Catalytic Oxidative Cross-Coupling Polymerization of Unsymmetric Binaphthol Derivatives Using Cu(I)-Bisoxazoline Complexes

Tomohisa TEMMA, Yusuke TAKAHASHI, Yasuhiro YOSHII, and Shigeki HABAUE[†]

Department of Chemistry and Chemical Engineering, Yamagata University, Yonezawa 992-8510, Japan

ABSTRACT: The asymmetric oxidative coupling polymerization of 6,6′-dihydroxy-2,2′-binaphthalene derivatives or methyl 3,7-dihydroxy-2-naphthoate, having an unsymmetric 2-naphthol structure, with copper catalysts under an O_2 atmosphere was carried out. The polymerization using the CuCl-(S)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) catalyst afforded a polymer with a high cross-coupling selectivity of up to 99%, which showed a number average molecular weight of $5.0–9.1 \times 10^3$. To estimate the stereoselectivity during the polymerization, a model reaction was examined which resulted in good to high cross-coupling selectivities, while the enantioselectivities were low. The polymer composed of a homo-coupling unit showed a photoluminescence spectral pattern similar to that of the model compound. In contrast, a very different emission, which may be due to the excimer, from that of the model was observed for the polymer consisted of the cross-coupling unit.   [doi:10.1295/polymj.PJ2006183]
    KEY WORDS   Asymmetric Oxidative Coupling / Cross-Coupling / Binaphthol /

Optically active and racemic 1,1′-binaphthyl-based polymers have been extensively studied, for example, as electroluminescent materials due to the fact that the conjugation length of a polymer could be controlled without inserting a nonconjugated spacer group into the polymer main chain.[1] Lin *et al.* investigated the synthesis and optical spectroscopic studies of a series of binaphthyl-based oligomers, from quaternaphthyls to decanaphthyls, and enantioselective fluorescence quenching of hexanaphthols by treatment with *trans*-1,2-diaminocyclohexane.[1b] Pu *et al.* reported that the 1,1′-binaphthyl-based polymer exhibits an electroluminescence property in a double-layered light emitting diode.[1c]

On the other hand, the oxidative coupling reaction of the 2-naphthol derivatives is a facile synthetic route for the 1,1′-bi-2-naphthol skeleton, and many chiral metal catalysts, such as Cu(I), Ru(II), and V(IV), have been developed to control its axially dissymetric stereochemistry.[2] Recently, we found that the asymmetric oxidative coupling reaction between two differently substituted 2-naphthol derivatives using the CuCl-(S)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) [CuCl-(S)Phbox] catalyst, affords a product with a high cross-coupling selectivity,[3] although few data have been available for the catalytic oxidative cross-coupling reaction leading to an unsymmetrical binaphthol structure. The cross-coupling- and stereo-selectivities were significantly affected by the substituents on 2-naphthol and the ester groups of 3-hydroxy-2-naphthoate.[3] This method was further used for the polymerization of the methyl 6,6′-dihydroxy-2,2′-binaphthalene-7-carboxylate as a monomer affording a

polymer with the high cross-coupling selectivity of 96%.[4]

Herein, the oxidative coupling polymerization of the new monomers, various unsymmetrically substituted 6,6′-binaphthol derivatives **1** and methyl 3,7-dihydroxynaphthalene-2-carboxylate **2**, with the copper-diamine catalysts, such as di-μ-hydroxo-bis[(N,N,N′,N′-tetramethylethylenediamine)copper(II)] chloride [CuCl(OH)-TMEDA], CuCl-(S)-Phbox, CuCl-(R)-(−)-2,2′-isopropulidenebis(4-benzyl-2-oxazoline) [(R)-Bnbox] CuCl-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)PMP], and CuCl₂-(−)-sparteine [(−)Sp] (Figure 1), is carried out, and the effect on the coupling selectivities of the substituents during the oxidative coupling polymerization and character-
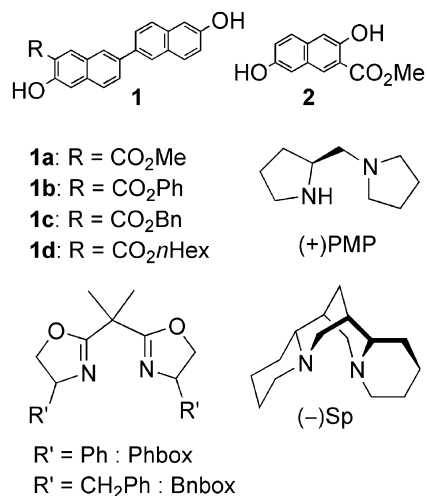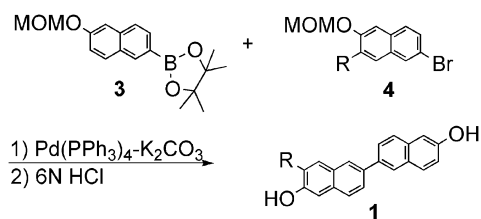

1a: R = CO₂Me
1b: R = CO₂Ph
1c: R = CO₂Bn
1d: R = CO₂nHex

(+)PMP

R′ = Ph : Phbox
R′ = CH₂Ph : Bnbox

(−)Sp

Figure 1.   Monomers and chiral ligands.

[†]To whom correspondence should be addressed (Tel/Fax: +81-238-26-3116, E-mail: habaue@yz.yamagata-u.ac.jp).

Scheme 1.

istics of the polybinaphthyls as an emissive material are investigated.

EXPERIMENTAL

Materials

Dry THF (Kanto) was used for the oxidative coupling reactions. The optically active diamines, (+)PMP (TCI) and (−)Sp (Sigma), were dried over CaH$_2$ and then distilled under reduced pressure. The bisoxazolines, (S)Phbox and (R)Bnbox (Aldrich), were used as received. The achiral copper complex, CuCl(OH)-TMEDA, was purchased from TCI.

Synthesis of Monomers 1[4] (Scheme 1).

Compound **3** was synthesized from 6-bromo-2-naphthol by methoxymethylation with NaH and chloromethyl methyl ether, followed by the reaction with 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane after lithiation with n-BuLi. Compound **4** was prepared from 7-bromo-3-hydroxy-2-naphthoic acid by esterification and methoxymethylation.

Monomer **1** was synthesized by the Suzuki coupling reaction between **3** and **4** in the presence of Pd(PPh$_3$)$_4$ and 1 M K$_2$CO$_3$, followed by treatment with 6 N HCl to remove the methoxymethyl ether, and purified by silica gel column chromatography.

1b: ^{1}H NMR (200 MHz, CDCl$_3$) 10.20 (s, 1H, –OH), 8.17–7.81 (m, 7H, aromatic), 7.54–7.13 (m, 9H, aromatic), 5.03 (s, 1H, –OH). IR (KBr, cm^{-1}) 3474, 3261, 1695, 1509, 1338, 1299, 1286, 1209, 1193, 1155. MS (FAB) m/z 406 [M]$^+$. Anal. calcd for C$_{27}$H$_{18}$O$_4$: C, 79.79; H, 4.46. Found: C, 79.61; H, 4.60.

1c: ^{1}H NMR (200 MHz, DMSO-d_6) 10.32 (s, 1H, –OH), 9.81 (s, 1H, –OH), 8.59–8.21 (s, 2H, aromatic), 8.04–7.75 (m, 6H, aromatic), 7.58–7.38 (m, 6H, aromatic), 7.14–7.09 (s, 2H, aromatic), 5.45 (s, 2H, –CH$_2$–). IR (KBr, cm^{-1}) 3355, 2360, 1683, 1513, 1463, 1409, 1336, 1307, 1284, 1211, 1155. MS (FAB) m/z 420 [M]$^+$. Anal. calcd for C$_{28}$H$_{20}$O$_4$: C, 79.98; H, 4.79. Found: C, 79.71; H, 5.15.

1d: ^{1}H NMR (200 MHz, CDCl$_3$) 10.59 (s, 1H, –OH), 8.57 (s, 1H, aromatic), 8.11–7.77 (m, 7H, aromatic), 7.35–7.12 (m, 3H, aromatic), 5.02 (s, 1H, –OH), 4.44 (t, 2H, $J = 6.8$ Hz, –OCH$_2$–), 1.91–1.83 (m, 2H,

–CH$_2$–), 1.43–1.36 (m, 6H, –CH$_2$–), 0.97–0.89 (m, 3H, –CH$_3$). IR (KBr, cm^{-1}) 3436, 3216, 2956, 2931, 1681, 1509, 1463, 1307, 1286, 1213. MS (FAB) m/z 414 [M]$^+$. Anal. calcd for C$_{27}$H$_{26}$O$_4$: C, 78.24; H, 6.32. Found: C, 78.24; H, 6.19.

Typical Polymerization Procedure

A monomer was added to a mixture of CuCl and a diamine in THF ([**1**] = 0.13 M, [Cu(I)]/[diamine]/[**1**] = 0.2/0.25/1). 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 (2/1/0.3 v/v/v)-insoluble fraction by centrifugation and drying in $vacuo$.

Cross-Coupling Reaction

The mono-methoxymethylated compounds, **5** and **6**, were prepared from **1** by methoxymethylation with NaH and chloromethyl methyl ether.[4]

A mixture of CuCl, diamine, and THF was stirred for 30 min under an O$_2$ atmosphere. To this mixture, **5** and **6** were added ([CuCl]/[diamine]/[**5**]/[**6**] = 0.2/0.25/0.5/0.5, [**5**] = 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 then afforded the crude products. The cross-coupling compound was isolated by silica gel column chromatography.

8b: ^{1}H NMR (200 MHz, CDCl$_3$) 10.62 (s, 1H, –OH), 9.09 (s, 1H, aromatic), 8.60 (s, 1H, aromatic), 8.82–7.24 (s, 28H, aromatic), 5.39 (s, 2H, –OCH$_2$–), 5.30 (s, 3H, –OCH$_2$O–, –OH), 3.59–3.53 (m, 6H, –OCH$_3$). IR (KBr, cm^{-1}) 3419, 1747, 1693, 1631, 1600, 1494, 1243, 1193, 1162, 1151. MS (FAB) m/z 898 [M]$^+$. Anal. calcd for C$_{58}$H$_{42}$O$_{10}$: C, 77.49; H, 4.71. Found: C, 77.50; H, 4.74.
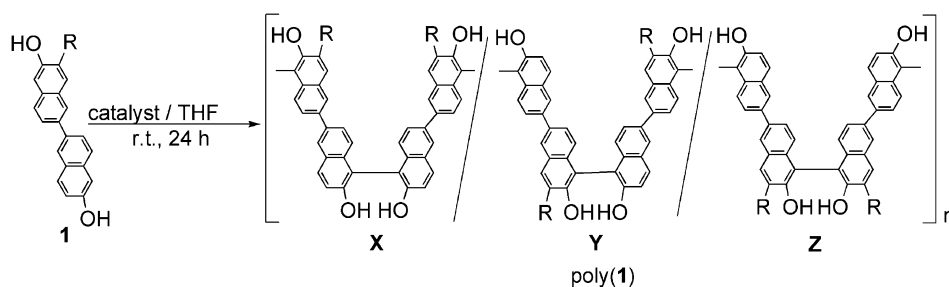
8c: ^{1}H NMR (200 MHz, CDCl$_3$) 10.93 (s, 1H, –OH), 8.83 (s, 1H, aromatic), 8.40–8.20 (s, 29H, aromatic), 5.52 (s, 2H, –OCH$_2$–), 5.42 (s, 2H, –OCH$_2$–), 5.36 (s, 2H, –OCH$_2$O–), 5.06 (s, 2H, –OCH$_2$O–), 3.54 (s, 3H, –OCH$_3$), 3.53 (s, 3H, –OCH$_3$). IR (KBr, cm^{-1}) 3372, 2953, 1716, 1677, 1629, 1600, 1498, 1272, 1195, 1151. MS (FAB) m/z 926 [M]$^+$. Anal. calcd for C$_{60}$H$_{46}$O$_{10}$: C, 77.74; H, 5.00. Found: C, 77.75; H, 4.97.

8d: ^{1}H NMR (200 MHz, CDCl$_3$) 11.05 (s, 1H, –OH), 8.84 (s, 1H, aromatic), 8.33–8.26 (s, 19H, aromatic), 5.37 (s, 2H, –OCH$_2$O–), 5.32 (s, 2H, –OCH$_2$O–), 5.08 (s, 1H, –OH), 4.50 (t, 2H, $J = 6.6$ Hz, –OCH$_2$–), 4.37 (t, 2H, $J = 6.6$ Hz, –OCH$_2$–), 3.57 (s, 3H, –OCH$_3$), 3.54 (s, 3H, –OCH$_3$), 1.96–1.75 (m, 4H, –CH$_2$–), 1.44–1.36 (m, 12H, –CH$_2$–), 0.96–0.90 (m, 6H, –CH$_3$). IR (KBr, cm^{-1}) 2945, 2929, 1724, 1716, 1677, 1600, 1504, 1344, 1195, 1151. MS (FAB) m/z

Table I. Asymmetric OCP of **1**[a]

Entry	**1**	Catalyst	Yield (%)[b]	M_n (×10³) (M_w/M_n)[d]	$[\alpha]_D$[e]	$[\phi]_D$[e]	Coupling ratio **X**:**Y**:**Z**[f]
1[g]	**1a** (Me)	CuCl(OH)TMEDA	55	2.0	—	—	18:79:3
2[g]	**1a** (Me)	CuCl-(S)Phbox	71 (47)[h]	4.5	+20	+68	3:96:1
3[g]	**1a** (Me)	CuCl-(R)Bnbox	98	3.5	−75	−257	3:92:5
4	**1b** (Ph)	CuCl(OH)TMEDA	62	3.4 (1.3)	—	—	11:71:18
5	**1b** (Ph)	CuCl-(S)Phbox	91 (33)[h]	5.0 (1.8)	−15	−60	3:95:2
6	**1b** (Ph)	CuCl-(R)Bnbox	71	3.8 (1.4)	−25	−101	14:71:15
7	**1b** (Ph)	CuCl-(+)PMP	0	—	—	—	—
8	**1c** (Bn)	CuCl(OH)TMEDA	27[c]	3.5 (1.2)	—	—	7:87:6
9	**1c** (Bn)	CuCl-(S)Phbox	78[c]	7.7 (1.3)	+40	+167	0:99:1
10	**1c** (Bn)	CuCl-(R)Bnbox	58[c]	5.1 (1.3)	−56	−234	4:89:7
11	**1d** (nHex)	CuCl(OH)TMEDA	81	4.1 (1.2)	—	—	12:87:1
12	**1d** (nHex)	CuCl-(S)Phbox	95	9.1 (2.3)	+55	+227	0:97:3
13	**1d** (nHex)	CuCl-(R)Bnbox	95	4.4 (1.4)	−80	−323	7:90:3

[a][Copper]/[ligand]/[**1**] = 0.20/0.25/1, [**1**] = 0.13 M, temp. = r. t., time = 24 h, O_2 atmosphere. [b]Methanol–ethyl acetate–1 N HCl (2/1/0.3, v/v)-insoluble part. [c]Methanol–ethyl acetate–1 N HCl (1/3/0.4, v/v)-insoluble part. [d]Determined by SEC in THF (polystyrene standard). [e]In THF. [f]Estimated by ^{1}H NMR analysis. [g]Reference 4. [h]Methanol-insoluble and THF-soluble part.

Scheme 2.

914 [M]⁺. Anal. calcd for $C_{58}H_{58}O_{10}$: C, 76.13; H, 6.39. Found: C, 76.14; H, 6.38.

8e: ^{1}H NMR (200 MHz, CDCl₃) 10.69 (s, 1H, –OH), 8.64 (s, 1H, aromatic), 7.82 (d, 1H, $J = 8.8$ Hz, aromatic), 7.56–7.38 (m, 4H, aromatic), 7.17–7.04 (m, 2H, aromatic), 5.31 (s, 2H, –OCH₂O–), 5.27 (s, 2H, –OCH₂O–), 4.89 (s, 1H, –OH), 4.06 (s, 3H, CO₂CH₃), 3.74 (s, 3H, CO₂CH₃), 3.55 (s, 3H, OCH₃), 3.52 (s, 3H, OCH₃). IR (KBr, cm⁻¹) 3399, 2921, 1708, 1681, 1602, 1506, 1440, 1386, 1274, 1151. Mass (FAB): 522 *m/z* [M]⁺. Anal. Calcd for $C_{28}H_{26}O_{10}$: C, 64.36; H, 5.02. Found: 64.35; H, 5.05.

Measurements

^{1}H and ^{13}C 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 JEOL 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 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. The UV-vis absorption (UV) spectra were recorded on a UV-2200A (Shimadzu). The fluorescence (FL) spectra were measured using a FluoreMax-2 spectrophotometer. The quantum yield was measured by PL quantum yield analyzer C9920-01 (Hamamatsu Photonics).

RESULTS AND DISCUSSION

Table I shows the results of the oxidative coupling polymerization (OCP) of **1b–d** with various copper catalysts (Scheme 2), together with those of the polymerization of **1a** (entries 1–3).[4a] The polymerization with the TMEDA catalyst afforded a product with a relatively lower number average molecular weight (M_n) in low to moderate yields (27–81%) (entries 4, 8, 11). The (+)PMP catalyst resulted in no yield (entry 7). The polymerization in the presence of the
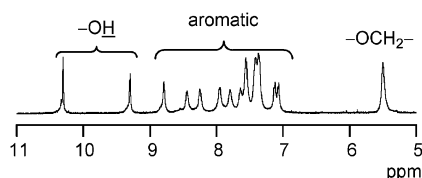
Figure 2. ^{1}H NMR spectrum of poly(**1c**) obtained with (*S*)Phbox (Table I, entry 9).
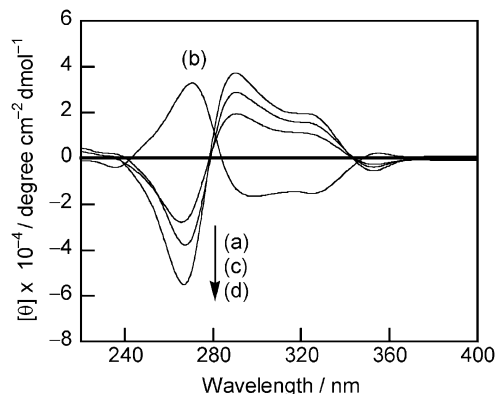

Figure 3. CD spectra of poly(**1**) obtained with (*S*)Phbox: (a) poly(**1a**) (Table I, entry 2), (b) poly(**1b**) (Table I, entry 5), (c) poly(**1c**) (Table I, entry 9), and (d) poly(**1d**) (Table I, entry 12) (monomer unit, in THF).

Figure 4. ^{1}H NMR spectra of hydroxyl protons of poly(**1b**) obtained with (A) CuCl-(*S*)Phbox (Table I, entry 5), (B) CuCl-(*R*)Bnbox (Table I, entry 6), and (C) CuCl(OH)-TMEDA (Table I, entry 4) (in DMSO-d_6, 50 °C).

CuCl-(*S*)Phbox catalyst produced a polymer with a good yield and an M_n value of the THF-soluble fraction, $\geq 5.0 \times 10^3$ (entries 5, 9, 12), especially, the polymer obtained by the polymerization of **1d** showed an M_n of 9.1×10^3, which is fully soluble in THF. These results are similar to those observed for the polymerization of **1a**.

The ^{1}H NMR spectrum of poly(**1c**) obtained with (*S*)Phbox is depicted in Figure 2, and the peaks are assigned as shown in the figure. The CD spectra of the obtained poly(**1**) using the CuCl-(*S*)Phbox catalyst are shown in Figure 3. The spectral patterns of the polymers with positive and negative specific rotations are mirror images of each other and indicates that the latter polymers are rich in the *S*-configuration,[5] whereas the *R*-structure is preferentially constructed during the polymerization of **1b**. The spectral patterns and absorption intensity are in good agreement with those of the observed specific rotation value. The structure of the ester group on the 6,6′-bi-2-naphthol significantly affected the coupling stereochemistry.

The coupling ratio X:Y:Z was calculated from the ^{1}H NMR analysis of the hydroxyl absorption intensities as previously reported.[4] The ^{1}H NMR spectra of the hydroxyl protons of poly(**1b**) using the (*S*)Phbox, (*R*)Bnbox, and TMEDA catalysts are shown in Figure 4. The internal and terminal hydroxyl protons with different chemical shifts appeared, and
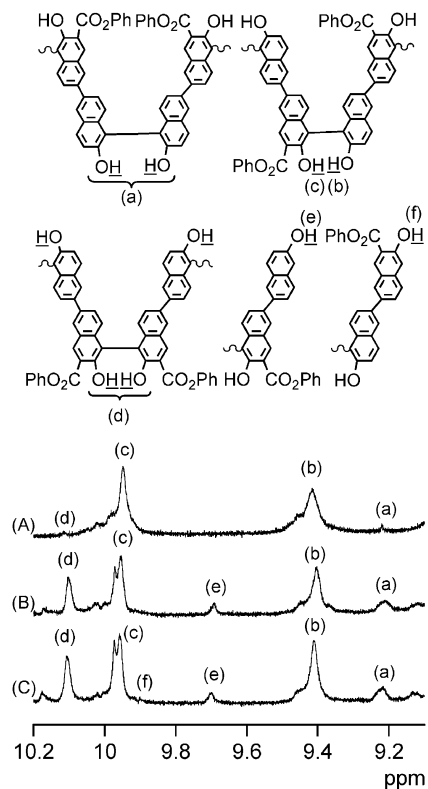
each observed peak was assigned as shown in the figure. The evaluated coupling ratios are shown in Table I. For polymerization with the (*S*)Phbox catalyst, the cross-coupling reaction predominantly proceeded with the cross-coupling selectivity Y of $\geq 95\%$. Especially, the polymer obtained from **1c** showed the highest Y-selectivity of 99%. The structure of the ester groups influenced the coupling-selectivity as well as the coupling enantioselectivity. The cross-coupling selectivity was also observed for the polymerization with the TMEDA and (*R*)Bnbox catalysts (71–90%), although they are much lower than those observed for the polymers obtained with the (S)Phbox catalyst.

The coupling stereoselectivity was estimated by the model reaction, that is, the oxidative coupling reaction between **5a–d** and **6a–d** with CuCl-(*S*)Phbox was conducted (Scheme 3) and the results are listed in Table II (entries 1–4). In every reaction, the corresponding cross-coupling compound **8** was produced in good yield (67–89%) with a high selectivity (>89%), whose value is quite comparable to that observed for the polymerization. In addition, the cross-coupling compounds **8a–d** showed an enantioselectivity of 31 (*S*), 10 (*R*), 28 (*S*), and 30% ee (*S*), respectively. The CD spectra of the obtained cross-coupling com-
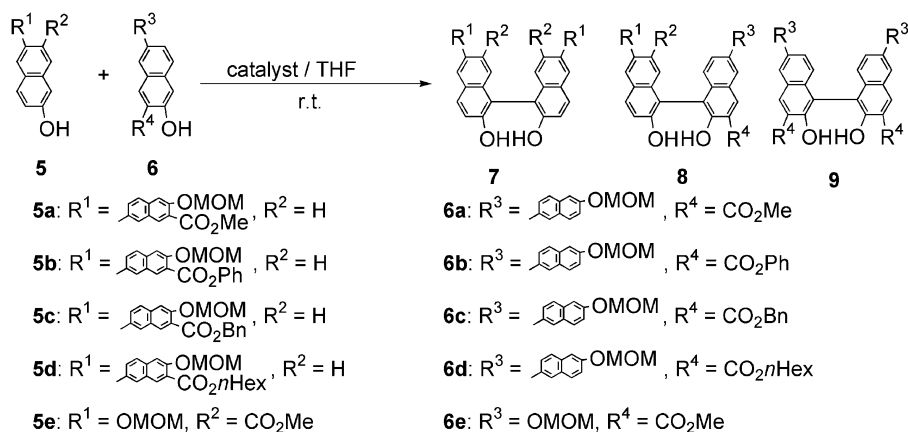
Scheme 3.

Table II. Asymmetric oxidative coupling reaction between **5** and **6**[a]

Entry	Catalyst	5	6	Time (h)	Coupling ratio 7:8:9[b]	Cross-coupling product **8**		
						8	Yield (%)[c]	ee (%)[d]
1[e]	CuCl-(S)Phbox	**5a**	**6a**	5	2:94:4	**8a**	89	31 (S)
2	CuCl-(S)Phbox	**5b**	**6b**	8	<1:89:10	**8b**	88	10 (R)
3	CuCl-(S)Phbox	**5c**	**6c**	8	<1:96:3	**8c**	67	28 (S)
4	CuCl-(S)Phbox	**5d**	**6d**	9	<1:95:4	**8d**	82	30 (S)
5	CuCl(OH)-TMEDA	**5e**	**6e**	9	30:66:4	**8e**	35	—
6	CuCl-(S)Phbox	**5e**	**6e**	5	8:80:12	**8e**	72	2 (R)
7	CuCl-(R)Bnbox	**5e**	**6e**	9	18:58:24	**8e**	46	25 (R)

[a]Conditions: [copper]/[diamine]/[**5**]/[**6**] = 0.20/0.25/1/1, [**5** + **6**] = 0.35 M, solvent = THF, O_2 atmosphere. [b]Ratio of isolated yields. [c]Isolated yield. [d]Determined by HPLC analysis (Chiralpak AD). [e]Reference 4.
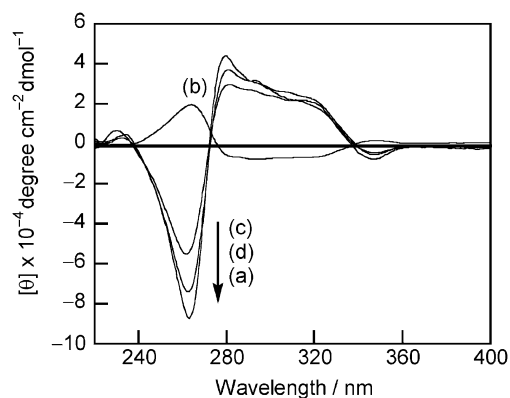

Figure 5. CD spectra of the cross-coupling compounds **8** obtained with (S)Phbox: (a) **8a** (Table II, entry 1), (b) **8b** (Table II, entry 2), (c) **8c** (Table II, entry 3), and (d) **8d** (Table II, entry 4) (binaphthalene unit, in THF).

Table III. Asymmetric OCP of **2**[a]

Entry	Catalyst	Yield (%)[b]	M_n (×10³) (M_w/M_n)[c]	$[\alpha]_D$ (deg)[d]
1	CuCl(OH)TMEDA	30	2.8 (1.4)	—
2	CuCl-(+)PMP	3	1.0 (1.7)	−14
3[e]	CuCl₂-(−)Sp	78	4.6 (1.4)	−49
4	CuCl-(S)Phbox	99 (25)[f]	12.7 (2.1)	0
5	CuCl-(R)Bnbox	92 (41)[f]	7.2 (2.0)	0

[a][Copper]/[diamine]/[**2**] = 0.20/0.25/1, [**2**] = 0.35 M, temp. = r. t., time = 24 h, O_2 atmosphere. [b]Methanol–1 N HCl (9/1, v/v)-insoluble part. [c]Determined by SEC in THF (polystyrene standard). [d]In THF. [e][CuCl₂]/[(−)Sp]/[**2**] = 0.5/1/1. [f]Methanol-insoluble and THF-soluble part.

pounds are demonstrated in Figure 5. The CD curves indicate that the cross-coupling compound having a phenyl ester group is rich in the *R*-configuration, and the others preferentially have the *S*-structure.[5] The spectral patterns are comparable to those of the corresponding polymers, and these results suggest that the stereochemisty constructed during the polymerization should be controlled in a degree similar to the

model reaction.

The OCP of the unsymmetric naphthalene monomer, **2**, with the various copper(I)-diamine catalysts was also carried out (Scheme 4) and the results are listed in Table III. The polymerizations with the TMEDA and (+)PMP catalysts afforded an oligomer as the methanol–1 N HCl (9/1, v/v)-insoluble fraction in a low yield (entries 1 and 2). In marked contrast, the polymerization with the bisoxazoline catalysts produced a polymer in quantitative yield, whose THF-soluble part showed an M_n of 12.7 × 10³ (entry 4).
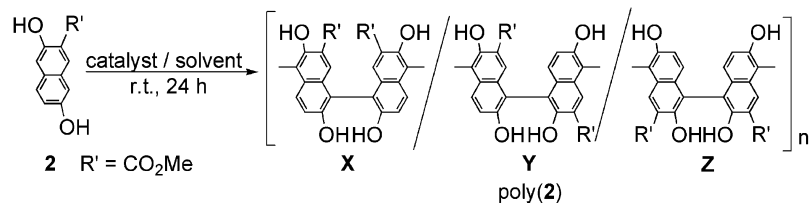
Scheme 4.
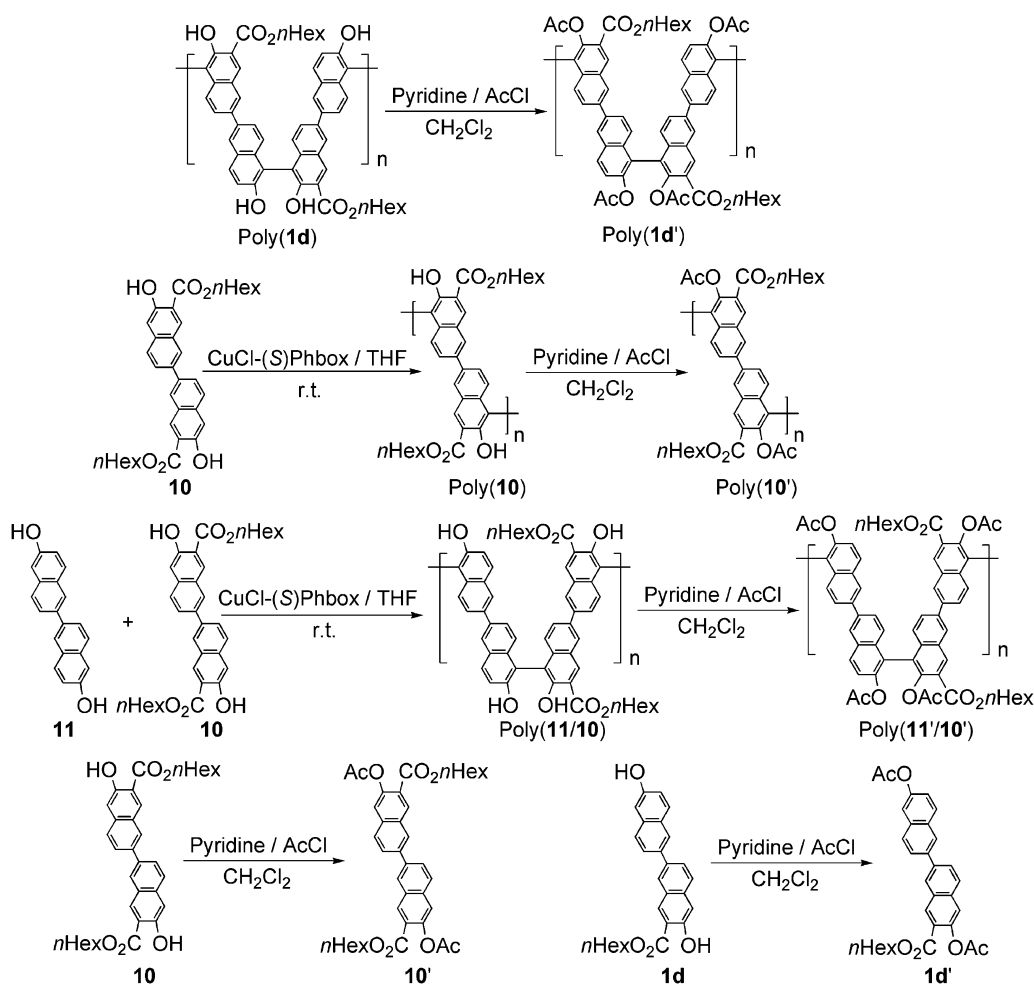
Scheme 5.

The polymerization with the (−)Sp and (R)Bnbox ligands also resulted in good yields with a much lower M_n value (entries 3 and 5).

The detailed cross-coupling selectivity of the obtained polymers was not clear at present, because some hydroxyl protons with almost the same chemical shift appeared in the ^{1}H NMR analysis. Accordingly, the cross-coupling selectivity, in addition to the stereoselectivity, were estimated from the model reaction between two naphthol derivatives, **5e** and **6e**, with various CuCl-diamine catalysts (Scheme 3, Table II, entries 5–7). The reaction with the (S)Phbox catalyst proceeded in the highly cross-coupling selective manner of 80%, whereas the obtained cross-coupl-

ing compound **8e** showed an enantioselectivity of 2% ee (R). The reactions with the TMEDA- and (R)Bnbox-catalysts resulted in a much lower yield and cross-coupling selectivity. Therefore, the CuCl-(S)Phbox catalyst should effectively produce a polymer mainly having a cross-coupling unit during the OCP of **2**.

To examine the UV- and FL-properties, the acetylation of the obtained poly(**1d**) (Table I, entry 12) was performed: poly(**1d′**), $M_n = 14.6 \times 10^3$, $M_w/M_n = 4.3$. The model compounds, such as poly(**10′**) ($M_n = 9.7 \times 10^3$, $M_w/M_n = 1.7$), poly(**11′/10′**) (cross-coupling selectivity = 93%, $M_n = 10.1 \times 10^3$, $M_w/M_n = 1.9$),[4b] **10′**, and **1d′**, were also prepared as shown in
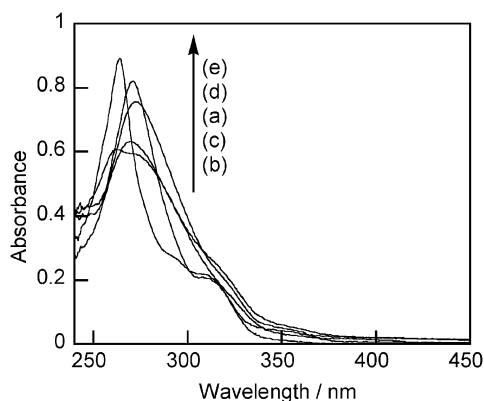
Figure 6. UV-vis absorption spectra of the obtained polymers and the model compounds: (a) poly(**10′**), (b) poly(**11′/10′**), (c) poly(**1d′**), (d) **10′**, and (e) **1d′** ($C = 1.0 \times 10^{-5}$ M, chloroform).
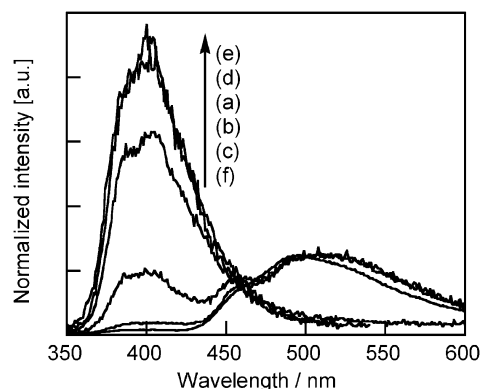

Figure 7. Fluorescence spectra of the obtained polymers and the model compounds (a) poly(**10′**) ($\lambda_{\mathrm{exc}} = 304$ nm), (b) poly-(**11′/10′**) ($\lambda_{\mathrm{exc}} = 315$ nm), (c) poly(**1d′**) ($\lambda_{\mathrm{exc}} = 313$ nm), (d) **10′** ($\lambda_{\mathrm{exc}} = 312$ nm), and (e) **1d′** ($\lambda_{\mathrm{exc}} = 312$ nm) ($C = 1.0 \times 10^{-5}$ M, chloroform), (f) poly(**1d′**) ($\lambda_{\mathrm{exc}} = 313$ nm) (thin film).

Scheme 5, and these acetylated polymers and model compounds were used for the UV and FL measurements.

The UV absorption spectra in chloroform are shown in Figure 6. The spectral patterns of these compounds were similar to each other with a strong absorption band around $\lambda_{\mathrm{max}} = 264$–271 nm and a shoulder around 304–315 nm. Figure 7 (a–e) shows the FL spectra of the polybinaphthols and model compounds in chloroform (concentration: 1.0×10^{-5} M), measured at an excitation wavelength of around 304–315 nm. The polymer consisting of only the homo-coupling unit, poly(**10′**), showed a spectrum similar to that observed for the model compound **10′**. The polymers mainly containing the cross-coupling unit, poly(**11′/10′**) and poly(**1d′**), exhibited red-shifted and broadened emission bands, probably due to the excimer coupling, especially, the FL intensity of the

emission around 400 nm is quite different between these two polymers. The FL spectrum of the poly(**1d′**) film was also measured (Figure 7, f). The similar spectral patterns to that of the dilute solution are observed, although the emission intensity around 400 nm slightly decreased. These results suggest the intermolecular excimer formation. The polymers, poly(**10′**) and poly(**1d′**), exhibited a quantum yield of $5 \pm 1\%$ and $7 \pm 1\%$, respectively. The coupling structure of the polymer significantly affected the emission properties.

CONCLUSIONS

The oxidative cross-coupling polymerization of various 6,6′-dihydroxy-2,2′-bianphtalene derivatives with the CuCl-(*S*)Phbox catalyst proceeded in a highly cross-coupling selective manner up to 99%. The polymer containing the cross-coupling unit showed significantly different FL spectra from their model compounds.

REFERENCES

1. a) L. Pu, *Chem. Rev.*, **104**, 1687 (2004).
   b) L. Ma, P. S. White, and W. Lin, *J. Org. Chem.*, **67**, 7577 (2002).
   c) A. K-Y. Jen, Y. Liu, Q-S. Hu, and L. Pu, *Appl. Phys. Lett.*, **75**, 3745 (1999).
2. a) M. Nakajima, I. Miyoshi, K. Kanayama, S. Hashimoto, M. Noji, and K. Koga, *J. Org. Chem.*, **64**, 2264 (1999).
   b) J. Gao, J. H. Reibenspies, and A. E. Martell, *Angew. Chem., Int. Ed.*, **42**, 6008 (2003).
   c) R. Irie, K. Masutani, and T. Katsuki, *Synlett*, 1433 (2000).
   d) Z. Luo, Q. Liu, L. Gong, X. Cui, A. Mi, and Y. Jiang, *Angew. Chem., Int. Ed.*, **41**, 4532 (2002).
   e) H. Somei, Y. Asano, T. Yoshida, S. Takizawa, H. Yamataka, and H. Sasai, *Tetrahedron Lett.*, **45**, 1841 (2004).
3. a) T. Temma and S. Habaue, *Tetrahedron Lett.*, **46**, 5655 (2005).
   b) T. Temma, B. Hatano, and S. Habaue, *Tetrahedron*, **62**, 8559 (2006).
4. a) T. Temma and S. Habaue, *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 6287 (2005).
   b) T. Temma, B. Hatano, and S. Habaue, *Polymer*, **47**, 1845 (2006).
5. S. R. Wyatt, Q.-S. Hu, X-L. Yan, W. B. Bare, and L. Pu, *Macromolecules*, **34**, 7983 (2001).