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Catalyzed oxidative polymerization to form poly(2,6-dimethyl-1,4-phenylene oxide) in water using water-soluble copper complex

Kei Saito, Norikazu Kuwashiro, Hiroyuki Nishide*

Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan

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Abstract

Simply stirring 2,6-dimethylphenol with a small amount of copper complex catalyst in alkaline water provided a green way to prepare poly(2,6-dimethyl-1,4-phenylene oxide) in water. We have searched for the optimum alkaline-resistant metal catalyst from a series of water-soluble copper complexes. The formed polymer was easily separated as an off-white powder by filtration after salting out.

Keywords: Oxidative polymerization; Polyphenylene oxide; Water solvent

1. Introduction

Polymerization reactions in water are green chemical reaction processes which can be applied on a large scale [1–3]. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is widely used as a high-performance engineering plastic and it is prepared both industrially and in the laboratory by the oxidative polymerization of 2,6-dimethylphenol (DMP) [4,5]. The polymerization proceeds at room temperature, and it is an ideal atom economical reaction that does not require any leaving groups in producing the polymer. In spite of its importance from the viewpoint of green chemistry, the only PPO preparation processes and mechanism studies to this time have been restricted to the oxidative polymerization of DMP using organic solvents such as toluene and benzene in the presence of a copper-amine catalyst under oxygen [6–11]. When an organic solvent is used for the reaction, both a solvent recovery process and an anti-explosive reactor are needed for industrial production. The use of water as the solvent for the oxidative polymerization to form PPO is the desired approach from a green chemical process. There has been, however, no report in which water was used as a solvent for the polymerization of DMP, except for a few studies using aqueous–organic biphasic solvents [12,13]. The oxidation of DMP in water is well known to predominantly give 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone (DPQ) which is formed by the C–C coupling of two monomeric phenols [14,15]. Recently we succeeded in oxidatively polymerizing DMP to form PPO in aqueous sodium hydroxide as the reaction solvent with an excess of oxidant, theme by suppressing DPQ formation [16–18]. The unresolved issue is that this reaction is not catalytic and the use of an oxidant such as potassium ferricyanide is not adequate from a green chemistry viewpoint.

A copper-amine catalyst in aqueous sodium hydroxide is known to form copper hydroxide by hydrolysis and the catalyst becomes inactive. To form a high molecular weight polymer by the oxidative polymerization in water using copper-amine catalysts, the catalysts need to be stable in the alkaline water and be regenerated with oxygen. To solve this problem, we have searched for the optimum metal catalyst from a series of water-soluble copper complexes and found that strong chelate copper complexes are stable in alkaline water and act as alkaline-resistant copper catalysts for oxidative polymerization. Here we report the oxidative polymerization

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* Corresponding author. Tel.: +81 3 3200 2669; fax: +81 3 3209 5522.
E-mail address: nishide@waseda.jp (H. Nishide).

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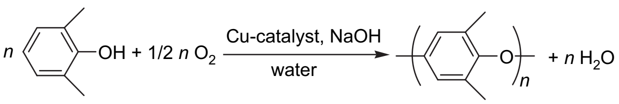

Scheme 1. Oxidative polymerization of 2,6-dimethylphenol in water by a water-soluble catalyst.

of DMP in water to form PPO using a water-soluble alkaline-resistant copper catalyst (Scheme 1).

2. Experimental section

2.1. Oxidative polymerization of 2,6-dimethylphenol (DMP) in water by a water-soluble catalyst

The following is a typical procedure for the polymerization (entry 3, Table 1). The aqueous solution (50 mL) of the complex of copper(II) dichloride dihydrate (0.85 g, 5 mmol) with diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (1.82 g, 5 mmol) was added to an aqueous solution (50 mL) of DMP (6.10 g, 50 mmol), sodium hydroxide (2.00 g, 50 mmol), and sodium *n*-dodecyl sulfate (1.45 g, 5 mmol) and then vigorously stirred (stirring speed 3000 rpm) in oxygen at 50 °C for 12 h. After salting out with the addition of sodium chloride (5.80 g, 0.1 mol) or 1-dodecyl pyridinium chloride hydrate (1.41 g, 5 mmol), the product was obtained by filtration (yield: 70%). ^{1}H NMR: (500 MHz, $CDCl_3$, TMS) δ 6.44 (2H, s, aromatic C–H), 2.09 (s, 6H, $-CH_3$); ^{13}C NMR: (125 MHz, $CDCl_3$, TMS) δ 16.8, 114.5, 132.5, 145.4, 154.7; IR (KBr): $\nu_{C-O-C} = 1186\ \mathrm{cm}^{-1}$. $M_w = 8.1 \times 10^3$, $M_w/M_n = 2.0$.

2.2. Thermal analyses

Thermal analyses of the polymer (entry 4, Table 2) were performed over a temperature range from 0 to 600 °C for the TG and from −100 to 350 °C for the DSC with a Seiko DSC 5200 thermal analyzer at a heating rate of 10 °C/min under nitrogen. DSC data are referred to the second heating cycle of annealing.

Table 1
Oxidative polymerization of 2,6-dimethylphenol (DMP)[a]

Entry	Ligand	Yield (%)	M_w (M_w/M_n)[b] ($\times 10^3$) (−)	Residual Cu[c] (contaminant)
1	EDTA	87	7.5 (2.7)	0.23
2	CyDTA	100	4.7 (1.8)	0.05
3	DTPA	70	8.1 (2.0)	0.12
4	EDTA-OH	37	3.3 (1.7)	1.60
5	TTHA	25	1.7 (1.1)	0.12
6	GEDTA	33	1.4 (1.4)	1.22
7	EDDP	42	1.4 (1.4)	0.84

[a] All of the polymerizations were carried out in water under oxygen at 50 °C; reaction time of 12 h; DMP 0.5 mol L^{-1}, sodium hydroxide 0.5 mol L^{-1}, copper catalyst 0.05 mol L^{-1}, and sodium *n*-dodecyl sulfate 0.05 mol L^{-1}.

[b] Determined by gel permeation chromatography relative to polystyrene standards in chloroform.

[c] The residual copper in the formed PPO after salting out with sodium chloride was measured by inductively coupled plasma emission spectroscopy.

Table 2
Surfactant effect on oxidative polymerization of 2,6-dimethylphenol (DMP)[a]

Entry	($C_nH_{2n} + OOSO_3Na$) Alkyl chain	mol L^{-1}	Yield (%)	M_w (M_w/M_n)[b] ($\times 10^3$) (−)
1	$n = 12$	0.05	70	8.1 (2.0)
2	$n = 12$	0.13	69	8.9 (2.1)
3	$n = 12$	0.25	98	9.3 (2.3)
4	$n = 12$	0.5	97	17 (2.6)
5	$n = 12$	1.0	97	16 (2.7)
6	$n = 6$	0.5	70	8.1 (2.0)
7	$n = 16$	0.5	95	9.6 (2.3)

[a] All of the polymerizations were carried out in water under oxygen at 50 °C; reaction time of 12 h using Cu–DTPA 0.05 mol L^{-1}; DMP 0.5 mol L^{-1}, sodium hydroxide 0.5 mol L^{-1}.

[b] Determined by gel permeation chromatography relative to polystyrene standards in chloroform.

2.3. UV–vis spectral detection of 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone (DPQ)

A 1.2 mg sample of the filtered product was removed and dissolved in toluene (10 mL). This toluene solution gave the UV–vis absorption with the maximum at 421 nm, which was ascribed to DPQ. The molar extinction coefficient ε was determined to be 54,000 M^{-1} cm^{-1} in toluene using pure DPQ. The amount of formed DPQ is given as a percentage of the feed amount of DMP. The amount of DPQ in the polymer formed in entry 4, Table 2 was 0.5%.

2.4. Residual copper yields measurement

The residual copper yields in the formed PPO were measured by inductively coupled plasma emission spectroscopy on a Varian VISTA-MPX by dissolving the polymer in 40% sulfonic acid. The precipitated out polymer from water was used to measure the residual copper yields without any copper removal. Previous procedure for the oxidative polymerization of DMP was carried out in toluene (100 mL) under oxygen at room temperature; reaction time of 6 h. The reaction mixture was poured into 5% HCl methanol solution to precipitate the polymer; DMP 0.5 mol L^{-1}, pyridine 5 mol L^{-1}, copper(I) chloride 0.05 mol L^{-1}.

2.5. Oxygen uptake measurement

An aqueous solution (10 mL) of DMP (1.22 g, 10 mmol), sodium hydroxide (0.40 g, 10 mmol), and sodium *n*-dodecyl sulfate (2.9 g, 10 mmol) was added to the sealed reaction vessel which is connected to the empty sealed vessel with manostat. Both bottles were filled with oxygen and the reaction was started by adding the aqueous solution (10 mL) of the complex of copper(II) dichloride dihydrate (0.17 g, 1 mmol) with diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (0.36 g, 1 mmol) by additional funnel and polymerization proceeds at 50 °C for 24 h. Oxygen uptake was calculated by measuring the water required to return the pressure of the empty vessel attached to the reaction vessel to the atmospheric pressure using a manostat.