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Polymer 44 (2003) 7377–7381
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Synthesis of poly(1,4-naphthylene) bearing crown ether side chain by asymmetric oxidative coupling polymerization

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Received 8 July 2003; received in revised form 4 September 2003; accepted 10 September 2003

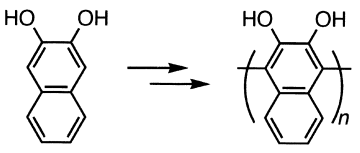
Abstract

The oxidative coupling polymerization of *racemic*-, (*R*)-, and (*S*)-2,2′,3,3′-tetrahydroxy-1,1′-binaphthyl derivatives bearing a crown ether moiety was carried out in the presence of a Cu(I) or Cu(II) catalyst with various ligands, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine, (−)-sparteine [(−)Sp], and (*S*)-(−)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline). Methanol-insoluble poly(binaphthyl crown ether) with a molecular weight up to $M_n = 4.1 \times 10^3$ was synthesized in moderate yields. Polymerization using (−)Sp proceeded in an *S*-selective manner; the polymer with the highest negative specific rotation was obtained with the (*S*)-monomer. The obtained polymers exhibited characteristic abilities for chiral recognition toward amino acids, such as 2-phenylglycine hydrochloride and 2-phenylglycine methyl ester hydrochloride.

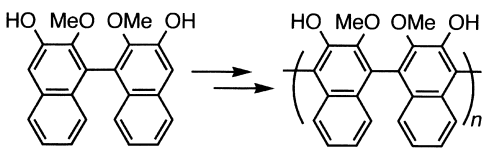
Keywords: Asymmetric oxidative coupling polymerization; Poly(1,4-naphthylene); Binaphthyl crown ether

1. Introduction

Due to the axial dissymmetry, 1,1′-bi-2-naphthol derivatives have been greatly utilized as chiral auxiliaries in organic reactions and chiral discriminations. Polymers that include the 1,1′-bi-2-naphthol structure are, therefore, attractive as functional chiral materials, and accordingly, numerous reports can be found on their syntheses and applications [1,2]. Among the polymers that feature the 1,1′-bi-2-naphthol moiety, poly(1,4-naphthylene) derivatives consisting of 1,1′-bi-2-naphthol units are especially of interest in terms of their chiroptical and physical properties, as well as their structure as a rigid polymer with a chiral backbone. We have recently reported on the first synthesis of poly(1,1′-bi-2-naphthol) derivatives via asymmetric oxidative coupling [3,4] polymerization (AOCP) of 2,3-dihydroxynaphthalene (**1**) or tetrahydroxybinaphthyl derivative (**2**) in the presence of copper complexes [5–7]. Polymerization of optically active **2** in combination with C_2-symmetric bisoxazoline ligands produced polymers with the preferential ···*RRRR*···/···*SSSS*··· and ···*RSRS*··· chain structures.



1 poly(**1**)



2 poly(**2**)

Binaphthyl based crown ethers have been recognized as possessing important chiral discrimination properties toward various molecules, such as amino acid derivatives [8–10]. Subsequently, the syntheses of polymers containing these crown ethers have been reported [11–15]. Herein, we report on the AOCP of binaphthyl crown ether **3** as a novel monomer. The ability of the obtained poly(1,4-naphthylene)

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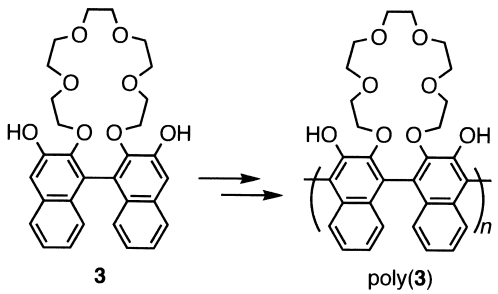
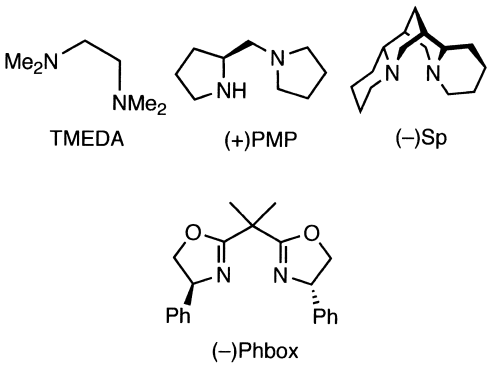
doi:10.1016/j.polymer.2003.09.017

bearing crown ether side chains for chiral discrimination was also examined.





2. Experimental

2.1. Measurements

^{1}H NMR spectra were measured on a Varian Gemini-2000 (400 MHz) spectrometer in $CDCl_3$. Infrared (IR) spectra were recorded on a JASCO FT/IR-620 spectrometer. Mass (MS) spectra were taken on a JEOL LMS-AX505HA or a Voyager Elite MALDI-TOF mass spectrometer (PE Biosystems). Optical rotation was measured on a JASCO P-1030 polarimeter at 25 °C. Circular dichroism (CD) spectra were obtained with a JASCO J-720L apparatus. Ultraviolet (UV) absorption spectra were taken on a JASCO V-570 spectrometer. The size exclusion chromatographic (SEC) analyses were performed on a Shodex GPC-System-21 equipped with Shodex UV-41 and Shodex RI-71S detectors using Shodex GPC KF-806L and KF-803 columns connected in series (eluent: tetrahydrofuran (THF), temp. = 40 °C, flow rate = 1.0 ml/min). Calibration was carried out using standard polystyrenes. Chromatographic separation was performed on a JASCO 980-PU chromatograph equipped with UV (JASCO 970-UV) and polarimetric (JASCO OR-990) detectors at room temperature.

2.2. Materials

The dry solvents, CH_2Cl_2 and THF (Kanto), were used for the polymerization. Optically active diamines, (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)PMP] (Aldrich) and (−)-sparteine [(−)Sp] (Sigma), were dried over calcium hydride and then distilled under reduced pressure. (*S*)-(−)-2,2′-Isopropylidenebis(4-phenyl-2-oxazoline) [(−)Phbox] (Aldrich) and di-μ-hydroxo-bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper(II)] chloride (CuCl-TMEDA) (TCI) was used as received.

Synthesis of **3**. The synthetic route of **3** is shown in Fig. 1. A solution of penta(ethylene glycol) di-*p*-toluenesulfonate (1.70 mmol) in THF (9 ml) was added to a mixture of 3,3′-dibenzyloxy-2,2′-dihydroxy-1,1′-binaphthyl (**4**) (1.70 mmol) and potassium *tert*-butoxide (5.0 mmol) in THF (8 ml). After stirring at reflux temperature for 4 h, 1N HCl was added, and the mixture was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel chromatography using hexane/$CHCl_3$/EtOH (50:4:1) to afford **5** (47% yield), which was subsequently converted to **3** via hydrogenolysis. The enantiomers of *rac*-**3** were separated by preparative high performance liquid chromatography (HPLC) using a chiral column (Daicel Chiralpak AD, 250 × 20 mm) with ethanol as the mobile phase.

Compound **3**. ^{1}H NMR ($CDCl_3$): δ 3.33–3.75 (m, 20H, –OCH_2C–), 7.08–7.10 (m, 4H, aromatic), 7.32–7.37 (m, 2H, aromatic), 7.46 (s, 2H, aromatic), 7.60 (br, 2H, –OH), 7.57 (d, J = 8.0 Hz, 2H, aromatic). IR (KBr, cm^{-1}): 3231, 2875, 1509, 1442, 1347, 1251, 1111, 1043, 951, 750. Mass (FAB): *m*/*z* 520 $[M]^+$. (*R*)-**3** (96%ee): $[\alpha]_D^{25} = -55.9°$ ($CHCl_3$, $c = 1.0$), (*S*)-**3** (>99%ee): $[\alpha]_D^{25} = +58.4°$ ($CHCl_3$, c = 0.83). The absolute configuration was confirmed by using (*S*)-**4** as a starting material [5,7].

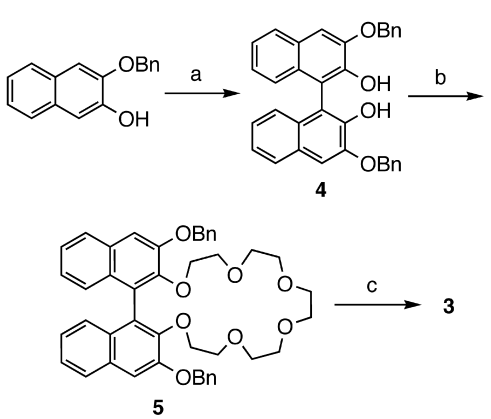


Fig. 1. Reagents and conditions for synthesis of **3**: (a) 10 mol% CuCl-TMEDA, CH_2Cl_2, O_2 atmosphere, (b) penta(ethylene glycol) di-*p*-toluenesulfonate, KO*t*-Bu, THF, (c) Pd/C, EtOH, H_2 atmosphere.

2.3. Polymerization procedure [5,7]

A solution of **3** (0.40 g, 0.77 mmol) in CH_2Cl_2 (6 ml) was added to a mixture of CuCl (15 mg, 0.15 mmol) and diamine (0.17 mmol) in CH_2Cl_2 (0.4 ml) at room temperature. After stirring at room temperature for 24 h under an O_2 atmosphere, the product was isolated as the methanol-insoluble fraction by centrifugation and drying in vacuo. The polymer was acetylated using an excess amount of acetyl chloride and pyridine in CH_2Cl_2 according to the previously reported procedure [5–7].

2.4. Enantioselective complexation experiment [16]

The polymer's ability for chiral recognition was estimated as follow: an aqueous solution (1.0 ml) of racemic amino acid hydrochloride (0.025 mmol) and $LiPF_6$ (0.25 mmol) was extracted with a solution of the polymer (0.0125 mmol, monomer unit) in $CHCl_3$ (1.0 ml) at room temperature for 15 min. After allowing the mixture to stand at room temperature for 24 h to attain complete phase separation, the amount of each enantiomer of the amino acid in the aqueous layer were determined by CD and UV analyses.

2.5. Benzylation of poly(3)

The polymer (81 mg) prepared with the $CuCl_2$-(−)Sp complex was benzylated using an excess amount of benzyl bromide (0.19 ml, 1.5 mmol) and K_2CO_3 (0.21 g) in a mixture of *N*,*N*-dimethylformamide (DMF, 2.5 ml) and THF (2.5 ml) at 60 °C for 24 h. The product was isolated as the methanol-insoluble part by centrifugation and drying in vacuo (overall yield: 50%): $M_w = 7.0 \times 10^3$, $M_n = 3.9 \times 10^3$, $[\alpha]_D^{25} = -120.2°$ ($CHCl_3$).

3. Results and discussion

The results of the oxidative coupling polymerization of **3** in the presence of various copper reagents at room temperature are summarized in Table 1. The polymerization of *rac*-**3** with the CuCl-TMEDA catalyst in CH_2Cl_2 afforded a polymer as the methanol-insoluble fraction in 50% yield with a number average molecular weight (M_n) of 4.0×10^3, which corresponds to about eight repeated units (entry 1). The obtained polymer was fully soluble in THF and $CHCl_3$.

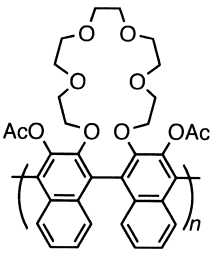
The ^{1}H NMR spectrum of this polymer is shown in Fig. 2. Previously, the stereochemistry of poly(**2**), with respect to the newly formed bonds during the polymerization process, was estimated using ^{13}C NMR analysis following acetylation of the hydroxyl groups [5]. However, in the case of the acetylated poly(**3**) [poly(**3′**)], comparable information was not obtained. As shown in the MALDI-MS spectrum of poly(*rac*-**3**) [matrix = α-cyano-4-hydroxycinnamic acid (αCHA)] (Fig. 3), peaks were observed for almost every multiple of the molecular weight of the monomer unit (518).

Table 1
Oxidative coupling polymerization of **3** in CH_2Cl_2 for 24 h

Entry	**3**	Catalyst	Yield[a] (%)	M_w[b] ($\times 10^3$)	M_n[b] ($\times 10^3$)	$[\alpha]_D^{25}$[c] (°)
1	*rac*	CuCl-TMEDA	50	5.6	4.0	–
2	*R*	CuCl-TMEDA	37	4.6	3.5	+74.3
3	*S*	CuCl-TMEDA	40	4.6	3.5	−78.7
4	*R*	CuCl-(+)PMP	33	3.7	3.1	+70.6
5	*S*	CuCl-(+)PMP	30	3.6	3.0	−73.4
6	*rac*	$CuCl_2$-(−)Sp[d]	61	6.2	4.1	−23.4
7	*R*	$CuCl_2$-(−)Sp[d]	40	3.9	3.0	+51.6
8	*S*	$CuCl_2$-(−)Sp[d]	48	3.8	2.9	−102.3
9	*R*	CuCl-(−)Phbox[e]	17	4.7	3.9	+52.9
10	*S*	CuCl-(−)Phbox[e]	<1	–	–	–

[a] Methanol-insoluble part.
[b] Determined by SEC in THF (polystyrene standard).
[c] In $CHCl_3$.
[d] [**3**]/[$CuCl_2$]/[(−)Sp] = 1/2/4, N_2 atmosphere.
[e] Solvent: THF.

Furthermore, a small peak was observed at an *m*/*z* value of approximately 5250, which corresponds to approximately 10 repeated units.



poly(**3'**)

Positive and negative $[\alpha]_D$ values were observed for the polymers obtained from (*R*)- and (*S*)-**3**, respectively. As shown in Table 1, poly((*R*)-**3**) and poly((*S*)-**3**), which were obtained using optically active catalyst, CuCl-(+)PMP, exhibited values for specific rotation of similar magnitude, but opposite in direction (entries 4 and 5). Furthermore, these values are comparable to those of the polymers that were obtained using achiral catalyst CuCl-TMEDA (entries 2 and 3). It can be suggested that the (+)PMP ligand would

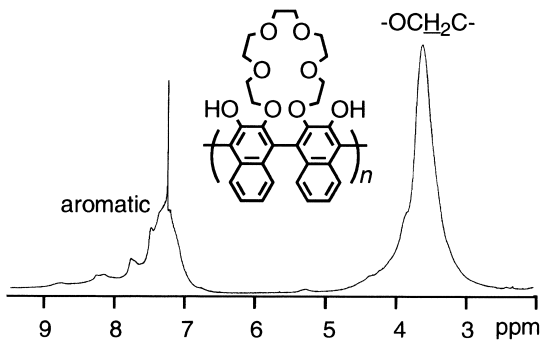


Fig. 2. ^{1}H NMR spectrum of poly(**3**) obtained from *rac*-**3** with (−)Sp (Table 1, entry 6) ($CDCl_3$, 60 °C).

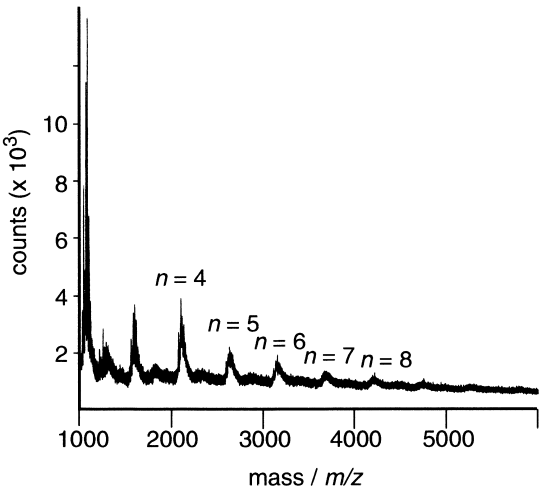


Fig. 3. MALDI-TOFMS spectrum of poly(*rac*-**3**) obtained with the $CuCl_2$-(−)Sp catalyst (Table 1, entry 6) (matrix = αCHA).

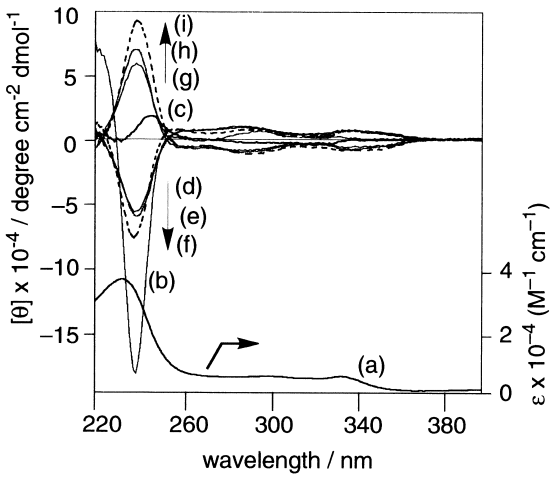


Fig. 4. UV spectrum of poly(*rac*-**3**) obtained with the $CuCl_2$-(−)Sp catalyst (Table 1, entry 6) (a) and CD spectra of (*R*)-**3** (b), poly(*rac*-**3**) obtained using (−)Sp (entry 6) (c), poly((*R*)-**3**) obtained using TMEDA (entry 2) (d), poly((*R*)-**3**) obtained using (+)PMP (entry 4) (e), poly((*R*)-**3**) obtained using (−)Sp (entry 7) (f), poly((*S*)-**3**) obtained using TMEDA (entry 3) (g), poly((*S*)-**3**) obtained using (+)PMP (entry 5) (h), poly((*S*)-**3**) obtained using (−)Sp (entry 8) (i) (naphthalene unit, in $CHCl_3$).

not have significant contributions to the stereocontrol during the polymerization of **3**. In contrast, for the polymers obtained using the $CuCl_2$-(−)Sp complex (entries 7 and 8), poly((*S*)-**3**) exhibited a negative specific rotation with a significantly larger absolute value than that of poly((*R*)-**3**). The polymer obtained using *rac*-**3** with this reagent showed a specific rotation of −23.4° (entry 6). Judging from the CD spectral patterns of these polymers, as shown in Fig. 4(c), (f), and (i), it can be reasoned that the polymerization with the (−)Sp ligand proceeds in an *S*-selective manner, however, details of the stereoselectivity of the polymerization remain unclear. Our studies show that poly((*S*)-**3**) produced with the (−)Sp ligand corresponds to the "···*SSS*···" main chain structure, and poly((*R*)-**3**) should correspond to the "···*RSR*···" structure (an underline part presents the stereostructure of the newly formed bond during the polymerization). In contrast, polymerization in the presence of the CuCl-(−)Phbox complex, which was effective for the polymerization of **1** and **2** [6,7], resulted in low or no yields (entries 9 and 10).

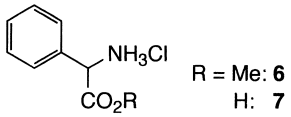
The ability of the obtained poly(**3**)s for enantiomer-selective complexation was estimated using 2-phenylglycine methyl ester hydrochloride (**6**) and 2-phenylglycine hydrochloride (**7**) as guest compounds. As shown in Table 2,

Table 2
Chiral recognition of poly(**3**) and poly(**3″**) toward amino acids

Entry	Guest	Poly(**3**) (used catalyst for preparation)	Extracted guest		Separation factor α[a]
			Amount (%)[b]	ee (%)[b]	
1	**6**	(*R*)-**3**	16.0	34.0 (*S*)	2.31
2		Poly((*R*)-**3**) (CuCl-TMEDA)	20.3	6.6 (*S*)	1.18
3		Poly((*S*)-**3**) (CuCl-TMEDA)	20.1	8.4 (*R*)	1.24
4		Poly((*R*)-**3**) (CuCl-(+)PMP)	20.1	5.4 (*S*)	1.14
5		Poly((*S*)-**3**) (CuCl-(+)PMP)	21.4	5.7 (*R*)	1.16
6		Poly((*R*)-**3**) ($CuCl_2$-(−)Sp)	20.8	6.1 (*S*)	1.16
7		Poly((*S*)-**3**) ($CuCl_2$-(−)Sp)	29.2	9.4 (*R*)	1.31
8		Poly((*S*)-**3″**) ($CuCl_2$-(−)Sp)	28.7	3.4 (*S*)	1.10
9	**7**	(*R*)-**3**	~0	–	–
10		Poly(*rac*-**3**) ($CuCl_2$-(−)Sp)	3.6	6.7 (*S*)	1.5
11		Poly((*R*)-**3**) (CuCl-TMEDA)	2.5	38.7 (*S*)	2.31
12		Poly((*S*)-**3**) (CuCl-TMEDA)	2.6	43.8 (*R*)	2.61
13		Poly((*R*)-**3**) (CuCl-(+)PMP)	2.2	48.1 (*S*)	2.92
14		Poly((*S*)-**3**) (CuCl-(+)PMP)	3.5	47.7 (*R*)	2.93
15		Poly((*R*)-**3**) ($CuCl_2$-(−)Sp)	4.3	36.4 (*S*)	2.22
16		Poly((*S*)-**3**) ($CuCl_2$-(−)Sp)	3.7	23.9 (*R*)	1.66
17		Poly((*S*)-**3″**) ($CuCl_2$-(−)Sp)	3.8	17.9 (*R*)	1.46

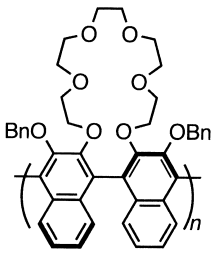
[a] $\alpha = [F_{major}/F_{minor}]/[E_{minor}/E_{major}]$. *F* : free analyte, *E* : extracted analyte.
[b] Determined by UV and CD analyses of the aqueous layer.

monomer (*R*)-**3** selectively formed a complex with (*S*)-**6** with a separation factor (α) [16] of approximately 2.31 (entry 1). Similarly, poly(**3**)s prepared from (*R*)- and (*S*)-**3** preferentially extracted (*S*)- and (*R*)-isomers, respectively, indicating that the stereochemistry of the monomer unit greatly influences the stereoselective complexation toward **6**. Although the polymers showed higher extractabilities, the observed selectivities were significantly lower than that of the monomer. Among the poly(**3**)s, poly((*S*)-**3**) that was prepared using the $CuCl_2$-(−)Sp complex exhibited the highest value for $[\alpha]_D$ (entry 7), and also demonstrated the highest selectivity ($\alpha = 1.31$). These results show that the stereochemistry between the binaphthyl crown ether units has a significant influence over the polymer's ability for chiral discrimination.



Although (*R*)-**3** was not able to extract **7**, the polymers showed higher extractabilities and α values (up to 2.93) for **7** than those observed for **6**. The (*R*)- and (*S*)-monomer units stereoselectively complexed with (*S*)- and (*R*)-**7**, respectively. Moreover, stereoselective complexation was even observed for the polymer prepared from *rac*-**3** using the $CuCl_2$-(−)Sp complex (entry 10).

The hydroxyl groups at the 3,3′-positions of the monomer unit of poly((*S*)-**3**) prepared with the $CuCl_2$-(−)Sp complex were benzylated [poly((*S*)-**3**″)]. This benzylated polymer showed a complexation towards **6** with an opposite and lower stereoselectivity than that of the original poly((*S*)-**3**) (entry 8). This clearly indicates that substituents on the 3,3′-positions significantly affect the stereoselectivity.



poly((*S*)-**3**")

4. Conclusion

In conclusion, novel poly(1,1′-bi-2-naphthol) bearing a crown ether moiety was stereoselectively synthesized by the oxidative coupling polymerization of *racemic*-, (*R*)-, and (*S*)-binaphthyl crown ether derivatives. The obtained polymers clearly demonstrated their characteristic ability to complex stereoselectively to 2-phenylglycine derivatives.

Acknowledgements

This work was partially supported by Grant-in-Aid for Scientific Research (No. 15350066) from the Ministry of Education, Science, Sports, and Culture of Japan.

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