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Copper(I)-Catalyzed Asymmetric Oxidative Coupling Polymerization of 2,3-Dihydroxynaphthalene Using Bisoxazoline Ligands

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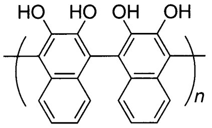
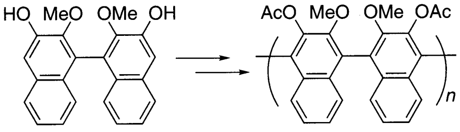
ABSTRACT: The asymmetric oxidative coupling polymerization of 2,3-dihydroxynaphthalene with the complexes of Cu(I)−bisoxazoline as a catalyst under an O_2 atmosphere was successfully accomplished to produce poly(2,3-dihydroxy-1,4-naphthylene) having a continuous 1,1′-bi-2-naphthol main chain structure. For example, the polymerization with (*S*)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) as a ligand at room temperature for 24 h afforded a methanol-insoluble polymer in 30% yield with a molecular weight of approximately 4.1×10^3 as estimated by ^{13}C NMR analysis, and the polymer was quantitatively obtained after 48 h. The obtained polymer was rich in the *S*-configuration. The structure of the bisoxazoline ligands significantly affected the catalyst activity and stereoselectivity.

Introduction

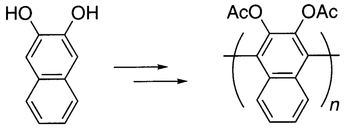
The π-conjugated polymers, such as the poly(*p*-phenylene)s, have attracted interest due to their applications as advanced materials with electronic and optical functions as well as their thermal and mechanical properties.[1] However, little attention has been paid to the poly(1,4-naphthylene)s, although the oligomers, such as the sexi- and octinaphthalene derivatives, from a stepwise synthesis have been reported.[2] The polymers having a 1,1′-bi-2-naphthol unit in the main chain are especially unique because the rigid C_2-symmetric structure can control the polymer conformation and functions, and many studies on the polymers partially bearing a 1,1′-bi-2-naphthol moiety in the main chain are available.[3] Accordingly, optically active poly(2,3-dihydroxy-1,4-naphthylene) derivatives are of great interest from the viewpoints of their synthesis, conformational structure, chiroptical and physical properties, and applications as a rigid polymer with a main-chain chirality.



Recently, we reported the first synthesis of poly(1,1′-bi-2-naphthol) derivative, in which the naphthalene units are connected at their 1,4-position, by the asymmetric oxidative coupling polymerization (AOCP) of optically active 3,3′-dihydroxy-2,2′-dimethoxy-1,1′-binaphthalene (**1**).[4] The polymer obtained after acetylation of the hydroxy groups had molecular weights (M_n) up to 5.2×10^3 based on the size exclusion chromatographic (SEC) analysis, which corresponds to about 24 repeat units with respect to the naphthalene unit. On the other hand, the AOCP of 2,3-dihydroxynaphthalene (**2**) using $CuCl_2$−(−)-sparteine [(−)Sp] and CuCl−(*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine [(+)PMP] complexes, which are known as effective reagents for the construction of the 1,1′-bi-2-naphthol skeleton,[5,6] resulted in a low yield and gave a low molecular weight oligomer, probably due to the low solubility of the monomer and products, along with some side reactions such as the generation of quinone derivatives.[7,8]

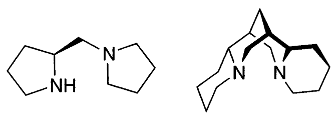


1 poly(**1'**)

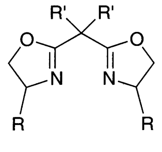


2 poly(**2'**)

Despite these unsuccessful results, the stereocontrolled polymerization of the commercially available and simple monomer **2** to produce poly(2,3-dihydroxy-1,4-naphthylene) is valuable in the development of novel functional polymer materials. In the course of our study on the AOCP of **2**, we found a novel highly active catalyst system, the copper(I) complexes of C_2-symmetric bisoxazoline derivatives, such as (*S*)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) [(*S*)IPhO], (*R*)-2,2′-isopropylidenebis(4-benzyl-2-oxazoline) [(*R*)IBnO], (*S*)-2,2′-isopropylidenebis(4-*tert*-butyl-2-oxazoline) [(*S*)ItBuO], and (*S*)-2,2′-methylenebis(4-phenyl-2-oxazoline) [(*S*)-MPhO].[9]



(+)PMP (−)Sp



R = Ph, R' = Me : IPhO
R = CH_2Ph, R' = Me : IBnO
R = *t*-Bu, R' = Me : ItBuO
R = Ph, R' = H : MPhO

10.1021/ma021797c CCC: $25.00

Table 1. AOCP of 2 at Room Temperature for 24 h

entry	catalyst (equiv)	solvent	yield (%)[a]	M_n ($\times10^3$)[b]
1	CuCl−(+)PMP (0.2)	THF	<1	1.9
2[c]	CuCl−(+)PMP (0.2)	THF	11[d]	1.8
3[e,f]	CuCl−(+)PMP (0.2)	THF	13[g]	2.1
4	CuCl−(+)PMP (0.2)	CH_2Cl_2	0	
5	$CuCl_2$-(−)Sp (1.0)[h]	MeOH	3	1.6
6[e]	$CuCl_2$-(−)Sp (2.0)[h]	MeOH	3	2.1

[a] Methanol-insoluble part of poly(**2′**). [b] Determined by SEC in THF (polystyrene standard). [c] Time = 48 h. [d] $[\alpha]^{25}_{D} = -12.8°$ ($CHCl_3$). [e] Reference 4. [f] Temperature = 50 °C. [g] $[\alpha]^{25}_{D} = -3.6°$ ($CHCl_3$). [h] $[CuCl_2]/[(-)Sp] = 1/2$; the polymerization was carried out under an N_2 atmosphere.

Experimental Section

Materials. 2 (Kishida Chem. Co.) and copper(I) salts [CuCl and $(CF_3SO_3Cu)_2\cdot C_6H_6$ (CuOTf); Aldrich] were used as received. The solvents, tetrahydrofuran (THF), dichloromethane, and methanol, used for polymerization were purchased from Kanto Chem. Co. as the dehydrate grade. The commercially available bisoxazolines (Aldrich) were used without further purification.

Measurements. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini-2000 (400 MHz for ^{1}H) spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. The 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, and THF was used as eluent (temperature = 40 °C, flow rate = 1.0 mL/min). Calibration was carried out using standard polystyrenes. 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. Thermogravimetric analyses (TGA) were carried out with a Seiko SSC-200 equipped with a TG/DTA-220 apparatus (at a heating rate of 40 °C/min).

Polymerization. 2 (0.28 g, 1.75 mmol) was added to a mixture of the Cu(I) salt and bisoxazoline in a solvent ([**2**] = 0.35 M, [Cu(I)]/[ligand]/[**2**] = 0.2/0.25/1). The mixture was stirred at room temperature under an O_2 atmosphere. After evaporation of the solvent, CH_2Cl_2 and an excess amount of acetyl chloride and pyridine were added. After a 12 h stirring, poly(**2′**) was isolated as the methanol-insoluble part by centrifugation, repeated washing with methanol, and drying in vacuo.[10]

Results and Discussion

The results of the AOCP of **2** using the CuCl−(+)-PMP and $CuCl_2$-(−)Sp complexes are listed in Table 1. The polymerizations were carried out under an O_2 atmosphere for the CuCl−(+)PMP catalyst system (entries 1−4) and under an N_2 atmosphere for the $CuCl_2$-(−)Sp (entries 5 and 6). In every case, however, the methanol-insoluble fraction after acetylation of the hydroxy groups was obtained in a poor or no yield (up to 13%) and an oligomer corresponding to the 7−9-mers as previously reported.[4]

Table 2 shows the AOCP of **2** using various Cu(I)−bisoxazoline complexes in THF or CH_2Cl_2 at room temperature under an O_2 atmosphere. The polymerization with the CuCl−(*S*)IPhO catalyst for 24 h afforded poly(**2′**) as a methanol-insoluble fraction in 30−34% yield, which showed $M_n = (1.06-1.53) \times 10^4$ (SEC) (entries 1 and 3). Furthermore, the polymer was quantitatively obtained from the polymerization for 48 h, although the obtained polymer was mostly insoluble in THF and $CHCl_3$ (entry 2). The counteranion of the copper salt, trifluoromethanesulfonate (OTf), also significantly influenced the catalyst activity to produce a polymer in quantitative even for the 24 h polymerization (entry 4). Both the polymer yield and M_n value were dramatically increased by using the bisoxazoline ligand in comparison with the Cu(I)−(+)PMP and Cu(II)−(−)Sp systems.

Table 2. AOCP of 2 with Bisoxazoline Ligands in THF at Room Temperature

entry	catalyst	time (h)	yield[a] (%)	M_n ($\times10^3$) (M_w/M_n)[b]	$[\alpha]^{25}_{D}$[c] (deg)
1	CuCl−(*S*)IPhO	24	30	10.6 (2.6)	−40.3
2	CuCl−(*S*)IPhO	48	>99[d] (3)[e]	6.2 (2.3)	
3[f]	CuCl−(*S*)IPhO	24	34 (31)[e]	15.3 (2.4)	+6.1
4	CuOTf-(*S*)IPhO	24	>99[d] (<1)[e]	9.4 (5.6)	
5	CuCl−(*R*)IBnO	24	21	9.8 (1.5)	+13.9
6	CuCl−(*S*)ItBuO	24	27 (25)[e]	8.5 (1.8)	+19.3
7	CuCl−(*S*)MPhO	24	>99[d] (4)[e]	6.9 (1.5)	
8	CuCl−(*S*)MPhO	3.5	56 (36)[e]	9.3 (1.6)	+46.1
9	CuCl−(*S*)iPrOPy	24	0		

[a] Methanol-insoluble part of poly(**2′**). [b] Determined by SEC in THF (polystyrene standard). [c] In $CHCl_3$. [d] Methanol-insoluble part of poly(**2**). [e] Methanol-insoluble and THF-soluble part of poly(**2′**). [f] Solvent = CH_2Cl_2.

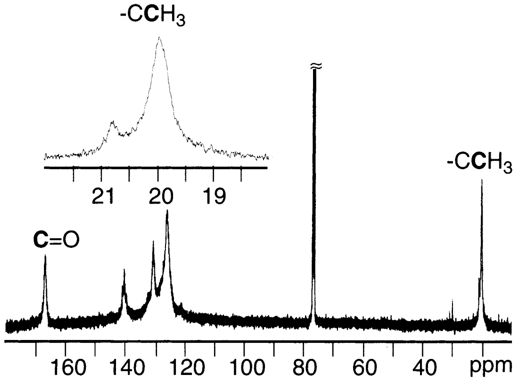


Figure 1. ^{13}C NMR spectrum of poly(**2′**) obtained with the CuCl−(*S*)IPhO catalyst (Table 2, entry 1) ($CDCl_3$, 60 °C).

Table 3. Asymmetric Oxidative Coupling of 3 at Room Temperature[a]

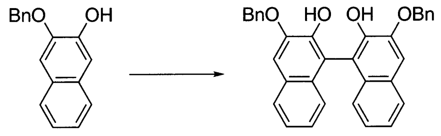
entry	catalyst	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	CuCl−(+)PMP[d]	CH_2Cl_2	7	84	10 (*S*)
2	CuCl−(*S*)IPhO	THF	2	92	43 (*S*)
3	CuCl−(*S*)IPhO	CH_2Cl_2	2	84	11 (*S*)
4	CuOTf−(*S*)IPhO	THF	3	94	12 (*S*)

[a] [Cu(I)]/[**3**] = 0.2, [**3**] = 0.35 M, O_2 atmosphere. [b] Isolated yield. [c] Determined by chiral HPLC (Chiralpak AD). [d] [Cu(I)]/[**3**] = 0.1.

Figure 1 demonstrates the ^{13}C NMR spectrum of poly(**2′**) obtained in THF (entry 1). The expanded spectrum of the methyl carbon in the acetyl groups shows a broad peak with a small shoulder around 21.0 ppm due to the terminal acetyl groups.[4] The molecular weight calculated from this intensity was approximately 4.1×10^3 [degree of polymerization (DP) ≈ 17], which is less than the half value estimated by SEC. This is due to the rigid main chain structure of the polymer. Although the stereochemistry of poly(**1′**) was evaluated from the absorption in this region,[4] significant information was not obtained for poly(**2′**).

The model reaction, coupling of 3-benzyloxy-2-naphthol (**3**) with the (*S*)IPhO ligand, was carried out (Table 3). The reactions proceeded in high yields to give a coupling product, 3,3′-dibenzyloxy-1,1′-binaphthalene-2,2′-diol (**4**),[5c,11] with an *S*-selective manner. The reaction in THF showed a moderate and higher enantioselectivity (43% ee, entry 2) than that obained in CH_2-

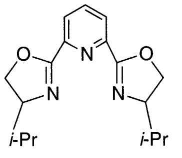
Cl_2. The CuOTf catalyst resulted in a low stereoselectivity (entry 4).



3 **4**

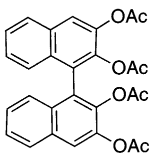
The polymer obtained with the CuCl−(*S*)IPhO system in THF exhibited a much higher specific rotation ($[\alpha]^{25}_D$ = −40.3°) than that obtained in CH_2Cl_2 (+6.1°). These are in good agreement with the results of the model reaction, although the sign for the specific rotations of the poly(**2′**)s are opposite to each other. The polymer obtained with (*S*)IPhO in THF should preferentially have an *S*-structure, whereas the *R*-structure should be in slight excess in poly(**2′**) obtained in CH_2Cl_2, although the degree of selectivity is not clear at present. These results are also supported by the circular dichroism (CD) spectra as will be mentioned later.

The effect of the structure of the bisoxazoline ligand on the AOCP of **2** in THF was examined. The ligands bearing the isopropylydene-bridge, (*R*)IBnO and (*S*)-ItBuO, were less effective for the stereocontrol during the polymerization than (*S*)IPhO based on the $[\alpha]_D$ value of the obtained polymers (Table 2, entries 5 and 6). On the other hand, the (*S*)MPhO having a methylene bridge showed a high catalyst activity to quantitatively produce a polymer for the polymerization of 24 h and in 56% yield even after 3.5 h (entries 7 and 8). In addition, the highest and positive specific rotation was observed for the obtained polymer. The complex of CuCl with 2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine [(*S*)^{i}PrOPy] resulted in no yield. The structure of the bisoxazoline ligand significantly affected the activity as well as the stereoselectivity.



iPrOPy

Figure 2 demonstrates the CD spectra of the obtained polymers and the model compound, (*S*)-2,2′,3,3′-tetraacetoxy-1,1′-binaphthyl (**5**) ($[\alpha]^{25}_D$ = +4.5, in $CHCl_3$).[12] The almost mirror-image spectral patterns were observed between the polymers with the negative and positive specific rotations, and the absorption intensity at 230 nm showed a good relation to the $[\alpha]_D$ values. The CD spectral pattern indicates that the polymer obtained with (*S*)IPhO in THF is rich in *S*-configuration, while the polymer obtained using (*S*)MPhO consists of the superior *R*-structure. However, when compared to the absorption intensity of the model (*S*)-**5**, that of the poly(**2′**)s was much smaller. Therefore, the enantioselectivity in the AOCP using the bisoxazoline ligands should be moderate or low as shown in the model reaction.



5

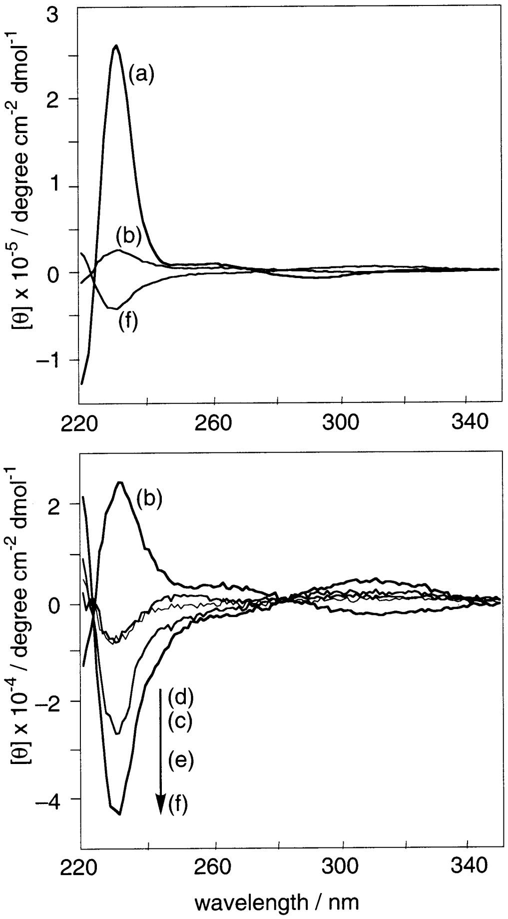
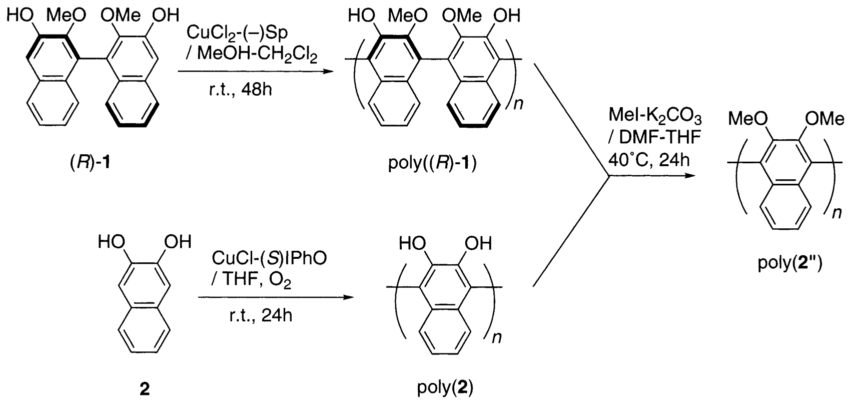


Figure 2. CD spectra of the model compound (*S*)-**5** (a), poly(**2′**) obtained with (*S*)IPhO in THF (b) (Table 2, entry 1), with (*S*)IPhO in CH_2Cl_2 (c) (entry 3), with (*R*)IBnO (d) (entry 5), with (*S*)ItBuO (e) (entry 6), and with (*S*)MPhO (f) (entry 8) (in $CHCl_3$).

To estimate the stereoselectivity in the AOCP of **2**, poly(2,3-dimethoxy-1,4-naphthylene) [poly(**2″**)] was synthesized using **1** and **2** as a monomer. The polymerization of (*R*)-**1** at room temperature using the $CuCl_2$−(−)Sp complex (1 equiv) in MeOH−CH_2Cl_2 (5/1 (v/v)) for 48 h afforded poly((*R*)-**1**). A part of the obtained polymer was acetylated to give poly(**1′**) [total yield 71% (MeOH-insoluble part), $M_n = 3.7 \times 10^3$, $M_w/M_n = 1.9$ (SEC), $[\alpha]^{25}_D$ = +200.2 (in $CHCl_3$)], whose stereochemistry was determined by ^{13}C NMR analysis[4] to be *R*:*S* = 81:19 with respect to the newly formed carbon−carbon bonds during the polymerization. Therefore, the obtained poly((*R*)-**1**) has a main-chain stereochemistry, *R*:*S* = 91:9. Another part of the obtained poly((*R*)-**1**) was methylated using an excess amount of methyl iodide and potassium carbonate at 40 °C in a mixture of *N*,*N*-dimethylformamide (DMF)−THF (1/1 (v/v)) to afford poly(**2″**) in 72% yield as a methanol-insoluble fraction [$M_n = 3.9 \times 10^3$, $M_w/M_n = 1.9$ (SEC)] with the specific rotation, $[\alpha]^{25}_D$ = +201.3° (in $CHCl_3$). Poly(**2″**) was also prepared by the polymerization of **2** with the CuCl−(*S*)IPhO catalyst (20 mol %) in THF at room temperature for 24 h followed by methylation of the hydroxy groups in 54% yield as a methanol-insoluble part (methanol-insoluble and THF-soluble part: 13%) [$M_n = 6.8 \times 10^3$, $M_w/M_n = 1.9$ (SEC), $[\alpha]^{25}_D$ = −28.5° (in $CHCl_3$)]. Assuming that the stereo-

Scheme 1



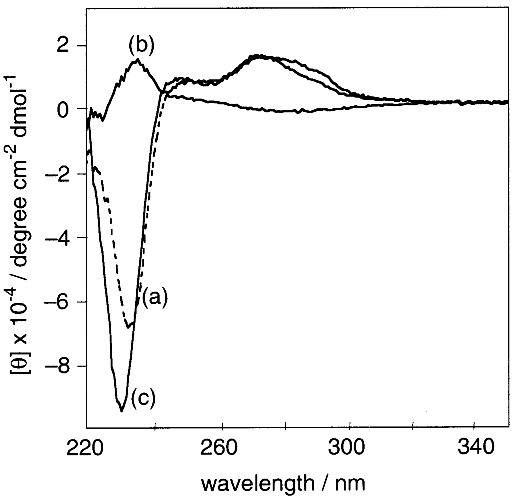


Figure 3. CD spectra of poly($\mathbf{2}''$) obtained from (*R*)-**1** (a), from **2** (b), and poly((*R*)-$\mathbf{1}'$) (c) (in $CHCl_3$).

selectivity (e.e.) of the main chain directly attributes to the specific rotation of the polymer, the specific rotations of the above two poly($\mathbf{2}''$) independently synthesized from (*R*)-**1** and **2** were compared. The stereoselectivity of poly($\mathbf{2}''$) prepared from **2** was evaluated to be R:S = 44:56 (12% ee) (see Scheme 1). This estimation again suggests that the enantioselectivity in the AOCP using the bisoxazoline ligands may not be high.

The CD spectra of poly($\mathbf{2}''$) and poly((*R*)-$\mathbf{1}'$) obtained from (*R*)-**1** and **2** are shown in Figure 3. The spectral patterns of poly($\mathbf{2}''$)s are almost mirror images of each other, although the intensity is quite different, supporting the above results.

A thermal property of poly(**2**) and poly($\mathbf{2}'$) was investigated by TGA (Figure 4). Two-step weight loss was observed for both polymers. Judging from the percentages of weight loss, the substituents on the naphthalene, acetyl and hydroxy groups, should be first decomposed around 350 °C, and then the polynaphthylene main chain starts to decompose around 400 °C.

In conclusion, the asymmetric oxidative coupling polymerization of a simple and commercially available monomer, 2,3-dihydroxynaphthalene, was first attained using the Cu(I)−bisoxazoline catalysts to produce poly(2,3-dihydroxy-1,4-naphthylene) having a continuous 1,1′-bi-2-naphthol main chain structure. The structure of the bisoxazoline ligands significantly affected the catalyst activity and stereoselectivity. The enantioselectivity attained in this polymerization was estimated to be low, although the actual selectivity is not clear at present.

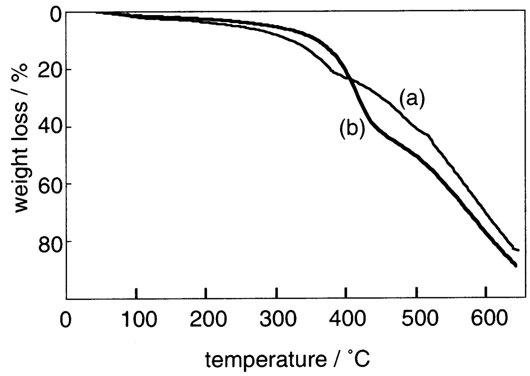


Figure 4. TGA traces of poly(**2**) (Table 2, entry 7) (a) and poly($\mathbf{2}'$) (Table 2, entry 3) (b).

References and Notes

(1) (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350−1377. (b) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747−1785.

(2) (a) Belohradsky, M.; Budesínsky, M.; Günterová, J.; Holy, P.; Závada, I.; Císarová, I.; Podlaha, J. *J. Org. Chem.* **1996**, *61*, 1205−1210. (b) Tanaka, K.; Furuta, T.; Fuji, K.; Miwa, Y.; Taga, T. *Tetrahedron: Asymmetry* **1996**, *7*, 2199−2202. (c) Fuji, K.; Furuta, T.; Tanaka, K. *Org. Lett.* **2001**, *3*, 169−171.

(3) (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405−2494. (b) Putala, M. *Enantiomer* **1999**, *4*, 243−262. (c) Pu, L. *Macromol. Rapid Commun.* **2000**, *21*, 795−809.

(4) Habaue, S.; Seko, T.; Okamoto, Y. *Macromolecules* **2002**, *35*, 2437−2439.

(5) (a) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, *35*, 7983−7984. (b) Nakajima, M.; Hashimoto, S.; Noji, M.; Koga, K. *Chem. Pharm. Bull.* **1998**, *46*, 1814−1815. (c) Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. *J. Org. Chem.* **1999**, *64*, 2264−2271. (d) Amou, S.; Takeuchi, K.; Asai, M.; Niizeki, K.; Okada, T.; Seino, M.; Haba, O.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3702−3709.

(6) (a) Smrcina, M.; Lorenc, M.; Hanus, V.; Sedmera, P.; Kocovsky, P. *J. Org. Chem.* **1992**, *57*, 1917−1920. (b) Smrcina, M.; Poláková, J.; Vyskocil, S.; Kocovsky, P. *J. Org. Chem.* **1993**, *58*, 4534−4538.

(7) The solid-state polymerization of 2,6-dihydroxynaphthalene was recently reported: Suzuki, M.; Yatsugi, Y. *Chem. Commun.* **2002**, 162−163.

(8) The enzymatic polymerization of 1,5-dihydroxynaphthalene: Wang, L.; Kobatake, E.; Ikariyama, Y.; Aizawa, M. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2855−2861.

(9) (a) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339−345. (b) Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297−2360. (c) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1−45.

(10) Elemental analysis of poly($\mathbf{2}'$) (Table 2, entry 1). Calcd for $(C_{14}H_{10}O_4)_n$: C, 69.42%; H, 4.16%. Found: C, 67.18%; H,

4.25%. The polymer may contain a trace amount of copper catalyst even after washing with methanol repeatedly.

(11) (a) Li, X.; Yang, J.; Kozlowski, M. C. *Org. Lett.* **2001**, *3*, 1137−1140. (b) Hon, S.-W.; Li, C.-H.; Kuo, J.-H.; Barhate, N. B.; Liu, Y.-H.; Wang, Y.; Chen, C.-T. *Org. Lett.* **2001**, *3*, 869−872.

(12) **5** was prepared from **4** by deprotection of benzyl groups and acetylation. The obtained racemic **5** was separated by HPLC using Chiralpak AD (Daicel, eluent: hexane/2-propanol = 9/1 (v/v)): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.92 (s, 6H, $-COCH_3$), 2.33 (s, 6H, $-COCH_3$), 7.13−7.89 (m, 10H, aromatic). IR (KBr, cm^{-1}): 2926, 1774, 1438, 1371, 1245, 1204, 1148, 1098, 1012. Mass (FAB) m/z 487 ($[M + H]^+$).

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