NOTES

Oxidative Coupling Polymerization
of Silicon-Tethered *p*-Alkoxyphenol Derivatives
with CuCl(OH)-*N,N,N′,N′*-Tetramethylethylenediamine Catalyst

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The catalytic oxidative coupling polymerization (OCP) of phenol derivatives is a very attractive process, especially, as an environmentally benign one, producing only water as the by-product, proceeding under mild conditions, and without using toxic formaldehyde to produce phenolic polymer materials. However, it is generally very difficult to control the coupling regio-chemistry of the phenoxy radical intermediate, therefore, the limited phenol monomers, such as 2,6-dimethylphenol affording poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), one of the most typical engineering plastics, have been practically used for the OCP.[1,2]

Recently, highly regio- or coupling selectivity-controlled polymerizations with the enzymatic and enzyme-model metal catalysts have been developed,[3–12] whereas, normally, a polymer consisting of a mixture of phenylene (*CC*) and oxyphenylene (*CO*) units can be produced during the OCP of phenol derivatives, and oligophenylenes having an *o*-phenol unit were synthesized in a stepwise fashion.[13–17] During the former enzymatic system in the presence of poly(ethylene glycol) as a template, the polymers predominantly composed of the *CC* unit up to 95% were constructed.[7] The regioselective polymerization leading to the poly(phenylene oxide)s was attained using the latter designed copper(II) complexes as the catalyst.[8–10] Accordingly, the further design of the OCP system will realize the more precise structure control of the polymer and expand its usefulness.[18–21]

The *p*-alkoxyphenol is one of the interesting phenolic monomers, because the obtained polymer possesses the poly(hydroquinone) skeleton, which is a typical redox-active polymer, therefore, it should be valuable for a wide range of electronic and electrochemical applications.[22–27] On the other hand, intramolecular reactions often enable to attain both high regio- and stereochemical control, and the substrates with a silyl linkage, which can be easily and selectively removed after the reaction, are especially useful.[28]

In this study, novel bifunctional *p*-alkoxyphenol monomers, **2**, were synthesized (Scheme 1) and polymerized using the commercially available copper catalyst, di-*μ*-hydroxo-bis[(*N,N,N′,N′*-tetramethylethylenediamine)copper(II)] chloride [CuCl(OH)-TMEDA], which is well known as an effective catalyst for the oxidative coupling of 2-naphthol derivatives,[29–31] and the coupling selectivity of the obtained polymers was investigated (Scheme 2).

EXPERIMENTAL

Materials

The CuCl(OH)-TMEDA complex (TCI) was used as received. The bifunctional monomers **2** were synthesized from the corresponding *p*-alkoxyphenols **1** and dichlorocyclohexylmethylsilane with imidazole and purified by silica gel column chromatography (hexane/AcOEt = 20/1) in 75–85% yield.

2-Me: ^{1}H NMR (CDCl$_3$): δ 0.21 (s, 3H, SiCH$_3$), 1.01 (m, 1H, SiCH), 1.18–1.25 (m, 5H, –CH$_2$–), 1.68–1.74 (m, 3H, –CH$_2$–), 1.82–1.85 (m, 2H, –CH$_2$–), 3.76 (s, 6H, –OCH$_3$), 6.74–6.78 (m, 4H, aromatic), 6.83–6.87 (m, 4H, aromatic). IR (neat, cm^{-1}): 2924, 2850, 1504, 1466, 1232, 1039, 935, 831. Mass (EI): m/z 372 [M]$^+$.

2-Et: ^{1}H NMR (CDCl$_3$): δ 0.21 (s, 3H, SiCH$_3$), 1.00 (m, 1H, SiCH), 1.18–1.29 (m, 5H, –CH$_2$–), 1.38 (t, 6H, $J = 7.0$ Hz, CCH$_3$), 1.68–1.73 (m, 3H, –CH$_2$–), 1.81–1.85 (m, 2H, –CH$_2$–), 3.96 (q, 4H, $J = 7.0$ Hz, –OCH$_3$), 6.73–6.77 (m, 4H, aromatic), 6.81–6.85 (m, 4H, aromatic). IR (neat, cm^{-1}): 2924, 2852, 1504,
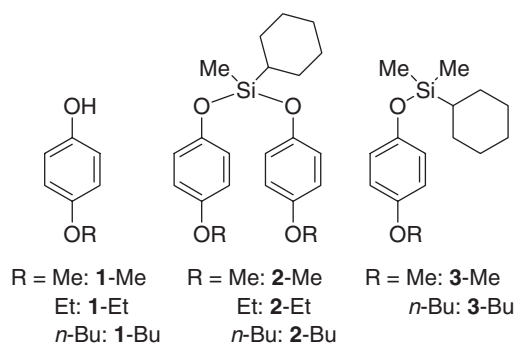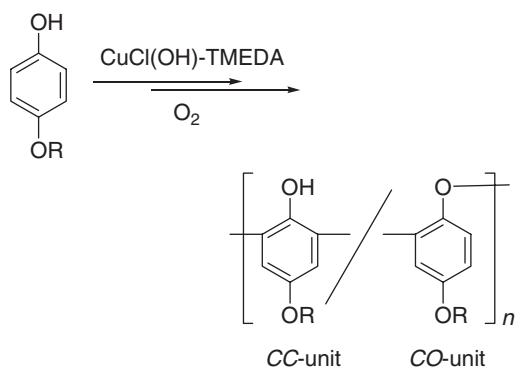
Scheme 1.

Scheme 2.

1475, 1232, 1213, 935, 831. Mass (EI): m/z 400 [M]$^+$.

2-Bu: ^{1}H NMR (CDCl$_3$): δ 0.21 (s, 3H, SiCH$_3$), 0.96 (t, 6H, $J = 7.0$ Hz, CCH$_3$), 1.00 (m, 1H, SiCH), 1.20–1.29 (m, 5H, –CH$_2$–), 1.43–1.52 (m, 4H, –CH$_2$–), 1.68–1.77 (m, 7H, –CH$_2$–), 1.81–1.85 (m, 2H, –CH$_2$–), 3.89 (t, 4H, $J = 6.5$ Hz, OCH$_2$), 6.73–6.78 (m, 4H, aromatic), 6.81–6.85 (m, 4H, aromatic). IR (neat, cm^{-1}): 2924, 2852, 1504, 1479, 1230, 1215, 1051, 935, 835. Mass (EI): m/z 456 [M]$^+$.

Polymerization (Typical Procedure)

A monomer was added to a solution of a copper catalyst ([phenol unit] = 0.60 M) in a solvent, and the mixture was stirred at room temperature for 48 h under an O$_2$ atmosphere. The product was isolated as the MeOH-1N HCl (10/1 (v/v))-insoluble part by centrifugation and drying under reduced pressure at 60 °C. The coupling selectivity (*CC/CO*) of the obtained polymers was estimated from the H$_2$ volume generated by adding a polymer solution in tetrahydrofuran (THF) (0.22 M) to a mixture of an excess amount of LiAlH$_4$ in THF (0.53 M).

Measurements

The ^{1}H and ^{13}C NMR spectra were measured using a Varian Unity-Inova (500 MHz for ^{1}H) or Mercury 200 (200 MHz for ^{1}H) spectrometer in CDCl$_3$. The infrared (IR) spectra were recorded using a Horiba

Table I. Polymerization of **1**-Me with CuCl(OH)-TMEDA in Various Solvents[a]

Run	Solvent	Yield[b] (%)	M_w[c] ($\times 10^3$)	M_n[c] ($\times 10^3$)	*CC/CO*[d]
1	CH$_2$Cl$_2$	73	3.6	1.3	32/68
2	THF	77	4.2	0.7	36/64
3	Nitrobenzene	64	1.9	1.2	33/67
4	DMA	57	2.4	1.2	71/29
5	DMF	54	2.5	1.4	64/36
6[e]	DMF	51	2.3	1.4	42/58
7	MeOH	49	3.6	1.9	42/58
8	2-Methoxyethanol	91	4.2	2.1	44/56

[a]Conditions: [Cu]/[**1**-Me] = 0.08, [**1**-Me] = 0.6 M, temp. = r.t., time = 48 h. [b]MeOH-1N HCl (10/1 (v/v))-insoluble part. [c]Determined by SEC in THF (polystyrene standard). [d]Estimated from the generated H$_2$ volume by the reaction of the obtained polymer with LiAlH$_4$. [e]Temp. = 90 °C.

FT-720 spectrometer. The mass (MS) spectra were taken using a Shimadzu QP-5000 mass spectrometer. The size exclusion chromatographic (SEC) analyses were performed using a JASCO PU-2080 Plus equipped with a JASCO UV-2075 Plus detector and Shodex KF-806L and KF-803L columns connected in series [eluent: THF, flow rate = 1.0 mL/min]. Calibration was carried out using standard polystyrenes.

RESULTS AND DISCUSSION

Several catalytic OCP's of hydroquinone derivatives have already been reported. For example, the polymerization of 4-hydroxyphenyl benzoate with the peroxidase catalyst gave a polymer with a coupling selectivity (*CC/CO*) of 61/39 ($M_w = 2300$, $M_w/M_n = 1.5$),[24] while the polymer having the unit ratio of 38/62 was obtained during the polymerization of *p*-methoxyphenol (**1**-Me) with the iron N,N'-ethylenebis(salicylideneamine) catalyst ($M_w = 1200$, $M_w/M_n = 1.7$).[26] The OCP of **1**-Me in the presence of the CuCl(OH)-TMEDA complex in various solvents at room temperature for 48 h under an O$_2$ atmosphere was carried out, and the regio-chemistry during the polymerization was evaluated (Table I).

The methanol-1N HCl (10/1 (v/v))-insoluble polymers were obtained in moderate to good yields, and the polymerization solvent significantly affected the coupling selectivity, as well as the catalyst activity. The polymerizations in CH$_2$Cl$_2$, THF, nitrobenzene, and alcoholic solvents, such as methanol and 2-methoxyethanol, gave a polymer rich in a *CO*-unit of 56–68%, while, in contrast, those in N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF) resulted in *CC*-selectivities of 71% and 64%, respectively (runs 4 and 5). However, during the polymerization in DMF at 90 °C, the polymer with a 58%

Table II. Polymerization of **2**-Me with CuCl(OH)-TMEDA[a]

Run	Catalyst (equiv.)[b]	Solvent	Yield[c] (%)	$M_w{}^{d}$ ($\times 10^3$)	$M_n{}^{d}$ ($\times 10^3$)	CC/CO[e]
1	0.08	DMF	11	1.9	1.0	86/14
2[f]	0.08	DMF	13	2.9	1.8	78/22
3	0.16	DMF	30	3.2	2.0	88/12
4	0.32	DMF	63	3.8	2.1	86/14
5	0.32	DMA	54	6.3	3.0	87/13
6[g]	0.08	DMF	60	1.5	1.1	38/62
7	0.08	Nitrobenzene	17	1.7	1.2	78/22
8	0.08	2-Methoxyethanol	27	3.0	1.2	65/35

[a]Conditions: [**2**-Me] = 0.3 M, temp. = r.t., time = 48 h. [b][Cu]/2[**2**-Me]. [c]MeOH-1N HCl (10/1 (v/v))-insoluble part. [d]Determined by SEC in THF (polystyrene standard). [e]Estimated from the generated H_2 volume by the reaction of the obtained polymer with LiAlH$_4$. [f]Time = 96 h. [g]Temp. = 90 °C.

CO-selectivity was obtained (run 6). Therefore, the hydrogen bond interaction between the monomer and the solvent, such as DMA and DMF, may cause a preferential formation of the carbon-carbon linkage during the polymerization.[7]

The results of the OCP of the bifunctional monomer, **2**-Me, with CuCl(OH)-TMEDA at room temperature for 48 h under an O_2 atmosphere are listed in Table II. The polymerizations in DMF, nitrobenzene, and 2-methoxyethanol resulted in a much lower yield than those of **1**-Me, and the obtained polymers were completely soluble in common organic solvents, such as CHCl$_3$ and THF (runs 1, 7, and 8). No silyl residue in the obtained polymers was detected based on the ^{1}H NMR analysis, and the deprotection of the hydroxyl groups occurred during the polymerization of **2**-Me as will be mentioned later. The polymer yield increased with the increasing [Cu]/2[**2**-Me] ratio and reached 63% when 0.32 equiv. of the catalyst was used in DMF (run 4), whereas the polymerization time showed a slight effect on the polymer productivity (run 2).

The polymerization of **2**-Me, even in nitrobenzene or 2-methoxyethanol, proceeded in a *CC*-selective manner, and the polymer obtained in DMF showed the highest *CC*-selectivity of 88%. Accordingly, the bifunctional monomer structure bearing the silyl linkage is quite effective for controlling the coupling regio-chemistry to some extent during the OCP. Figure 1 depicts the ^{1}H NMR spectrum of the methanol-insoluble polymer obtained in DMF (run 4). The coupling selectivity estimated from the observed peak intensities was $CC/CO \approx 87/13$, whose value is quite consistent with that evaluated from the H_2 volume generated from the reaction between the obtained polymer and LiAlH$_4$ in THF.

Table III shows the OCP of various mono- and bifunctional monomers at room temperature. The
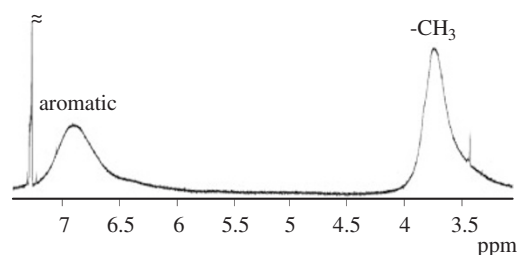
Figure 1. ^{1}H NMR spectrum of poly(**2**-Me) (Table II, run 4) (CDCl$_3$, 60 °C).

Table III. Polymerzation of Various Monomers with CuCl(OH)-TMEDA[a]

Run	Monomer	Solvent	Yield[b] (%)	$M_w{}^{c}$ ($\times 10^3$)	$M_n{}^{c}$ ($\times 10^3$)	CC/CO[d]
1	**1**-Et	Nitrobenzene	52	2.2	1.7	42/58
2	**1**-Bu	Nitrobenzene	46	2.0	1.5	40/60
3	**2**-Et	Nitrobenzene	14	1.7	1.2	80/20
4[e]	**2**-Et	DMF	66	4.4	2.2	84/16
5	**2**-Bu	Nitrobenzene	10	2.4	1.7	76/24
6[e]	**2**-Bu	DMF	76	4.1	2.4	76/24
7	**3**-Me	Nitrobenzene	0	—	—	—
8	**3**-Bu	Nitrobenzene	0	—	—	—

[a]Conditions: [Cu]/[phenol unit] = 0.08, [monomer] = 0.6 M for **1** and **3** and 0.3 M for **2**, temp. = r.t., time = 48 h. [b]MeOH-1N HCl (10/1 (v/v))-insoluble part. [c]Determined by SEC in THF (polystyrene standard). [d]Estimated from the generated H_2 volume by the reaction of the obtained polymer with LiAlH$_4$. [e][Cu]/2[**2**] = 0.32.

polymer prepared from **1**-Et or **1**-Bu was rich in the *CO*-unit (runs 1 and 2), whereas the *CC*-unit was predominantly constructed during the polymerization of **2**-Et or **2**-Bu (runs 3–6), similar to those of **1**-Me and **2**-Me. The obtained polymers were totally soluble in THF and CHCl$_3$, and no silyl residue was again detected in the poly(**2**)'s.

The polymerization of the *p*-alkoxyphenol derivatives having a cyclohexyldimethylsilyl group, **3**-Me and **3**-Bu, resulted in no yield (runs 7 and 8), and an 84% of the **3**-Me was recovered from the MeOH-1N HCl (10/1)-soluble fraction. On the other hand, the polymerization of **2**-Me at 90 °C in DMF produced a polymer with a *CO*-selectivity of 62% in 60% yield (Table II, run 6), which are almost comparable with those of **1**-Me under the same conditions (Table I, run 6), suggesting that the fast deprotection of the silyl group takes place at 90 °C. Therefore, the deprotection and oxidative coupling reactions may concertedly proceed to control the coupling regio-chemistry during the polymerization of **2**-Me at room temperature, although the detail mechanism is not clear at present.

In conclusion, a novel bifunctional monomer **2** was polymerized using a conventional copper catalyst

under an O_2 atmosphere to preferentially afford a polymer having a polyphenylene structure. A simple design of the monomer structure effectively controlled the regio- or coupling selectivity to some extent during the oxidative coupling polymerization.

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