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Asymmetric oxidative coupling polymerization of dihydroxynaphthalene derivatives with cobalt-salen complexes

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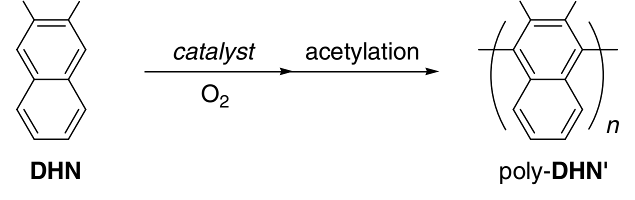
Summary

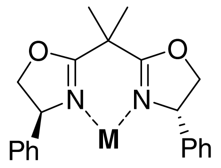
The oxidative coupling polymerization of dihydroxynaphthalene derivatives with a novel catalyst system, the cobalt(II)-salen complexes, was investigated. For example, the asymmetric polymerization of 2,3-dihydroxynaphthalene with (*R,R*)-(−)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) in a dichloromethane-methanol mixed solvent at room temperature for 0.5 h under an oxygen atmosphere, followed by acetylation of the hydroxyl groups, produced a methanol-insoluble polymer with the specific rotation value $[\alpha]_D$ of +165, which was rich in the *R*-configuration. To estimate the enantioselectivity during the polymerization, the corresponding acetylated dimer product was isolated from a polymerization mixture and determined to be 58% *e.e.*

Introduction

The catalytic oxidative coupling reaction of 2-naphthol derivatives is well known and one of the most facile and effective synthetic routes for the 1,1'-bi-2-naphthol derivatives, that have been widely utilized in asymmetric synthesis, catalysis, and resolution [1]. Many reports on their enantioselective synthesis using chiral metal catalysts, such as copper(I) [2–4], oxovanadium(IV) [5–7], and ruthenium(II) [8], are available.



Scheme 1.



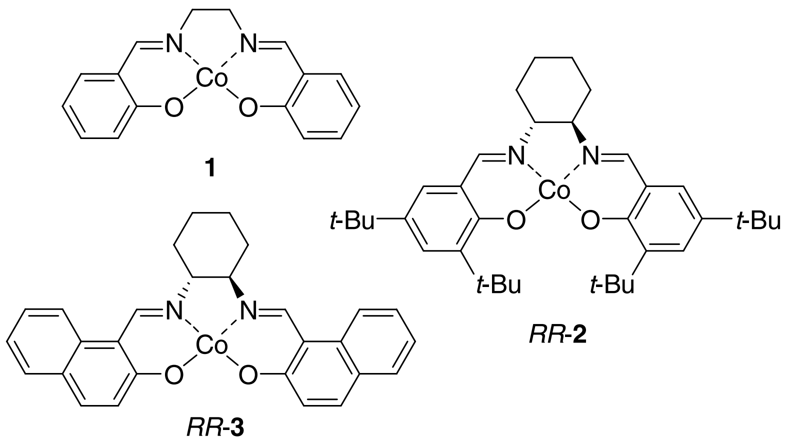
M = CuCl or $VOSO_4$

M-(*S*)Phbox

Scheme 2.

Recently, we reported the first oxidative coupling polymerization (OCP) of 2,3-dihydroxynaphthalene (**DHN**) (Scheme 1), in which new catalyst systems for the oxidative coupling, such as CuCl-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (Phbox) and $VOSO_4$-Phbox (Scheme 2) [9–11], were introduced. The poly-**DHN** has a main-chain comprised of continuously linked binaphthol units at the 4,4'-positions, and are interesting as optically active and functional polyaromatics [12–14]. For example, the polymerization with the latter catalyst afforded poly-**DHN'** with the absolute specific rotation value ($[\alpha]_D$) of about 140, and the enantioselectivity was estimated to be 80% *e.e.* [11]. In contrast, the aforementioned conventional copper and oxovanadium catalysts used for the oxidative coupling reaction showed a poor or no polymer-productivity. Therefore, the development of a novel catalyst for the oxidative coupling reactions is significant.

During the course of our study, we found that the cobalt-salen complexes [15], such as **1**–**3** (Scheme 3), can act as a catalyst for the OCP of **DHN**, although there are few reports of the asymmetric oxidative coupling reaction, as well as the polymerization, with the cobalt complexes. In this article, we report the effect of the cobalt complexes as an OCP-catalyst of the dihydroxynaphthalene derivatives.



Scheme 3.

Experimental

Materials

The monomer **DHN** and Phbox were purchased from Aldrich and used as received for the polymerization. The cobalt-salen complexes **1**–**3** were purchased (**1** and **2**: Aldrich) or prepared according to reported procedures [16,17].

Polymerization

The **DHN** monomer was added to a mixture of the catalyst ([catalyst]/[**DHN**] = 1/10), dichloromethane, and methanol [CH_2Cl_2/ MeOH = 7/1 or 20/1 (v/v), [**DHN**] = 0.35 or 0.20 M]. After stirring under an O_2 atmosphere, the solvents were evaporated, and dichloromethane and an excess amount of acetyl chloride and pyridine were added. After 24 h stirring under an N_2 atmosphere, the reaction mixture was poured into a large excess of MeOH-1N HCl [10/1 (v/v)]. The insoluble fraction was collected by centrifugation, repeatedly washed with methanol, and then dried *in vacuo*.

Measurements

The ^{1}H and ^{13}C NMR spectra were measured using a Varian Unity-Inova spectrometer (500 MHz for ^{1}H) in $CDCl_3$. The size exclusion chromatographic (SEC) analyses were performed using a JASCO PU-2080 equipped with a JASCO RI-2031 detector and Tosoh TSKgel G3000H and G7000H columns connected in series (eluent: *N,N*-dimethylformamide (DMF), temp. = 40°C, flow rate = 0.6 mL/min). Calibration was carried out using standard polystyrenes. Circular dichroism (CD) spectra were recorded using a JASCO J-720L apparatus. The optical rotation was measured using a JASCO P-1010 polarimeter in $CHCl_3$ at 25°C. The HPLC analyses were performed on a JASCO 986-PU chromatograph equipped with an UV (JASCO 970-UV) detector and Daicel Chiralpak AD [eluent = hexane/*i*-propanol = 9/1 (v/v), flow rate = 0.5 mL/min]. The infrared (IR) spectra were recorded on a Horiba FT-720 spectrometer.

Results and discussion

Table 1 shows the results of the OCP of **DHN** with cobalt salts at room temperature, together with those of the polymerization using the copper(II) and oxovanadium(IV)

Table 1. OCP of **DHN** with various catalysts
[Catalyst]/[**DHN**] = 0.1, [**DHN**] = 0.35 M, temp. = room temperature, time = 48 h, O_2 atmosphere)

Entry	Catalyst	Solvent	Yield (%)[a]	M_n x 10^{-3} (M_w/M_n)[b]
1	Cu(acac)$_2$	CH_2Cl_2-MeOH[c]	0	---
2[d]	VO(acac)$_2$	CH_2Cl_2-MeOH[c]	91 (19)	3.3 (4.5)
3	Co(acac)$_2$	CH_2Cl_2-MeOH[c]	0	---
4	Co(OAc)$_2$	CH_2Cl_2-MeOH[c]	0	---
5	**1**	CH_2Cl_2-MeOH[c]	87 (27)	11 (4.5)
6	**1**	CH_2Cl_2-MeOH[e]	72	13 (1.3)
7	**1**	CH_2Cl_2	2	5.1 (1.4)
8	**1**	THF	0	---

[a]MeOH-insoluble part of poly-**DHN’**, in parentheses, the value for the MeOH-insoluble and THF-soluble part is given; [b]determined by SEC in DMF or THF (polystyrene standard); [c]CH_2Cl_2 / MeOH = 7 / 1 (v/v); [d]ref. 11; [e]CH_2Cl_2 / MeOH = 20 / 1 (v/v)

Table 2. Asymmetric OCP of **DHN** with chiral catalysts
([Catalyst]/[**DHN**] = 0.1, [**DHN**] = 0.35 M, solvent = CH_2Cl_2-MeOH (7/1 (v/v)), temp. = room temperature, time = 48 h, O_2 atmosphere)

Entry	Catalyst	Yield (%)[a]	M_n x 10^{-3} (M_w/M_n)[b]	$[\alpha]_D$[c]
1	CuCl-(*S*)Phbox[d]	54	14 (1.2)	−3
2[e]	VO(acac)$_2$-(*S*)Phbox	90 (45)	5.9 (11)	+57
3[e]	VOSO$_4$-(*S*)Phbox	72 (36)	4.7 (19)	+140
4	Co(acac)$_2$-(*S*)Phbox	0	---	---
5	**1**-(*S*)Phbox[f]	31	6.7 (1.2)	−5
6	*RR*-**2**[g]	20	5.5 (1.1)	+165[h]

[a] MeOH-insoluble part of poly-**DHN'**, in parentheses, the value for the MeOH-insoluble and THF-soluble part is given; [b] determined by SEC in DMF or THF (polystyrene standard); [c] in $CHCl_3$; [d] solvent = CH_2Cl_2-MeOH (20/1 (v/v)), temp. = −20°C; [e] ref. 11; [f] temp. = 0°C; [g] solvent = CH_2Cl_2-MeOH (20/1 (v/v)), [DHN] = 0.20 M, time = 0.5 h; [h] $[\phi]_D$ +399

salts. Although the vanadium-catalyst produced a methanol-insoluble polymer in a good yield, the polymerization with Co(acac)$_2$ and Co(OAc)$_2$, as well as Cu(acac)$_2$, in CH_2Cl_2-MeOH resulted in no yield (entries 1–4). In contrast, the salen-cobalt complex, **1**, showed a good activity to afford a polymer in 87% yield (entry 5), the value of which is almost comparable with that of VO(acac)$_2$. These results indicate that the ligand structure significantly affects the catalyst activity, and the cobalt-salen complex can be a good candidate for the asymmetric OCP. The solvent effect was also examined (entries 6–8), and the mixed solvent of CH_2Cl_2 with MeOH showed a result much better than that of the polymerization in CH_2Cl_2 or THF.

The asymmetric OCP with various chiral catalysts in CH_2Cl_2-MeOH was carried out (Table 2). Although the CuCl-(*S*)Phbox catalyst produced a polymer with an $[\alpha]_D$ of −40 during the polymerization in THF [9], its stereocontrol effect was significantly reduced (entry 1). As previously reported, the polymer obtained using VOSO$_4$-(*S*)Phbox showed a specific rotation of +140 (entry 3) [11]. The polymerization with the cobalt salts, such as Co(acac)$_2$ and **1**, in the presence of (*S*)Phbox resulted in no and low yields, in addition, which hardly showed any optical activity (entries 4 and 5). In contrast, the chiral cobalt-salen complex, *RR*-**2**, produced a polymer with an $[\alpha]_D$ of +165 during the polymerization for 0.5 h, indicating that it is quite effective for the stereocontrol during the OCP of **DHN**.

Table 3. AOCP of **DHN** with cobalt-salen complexes
([Co]/[**DHN**] = 0.1, [**DHN**] = 0.20 M, solvent = CH_2Cl_2-MeOH (20/1 (v/v)), temp. = room temperature, O_2 atmosphere)

Entry	Catalyst	Time (h)	Yield (%)[a]	M_n x 10^{-3} (M_w/M_n)[b]	$[\alpha]_D$[c]
1	*SS*-**2**	0.5	22	5.8 (1.1)	−132[d]
2	*RR*-**2**	6	91 (4)	8.6 (4.1)	+31
3	*RR*-**2**	48[e]	58	9.1 (1.6)	+75
4	*RR*-**2**	72[f]	6	5.4 (1.3)	+71
5	*SS*-**2**	24[g]	92 (58)	17 (3.9)	−50
6	*RR*-**3**	24	93 (25)	20 (2.5)	+27

[a] MeOH-insoluble part of poly-**DHN'**, in parentheses, the value for the MeOH-insoluble and THF-soluble part is given; [b] determined by SEC in DMF (polystyrene standard); [c] in $CHCl_3$; [d] $[\phi]_D$ −319; [e] temp. = −20°C; [f] temp. = −40°C; [g] under air

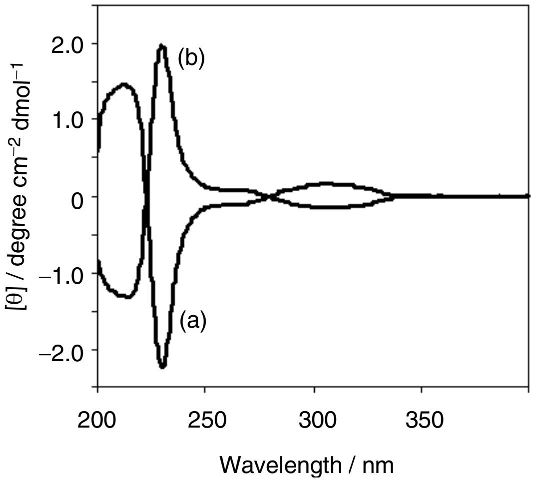
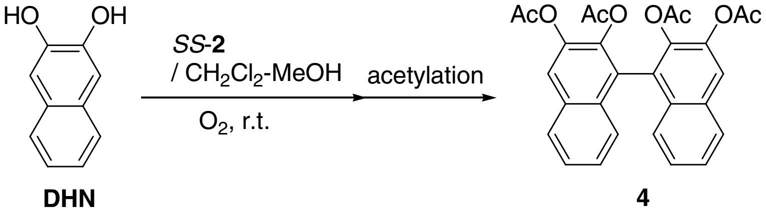


Figure 1. CD spectra of poly-**DHN'** obtained with (a) *RR*-**2** (Table 2, entry 6) and (b) *SS*-**2** (Table 3, entry 1) (in THF)

The polymerization with *SS*-**2** at room temperature for 0.5 h afforded an optically active polymer with the specific rotation of −132, which is opposite in sign to that of the polymer obtained with *RR*-**2** (Table 3, entry 1). Figure 1 shows the CD spectra of these polymers. Mirror image spectral patterns were clearly observed, and the patterns show that the polymer obtained with *RR*-**2** consists of the superior *R*-structure, whereas the *SS*-catalyst produces a polymer rich in the *S*-configuration [9,10].

The OCP with the *SS*-**2** catalyst in CH_2Cl_2-MeOH [20/1 (v/v)] at room temperature for 20 min. under an O_2 atmosphere was also performed, and after acetylation, the dimer product **4** was isolated from the reaction mixture by silica gel column chromatography in an 11% yield with 58% *e.e.* (*S*) (Scheme 4) [9,11]. The configuration of the obtained **4** is consistent with that of the polymer. Accordingly, the polymerization of **DHN** with **2** should proceed with approximately this stereoselectivity at least during the initial stage.

The OCP with **2** for 6 h under O_2 or for 24 h in air produced a polymer in a high yield, however, the methanol-insoluble and THF-soluble fraction showed a much lower $[\alpha]_D$ value than that observed for the polymers obtained by the 0.5 h-polymerization (Table 3, entries 2 and 5). The OCP with *RR*-**2** at a lower temperature, such as −20 and −40°C, for 48 and 72 h also afforded a polymer with a specific rotation around +70 (entries 3 and 4). These results suggest that the stereocontrol ability of the cobalt-catalyst may be significantly reduced with polymerization time.



Scheme 4.

Table 4. AOCP of **DHN** with *RR*-**2**
([Co]/[**DHN**] = 0.1, [**DHN**] = 0.20 M, solvent = CH_2Cl_2-MeOH (20/1 (v/v)), temp. = room temperature, O_2 atmosphere)

Entry	Time (h)	Yield (%)[a]	M_n x 10^{-3} (M_w/M_n)[b]	$[\alpha]_D$[c]
1	0.5	28	6.6 (1.1)	+172
2	1	78	12 (1.5)	+130
3	3	82 (14)	15 (2.7)	+69
4	6	87 (8)	11 (2.9)	+11
5	24	93 (3)	8.6 (3.1)	+9

[a]MeOH-insoluble part of poly-**DHN'**, in parentheses, the value for the MeOH-insoluble and THF-soluble part is given; [b]determined by SEC in DMF (polystyrene standard); [c]in $CHCl_3$

The OCP with *RR*-**2** at room temperature was carried out by removing small portions of the reaction mixture as a function of the reaction time. Table 4 lists the results of each portion. After 0.5 h, the polymer was obtained in a 28% yield with a specific rotation of +172. The $[\alpha]_D$ values of the obtained polymer decreased with the degree of the polymerization, and, after 24 h, the polymerization resulted in a 93% yield with a specific rotation of the THF-soluble part of +9, while the yield of the THF-insoluble part increased with the polymerization.

Figure 2 depicts the CD spectra of the obtained polymers. The absorption intensity around 230 and 310 nm showed a good relation to the $[\alpha]_D$ values. These results support the fact that the stereoselectivity of the cobalt complex significantly decreased, probably due to the structure of the active catalyst species that may change during the polymerization, although such details are not clear at present.

The methanol-insoluble fraction was only slightly obtained by the polymerization with *RR*-**3** at room temperature for 30 min, while the 24 h-polymerization produced a polymer in a 93% yield with a low optical rotation power (Table 3, entry 6).

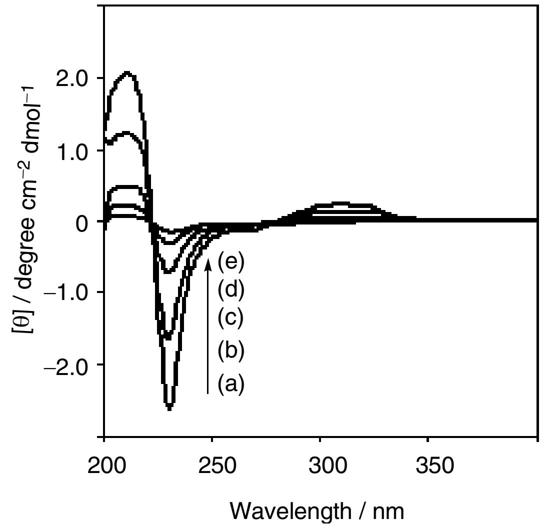


Figure 2. CD spectra of poly-**DHN'** obtained with *RR*-**2** (a) for 0.5 h (Table 4, entry 1), (b) for 1 h (entry 2), (c) for 3 h (entry 3), (d) for 6 h (entry 4), and (e) for 24 h (entry 5) (in THF)

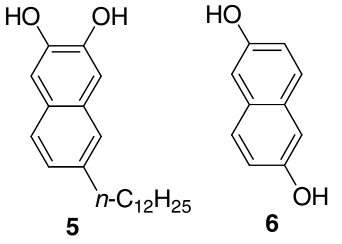
Table 5. OCP of **5** and **6**
([Catalyst]/[monomer] = 0.1, [monomer] = 0.20 M, solvent = CH_2Cl_2-MeOH (20/1 (v/v)), temp. = room temperature, time = 24 h, O_2 atmosphere)

Entry	Monomer	Catalyst	Yield (%)[a]	M_n x 10^{-3} (M_w/M_n)[b]	[α]$_D$[c]
1[d]	**5**	VOSO$_4$-(*S*)Phbox[e,f]	94	8.0 (2.0)	+60[g]
2	**5**	**1**[e]	81	5.8 (1.7)	---
3	**5**	*RR*-**2**[h]	79	4.8 (1.4)	+79[i]
4	**6**	VOSO$_4$-(*R*)Phbox[e,f]	0	---	---
5	**6**	**1**	91 (6)[j]	6.5 (1.2)	---
6	**6**	*SS*-**2**	99 (7)[k]	5.8 (1.1)	0

[a]MeOH-insoluble part of the acetylated polymer, in parentheses, the value for the MeOH-insoluble and THF-soluble part is given; [b]determined by SEC in DMF (polystyrene standard); [c]in $CHCl_3$; [d]ref. 18; [e]time = 48 h; [f]CH_2Cl_2-MeOH = 7/1 (v/v); [g][ϕ]$_D$ +246; [h]time = 0.5 h; [i][ϕ]$_D$ +335; [j]*m* : *r* = 58 : 42; [k]*m* : *r* = 55 : 45

Therefore, the salen-ligand structure significantly influenced the catalyst activity and stereoselectivity.

The OCP of the other dihydroxynaphthyl monomers, such as 6-dodecyl-2,3-dihydroxynaphthalene **5** [18,19] and 2,6-dihydroxynaphthalene **6** [20–22] (Scheme 5), with the cobalt-salen complexes at room temperature was examined (Table 5). The results of the polymerization with the VOSO$_4$-Phbox catalyst [11] are also listed in the table for comparison. Every polymerization with the cobalt complex resulted in a good yield. Poly-**5'** obtained with *RR*-**2** for 0.5 h, followed by acetylation of the hydroxyl groups, showed a specific rotation of +79 (entry 3), whose value is roughly consistent with the optical activities of poly-**DHN'**, when the molar rotation, [ϕ]$_D$ (+335 for poly-**5'**), are compared. The value for the polymer obtained with the oxovanadium catalyst was +246 (entry 1). Accordingly, regarding the stereocontrol during the OCP of **5**, the cobalt-catalyst should be more effective than the vanadium one, and the substituent at the 6-position of **DHN** has only a slight affect. The VOSO$_4$-Phbox catalyst did not afford any methanol-insoluble polymer during the polymerization of **6** in contrast to the polymerization with the cobalt-salen complexes (entries 4-6). However, the polymerization with the latter catalyst systems gave an almost atactic (*meso* : *rasemo* ratio) and optically inactive polymer [20]. Although the polymers containing a large amount of THF-insoluble fraction, they showed a quite resemble IR spectral pattern to that of the reported poly(2,6-dihydroxy-1,5-naphthylene) [22].



Scheme 5.

Conclusions

A novel catalyst system for the oxidative coupling polymerization, the cobalt-salen complexes, was developed. The enantioselectivity during the polymerization with the chiral salen complexes was significantly affected by the structure of the monomer and polymerization conditions, such as the polymerization time, and the result nearly reached that for the previously reported $VOSO_4$-Phbox catalyst, as well as the CuCl-Phbox system.

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19. **5**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7.0 Hz, CH_3), 1.27-1.37 (m, 18H, $-CH_2-$), 1.65-1.71 (m, 2H, $-CH_2-$), 2.71 (t, 2H, J = 8.0 Hz, $-CH_2-$), 5.43 (s, 1H, -OH), 5.49 (s, 1H, -OH), 7.17-7.57 (m, 5H, aromatic). IR (KBr, cm^{-1}): 3268, 2913, 2840, 1527, 1265, 1112, 860. MS (EI) m/z 328 ($[M]^+$) M.P.: 135-136°C. Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H: 9.82. Found: C, 80.61; H: 10.05
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