. Renkema, G. Challa, J. Reedijk, *J. Polym. Sci. Part A* **1992**, *30*, 901–911.
- [14] Normalized plots of magnetization versus the ratio of the magnetic field and effective temperature for the powder product obeyed a theoretical curve corresponding to the $S = 1/2$ Brillouin function (S = spin quantum number). This showed no contribution of the contaminants such as the potassium ferricyanide oxidant to the measurement of the radical concentration.
- [15] The half-life of the phenoxyl radical was determined to be approximately 4 min by ESR spectroscopic analysis of the powder sample.