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Novel vanadium catalyst system with tartaric acid salts for highly selective asymmetric oxidative coupling polymerization

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Abstract

The asymmetric oxidative coupling polymerization (AOCP) of 2,3-dihydroxynaphthalene (DHN) with a novel catalyst system, oxovanadium(IV) stearate in the presence of the sodium or lithium salt of tartaric acid, under an O_2 atmosphere was carried out. For example, the polymerization with a catalytic amount of the D-(−)-tartaric acid disodium salt in THF at room temperature for 48 h followed by acetylation of the hydroxyl groups gave a methanol-insoluble polymer in a 40% yield, which showed the highest specific rotation value ($[\alpha]_D$) of −223 among the polymers so far obtained by the AOCP of DHN. The enantioselectivity during the polymerization was estimated to be an 88% enantiomeric exess (*S*).

Keywords: Vanadium catalyst; Tartaric acid salt; Asymmetric oxidative coupling polymerization

1. Introduction

The asymmetric synthesis of high-functional molecules, especially, based on the asymmetric induction reaction with the metal catalysts is an important research area. Optically active 1,1′-bi-2-naphthol derivatives with an axially dissymmetric structure are some of the most important compounds in organic chemistry and have been widely utilized in asymmetric synthesis, optical resolution, etc. [1,2]. The catalytic oxidative coupling reaction is an effective and facile method to obtain these compounds. Many asymmetric metal catalysts have been developed [3–6]. For instance, the optically active mono- and binuclear-type oxovanadium(IV) complexes prepared from $VOSO_4$, aldehydes, and amino acids have been reported as catalysts with a high stereoselectivity [7–10].

In polymer chemistry, the polymers bearing the binaphthol unit in the main chain have also attracted interests as optically active and functional materials and many reports on their synthesis and application could be found [1,2]. Recently, we reported the first catalytic and asymmetric oxidative coupling polymerization (AOCP) of 2,3-dihydroxynaphthalene (DHN) producing poly(2,3-dihydroxy-1,4-naphthylene) [poly(DHN)] consisting of straight binaphthol units (Scheme 1), in which the novel Cu(I)- or V(IV)-bisoxazoline catalyst was employed (Scheme 2) [11–16]. Especially, the latter vanadium catalyst system showed a much higher stereocontrol ability and the specific rotation ($[\alpha]_D$) of the polymer obtained using the vanadyl sulfate [$VOSO_4$]–(*R*)-2,2′-isopropylidenebis(4-phenyl-2-oxazoline) [(*R*)Phbox] catalyst reached −147.

On the other hand, the OCP is known as an industrial process for producing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which is an amorphous engineering plastic [17]. However, the use of this method is quite limited because of the difficulty in coupling-regiocontrolling the phenoxy radical intermediate. The coupling-selectivity control has been attained to some extent by using enzyme and enzyme–model catalysts in recent years [18,19]. Therefore, the development of a novel metal catalyst is practical and effective for realizing precise structure control during the OCP.

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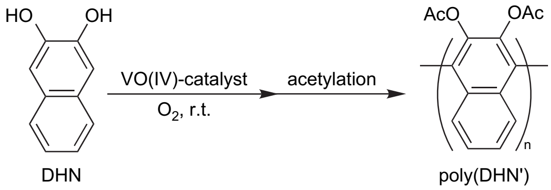
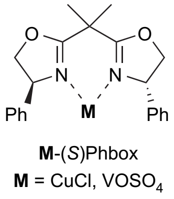


Scheme 1.



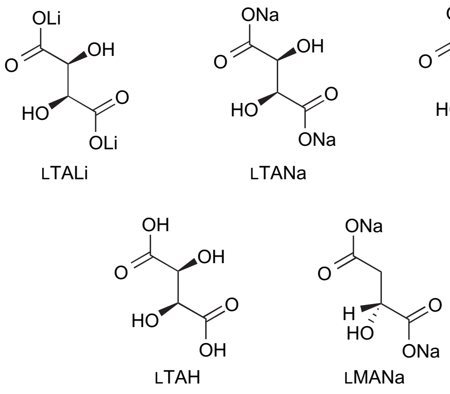
Scheme 2.

During the course of our study on the stereocontrolled synthesis of poly(DHN) by AOCP, we found that the novel system, VO(stearate)$_2$–L- or D-tartaric acid salt of sodium or lithium [L(or D)TAM (M = Na, Li)] (Scheme 3), shows a catalytic activity with a much higher stereocontrol ability than that of the above-mentioned $VOSO_4$–Phbox catalyst system. The reaction with titanium and vanadium catalysts in combination with dialkyl tartrate is well known as the Katsuki–Sharpless asymmetric oxidation, that is, the asymmetric epoxidation of allylic alcohols [20–24]. The aqueous polymerization of acrylonitrile initiated by V^{5+}–tartaric acid in sulfuric acid has also been investigated in the literature [25]. However, the OCP with the oxovanadium in the presence of tartaric acid salts has never been reported to the best of our knowledge.

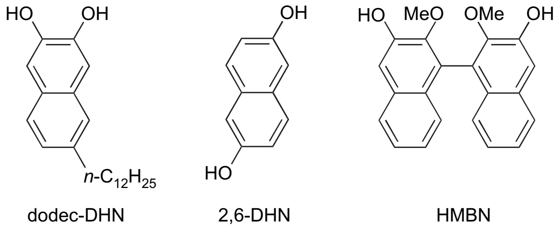
2. Experimental section

2.1. Measurements

^{1}H NMR spectra were measured on a Varian Unity Inova (500 MHz for ^{1}H) spectrometer. The optical rotation was measured on a Jasco P-1010 polarimeter at 25 °C. Circular dichroism (CD) spectra were obtained with a Jasco J-720WI apparatus. The size exclusion chromatographic (SEC) analyses were performed on a Jasco PU-2080 Plus equipped with a Jasco RI-2031-Plus RI detector with TSKgel G3000H$_{HR}$ and TSKgel G7000H$_{HR}$ columns connected in series (eluent = DMF, temperature = 25 °C, flow rate = 0.6 mL/min). Calibration was carried out with standard polystyrenes. High-performance-liquid-chromatography analyses were performed on a Jasco 986-PU chromatograph equipped with UV (Jasco 970-UV) detector [column = Chiralpak AD, eluent = hexane/2-propanol = 9/1 (v/v), temperature = 40 °C, flow rate = 0.5 mL/min].



Scheme 3.



Scheme 4.

2.2. Materials

The monomers, DHN (Aldrich), 2,6-dihydroxynaphthalene (2,6-DHN, Aldrich), 6-dodecyl-2,3-dihydroxynaphthalene (dodec-DHN), and 3,3′-dihydroxy-2,2′-dimethoxy-1,1′-binaphthalene (HMBN), were purchased or synthesized as previously reported [13,14,16] (Scheme 4). The dry solvents, CH_2Cl_2, tetrahydrofuran (THF), and methanol (Kanto), and the vanadium salts, such as VO(stearate)$_2$ and $VOSO_4$ (Wako), were used for the polymerization as-received. The optically active tartaric acids, L-(+)-tartaric acid (LTAH, Aldrich) and D-(−)-tartaric acid (DTAH, TCI), were used and their salts [L(or D)TAM] (M = Na, Li) (Scheme 3) were prepared as follows: a solution of sodium ethoxide (0.45 g, 6.66 mmol) in MeOH (30 mL) was gradually added to a solution of tartaric acid (0.5 g, 3.33 mmol) in MeOH (20 mL). After stirring at room temperature for 1.5 h, the mixture was filtered under an N_2 atmosphere and the filtrate was dried *in vacuo*.

2.3. Polymerization procedure

A monomer was added to a mixture of VO(stearate)$_2$ and TAM (M = Na, Li) ([DHN]/[VO(stearate)$_2$]/[TAM] = 1/0.1/0.1) in a solvent (0.35 M). After the mixture was stirred under an O_2 atmosphere, the solvent was evaporated, and CH_2Cl_2 and an excess amount of acetyl chloride and pyridine were added. The acetylated polymer was isolated as the MeOH-insoluble fraction by centrifugation and drying *in vacuo*.

3. Results and discussion

The results of the OCP of DHN with various catalyst systems at room temperature are summarized in Table 1.