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# Oxidative coupling polymerization of racemic 3,3'-dihydroxy-2,2'-dimethoxy-1,1'-binaphthalene with copper(II)-(-)-sparteine complex

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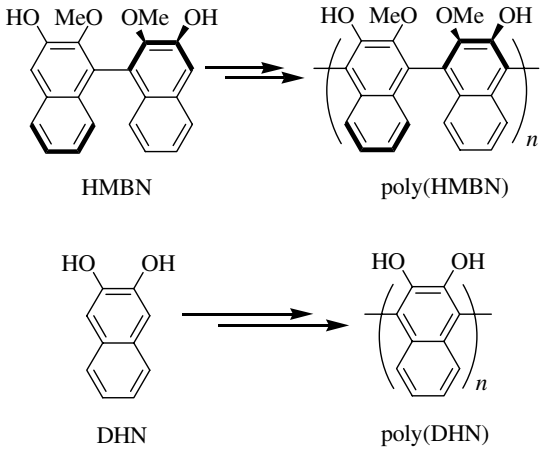
## Summary

The oxidative coupling polymerization of racemic 3,3'-dihydroxy-2,2'-dimethoxy-1,1'-binaphthalene with copper(II) chloride-(-)-sparteine [(-)Sp] in methanol at room temperature was carried out and the enantiomer-selectivity during the polymerization was examined. The (*R*)-monomer preferentially reacted, and the purity of the unreacted monomer reached 80%*ee* (*S*) after 15 h, while that of the polymerized monomer gradually decreased from 26%*ee* (*R*) as a function of the polymerization. The ratio of the rate constants of both enantiomers, $s = k_R/k_S$, was determined to be 2.3. The model coupling reaction of the mono-benzylated (*R*)-monomer with $CuCl_2$-(-)Sp showed that the *R*-configuration with respect to the carbon-carbon bonds between the monomer units was selectively constructed during the polymerization.

## Introduction

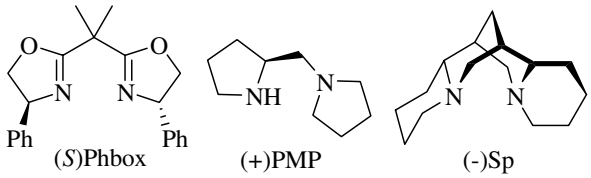
Recently, we reported the asymmetric oxidative coupling polymerization (AOCP) of the optically active 3,3'-dihydroxy-2,2'-dimethoxy-1,1'-binaphthalene (HMBN) or 2,3-dihydroxynaphthalene (DHN) using copper catalysts that produced poly(2,3-dihydroxy-1,4-naphthylene) derivatives, which are novel types of polyarylenes bearing a rigid main chain with continuous axial dissymmetry, therefore, of great interest as a functional polymeric material (Scheme 1) [1-5]. The stereoselectivity of the newly formed carbon-carbon bonds (*R* : *S*) during the polymerization of (*R*)- or (*S*)-HMBN significantly depends on the structure of the chiral diamine-type ligands. The polymerization with bisoxazoline, (*S*)- or (*R*)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (Phbox) proceeds under an almost complete ligand stereochemical control, that is, the polymer with an *S*- or *R*-selectivity regardless of the monomer chirality was obtained by the polymerization with (*S*)- or (*R*)-Phbox, respectively. On the other hand, the monomer chirality significantly affected the stereoselectivity during the polymerization with chiral diamine ligands, such as (+)-1-(2-pyrrolidinyl-methyl)pyrrolidine [(+)PMP] [6,7] and (-)-sparteine [(-)Sp] [8,9] (Scheme 2), which are well known as effective reagents for the oxidative coupling reaction leading to a 1,1'-bi-2-naphthol skeleton, and a clear match/mismatch effect between the monomer and the diamine was observed [1,2]. For example, the polymerization of (*R*)- or (*S*)-HMBN with $CuCl_2$-(-)Sp gave a polymer with the stereoselectivity of the




**Scheme 1.**

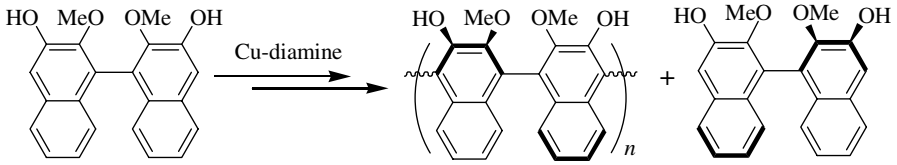
newly constructed bonds between the monomer units, *R* : *S* = 84 : 16 or 52 : 48, respectively.

Enantiomer- or asymmetric-selective polymerization, in which one enantiomer of a racemic monomer is preferentially polymerized by a chiral initiator, is attractive as a process affording a kinetically resolved monomeric compound, as well as an optically active polymer. Many studies on the enantiomer-selective chain-type polymerization of cyclic and vinyl monomers, such as the oxiranes, thiiranes, lactones, lactide, α-olefins, and (meth)acrylates, are available [10-20]. To the best of our knowledge, there are few reports on the enantiomer-selectivity during the successive homo-polymerization, in contrast to that through the chain polymerization mechanisms. In addition, the kinetic resolution method for 1,1'-bi-2-naphthol derivatives through enantiomer-differentiating reactions with chiral reagents or catalysts, even including the enzymatic ones, is unexpectedly limited [21-26].




**Scheme 2.**

In this study, the oxidative coupling polymerization of racemic HMBN with chiral copper-diamine catalysts was carried out, and the enantiomer-selectivity during the polymerization was investigated (Scheme 3). To discriminate the stereochemistry between the enantiomer-selectivity and stereoselectivity of the carbon-carbon bonds generated by the coupling reaction, the underlined absolute configurations, *R* and *S*, are used for describing the latter stereochemistry in this study.




*rac*-HMBN poly((*R*)-HMBN) (*S*)-HMBN

**Scheme 3.**

## Experimental

*Materials*

The monomer HMBN, reagents, and solvents used in the polymerization were synthesized or purchased as previously reported [1-4].

*Polymerization*

The HMBN monomer was added to a mixture of $CuCl_2$ and (-)Sp ([HMBN] = 0.16 M, [Cu(II)]/[(-)Sp]/[HMBN] = 1/2/1) in MeOH. During the polymerization at room temperature under an $N_2$ atmosphere, small portions of the reaction mixture were removed using a syringe. Each reaction mixture was poured into a large excess of MeOH-1N HCl [10/1 (v/v)]. The insoluble fraction was collected by centrifugation and drying in vacuo. The obtained polymer was further acetylated using an excess amount of acetyl chloride and pyridine (5 equiv.) in $CH_2Cl_2$ to measure the molecular weights and optical properties. The ratio of acetylation was over 88%. After evaporation of the solvents, the MeOH-1N HCl-soluble part was further extracted with 1N HCl and $CHCl_3$. The residual monomer was isolated by silica gel column chromatography (hexane/AcOEt/$CHCl_3$ = 3/1/1), and the enantiomer excess (*ee*) was determined by high-performance-liquid-chromatography (HPLC) [column: Daicel Chiralpak AD-H, eluent: hexane/ethanol = 45/55 (v/v), flow rate = 0.5 ml/min].

*Measurements*

The $^1H$ and $^{13}C$ NMR spectra were measured using a Varian Unity-Inova spectrometer (500 MHz for $^1H$) in $CDCl_3$. The size exclusion chromatographic (SEC) analyses were

**Table 1.** OCP of *rac*-HMBN with various copper reagents at room temperature ([CuCl]/[ligand]/[HMBN] = 0.16/0.20/1, [HMBN] = 0.16 M, solvent = THF, $O_2$ atmosphere)

| | | Monomer | | Polymer | | | |
|---|---|---|---|---|---|---|---|
| Reagent | Time (h) | Recovery (%)[a] | *ee* (%)[b] | Yield (%)[c] | *ee* (%)[d] | $M_n$ (x $10^3$) ($M_w/M_n$)[e] | $[\alpha]_D$[f] |
| CuCl-(*S*)Phbox | 0.5 | 3 | 26 (*R*) | 53 | 1 (*S*) | 9.8 (1.3) | -92 |
| CuCl-(+)PMP[g] | 2 | 27 | 17 (*S*) | 10 | 7 (*R*) | 8.7 (1.3) | +21 |
| $CuCl_2$-(-)Sp[h] | 1 | 42 | 36 (*S*) | 16 | 26 (*R*) | 11.9 (1.3) | +186 |

[a]isolated value; [b]determined by HPLC; [c]MeOH-1N HCl (10/1 (v/v))-insoluble part of poly(HMBN); [d]calculated value for the reacted monomer; [e]determined by SEC using the polymer after acetylation (MeOH-1N HCl (10/1 (v/v))-insoluble part); [f]measured in $CHCl_3$ using the acetylated polymer; [g]solvent = $CH_2Cl_2$; [h]$[CuCl_2]/[(-)Sp]/[HMBN]$ = 1/2/1, [HMBN] = 0.16 M, solvent = MeOH, $N_2$ atmosphere

performed using a Hitachi 655A-11 equipped with a Shimadzu SPD-6A UV detector and TSK G5000H and Shodex AC-802.5 columns connected in series (eluent: $CHCl_3$, temp. = 40 $^oC$, flow rate = 1.0 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 $^oC$. The HPLC analyses were performed on a JASCO 986-PU chromatograph equipped with an UV (JASCO 970-UV) detector at room temperature.

## Results and discussion

Table 1 shows the results of the polymerization of *rac*-HMBN with chiral copper complexes at room temperature. The polymerization with the CuCl-(*S*)Phbox catalyst proceeded quite fast. Even after a 0.5 h polymerization, a 3% monomer was recovered. On the other hand, a relatively slower polymerization was observed for the (+)PMP and (-)Sp systems, and the unreacted monomer during the polymerization with $CuCl_2$-(-)Sp showed the higher *ee* value of 36% (*S*), when the monomer conversion was 58%. Accordingly, the polymerized monomer *ee* was calculated to be 26% (*R*). The obtained polymer after acetylation of the hydroxyl groups [poly(HMBN')] showed a specific rotation ($[\alpha]_D$) of +186, whose value was almost comparable to that of the polymer obtained from (*R*)-HMBN using $CuCl_2$-(-)Sp ($[\alpha]_D$ = +185) [1], suggesting that the stereochemistry of the carbon-carbon bonds formed by the coupling reaction should also be controlled, in addition to the *R*-isomer-selectivity of the polymerization system. In contrast, the $[\alpha]_D$ value of the polymer obtained with CuCl-(+)PMP, +21, is much smaller than that of poly[(*R*)-HMBN'] ($[\alpha]_D$ = +157) [12]. These results indicate that the $CuCl_2$-(-)Sp system is suitable for further investigation of the enantiomer-selectivity during the AOCP.

**Table 2.** OCP of *rac*-HMBN with $CuCl_2$-(-)Sp at room temperature ($[CuCl_2]/[(-)Sp]/[HMBN]$ = 1/2/1, [HMBN] = 0.16 M, solvent = MeOH, $N_2$ atmosphere)

| | Monomer | | Polymer | | |
|---|---|---|---|---|---|
| Time (h) | Recovery (%)[a] | *ee* (%)[b] | Yield (%)[c] | *ee* (%)[d] | $M_n$ (x $10^4$) ($M_w/M_n$)[e] |
| 2 | 32 | 36 (*S*) | 19 | 17 (*R*) | 1.19 (1.3) |
| 3 | 23 | 39 (*S*) | 19 | 12 (*R*) | 1.19 (1.3) |
| 5 | 14 | 49 (*S*) | 19 | 8 (*R*) | 1.13 (1.3) |
| 7 | 14 | 61 (*S*) | 23 | 10 (*R*) | 1.18 (1.3) |
| 15 | 4 | 80 (*S*) | 42 | 4 (*R*) | 1.08 (1.3) |
| 24 | 2 | 68 (*S*) | 77 | 2 (*R*) | 1.05 (1.6) |

[a]isolated value; [b]determined by HPLC; [c]MeOH-1N HCl (10/1 (v/v))-insoluble part; [d]calculated value for the reacted monomer; [e]determined using the polymer after acetylation (MeOH-1N HCl (10/1 (v/v))-insoluble part) by SEC

Table 2 lists the results of a polymerization run with $CuCl_2$-(-)Sp for 24 h and changes in the monomer conversion, monomer *ee*, polymer yield of the methanol-1N HCl (10/1 (v/v))-insoluble fraction, and calculated *ee* values for the monomer unit from the residual monomer *ee* as a function of the polymerization time are demonstrated in Figure 1. The monomer conversion and polymer yield increased with time and reached almost 100% and 77%, respectively, after 24 h. The purity of the unreacted

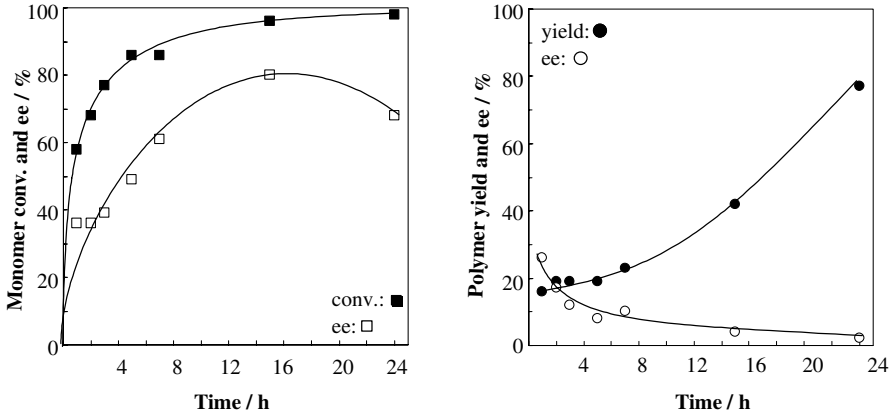



**Figure 1.** Monomer conversion, *ee* (*S*) of the residual monomer, polymer yield, and calculated *ee* (*R*) of the monomer units as a function of polymerization time (monomer: *rac*-HMBN; catalyst: $CuCl_2$-(-)Sp)

monomer reached 80%*ee* (*S*) after 15 h, while that of the polymerized monomer gradually decreased from 26%*ee* (*R*) with the increasing degree of polymerization.
The (*R*)-monomer preferentially reacted in this polymerization system. The ratio of the rate constants of both enantiomers, $s = k_R/k_S$, was determined to be 2.3, based on the observed values for the 1 h polymerization [15,17]. Figure 2 shows the plots of the measured *ee* values for the residual monomer (*S*) and the monomer unit introduced into the polymer chain (*R*) versus the monomer conversion, together with the theoretical values calculated on the basis of the s value of 2.3 for the monomer conversion of 50% or below. The polymers consisting of approximately 40%*ee* of the monomeric units during the initial stage of the polymerization and 28%*ee* at the half-reaction (50% conversion) may be produced during the polymerization.
As the purity of the reacted monomer decreased, the specific rotation observed for poly(HMBN') gradually decreased from +186 to +68 (Figure 3). The CD spectra of the obtained polymers are shown in Figure 4. The absorption intensity around 240 nm

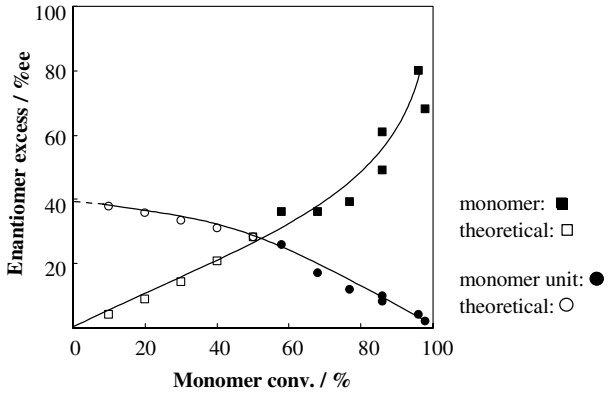



**Figure 2.** Monomer conversion vs. *ee* values of the residual monomer and calculated *ee* values for the monomer unit (monomer: *rac*-HMBN; catalyst: $CuCl_2$-(-)Sp)

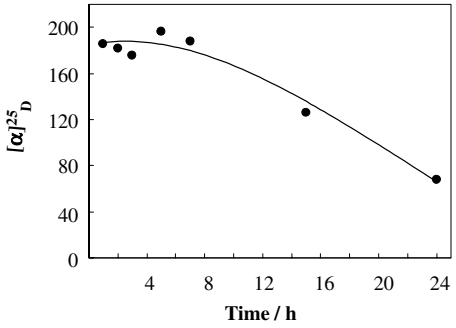



**Figure 3.** Plots of the specific rotation of poly(HMBN') obtained with $CuCl_2$-(-)Sp (in $CHCl_3$)

showed a good relation to the $[\alpha]_D$ values and the spectral patterns indicated that these polymers are rich in the *R*-configuration [1-4].

Figure 5 shows the $^{13}C$ NMR spectrum of poly(HMBN') obtained by the 15 h polymerization, and each peak is assigned as shown in the figure. Although the stereochemistry of the newly constructed carbon-carbon bonds (*R* : *S*) during the polymerization of the optically active HMBN can be estimated from the methyl carbon absorption of the acetyl groups, as previously reported [1,2], the stereochemistry cannot be directly determined here because the racemic monomer was used. The 1 : 1 absorption is always observed for the "-*RRS*-" and "-*SSR*-" chains [1], therefore, the selectivity was estimated to be [*RRR* + *SSS* + 1/2(*RRS* + *SSR*)] : [*SRS* + *RSR* + 1/2(*RRS* + *SSR*)] = 63 : 37 from the absorption intensity. This result indicates that the (*RRR*)- and/or (*SSS*)-dimer units should be selectively constructed during the polymerization.

The model coupling reaction of the mono-benzylated monomer, BnHMBN, with $CuCl_2$-(-)Sp in methanol at room temperature for 2 h was conducted ([BnHMBN] = 0.16 M, [BnHMBN]/[$CuCl_2$]/[(-)Sp] = 1/2/1) (Scheme 4) [27,28]. The coupling

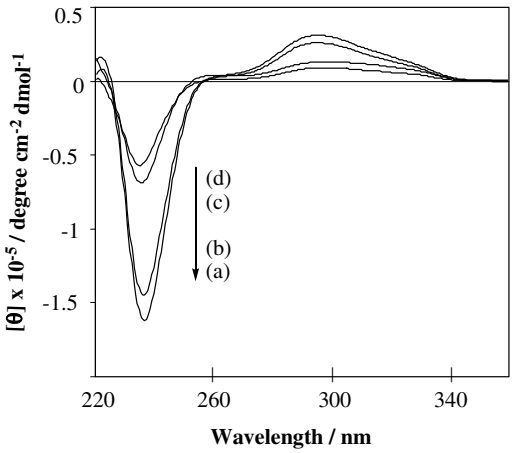
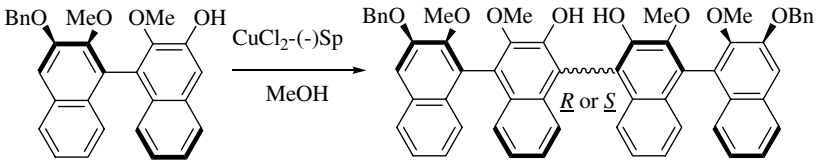



**Figure 4.** CD spectra of poly(HMBN') obtained with $CuCl_2$-(-)Sp, polymerization time: (a) 1 h; (b) 3 h; (c) 15 h; (d) 24 h (in $CHCl_3$)




(*R*)-BnHMBN

**Scheme 4.**

reaction of (*R*)-BnHMBN gave a mixture of the (*RRR*)- and (*RSR*)-isomers in 36% and 16% yields, respectively, whereas the coupling product was obtained in 31% yield (*SSS* : *SRS* = >99 : <1) for the reaction of (*S*)-BnHMBN. Accordingly, the coupling reaction of (*R*)-BnHMBN proceeded much faster than that of the (*S*)-isomer, and the (*RRR*)-quaternaphthyl structure was preferentially formed during the reaction. These results are very consistent with those observed for the polymerization of *rac*-HMBN. On the other hand, the observed setereoselectivity (*R* : *S* = 69 : 31) for the model coupling of (*R*)-BnHMBN showed a tendency similar to that estimated for the polymer synthesized from (*R*)-HMBN (84 : 16), while that for the reaction of (*S*)-BnHMBN is quite different from the evaluated selectivity for the 24 h polymerization of the (*S*)-monomer (52 : 48) [1]. It is known that the deracemization of the 1,1'-bi-2-naphthol derivatives is caused by the $CuCl_2$-(-)Sp complex [8,9,29]. Accordingly, this may be due to the fact that the epimerization of the formed 1,1'-bi-2-naphthol units during the coupling process takes place.

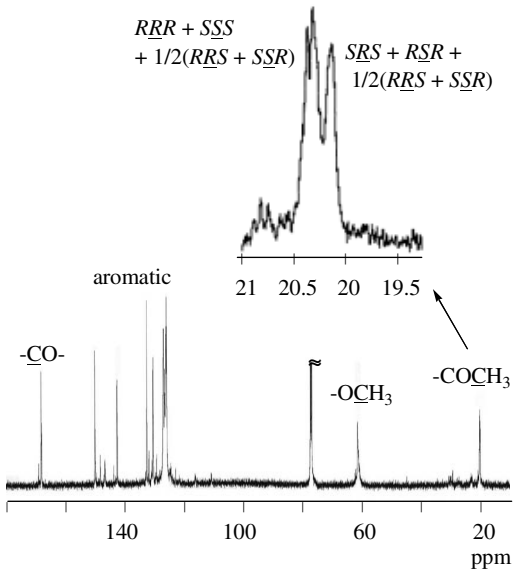



**Figure 5.** $^{13}C$ NMR spectrum of poly(HMBN') obtained by the polymerization for 15 h ($CDCl_3$, 60 °C)

## Conclusions

During the asymmetric oxidative coupling polymerization of the racemic monomer, HMBN, with $CuCl_2$-(-)Sp, the (*R*)-monomer was preferentially incorporated into the polymer chain, and the purity of the residual monomer attained 80%*ee* (*S*) after 15 h. In addition, the *R*-configuration was selectively produced that afforded the *RRR*-mainchain-structure.

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