

Oxidative coupling polymerization of *p*-alkoxyphenols with Mn(acac)₂-ethylenediamine catalysts

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ABSTRACT

The oxidative coupling polymerization of *p*-alkoxyphenols with Mn(acac)₂-ethylenediamine catalysts was carried out. The polymerization of *p*-methoxyphenol with the manganese(II) acetylacetonate [Mn-(acac)₂]-*N,N'*-diethylethylenediamine catalyst in CH₂Cl₂ at room temperature under an O₂ atmosphere afforded a polymer, which mainly consists of the *m*-phenylene unit, whereas the polymer obtained with Mn(acac)₂ was rich in the oxyphenylene structure. The polymer yield and regioselectivity were significantly affected by the monomer and catalyst structures. The former catalyst system was also used for the coupling reaction of 2-methoxy-4-methylphenol. The corresponding carbon-carbon coupling product was isolated with a regioselectivity of 95%.

Keywords: Oxidative Coupling Polymerization; Phenol; Polyphenylene; Manganese Catalyst; Regioselectivity

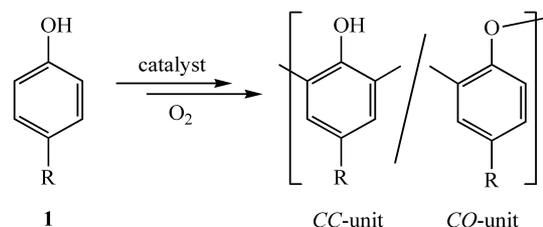
1. INTRODUCTION

Phenolic polymers bearing a polyphenylene main chain structure have been mainly synthesized by the transition-metal-catalyzed coupling reactions of aryl halides, such as the Wurtz coupling, Ullmann reaction, Kumada-Tamao-Corriu coupling, etc [1-4]. These reactions are suitable for the regio and/or coupling selective formation of carbon-carbon bonds between aromatics. However, from the viewpoint of a convenient and green chemical method, they have some problems, such as the synthesis of aryl halides, protection of the hydroxyl group, and disposing of a large amount of the metal hal-

ide from the reaction system.

On the other hand, the catalytic oxidative coupling polymerization (OCP) of 2,6-dimethylphenol is industrially utilized for the synthesis of poly(2,6-dimethyl-1,4-phenylene ether) (PPE), which is one of the most common engineering plastics [5-7]. The OCP is known as the environmentally conscious method, due to the fact that the reaction proceeds under mild conditions producing only water as the by-product. Meanwhile, the OCP mediates a free radical coupling process; therefore, it is generally very difficult to control the coupling regioselectivity of the phenoxy radicals without producing a branched chain. For example, the OCP of *p*-substituted phenols **1** generally affords a polymer composed of a mixture of the phenylene (CC) and oxyphenylene (CO) units (Scheme 1).

The highly regiocontrolled polymers having a poly(*m*-phenylene) skeleton should have a conjugated higher-order structure which is applicable as novel electronic and electrochemical materials [8-11]. For instance, a unique conformation change caused by the cisoid and transoid main chain structures was reported [1], and a helix-induction in a chiral environment was also achieved [2]. The precise coupling regiocontrol of the phenoxy radicals during the OCP will significantly contribute to the facile synthesis of novel phenolic polymer materials.



Scheme 1. OCP of **1**.

Studies of the catalyst systems for the regioselective OCP leading to a poly(phenylene ether) or poly(phenylene) derivative, such as the enzymatic and enzyme-model metal ones, and the copper-amine immobilized on mesopores, have been reported [12-16]. We also reported that the OCP of the bifunctional *p*-alkoxyphenol monomer **2** (Scheme 2) using the commercially available and typical copper catalyst, di- μ -hydroxo-bis[*N,N,N',N'*-tetramethylethylenediamine]copper(II) chloride [CuCl(OH)-TMEDA] proceeds in a regioselective manner to afford a polymer with a *CC*-unit selectivity of up to 88% [17]. However, the regioselectivity has still not been sufficiently controlled.

p-Alkoxyphenol is one of the attractive phenolic monomers, because its polymer possesses the poly(hydroquinone) structure, which is a typical redox-active polymer. In this study, the OCP of the *p*-alkoxyphenols **1** with various metal catalysts was investigated, and novel manganese (II) acetylacetonate [Mn(acac)₂]-ethylenediamine catalysts for the *CC*-selective coupling formation were found.

2. EXPERIMENTAL

2.1. Materials

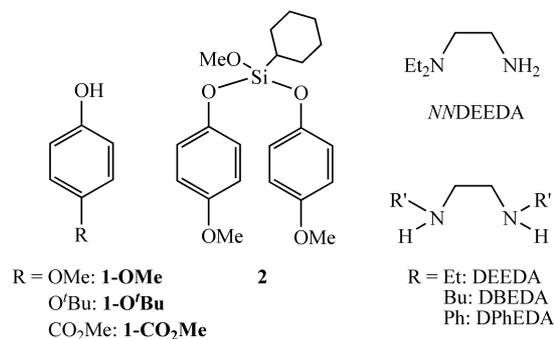
The monomers, *p*-methoxyphenol (**1-OMe**, Kanto), 4-*tert*-butoxyphenol (**1-O'Bu**, TCI), *p*-hydroxybenzoic acid methyl ester (**1-CO₂Me**, TCI) (Scheme 2), and **2**, were purchased or synthesized as previously reported [17]. Mn(acac)₂, Mn(acac)₃ (Wako), manganese(II) acetate [Mn(OAc)₂] (Kanto), VO(acac)₂, and Co(acac)₂ (TCI) were used as received. The dry solvents, CH₂Cl₂, tetrahydrofuran (THF), MeOH, and *N,N*-dimethylformamide (DMF) (Kanto), were employed for the oxidative coupling. The diamines (Scheme 2) were used without further purification.

2.2. Polymerization

A monomer was added to a mixture of Mn(acac)₂ and ethylenediamine ([monomer]/[Mn(acac)₂]/[ethylenediamine] = 1/0.08/0.08) in a solvent (0.6 M), and the mixture was stirred at room temperature under an O₂ atmosphere. The product was isolated as the MeOH-1N HCl (10/1 (v/v))-insoluble part by centrifugation and drying under reduced pressure at 50°C. The regioselectivity (*CC/CO*) of the obtained polymers was estimated from H₂ volume generated by adding a polymer solution in THF to a mixture of an excess amount of lithium aluminum hydride (LiAlH₄) in THF [10,12-14,17].

2.3. Measurements

The ¹H NMR spectra were measured using a Varian Unity-Inova (500 Mz) or Mercury 200 (200 MHz) spec-



Scheme 2. Monomers and ligands.

trometer in CDCl₃. The infrared (IR) spectra were recorded using a HORIBA FT-720 spectrometer. The ultraviolet (UV) absorption spectra were taken by a JASCO V-630 spectrophotometer. The size exclusion chromatographic (SEC) analyses were performed using a JASCO PU-2080-Plus equipped with a JASCO UV-2075-Plus detector and Shodex AC-8025 and TSK-GEL columns connected in series [eluent: CHCl₃, flow rate = 1.0 mL/min]. Calibration was carried out using standard polystylenes.

3. RESULTS AND DISCUSSION

3.1. OCP with Manganese Catalyst

The OCP of **1-OMe** with various catalysts was carried out. The results are summarized in Table 1. The regioselectivity of *CC/CO* could not be estimated from the ¹H NMR spectra, because the peaks of the aromatic rings and hydroxyl group were broad and overlapped, as reported in previous studies [10,12-14,17]. Therefore, it was evaluated by titration of the hydroxyl group of the poly(**1-OMe**).

The polymerization with VO(acac)₂ or Co(acac)₂, the former of which was effective as a catalyst for the OCP of 2,3-dihydroxynaphthalene [18-20], in CH₂Cl₂-MeOH [7/1 (v/v)] at room temperature under an O₂ atmosphere did not proceed (entries 1 and 2), whereas Mn(acac)₂ showed a catalytic activity to afford a polymer as a methanol-1N HCl [10/1 (v/v)]-insoluble fraction in 69% yield with a regioselectivity (*CC/CO*) of 24/76 (entry 3). The polymerization in CH₂Cl₂ also resulted in good to high yields, and the selectivity was slightly affected by the solvent (entries 4 and 5). The polar solvents, such as THF and DMF, however, prevented the production of a polymer (entries 6 and 7). Therefore, the polymerization solvent significantly influenced the catalytic activity during the polymerization with Mn(acac)₂. The polymerization with Mn(acac)₃ also gave a polymer, although the catalytic activity was lower than that of Mn(acac)₂ (entry 8). This result suggests that the polymerization

proceeds through the Mn(III) species generated by the one-electron oxidation of the Mn(II) ones as mentioned later. The counter anion also affected the catalyst performance (entry 9).

3.2. OCP with Mn(acac)₂-Diamine Catalyst

The OCP of **1-OMe** with Mn(acac)₂ in the presence of various ethylenediamines ([Mn(acac)₂]/[ethylenediamine] = 1) in CH₂Cl₂ was then examined (**Table 2**). The OCP with TMEDA resulted in a poor yield (entry 1). However, the polymerizations with pyridine (2 equiv.) and the ethylenediamines having primary and secondary amino groups, such as *N,N*-diethylethylenediamine [*N*NDEEDA],

N,N'-diethylethylenediamine [DEEDA], *N,N'*-di-*n*-butylethylenediamine [DBEDA], and *N,N'*-diphenylethylenediamine [DPhEDA] (**Scheme 2**), gave a polymer in moderate to good yields, whose regioselectivity was quite different from that of the polymer obtained without the amine ligand, especially, the polymers obtained with the ethylenediamine were rich in the CC-unit (entries 3-6). For example, the polymerization with DEEDA for 96 h gave a polymer in 47% yield with the regioselectivity (CC/CO) of 87/13.

The effects of the Mn(acac)₂-DEEDA catalyst system during the polymerization under various conditions were further investigated (**Table 3**). Although the 24 h-po-

Table 1. OCP of **1-OMe** with Various Catalysts^a.

Entry	Catalyst ^a	Solvent	Time (h)	Yield (%) ^b	$M_w \times 10^{-3} (M_w/M_n)^c$	Selectivity ^d (CC/CO)
1	VO(acac) ₂	CH ₂ Cl ₂ -MeOH ^c	72	0	—	—
2	Co(acac) ₂	CH ₂ Cl ₂ -MeOH ^c	72	0	—	—
3	Mn(acac) ₂	CH ₂ Cl ₂ -MeOH ^c	48	69	5.8 (1.1)	24/76
4	Mn(acac) ₂	CH ₂ Cl ₂	48	72	5.1 (1.2)	33/67
5	Mn(acac) ₂	CH ₂ Cl ₂	96	91	5.6 (1.2)	28/72
6	Mn(acac) ₂	THF	48	0	—	—
7	Mn(acac) ₂	DMF	48	0	—	—
8	Mn(acac) ₃	CH ₂ Cl ₂	48	40	4.6 (1.2)	31/69
9	Mn(OAc) ₂	CH ₂ Cl ₂	48	0	—	—

^aConditions: [catalyst]/[**1-OMe**] = 0.08, [**1-OMe**] = 0.6 M, temp. = room temperature, O₂ atmosphere. ^bMeOH-1N HCl (10/1 (v/v))-insoluble part.

^cDetermined by SEC in CHCl₃ (polystyrene standard). ^dEstimated from the generated H₂ volume by the reaction of the obtained polymer with LiAlH₄.

^eCH₂Cl₂/MeOH = 7/1 (v/v).

Table 2. OCP of **1-OMe** with Mn(acac)₂-Ethylenediamine Catalysts^a.

Entry	Catalyst ^a	Yield (%) ^b	$M_w \times 10^{-3} (M_w/M_n)^c$	Selectivity ^d (CC/CO)
1	Mn(acac) ₂ -TMEDA	7	—	—
2	Mn(acac) ₂ -2Pyridine	60	7.4 (1.3)	50/50
3	Mn(acac) ₂ - <i>N</i> NDEEDA	77	4.4 (1.3)	56/44
4	Mn(acac) ₂ -DEEDA	47	5.2 (1.2)	87/13
5	Mn(acac) ₂ -DEEDA	37	5.7 (1.2)	68/32
6	Mn(acac) ₂ -DPhEDA	62	5.6 (1.2)	79/21

^aConditions: [catalyst]/[**1-OMe**] = 0.08, [**1-OMe**] = 0.6 M, solvent = CH₂Cl₂, temp. = room temperature, time = 96 h, O₂ atmosphere. ^bMeOH-1N HCl

(10/1 (v/v))-insoluble part. ^cDetermined by SEC in CHCl₃ (polystyrene standard). ^dEstimated from the generated H₂ volume by the reaction of the obtained polymer with LiAlH₄.

Table 3. OCP of **1-OMe** with Mn(acac)₂-DEEDA under Various Conditions^a.

Entry	Catalyst ^a	Time (h)	Yield (%) ^b	$M_w \times 10^{-3} (M_w/M_n)^c$	Selectivity ^d (CC/CO)
1	Mn(acac) ₂ -DEEDA	24	14	4.4 (1.2)	92/8
2	Mn(acac) ₂ -DEEDA ^e	96	0	—	—
3	Mn(acac) ₂ -DEEDA ^f	96	61	5.6 (1.6)	67/33
4	Mn(acac) ₂ -DEEDA ^g	96	86	7.3 (1.4)	64/36
5	Mn(acac) ₂ -2DEEDA	96	30	6.1 (1.4)	61/39

^aConditions: [catalyst]/[**1-OMe**] = 0.08, [**1-OMe**] = 0.6 M, solvent = CH₂Cl₂, temp. = room temperature, O₂ atmosphere. ^bMeOH-1N HCl (10/1 (v/v))-insoluble part. ^cDetermined by SEC in CHCl₃ (polystyrene standard). ^dEstimated from the generated H₂ volume by the reaction of the obtained polymer with LiAlH₄.

^eTemperature = 50°C. ^f[Catalyst]/[**1-OMe**] = 0.16. ^gSolvent = CH₂Cl₂/MeOH [7/1 (v/v)].

lymerization produced a polymer in a low yield, the regioselectivity of the obtained polymer was $CC/CO = 92/8$ (entry 1). Accordingly, during the first stage of the polymerization, a highly regioselective coupling reaction should occur. The polymerization at 50°C did not give a polymer. The other polymerization conditions, such as catalyst ratio and solvent, also affected the regioselectivity and catalytic activity (entries 2-4). When two equivalents of DEEDA to $\text{Mn}(\text{acac})_2$ was used, both the polymer yield and CC -unit ratio significantly decreased (entry 5), indicating that the 1:1 complex of $\text{Mn}(\text{acac})_2$ and DEEDA should be an active species. Although this catalyst system showed a lower catalytic activity than that of the polymerization without the diamine, the CC -unit selectivity was much higher.

The OCP of various monomers, such as **1-O'Bu**, **1-CO₂Me**, **2**, with the $\text{Mn}(\text{acac})_2$ -DEEDA catalyst in CH_2Cl_2 at room temperature for 96 h under an O_2 atmosphere was also performed. The polymerizations of **1-O'Bu** and **1-COOMe** did not afford a MeOH - 1N HCl (10/1 (v/v))-insoluble fraction, and the polymerization of **2** resulted in a trace yield. These results suggest that the steric and/or electronic effects of the *p*-substituent significantly influence the polymerizability.

Figure 1 shows the FT-IR spectra of poly(**1-OMe**) with a unit ratio of (A) $CC/CO = 28/72$ and (B) $92/8$. In each spectrum, the absorptions due to the vibrations of the O-H and C-O-C linkages were observed, indicating that the polymers are composed of a mixture of CC - and CO -units. The latter spectrum showed a much larger phenolic O-H peak due to the fact that this polymer is rich in the CC -unit [12].

Both polymers with $CC/CO = 28/72$ and $92/8$ were completely soluble in chloroform, acetone, THF, DMF, and dimethyl sulfoxide, whereas insoluble in hexane and methanol. However, the latter polymer was almost solu-

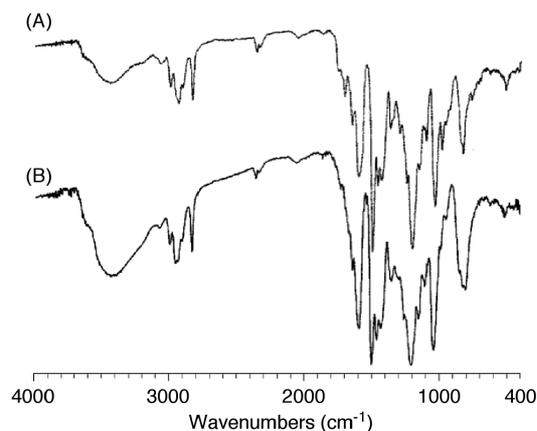
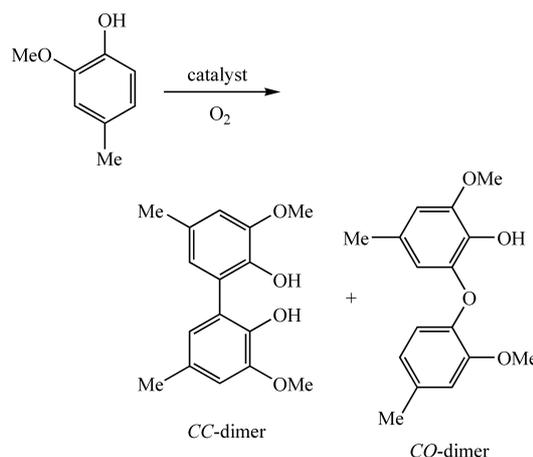


Figure 1. IR spectra of poly(**1-OMe**) with (A) $CC/CO = 28/72$, and (B) $CC/CO = 92/8$.

ble in an equivolume mixture of methanol and a 2N NaOH aqueous solution, while the former was insoluble.

In order to clarify the applicability of this $\text{Mn}(\text{acac})_2$ -DEEDA catalyst, the oxidative coupling reaction of 2-methoxy-4-methylphenol **3**, which can afford two coupling dimer products, the CC -dimer and CO -dimer [21-23], as well as the polymeric compounds, was investigated (**Scheme 3**). The reaction was conducted under the same reaction conditions as the polymerization in CH_2Cl_2 for 96 h at room temperature under an O_2 atmosphere, and the dimers were isolated by silica gel column chromatography (hexane/ $\text{AcOEt} = 10/1$). The coupling reaction with only $\text{Mn}(\text{acac})_2$ afforded a 31% yield of the CC -dimer and 10% yield of the CO -dimer, that is, the regioselectivity (CC/CO) was 76/24. In the case of the reaction using $\text{Mn}(\text{acac})_2$ -DEEDA, the isolated yields were 57% and 3%, respectively, giving a selectivity of $CC/CO = 95/5$. The $\text{Mn}(\text{acac})_2$ -DEEDA catalyst was quite effective for the regioselective oxidative coupling.

The UV-Vis spectra of poly(**1-OMe**) and the obtained dimeric products of **3** are shown in **Figure 2**. The maxi-



Scheme 3. Oxidative coupling reaction of **3**.

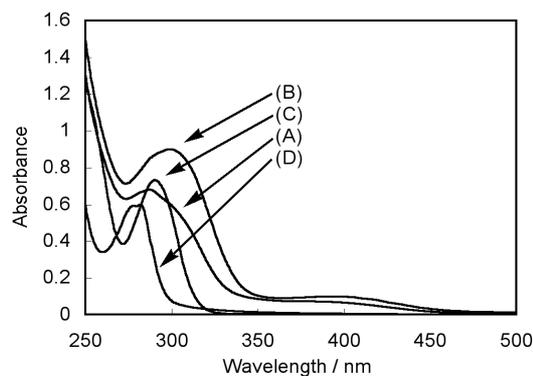


Figure 2. UV-Vis spectra of poly(**1-OMe**) with (A) $CC/CO = 28/72$, (B) $CC/CO = 92/8$, (C) CC -dimer, (D) CO -dimer (in CHCl_3).

mum absorption wavelength was observed at 287 nm for the polymer with $CC/CO = 28/72$, whereas the red-shifted absorption with the maximum of 299 nm was observed for the polymer with $CC/CO = 92/8$. This should be explained by the extension of the π -conjugation length due to the phenylene main chain structure for the latter polymer. Actually, the CC -dimer of **3** also showed a maximum absorption at 290 nm, which is greater than that of the CO -dimer of 282 nm.

The plausible OCP mechanism with $Mn(acac)_2$ -DEEDA was proposed as follows (**Figure 3**): The complex of an *in situ* generated $Mn(III)$ species and **1-OMe** causes the one-electron oxidation of the phenol to form a species of $Mn(II)$ and the phenoxy radical, which concertedly induces the regioselective intermolecular radical-radical coupling to produce the corresponding carbon-carbon coupling product [15]. The dissociated manganese species are oxidized by dioxygen to regenerate the active $Mn(III)$ species.

4. CONCLUSIONS

The OCP with $Mn(acac)_2$ -ethylenediamine catalyst systems, that regioselectively produces a polymer with the poly(*m*-phenylene) backbone, was developed. The catalytic activity and regioselectivity during the polymerization were significantly affected by the monomer and catalyst structures, and polymerization conditions. Especially, the $Mn(acac)_2$ -DEEDA catalyst showed a high regiocontrol ability. The catalyst can be readily and simply prepared by mixing of the commercially available $Mn(acac)_2$ and DEEDA.

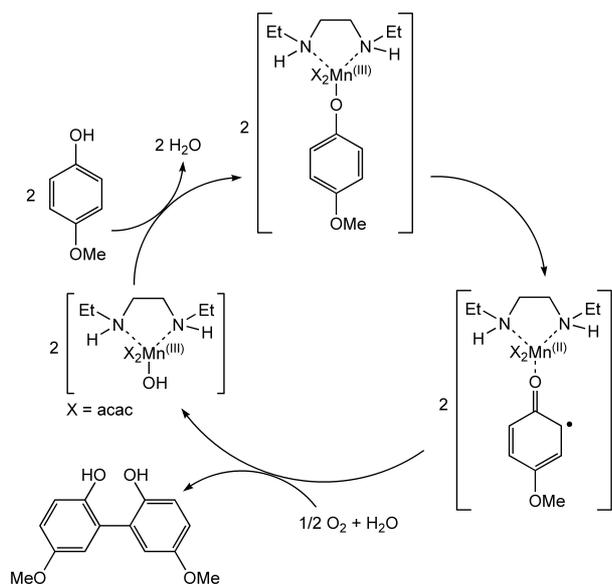


Figure 3. Plausible mechanism for OCP of **1-OMe** with $Mn(acac)_2$ -DEEDA.

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