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Copper(I) catalyzed asymmetric oxidative cross-coupling copolymerization leading to alternating copolymers

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Abstract

The asymmetric oxidative coupling copolymerization of 6,6′-dihydroxy-2,2′-binaphthalene and dihexyl 6,6′-dihydroxy-2,2′-binaphthalene-7,7′-dicarboxylate with the copper(I)-diamine catalysts under an O_2 atmosphere was carried out. The copolymerization using the CuCl-(*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) catalyst [(*S*)Phbox], afforded a polymer with the high cross-coupling selectivity of 93%, that is, a copolymer with a mainly alternating structure, in 80% yield. The number-average molecular weight of the methanol-ethylacetate (1/3 v/v)-insoluble part of the copolymer was 1.1×10^4. To estimate the enantioselectivity with respect to the cross-coupling linkage in the obtained copolymer, the model asymmetric oxidative cross-coupling reaction with CuCl-(*S*)Phbox was also examined, and the products showed a 96% cross-coupling selectivity and enantioselectivity of 43% ee (*S*).

Keywords: Copolymerization; Cross-coupling; Asymmetric oxidative coupling

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1. Introduction

Optically active 1,1′-bi-2-naphthol and its derivatives are of great synthetic interest, as they have been extensively utilized in asymmetric synthesis, catalyses, and resolutions, based on their axially dissymmetric structure [1,2]. The asymmetric oxidative coupling reaction is one of the most facile routes for them and has been attained by treating naphthols with various chiral metal catalysts, such as Cu(I), Ru(II), and V(IV) [3–7] to produce a symmetrical binaphthol skeleton. In marked contrast, the catalytic selective cross-coupling between two different types of naphthols affording an unsymmetrical molecule has rarely been available, although several reactions using a stoichiometric or excess amount of a metal complex were reported [8–12].

We recently found that the oxidative cross-coupling reaction between 2-naphthol derivatives and 3-hydroxy-2-naphthoates in the presence of a catalytic amount of the CuCl-2,2′-(*S*)-isopropylidenebis(4-phenyl-2-oxazoline) [(*S*)Phbox] complex proceeded in a highly cross-coupling selective manner up to 99.7% [13]. Furthermore, we also reported that the polymerization of the unsymmetric 6,6′-bi-2-naphthol derivative, methyl 6,6′-dihydroxy-2,2′-binaphthalene-7-carboxylate, with the CuCl-(*S*)Phbox catalyst afforded a polymer with the high cross-coupling selectivity of 96% [14].

The polymers comprised of the continuous 1,1′-bi-2-naphthol units are unique because the rigid C_2-symmetric framework can control the polymer conformation and functions [1]. Therefore, their synthesis by regulating the main chain structure is quite attractive [15–18]. The controlled copolymerization is a useful method for constructing a more complicated and precise polymer structure. However, there is no report on the alternating sequence control during the oxidative coupling copolymerization (OCCP), as far as we know, although the synthesis of random phenolic copolymers is known [19,20]. The developed cross-coupling catalyst system, the complex of copper(I) with bisoxazoline, for the oxidative coupling reaction will work for the controlled synthesis of a copolymer bearing an alternating main chain structure.

In this study, the OCCP of 6,6′-dihydroxy-2,2′-binaphthalene **1** and dihexyl 6,6′-dihydroxy-2,2′-binaphthalene-7,7′-dicarboxylate **2** using various copper(I)-diamine catalysts was carried out (Scheme 1), and the cross-coupling selectivity, that is, the alternating copolymerizability, and enantioselectivity of the cross-coupling reaction were examined.

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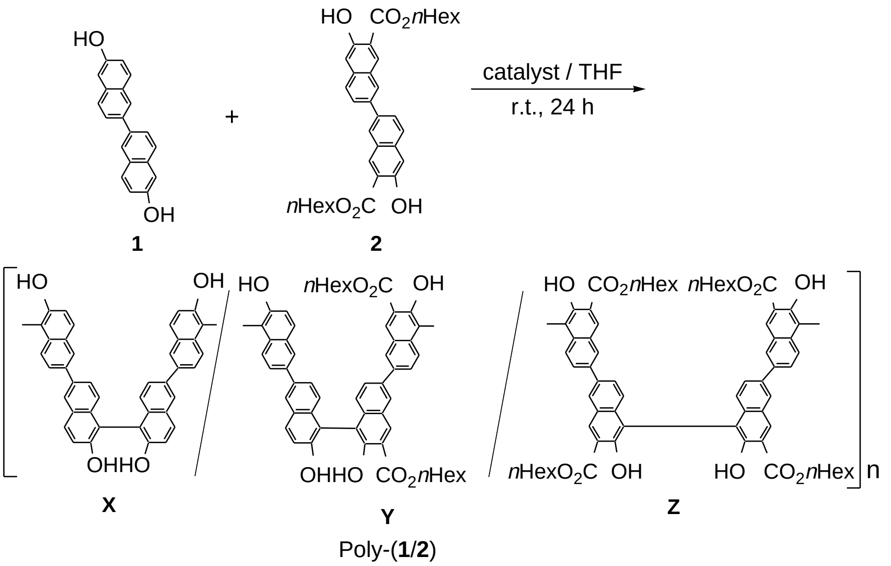


Scheme 1. OCCP of **1** and **2**.

2. Experimental section

2.1. Measurements

^{1}H NMR spectra were measured on a Varian Unity Inova (500 MHz for ^{1}H) or mercury 200 (200 MHz for ^{1}H) spectrometer. The infrared (IR) spectra were recorded on a Horiba FT-720 spectrometer. The mass (MS) spectra were obtained using a JOEL AX505H. The optical rotation was measured on a Jasco P-1010 polarimeter at 25 °C. The circular dichroism (CD) spectra were obtained with a Jasco J-720WI apparatus. The size exclusion chromatography (SEC) analyses were performed on a Jasco PU-2080 plus equipped with a Jasco UV-2075 plus UV detector with KF-806F and KF-803F columns connected in series (eluent = THF, temperature = 25 °C, flow rate = 1.0 mL/min). Calibration was carried out with standard polystyrenes. The molecular weight was also determined using a DP-8020 (Tosoh) equipped with a UV-8020 (Tosoh) and a Wyatt Technology DAWN-DSP multi-angle light scattering (MALS) detectors with Shodex KF-802 and KF-806L × 2 columns connected in series, and tetrahydrofuran (THF) was used as the eluent at 40 °C. The high-performance-liquid-chromatography (HPLC) analyses were performed on a Jasco 986-PU chromatograph equipped with UV (Jasco 970-UV) and polarimetric (Jasco OR-990) detectors at room temperature.

2.2. Materials

Dry THF (Kanto) was used for the oxidative coupling reactions. The optically active diamines, (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)PMP] (TCI) and (−)-sparteine [(−)Sp] (Sigma), were dried over CaH$_2$ and then distilled under reduced pressure. The bisoxazolines, (*S*)Phbox and (*R*)-(+)-2,2′-isopropylidenebis(4-benzyl-2-oxazoline) [(*R*)Bnbox] (Aldrich) (Scheme 2), were used as received. The achiral copper complex, di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper(II)] chloride [CuCl(OH)-TMEDA], was purchased from TCI.

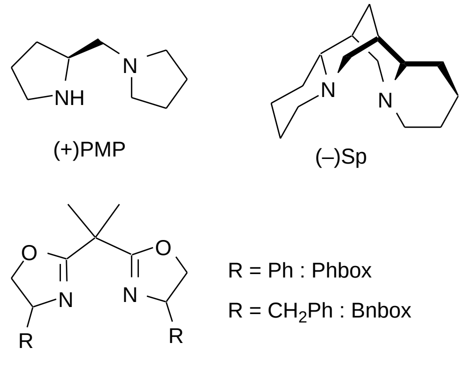
Monomer **1** and, Monomer **2** were synthesized from 6-bromo-2-naphthol and hexyl 7-bromo-3-hydroxy-2-naphthoate, respectively, by reaction with hexamethylditin and catalytic Pd(PPh$_3$)$_4$ [21].

1. ^{1}H NMR (DMSO-d_6): δ 7.11–7.15 (m, 4H, aromatic), 7.81–7.88 (m, 6H, aromatic), 8.18 (s, 2H, aromatic), 9.79 (br, 2H, –OH). IR (KBr, cm^{-1}): 3305, 1633, 1604, 1517, 1473, 1436, 1292, 1268, 1251, 1209. Mass (FAB): *m/z* 286 [M]$^+$.

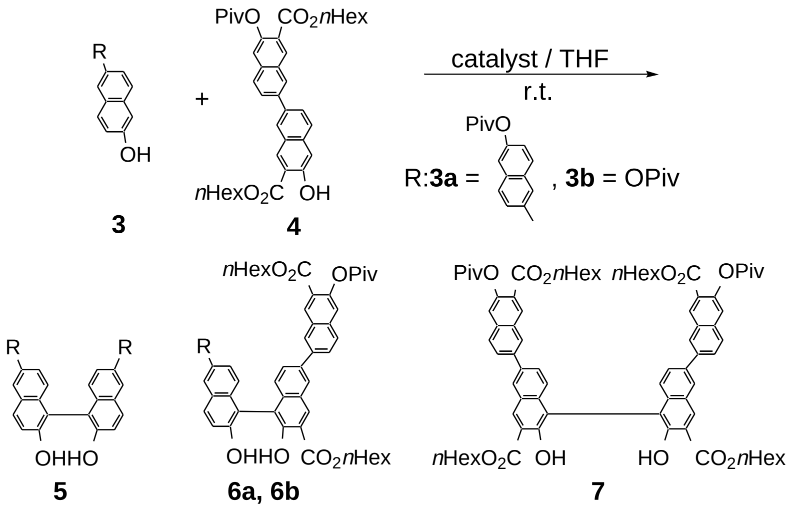
Mono-trimethylacetylated compounds, **3a** and **4** were prepared from **1** and **2** by esterification with trimethylacetyl chloride (pivaloyl chloride, PivCl) and Et$_3$N.

3a. ^{1}H NMR (DMSO-d_6): δ 1.35 (s, 9H, –CH$_3$), 7.11 (s, 1H, aromatic), 7.26–7.32 (d, J = 10.4 Hz, 2H, aromatic), 7.68 (s, 1H, aromatic), 7.79–7.90 (m, 3H, aromatic), 8.01–8.08 (m, 3H, aromatic), 8.24 (s, 1H, aromatic), 8.35 (s, 1H, aromatic), 9.80 (br, 1H, –OH). IR (KBr, cm^{-1}): 3459, 2975, 1733, 1600, 1469, 1396, 1288, 1207, 1157, 865. Mass (FAB): *m/z* 370 [M]$^+$.

4. ^{1}H NMR (CDCl$_3$): δ 0.88–0.97 (m, 6H, –CH$_3$), 1.38–1.45 (m, 21H, –CH$_2$–, –CH$_3$), 1.76–1.91 (m, 4H, –CH$_2$–), 4.30–4.39 (t, J = 6.8 Hz, 2H, –OCH$_2$–), 4.42–4.48 (t, J = 6.6 Hz, 2H, –OCH$_2$–), 7.37 (s, 1H, aromatic), 7.53 (s, 1H, aromatic), 7.80–



Scheme 2. Chiral ligands.



Scheme 3. Model reaction of **3** and **4**.

7.94 (m, 4H, aromatic), 8.14 (s, 1H, aromatic), 8.21 (s, 1H, aromatic), 8.59–8.60 (d, $J=2.2$ Hz, 2H, aromatic), 10.62 (s, 1H, –OH). IR (KBr, cm^{-1}): 3234, 2960, 2933, 1743, 1725, 1681, 1313, 1240, 1230, 1110. Mass (FAB): *m/z* 627 [M]$^+$.

2.3. Polymerization

Monomers **1** (0.047 g, 0.166 mmol) and **2** (0.09 g, 0.166 mmol) were added to a mixture of CuCl and a diamine in THF ([**1**] = 0.065 M, [Cu(I)]/[diamine]/[**1**]/[**2**] = 0.2/0.25/0.5/0.5). The mixture was stirred at room temperature under an O_2 atmosphere. After stirring for 24 h, the polymer was isolated as the methanol-ethyl acetate-1 N HCl (1/3/0.2 v/v/v)-insoluble fraction by centrifugation and drying *in vacuo*.

2.4. Cross-coupling reaction

A mixture of CuCl, diamine, and THF was stirred for 30 min under an O_2 atmosphere. To this mixture, **3** and **4** were added ([CuCl]/[diamine]/[**3**]/[**4**] = 0.2/0.25/0.5/0.5, [**3**] = 0.065 M). The reaction mixture was stirred at room temperature for 3 h, diluted with $CHCl_3$, and washed with 1 N HCl. The organic layer was then dried over $MgSO_4$. Filtration and concentration afforded the crude products. The cross-coupling compound was isolated by silica gel column chromatography (hexane/ethyl acetate = 1/2) (Scheme 3).

6a. ^{1}H NMR ($CDCl_3$): δ 0.86–0.99 (m, 6H, –CH_3), 1.34–1.49 (m, 30H, –CH_2–, –CH_3), 1.75–1.96 (m, 4H, –CH_2–), 4.29–4.36 (t, $J=7.0$ Hz, 2H, –OCH_2–), 4.48–4.54 (t, $J=6.8$ Hz, 2H, –OCH_2–), 5.09 (s, 1H, –OH), 7.19–8.3 (m, 18H, aromatic), 8.58 (s, 1H, aromatic), 8.85 (s, 1H, aromatic), 11.08 (s, 1H, –OH). IR (KBr, cm^{-1}): 3459, 2958, 2929, 1751, 1725, 1675, 1276, 1195, 1145, 1106. Mass (FAB): *m/z* 995 [M]$^+$.

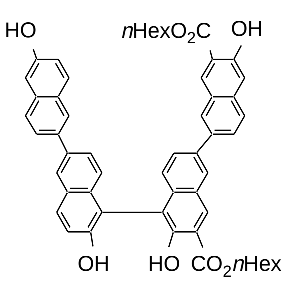
6b. ^{1}H NMR ($CDCl_3$): δ 0.91–0.98 (m, 6H, –CH_3), 1.38–1.48 (m, 30H, –CH_2–, –CH_3), 1.76–1.95 (m, 4H, –CH_2–), 4.29–4.36 (t, $J=6.8$ Hz, 2H, –OCH_2–), 4.46–4.53 (t, $J=6.6$ Hz, 2H, –OCH_2–), 5.03 (s, 1H, –OH), 6.95–7.92 (m, 10H, aromatic), 8.19 (s, 1H, aromatic), 8.27 (s, 1H, aromatic), 8.59 (s, 1H, aromatic), 8.82 (s, 1H, aromatic), 11.04 (s, 1H, –OH). IR (KBr, cm^{-1}): 3438, 2958, 2931, 1756, 1720, 1671, 1280, 1226, 1149, 1110. Mass (FAB): *m/z* 869 [M]$^+$.

The model dimer **8** was prepared from **6a** by hydrolysis of the pivaloyl groups with potassium hydroxide in THF, followed by esterification with 1-hexanol (Scheme 4).

8 ^{1}H NMR ($CDCl_3$/DMSO-d_6 v/v = 1/1): δ 0.89–0.96 (m, 6H, –CH_3), 1.25–1.57 (m, 12H, –CH_2–), 1.81–1.93 (m, 4H, –CH_2–), 4.41–4.44 (t, $J=6.5$ Hz, 2H, –OCH_2–), 4.48–4.50 (t, $J=6.5$ Hz, 2H, –OCH_2–), 7.09–7.42 (m, 5H, aromatic), 7.61–8.02 (m, 10H, aromatic), 8.17 (s, 1H, aromatic), 8.23 (s, 1H, aromatic), 8.38 (s, 1H, aromatic), 8.57 (s, 1H, aromatic), 8.79 (s, 1H, aromatic), 9.03 (s, 1H, –OH), 9.38 (s, 1H, –OH),10.38 (s, 1H, –OH), 10.63 (s, 1H, –OH). IR (KBr, cm^{-1}): 3372, 2954, 2927, 2856, 1677, 1508, 1346, 1280, 1201, 1157. Mass (FAB): *m/z* 827 [M]$^+$.

3. Results and discussion

The results of the OCCP between two differently substituted 6,6′-dihydroxy-2,2′-binaphthalene derivatives, **1** and **2** (1: 1), in the presence of various copper catalysts at room temperature for 24 h are listed in Table 1. The copolymerization with the CuCl(OH)-TMEDA catalyst afforded poly-(**1/2**) as the methanol-ethyl acetate-1 N HCl (1/3/0.2, v/v/v)-insoluble fraction in 40% yield with a number average molecular weight (M_n) of 6.9×10^3, and the unit ratio in the copolymer was estimated



8

Scheme 4. Model dimer **8**.

Table 1
Asymmetric oxidative coupling copolymerizaion between **1** and **2** at room temperature for 24 h

Entry	Catalyst	Yield (%)[a]	M_n ($\times 10^3$) (M_w/M_n)[b]	$[\alpha]_D^{25}$[c]	Coupling ratio	
					X:Y:Z[d]	**1**:**2**[e]
1	CuCl(OH)-TMEDA	40	6.9(1.6)	–	23:75:2	56.2:43.8
2	CuCl-(+)PMP	23	2.8 (1.8)	+6	87:13:0	84.4: 15.6
3	CuCl-(−)Sp	15	3.7(1.8)	0	86:14:0	83.6:16.4
4	CuCl-(*S*)Phbox	80	11.0(1.9)	+56	3:93:4	49.8:50.2
5	CuCl-(*R*)Bnbox	51	7.4(1.4)	−71	4:89:7	51.3:48.7
6[f]	CuCl-(*S*)Phbox	60[h]	3.5(1.3)	+111	12:87:1	53.5:46.5
7[g]	CuCl-(*S*)Phbox	81	13.4(3.3)	+64	39:61:<1	63.3:36.7

[a] Methanol-ethyl acetate-1 N HCl (1/3/0.2 v/v/v)-insoluble part.
[b] Determined by SEC in THF (polystyrene standard).
[c] In THF.
[d] Estimated by ^{1}H NMR analysis.
[e] Estimated by ^{1}H NMR analysis of acetylated polymer.
[f] [**1**]/[**2**]=2/1, time=0.5 h.
[g] Methanol-1 N HCl (1/9 v/v)-insoluble part.
[h] [**1**]/[**2**]=2/1, time=24 h.

from the ^{1}H NMR analysis of the acetylated poly-(**1**/**2**) to be **1**:**2**=56:44 (entry 1). In contrast, the chiral conventional diamine ligands, such as (+)PMP and (−)Sp, gave a product in low yields with an M_n of 3.7×10^3 or less (entries 2 and 3), and showed the unit ratio of **1**:**2** to be around 84:16. The monomer **1** preferentially reacted in these polymerization systems. As is the case with the (*S*)Phbox ligand, in contrast, poly-(**1**/**2**) was obtained in a good yield with an M_n value of 1.1×10^4. Its unit ratio was evaluated to be 50:50 (entry 4). The ^{1}H NMR spectrum of the copolymer obtained with (*S*)Phbox is depicted in Fig. 1, and the peaks are assigned as shown in the figure. The ligand structure significantly affected the monomer reactivity ratio during the OCCP.

In the copolymer, three different binaphthol units can exist (Scheme 1). To estimate the homo- (X and Z) and cross-coupling (Y) ratio, the model compound **8** having the cross-coupling unit Y and the model polymers, poly-**1** and poly-**2**, which consist of only the homo-coupling unit X and Z, were synthesized. The latter homo-polymers were prepared through the polymerization of **1** or **2** as shown in Scheme 5 [poly-**1**:91% yield (MeOH-AcOEt-1 N HCl (1/1/0.2 v/v/v)-insoluble part), $M_n=3.2\times 10^3$, $M_w/M_n=1.4$; poly-**2**: 92% yield (MeOH–AcOEt–1 N HCl (3/1/0.4 v/v/v)-insoluble part), $M_n=9.2\times 10^3$, $M_w/M_n=2.0$]. The ^{1}H NMR spectra of the hydroxyl protons of these model compounds are shown in Fig. 2(A–C). The internal and terminal hydroxyl protons with different chemical shifts appeared as shown in the figure. Fig. 2(D) shows the ^{1}H NMR spectrum of the same region of the copolymer obtained using the (*R*)Bnbox catalyst (Table 1, entry 5). Its spectral pattern was in good agreement with those of the model compound **8** and polymers, and each observed peak was assigned as shown in the figure. Thus, the cross-coupling selectivity (X:Y:Z) calculated from the ^{1}H NMR analysis is also summarized in Table 1.

During the polymerization with (+)PMP and (−)Sp, the homo-coupling reaction predominantly proceeded to give a polymer with an X-unit of 86–87%, whereas the reaction with the bisoxazoline ligands, such as (*S*)Phbox and (*R*)Bnbox, preferentially formed a cross-coupling bond with a high selectivity, Y of 93 and 89%, respectively. It is postulated that the ester moiety may act as an accepter in the coupling reactions with the CuCl–bisoxazoline catalysts because of its electron-deficient character, while the one-electron oxidation should be predominantly promoted on the 2-naphthol part to give a radical intermediate, and then, the cross-coupling reaction between these two naphthols may selectively occur [12,13]. The molecular weight calculated from the ^{1}H NMR

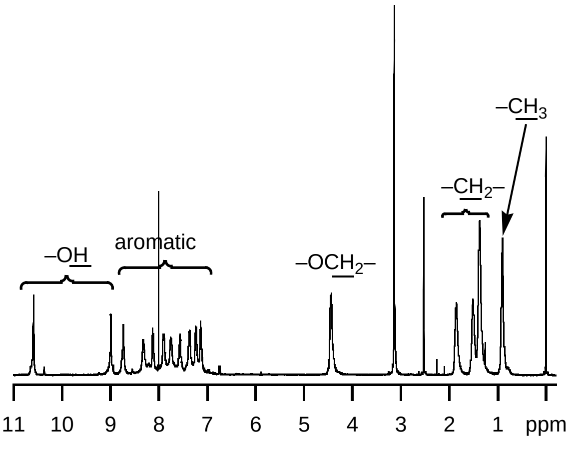
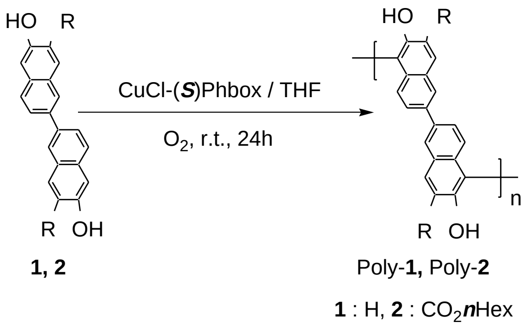


Fig. 1. ^{1}H NMR spectrum of poly-(**1**/**2**) obtained with (*S*)Phbox (Table 1, entry 4) (in $CDCl_3$/DMSO-d_6, (1/1 v/v), 50 °C).



Scheme 5. Oxidative homo-coupling polymerization of **1** or **2**.

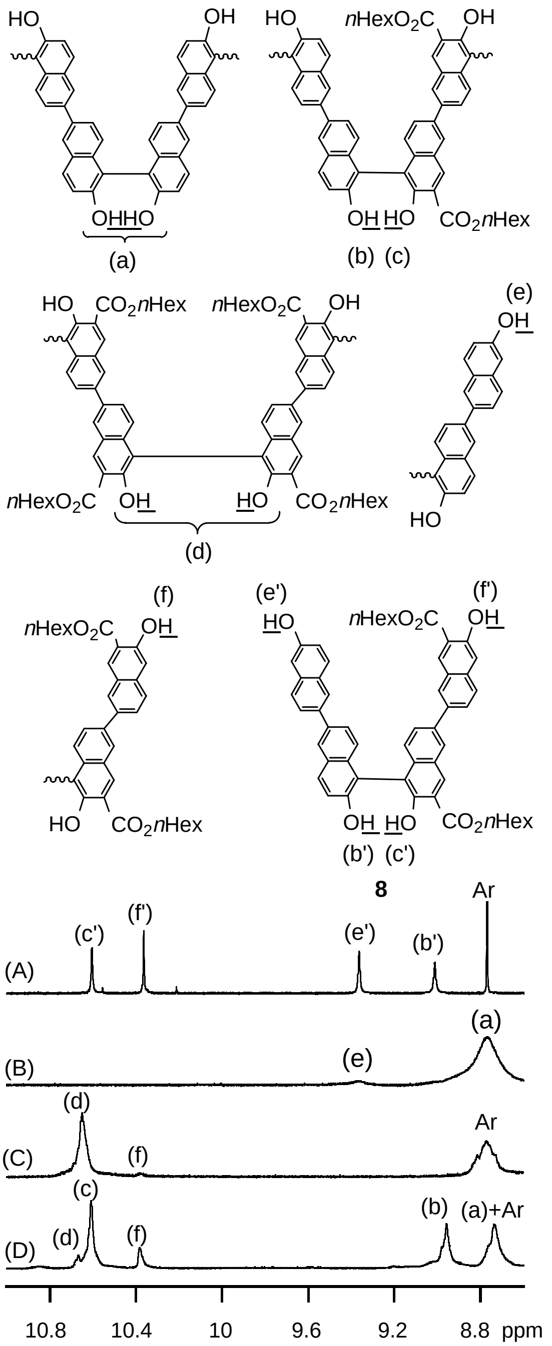


Fig. 2. ^{1}H NMR spectra of hydroxy protons of (A) model compound **8**, (B) poly-**1**, (C) poly-**2**, and (D) poly-(**1/2**) obtained with the CuCl-(*S*)Bnbox catalyst (Table 1, entry 5) (in CDCl$_3$/DMSO-d_6, (1/1 v/v), 50 °C).

absorption intensities of the terminal protons was 10.7×10^3 for the polymer obtained with (*S*)Phbox (entry 4), which is quite identical with that estimated by the SEC analyses ($M_n=10.0\times10^4$ determined by MALS in THF).

The OCCP between **1** and **2** in the 2:1 feed with the CuCl-(*S*)Phbox catalyst was also conducted (entries 6 and 7). These results indicate that, during the early stage of the polymerization, the cross-coupling reaction preferentially occurred, and then the homo-coupling unit *X* was constructed from the residual monomer. Assuming that the copolymerization (**1**:**2**=2:1 in feed) proceeds with the coupling selectivity, *X*:*Y*:*Z*=3:93:4, followed by the homo-coupling unit formation of the residual monomer **1** to produce a polymer with an M_n value of 1.3×10^4, the copolymer will show a cross-coupling selectivity (*X*:*Z*) of approximately 36:64:<1. The obtained copolymer showed a selectivity of 39:61:<1, which is quite similar to the ideal value.

The CD spectra of the obtained poly-(**1/2**) are shown in Fig. 3. The spectral patterns for the copolymers prepared with (+)PMP and (−)Sp were quite different from those obtained using the bisoxazolines due to the fact that the polymers have different unit ratios from one another. The absorption intensities of the latter copolymers around 260 and 290 nm showed a good relation to the $[\alpha]_D$ values and the spectral patterns indicate that the copolymer obtained with the CuCl-(*S*)Phbox catalyst is rich in the *S*-configuration [22,23].

The OCCP between **2** and the commercially available monomer, 2,6-dihydroxynaphthalene **9** (1:1), with the CuCl-diamine catalysts was also conducted (Scheme 6), and results are listed in Table 2. The cross-coupling selectivity of the obtained copolymer was estimated from the absorption intensity ratio of the hydroxyl protons in the ^{1}H NMR spectrum and the M_n value determined by SEC, because some protons with almost the same chemical shifts appeared in the ^{1}H NMR analysis. The polymerization with the CuCl(OH)-TMEDA afforded a polymer with a molecular weight (M_n) of 4.0×10^3 in a low yield, and the homo-coupling reaction generating an *X*-unit predominantly occurred (entry 1). On the other hand, the polymerization using the CuCl-(*S*)Phbox catalyst gave poly-(**9/2**) in a 79% yield, whose THF soluble part showed an M_n of 7.2×10^3 (entry 2). Although the polymerization also proceeded in a cross-coupling selective manner, poly-(**9/2**) showed a lower selectivity, *Y* of 74%, and unit ratio of **9**:**2**=46:54, than those for poly-(**1/2**) obtained using the CuCl-(*S*)Phbox. The copolymerization with the (*R*)Bnbox ligand also resulted in a much lower *Y*-selectivity. These results indicate that the cross-coupling selectivity during the OCCP significantly affected by the monomer structure.

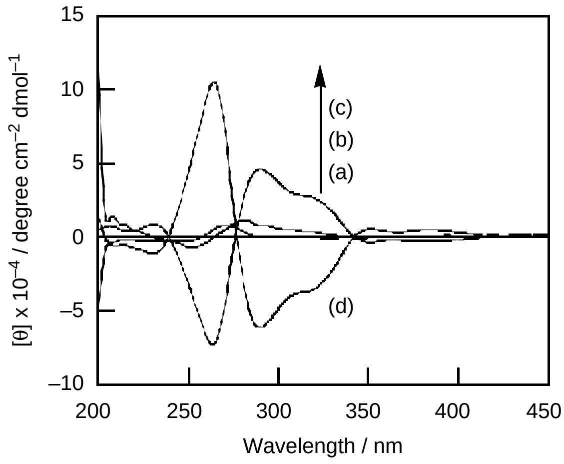
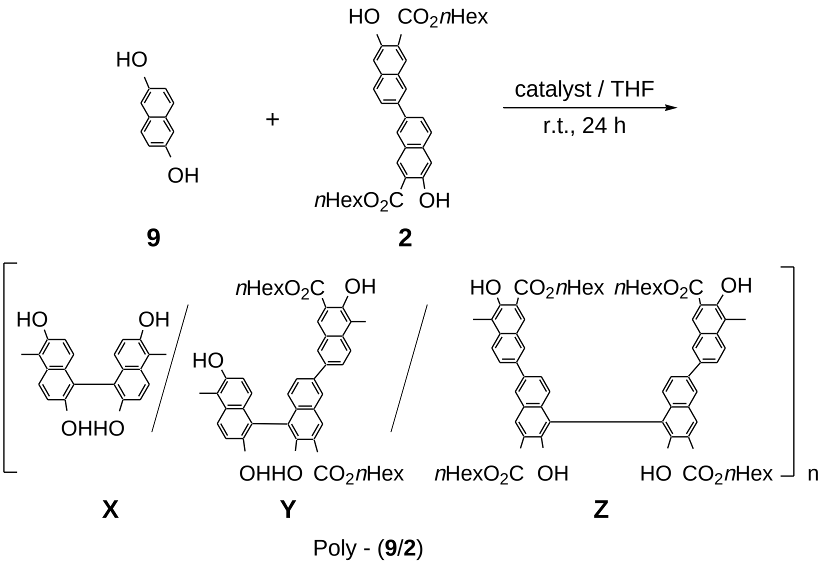


Fig. 3. CD spectra of poly-(**1/2**) obtained with (a) (+)PMP (Table 1, entry 2), (b) (−)Sp (entry 3), (c) (*S*)Phbox (entry 4), and (d) (*R*)Bnbox (entry 5) (monomer unit, in THF).



Scheme 6. OCCP of **9** and **2**.

Table 2
Asymmetric Oxidative Coupling Copolymerizaion between **9** and **2** at Room Temperature for 24 h

Entry	Catalyst	Yield (%)[a]	M_n ($\times 10^3$)(M_w/M_n)[b]	$[\alpha]_D^{25}$[c]	Coupling ratio[d]	
					X:*Y*:*Z*	**9**:**2**
1	CuCl(OH)-TMEDA	18	4.0 (1.5)	–	57:23:20	62.6:37.4
2	CuCl-(*S*)Phbox	79 (58)[e]	7.2 (2.1)	−53	8:74:18	45.9:54.1
3	CuCl-(*R*)Bnbox	55	4.0 (1.4)	−25	25:42:33	41.7:58.3

[a] Methanol-ethyl acetate-1 N HCl (1/3/0.2 v/v/v)-insoluble part.

[b] Determined by SEC in THF (polystyrene standard).

[c] In THF.

[d] Estimated by ^{1}H NMR analysis.

[e] THF-soluble part of the polymer.

To estimate the stereoselectivity during the OCCP, a model reaction, that is the oxidative coupling of **3** and **4** with TMEDA, (*S*)Phbox, and (*R*)Bnbox, was performed (Table 3). In every catalyst system, the cross-coupling reaction preferentially took place. Particularly, the cross-coupling reaction with (*S*)Phbox proceeded with a good yield in a highly selective manner $Y = 96\%$ (entry 2), whose value was almost identical to that observed for the copolymerization. The cross-coupling compound **6a** obtained with (*S*)Phbox and (*R*)Bnbox showed enantioselectivities of 43% ee (*S*) and 57% ee (*R*), respectively. The model reaction of **3b** and **4** with the CuCl-(*S*)Phbox catalyst was also carried out (entry 4). The cross-coupling selectivity was 89%, the value of which is higher than that observed for the copolymer poly-(**9**/**2**). This may be due to the substituent effect of the pivaloyl group on **3b**.

Fig. 4 shows the CD spectra of the obtained model compounds in THF. The spectral patterns quite closely resemble those of polymers mainly having the cross-coupling unit *Y*.

Table 3
Asymmetric Oxidative Cross-Coupling Reaction between **3** and **4**

Entry	**3**	Catalyst	Time (h)	Coupling ratio *X*:*Y*:*Z*[a]	Cross-coupling product *Y*	
					Yield (%)[b]	ee (%)[c]
1	**3a**	CuCl(OH)-TMEDA	5	25:75:<1	54	–
2	**3a**	CuCl-(*S*)Phbox	3	<1:96:4	90	43(*S*)
3	**3a**	CuCl-(*R*)Bnbox	5	7:84:9	65	57 (*R*)
4	**3b**	CuCl-(*S*)Phbox	3	3:89:8	75	18 (*S*)

[a] Ratio of isolated yields.

[b] Isolated yield.

[c] Determined by HPLC analysis (Chiralpak AD or AS).

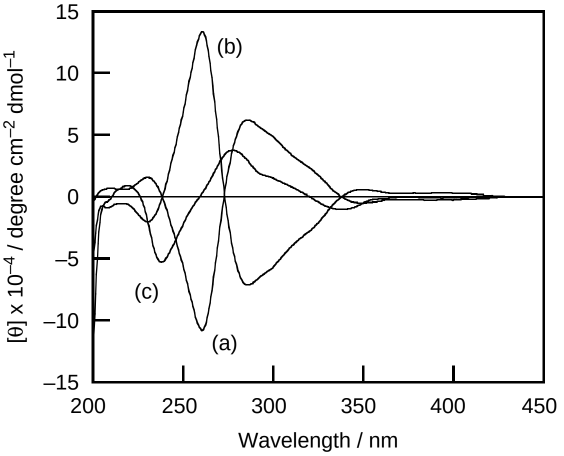


Fig. 4. CD spectra of the cross-coupling compound **6a** obtained with (a) (*S*)Phbox (Table 3, entry 2), (b) (*R*)Bnbox (entry 3), and (c) the cross-coupling compound **6b** obtained with (*S*)Phbox (entry 4) (in THF).

4. Conclusions

The oxidative coupling copolymerization of two differently substituted 6,6′-dihydroxy-2,2′-binaphthalene derivatives with the CuCl-(*S*)Phbox catalyst at room temperature proceeded in a highly cross-coupling selective manner (93%) to produce an alternating-type copolymer. The enantioselectivity of the cross-coupling unit was estimated to be 43% ee (*S*), based on the result of the model coupling reaction.

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