Asymmetric Oxidative Coupling Polymerization of Optically Active Tetrahydroxybinaphthalene Derivative

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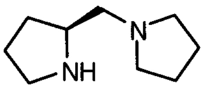
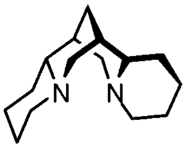
1,1′-Bi-2-naphthol derivatives are some of the most important artificial chiral auxiliaries and have been extensively used in asymmetric syntheses and chiral discriminations. Optically active oligo- and poly(1,1′-bi-2-naphthol) derivatives, in which the naphthalene units are connected at their 1,4-positions, are of great interest from the viewpoints of synthesis, conformational structure, chiroptical and physical properties, and applications as a conjugated polymer with a main-chain chirality. Although studies on the synthetic approach to oligomers, such as the sexi- and octinaphthalene derivatives, in addition to the polymers partially having a 1,1′-bi-2-naphthol unit in the main chain are available,[1−4] there is no report on the synthesis of the poly(1,1′-bi-2-naphthol) derivatives by the polymerization process as far as we know.

Recently, the asymmetric syntheses of the 1,1′-bi-2-naphthol skeleton by the oxidative coupling reaction of 2-naphthol derivatives have been reported.[5,6] For example, the asymmetric aerobic oxidative coupling of 2-naphthol derivatives using the chiral CuCl−diamine complexes proceeded in good yields with high enantioselectivity.[5b,d] In the present study, these methods were applied to the polymerization of 2,3-dihydroxynaphthalene as a monomer affording poly(1,1′-bi-2-naphthol).[7] The polymerization was carried out using the CuCl-(*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)PMP][5,8] or $CuCl_2$-(−)-sparteine [(−)Sp] complex,[6f,g,9] and the polymer was obtained as a methanol-insoluble part after acetylation of the hydroxy groups. However, these polymerizations gave low molecular weight oligomers in a low yield,[8,9] probably due to the low solubility of the monomer and some side reaction such as the generation of quinone derivatives.

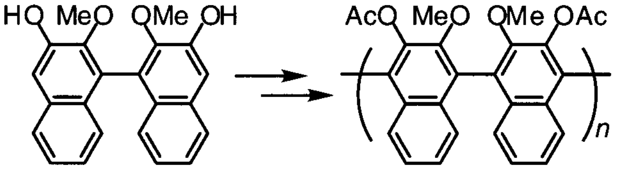


(+)PMP



(−)Sp

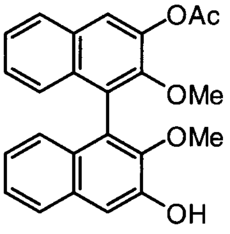
To improve the polymerization yield and the molecular weight of the obtained polymer, optically active 3,3′-dihydroxy-2,2′-dimethoxy-1,1′-binaphthalene (**1**)[2b,10] was adopted as a monomer during the oxidative coupling polymerization using the CuCl-(+)PMP, $CuCl_2$-(−)Sp, and CuCl−*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)[5a,c] complexes (Table 1). The produced polymer was also isolated as a methanol-insoluble fraction after acetylation of the hydroxy groups.



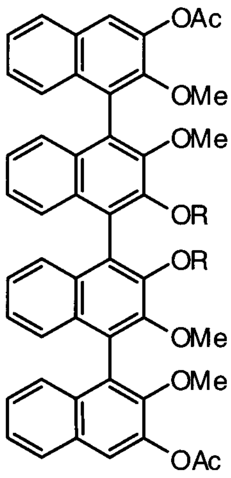
1 poly(**1**)

The polymerizations proceeded with much better yields than those for the polymerization of 2,3-dihydroxynaphthalene.[8,9] The obtained polymers had molecular weights up to 5.2 × 10^3 based on the size exclusion chromatographic (SEC) analysis, which corresponds to about 24-mer with respect to the naphthalene unit. These values were comparable to the molecular weight estimated by the ^{13}C NMR analysis as will be mentioned later.

As the model compounds of the obtained polymers, the optically active octahydroxyquaternaphthalene derivatives **2c** were prepared by the oxidative coupling reaction of **2a** using the CuCl-(+)PMP catalyst followed by acetylation.[2b,e,11] The ^{13}C NMR spectra of the methyl carbon in the acetyl groups of the optically active and racemic **2c** are demonstrated in Figure 1. The peaks were assigned as shown in the figure, and the chemical shifts of the internal acetyl groups are clearly affected by the stereostructure.



2a



R = H: **2b**
Ac: **2c**

Figure 2 shows the ^{13}C NMR spectra of the methyl carbon in the acetyl groups of the poly(**1**)s. The peaks around 20.7 ppm are based on the terminal acetyl groups, as mentioned above, and the molecular weight of the polymers can be estimated from this intensity. On the other hand, the two peaks around 19.9 and 20.2 ppm for the internal acetyl groups are considered to show the stereochemistry of the bonds newly formed during the polymerization from the results shown in Figure 1. The former must be based on the absorption of the (*R*)-structure existing between the (*S*)-structure ($\cdots S\underline{R}S\cdots$) or the (*S*)-form between the (*R*)-form ($\cdots R\underline{S}R\cdots$), while the latter must be due to the structures $\cdots S\underline{S}S\cdots$ or $\cdots R\underline{R}R\cdots$. Therefore, the match/mismatch stereochemistry between the mono-

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Table 1. Oxidative Coupling Polymerization of 1 at Room Temperature for 24 h

entry	**1**	reagent	yield (%)^a	M_n ($\times 10^3$)^b	M_w/M_n^{b}	*R*:*S*^{c}	$[\alpha]^{25}_D$ (deg)^d
1	*R*	CuCl-TMEDA^e	71	5.2	1.6	*f*	+144.9
2	*R*	CuCl−(+)PMP^e	59	4.1	1.6	71:29	+156.5
3	*S*	CuCl−(+)PMP^e	36	3.8	1.3	53:47	−129.2
4	*R*	$CuCl_2$-(−)Sp^g	61	3.4	2.3	84:16	+185.0
5	*S*	$CuCl_2$-(−)Sp^g	70	3.1	1.4	52:48	−70.9

[a] Methanol-insoluble part of poly(**1**). [b] Determined by SEC in THF (polystyrene standard). [c] Estimated by ^{13}C NMR analysis. [d] In $CHCl_3$. [e] [**1**] = 0.13 M, [CuCl]/[diamine]/[**1**] = 0.20/0.25/1, solvent = CH_2Cl_2, O_2 atmosphere. [f] Not determined. [g] [**1**] = 0.077 M, [$CuCl_2$]/[(−)Sp]/[**1**] = 1/2/1, solvent = MeOH, N_2 atmosphere.

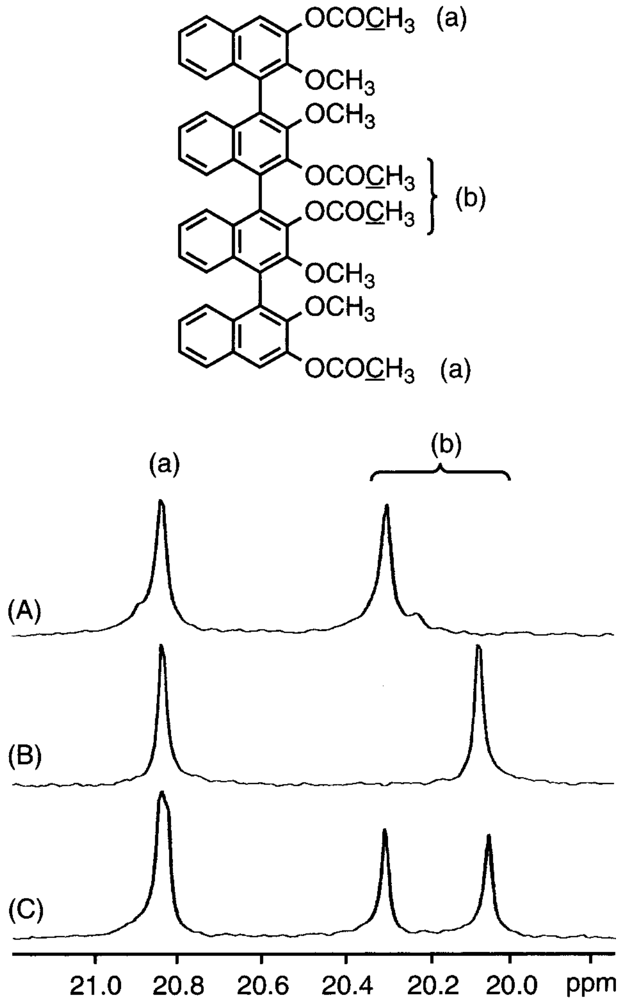

Figure 1. ^{13}C NMR spectra of methyl carbon in acetyl groups of (A) (*SSS*)-**2c**, (B) (*SRS*)-**2c**, and (C) (*RRS*/*SSR*)-**2c** ($CDCl_3$, room temperature).

mers and the ligands was clearly observed during the asymmetric oxidative coupling polymerization. In both systems with (+)PMP and (−)Sp as a ligand, the polymerization of (*R*)-**1** proceeded much more selectively to produce the ···*RRR*··· structure than those of (*S*)-**1**, as well as (*R*)-**1** with the achiral catalyst (entry 1), which showed almost no selectivity. During the polymerization of the (*R*)-monomer with (−)Sp, the selectivity was determined to be *R*:*S* ≈ 84:16 (Figure 2C), suggesting that the obtained polymer consists of about 1 (*S*)- and 14 (*R*)-configurations with regard to the bonds between the naphthyl groups. The estimated selectivities (*R*:*S*) for poly(**1**)s are listed in Table 1. The spectral pattern of the polymer prepared with the achiral catalyst (entry 1) was much broader than those of poly(**1**)s obtained with the chiral complexes.

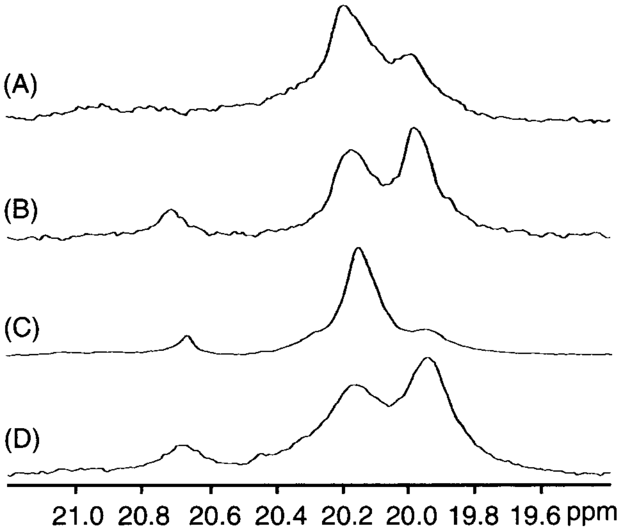

Figure 2. ^{13}C NMR spectra of methyl carbon in acetyl groups of poly(**1**)s (A) obtained from (*R*)-**1** with (+)PMP (entry 2), (B) (*S*)-**1** with (+)PMP (entry 3), (C) (*R*)-**1** with (−)Sp (entry 4), and (D) (*S*)-**1** with (−)Sp (entry 5) ($CDCl_3$, 60 °C).

The model reactions of the optically active **2a** using the CuCl-(+)PMP catalyst were performed in CH_2Cl_2 under an O_2 atmosphere at room temperature. The oxidative coupling of (*R*)-**2a** for 4 h gave (*RRR*)- and (*RSR*)-**2b** in 27 and 6% yields (*R*:*S* = 82:18), respectively, whereas (*SSS*)- and (*SRS*)-**2b** were obtained in 31 and 19% yields, respectively, for the reaction of (*S*)-**2a** for 7 h (*S*:*R* = 62:38).[12] Although *S*-selectivity was observed during the reaction of (*S*)-**2a**, it was much lower than the *R*-selectivity during the coupling of the (*R*)-isomer. These results support the stereoselectivities observed for polymerization of **1**.

Figure 3 depicts the circular dichroism (CD) spectra of the model compounds, (*SSS*)- and (*SRS*)-**2c**, and poly(**1**)s obtained with the chiral complexes. The spectral patterns of the poly(**1**)s obtained from (*R*)- and (*S*)-**1** are almost mirror images of each other and mainly determined on the basis of the monomer configuration, although the peak intensities are significantly different. The CD intensity at 235 nm except for poly(**1**) having a lower stereoselectivity (entry 5) was almost comparable to those of the model compounds.

In conclusion, poly(1,1′-bi-2-naphthol) derivatives, in which the naphthalene units are connected at their 1,4-positions, with a high stereoregularity were first synthesized by the asymmetric oxidative coupling polymerization of optically active 3,3′-dihydroxy-2,2′-dimethoxy-1,1′-binaphthalene with chiral copper reagents. Further investigations into the stereoselective coupling polymerization of tetrahydroxybinaphthalene derivatives and functions of the obtained polymers are now in progress.

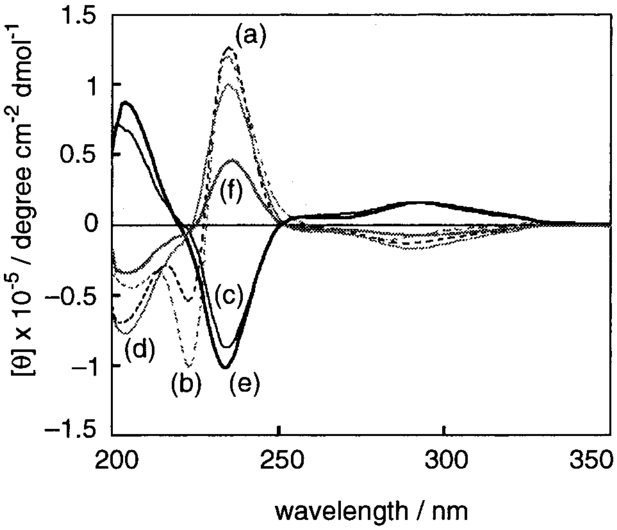

Figure 3. CD spectra of (a) (*SSS*)-**2c**, (b) (*SRS*)-**2c**, (c) poly(**1**) obtained from (*R*)-**1** with (+)PMP (entry 2), (d) poly(**1**) obtained from (*S*)-**1** with (+)PMP (entry 3), (e) poly(**1**) obtained from (*R*)-**1** with (−)Sp (entry 4), and (f) poly(**1**) obtained from (*S*)-**1** with (−)Sp (entry 5) (naphthalene unit, in THF).

Supporting Information Available: Text giving ^{1}H NMR, ^{13}C NMR, and CH analysis of poly(**1**) and spectral data of the model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(7) Typical procedure: A monomer was added to a mixture of copper chloride and diamine in a solvent. After stirring the mixture for 24 h, a solvent was evaporated, and CH_2Cl_2 and an excess amount of acetyl chloride and pyridine were added. The acetylated polymer was isolated as a methanol-insoluble part by centrifugation and drying in vacuo.

(8) Conditions: solvent = tetrahydrofuran, temperature = 50 °C, [2,3-dihydroxynaphthalene] = 0.35 M, [CuCl]/[(+)PMP]/[monomer] = 0.2/0.25/1, O_2 atmosphere. Yield: 13%, M_n = 2.1 × 10^3 (SEC, polystyrene standard).

(9) Conditions: solvent = methanol, temperature = room temperature, [2,3-dihydroxynaphthalene] = 0.17 M, [$CuCl_2$]/[(−)Sp]/[monomer] = 1/2/1, N_2 atmosphere, Yield: 3%, M_n = 1.6 × 10^3 (SEC, polystyrene standard).

(10) The *rac*-**1** was preparatively separated by HPLC using Chiralpak AD (Daicel, 25 × 2 cm column, eluent: hexane/ethanol = 45/55 (v/v)).

(11) The absolute configuration of **2c** was confirmed by conversion of acetyl groups of **2c** to methyl groups.[2b,e]

(12) The oxidative coupling of (*S*)-**2a** with the CuCl−TMEDA catalyst for 5 h gave ($S\underline{S}S$)- and ($S\underline{R}S$)-**2b** in 21 and 17% yields ($\underline{S}$:$\underline{R}$ = 55:45), respectively.

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