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# The First Optically Active and Sterically Regular Poly(1,1′-bi-2-naphthol)s: Precursors to a New Generation of Polymeric Catalysts

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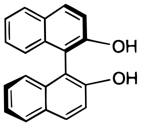
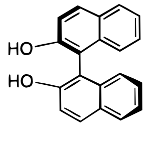
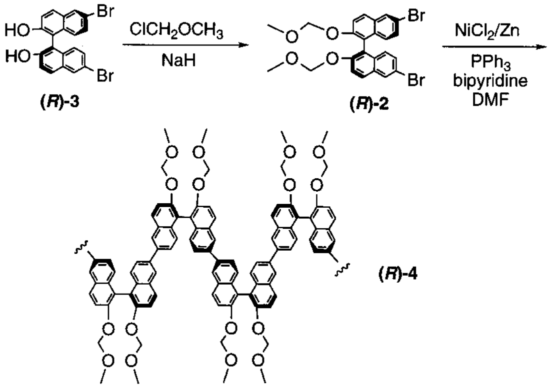
The application of optically active 1,1′-bi-2-naphthols, (*R*)-**1** and (*S*)-**1**, in asymmetric organic reactions has attracted very extensive attention.[1] These molecules and their derivatives have demonstrated excellent chiral induction in a number of organic transformations when used either as chiral auxiliaries or as chiral ligands.[1−3] In our laboratory, we are interested in synthesizing chiral conjugated polybinaphthyls[4] and developing sterically regular polymeric binaphthyl-based catalysts to carry out organic reactions. Using polymer-supported catalysts in industrial processes has several advantages, such as durable catalytic activity and easy recovery of the catalysts.[5,6] Traditionally, polymeric chiral catalysts are prepared by attaching chiral metal complexes to an achiral and sterically irregular polymer backbone.[5,6] In these systems, the catalytic sites are randomly oriented along the polymer chain, which makes it very difficult to systematically modify the microenviroment of the catalytic centers to optimize the reactivity and the stereoselectivity of the catalysts. Herein, we report our synthesis and characterization of the first optically active and sterically regular poly(1,1′-bi-2-naphthol). We have shown that this polymer can be used to prepare a new generation of polymeric catalysts where the catalytic centers are highly organized along the polymer chain. This polymeric catalyst has exhibited greatly enhanced catalytic activity over the corresponding monomeric catalyst when used in the Mukaiyama aldol condensation.


**(*R*)-1**


**(*S*)-1**

**Scheme 1. Preparation of the Chiral Polybinaphthyl (*R*)-4**



A chiral binaphthyl monomer (*R*)-**2** is synthesized from the reaction of 6,6′-dibromo-1,1′-bi-2-naphthol, (*R*)-**3**, with chloromethyl methyl ether in the presence of sodium hydride.[7,8] The specific optical rotation of (*R*)-**2** is $[\alpha]_D = +23.1°$ ($c = 1.0$, THF). In the presence of a catalytic amount of nickel(II) chloride and excess zinc, (*R*)-**2** is polymerized to generate an optically active polybinaphthyl (Scheme 1).[9] The best polymerization condition we have found so far is to heat a mixture of (*R*)-**2**, nickel(II) chloride (10 mol %), zinc (3 equiv), triphenylphosphine (40 mol %), and bipyridine (10 mol %) in DMF under nitrogen at 85−90 °C for 24 h. After the insolubles are filtered away, (*R*)-**4** is purified by precipitation of its methylene chloride solution with methanol several times. Gel permeation chromatography (GPC) analysis of (*R*)-**4** shows $M_w = 6000$ and $M_n = 3800$ (PDI = 1.6).[10] Its specific optical rotation is $[\alpha]_D = -301.9°$ ($c = 1.0$, THF). (*R*)-**4** is soluble in common organic solvents such as THF, methylene chloride, and chloroform and has been characterized by spectroscopic methods including $^1$H and $^{13}$C NMR.

We have prepared another chiral binaphthyl monomer (*R*)-**5** from the reaction of (*R*)-**3** with acetic anhydride. (*R*)-**5** is polymerized in the presence of 10 mol % nickel(II) chloride and excess zinc to generate (*R*)-**6** (Scheme 2). This polymer is also soluble in methylene chloride, chloroform, and THF. GPC analysis of (*R*)-**6** shows its molecular weight $M_w = 6400$ and $M_n = 3600$ (PDI = 1.8). The specific optical rotation of (*R*)-**6** is $[\alpha]_D = -353°$ ($c = 0.5$, THF). When a mixture of the THF solution of (*R*)-**6** and aqueous potassium hydroxide is heated at reflux, the ester functions of the polymer are readily hydrolyzed and an optically active polybinaphthol (*R*)-**7** is obtained. (*R*)-**7** is found to be soluble in basic water solution and insoluble in regular organic solvents. It is purified by dissolution in aqueous potassium hydroxide solution followed by precipitation with hydrogen chloride. The specific optical rotation of (*R*)-**7** is $[\alpha]_D = -139.8°$ ($c = 0.5$, 0.5 M aqueous KOH). (*R*)-**7** gives a relatively well-

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(6) Pittman, C. U., Jr. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1983; Vol. 8, p 553.

(7) (*R*)-**3** is prepared from the bromination of (*R*)-**1**: Sogah, G. D. Y.; Cram, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 3035.

(8) An efficient resolution of 1,1′-bi-2-naphthol has been developed in this laboratory: Hu, Q.-S.; Vitharana, D. R.; Pu, L. *Tetrahedron: Asymmetry* **1995**, *6*, 2123.

(9) (a) Wang, Y.; Quirk, R. P. *Macromolecules* **1995**, *28*, 3495. (b) Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 2354.

(10) THF was used as the eluting solvent in the GPC analysis of the polymers in this paper, and polystyrene standards were used. A laser light scattering study on another rigid and sterically regular polybinaphthyl prepared in our laboratory shows that the actual molecular weights of the binaphthyl-based polymers are about 1.4−2.5 times higher than the data obtained from GPC analysis.[4c]

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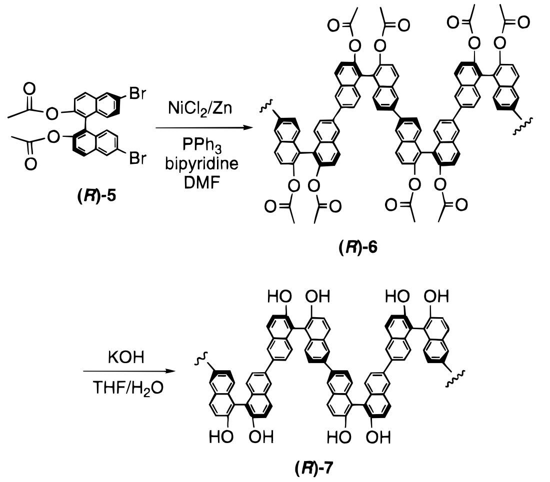
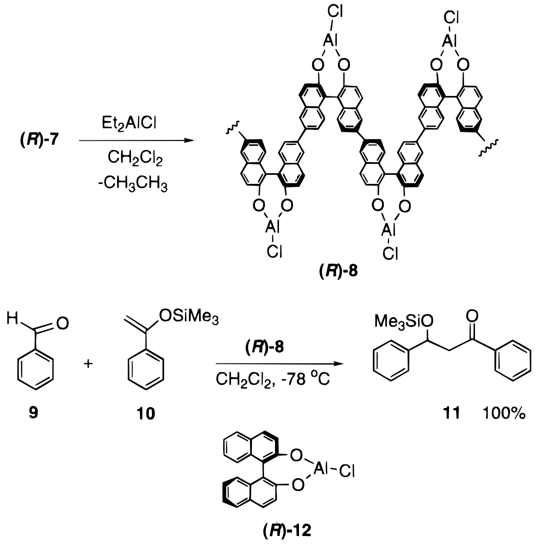
**Scheme 2. Preparation of the Chiral Polybinaphthyl (*R*)-6 and the Chiral Poly(1,1′-bi-2-naphthol) (*R*)-7**



**Scheme 3. Preparation of a Polybinaphthyl Aluminum(III) Catalyst (*R*)-8 and Its Application in the Mukaiyama Aldol Condensation**



resolved $^1$H NMR spectrum, which is consistent with the polymer structure. The UV spectrum of the polymer in 0.5 M aqueous KOH solution displays $\lambda_{\max} = 274, 340$ nm. In the same solution, the circular dichroism spectrum of (*R*)-**7** shows positive and negative Cotton effects: $[\theta]_{252} = 2.45 \times 10^3$, $[\theta]_{276} = -2.57 \times 10^3$, $[\theta]_{336} = -1.30 \times 10^3$, and $[\theta]_{364} = 9.06 \times 10^3$, $[\theta]_{377(\mathrm{sh})} = 6.62 \times 10^3$.[11] In the presence of hydrochloric acid, (*R*)-**4** also undergoes facial hydrolysis to generate the optically active polybinaphthol.

Treatment of the polybinaphthol (*R*)-**7** with diethyl aluminum chloride produces a novel polymeric Lewis acid complex (*R*)-**8** (Scheme 3).[12] In (*R*)-**8**, the aluminum centers are expected to be highly organized along the rigid and sterically regular polymer chain. When the reaction of (*R*)-**7** with 0.8 equiv of diethylaluminum chloride is carried out in deuterated methylene chloride, after 3 h, the $^1$H NMR spectrum of the reaction mixture shows the complete consumption of diethyl aluminum chloride. We have discovered that the resulting heterogeneous polymeric aluminum catalyst (*R*)-**8** is an excellent catalyst for the Mukaiyama aldol condensation of benzaldehyde, **9**, with 1-phenyl-1-[(trimethylsilyl)oxy]ethylene, **10**.[13] In the presence of 16 mol % (based on the monomeric unit) of (*R*)-**8**, **11** is produced quantitatively from this reaction in less than 3.5 h at −78 °C. However, under similar conditions, when 16 mol % of the monomeric aluminum complex (*R*)-**12**, prepared from the reaction of (*R*)-**1** with diethylaluminum chloride (0.8 equiv) in methylene chloride solution, is used as the catalyst, the rate of the Mukaiyama condensation is very slow. After 3.5 h, only ca. 5% conversion is observed. Thus, from the monomeric catalyst to the polymeric catalyst, there is a dramatic increase of the catalytic activity. In solution, (*R*)-**12** may exist as oligomers through the stable Al−O−Al bridging bonds to fill the empty p orbitals of the aluminum(III) atoms, which greatly reduces the catalytic activity of the complex.[14] However, in the polymeric complex (*R*)-**8**, formation of the Al−O−Al bridging bonds is very difficult, and the vacant p orbitals of the aluminum atoms in the polymeric complex will be available to activate the carbonyl group of **9** in the condensation reaction, leading to the excellent catalytic activity. Neither (*R*)-**8** nor (*R*)-**12** shows enantioslectivity in this reaction. We are currently exploring the reaction conditions and modifying the structure of the polymeric catalyst, e.g., by introduction of substituents to the 3,3′-positions of the binaphthol units in the polymer, in order to develop a class of enantioselctive polymeric catalysts.

In summary, the first optically active and sterically regular poly(1,1′-bi-2-naphthol)s have been synthesized through the hydrolysis of chiral polybinaphthyls that contain ester or acetal functional groups. These chiral polybinaphthols are soluble in basic water solution and have been characterized by a number of spectroscopic methods. The Lewis acid complex made from the polybinaphthol shows greatly enhanced catalytic activity over the corresponding monomeric complex when applied in the Mukaiyama aldol condensation. Because of the stereoregularity of the main chain chiral polybinaphthol, the catalytic centers in the polymeric catalyst are highly organized along the polymer chain, which makes it possible to systematically modify the microenvironment of the catalysts and to tune their reactivity and stereoselectivity. Work along this line is in progress.

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**Supporting Information Available:** Detailed experimental procedures and characterizations involving (*R*)-**2**, (*R*)-**4**, (*R*)-**5**, (*R*)-**6**, and (*R*)-**7** (3 pages).

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[11] The molar ellipiticity is calculated on the basis of the concentration of the monomer unit of (*R*)-**7**.

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