

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 O₂ 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 excess (*S*).

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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 VOSO₄, aldehydes, and amino acids have been reported as catalysts with a high stereoselectivity [7–10].

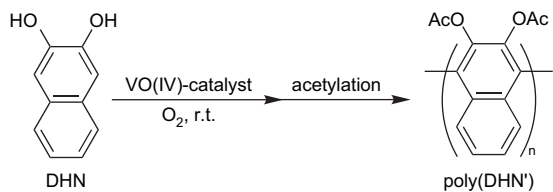
In polymer chemistry, the polymers bearing the binaphthol unit in the main chain have also attracted interests as optically active and functional materials and many reports on their

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 [VOSO₄]-(*R*)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) [(*R*)Phbox] catalyst reached –147.

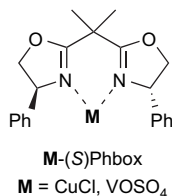
On the other hand, the OCP is known as an industrial process for producing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), which is an amorphous engineering plastic [17]. However, the use of this method is quite limited because of the difficulty in coupling-regiocontrolling the phenoxy radical intermediate. 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.



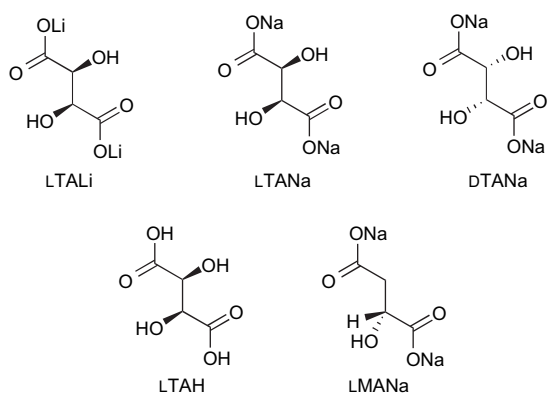
Scheme 2.

During the course of our study on the stereocontrolled synthesis of poly(DHN) by AOCPP, 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 VOSO₄-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 V⁵⁺-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.

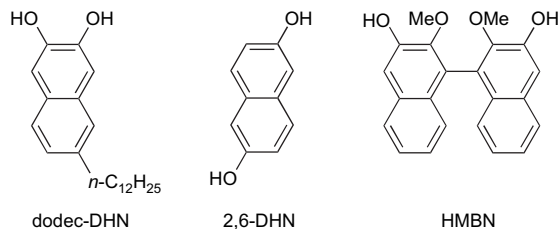
2. Experimental section

2.1. Measurements

¹H NMR spectra were measured on a Varian Unity Inova (500 MHz for ¹H) spectrometer. The optical rotation was measured on a Jasco P-1010 polarimeter at 25 °C. Circular



Scheme 3.



Scheme 4.

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].

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, CH₂Cl₂, tetrahydrofuran (THF), and methanol (Kanto), and the vanadium salts, such as VO(stearate)₂ and VOSO₄ (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 N₂ 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 O₂ atmosphere, the solvent was evaporated, and CH₂Cl₂ 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.

Table 1
AOC of DHN with VO(stearate)₂–TAM catalysts at room temperature under an O₂ atmosphere^a

Run	Catalyst	Solvent	Time (h)	Yield ^b (%)	$M_n \times 10^{-3c}$ (M_w/M_n)	$[\alpha]_D^d$
1	VO(stearate) ₂	CH ₂ Cl ₂ –MeOH	96	89	11 (2.9)	–
2	VO(stearate) ₂	THF	48	0	–	–
3	VO(stearate) ₂ –DTANa	CH ₂ Cl ₂ –MeOH	48	68	14 (4.9)	0
4	VO(stearate) ₂ –DTANa	THF	48	40	6.9 (1.3)	–223
5	VOSO ₄ –LTANa	THF	48	0	–	–
6	VO(acac) ₂ –LTANa	THF	48	0	–	–
7	Cu(OAc) ₂ –DTANa	THF	48	0	–	–

^a Conditions: [V]/[DHN] = 0.1, [DHN] = 0.35 M, solvent = CH₂Cl₂–MeOH [7/1 (v/v)].

^b MeOH-insoluble part of poly(DHN').

^c Determined by SEC in DMF (polystyrene standard).

^d In CHCl₃.

VO(stearate)₂ alone showed a catalytic activity in CH₂Cl₂–MeOH [7/1 (v/v)] [7,26] to afford a polymer as a methanol-insoluble fraction in 89% yield with the number average molecular weight (M_n) of 11×10^3 (run 1), whereas the polymerization in THF did not proceed (run 2). The polymerization was carried out in the presence of a catalytic amount of DTANa. The increase in the M_n value was observed for the polymerization in CH₂Cl₂–MeOH, although the obtained polymer did not show any optical activity (run 3). In marked contrast, the polymerization in THF gave a polymer in a moderate yield with specific rotation ($[\alpha]_D$) of –223 (run 4), which is the highest value in the reported poly(DHN') [11,15,16]. Therefore, in THF, a novel active catalyst species is generated from VO(stearate)₂ and tartaric acid salt, and stereoselectively forms a carbon–carbon bond between the naphthalene units during the polymerization.

Fig. 1 demonstrates the ¹³C NMR spectrum of poly(DHN') obtained with VO(stearate)₂–DTANa in THF for 48 h (run 4). The molecular weight can be calculated from the methyl carbon in the acetyl groups as previously reported [11,13], and estimated to be approximately 5.8×10^3 [degree of polymerization (DP) = 24], which is slightly lower than the value measured by SEC. This should be attributed to the rigid main chain structure of the polymer.

Fig. 2 shows the CD spectra of the polymer obtained using VO(stearate)₂–DTANa in THF, together with that of the model compound, (*S*)-2,2',3,3'-tetraacetoxy-1,1'-binaphthyl (**1**) [11], and poly(DHN') obtained with the previously reported VOSO₄–(*R*)Phbox ($[\alpha]_D = -147$) [15]. The CD spectral

pattern indicates that the polymer obtained using the VO(stearate)₂–DTANa catalyst is rich in the (*S*)-configuration, and the absorption intensity at around 230 nm is almost comparable to that of the model dimer. Based on the CD intensity, the polymerization with the VO(stearate)₂–DTANa catalyst system proceeded with a much higher stereoselectivity than that with the VOSO₄–(*R*)Phbox catalyst.

The polymerization in THF with various catalysts in the presence of TANa was also performed (runs 5–7), and the VOSO₄, VO(acac)₂, and Cu(OAc)₂ salts, in contrast to VO(stearate)₂, hardly showed any catalytic activity. These results indicate that the counter anion of the oxovanadium, as well as the center metal, plays an important role. In addition, the combination between the catalyst and the solvent significantly influences the catalytic activity and the stereoselectivity. The VO(stearate)₂–DTANa catalyst is quite effective for the AOC of DHN.

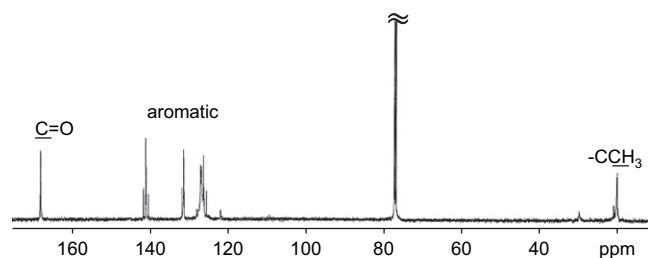


Fig. 1. ¹³C NMR spectrum of poly(DHN') obtained with VO(stearate)₂–DTANa for 48 h (Table 1, run 4) (CDCl₃, 57 °C).

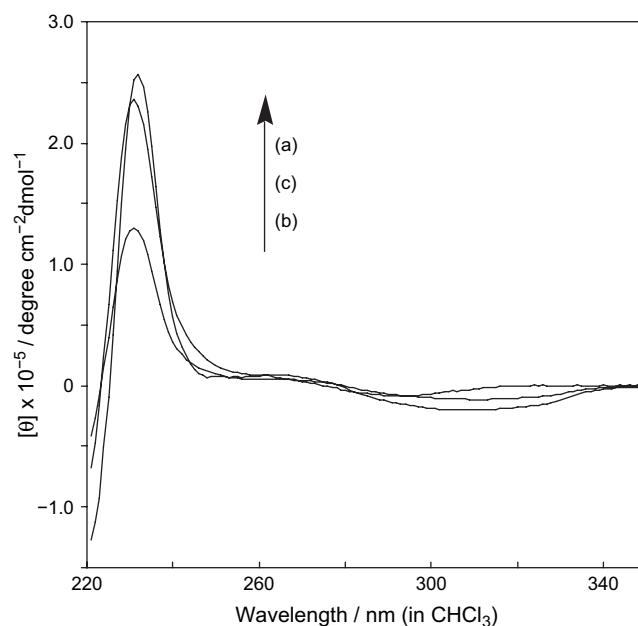


Fig. 2. CD spectra of (a) (*S*)-**1**, (b) poly(DHN') obtained with VOSO₄–(*R*)Phbox [15], and (c) poly(DHN') obtained with VO(stearate)₂–DTANa (Table 1, run 4); θ = molar ellipticity.

Table 2
AOCF of DHN with VO(stearate)₂–TAM (M = Na, Li) catalyst at room temperature under an O₂ atmosphere^a

Run	Catalyst	Solvent	Time (h)	Yield ^b (%)	$M_n \times 10^{-3c}$ (M_w/M_n)	$[\alpha]_D^d$
1	VO(stearate) ₂ –LTANa	THF	96	31	8.6 (1.2)	+217
2 ^e	VO(stearate) ₂ –2DTANa	THF	48	48	6.8 (1.2)	–172
3 ^f	VO(stearate) ₂ –DTANa	THF	48	77	8.3 (1.3)	–134
4 ^g	VO(stearate) ₂ –DTANa	THF	48	96 (65)	9.9 (1.7)	–86
5	VO(stearate) ₂ –LTALi	THF	48	15	8.3 (1.6)	+205
6	VO(stearate) ₂ –DTALi	THF	48	18	6.6 (1.2)	–230
7	VO(stearate) ₂ –DTALi	THF	96	42	7.1 (1.2)	–234
8	VO(stearate) ₂ –DTALi	CH ₂ Cl ₂ –MeOH	48	>99	10.8 (2.9)	0
9	VO(stearate) ₂ –LTAH	THF	48	0	–	–
10	VO(stearate) ₂ –LMANa	THF	48	0	–	–

^a Conditions: [V]/[DHN] = 0.1, [DHN] = 0.35 M, solvent = CH₂Cl₂–MeOH [7/1 (v/v)].

^b MeOH-insoluble part of poly(DHN'). In parentheses, the values for the MeOH-insoluble and THF-soluble parts are given.

^c Determined by SEC in DMF (polystyrene standard).

^d In CHCl₃.

^e [V]/[DTANa] = 1/2.

^f [DHN] = 0.70 M.

^g Temperature = 60 °C.

The polymerization with LTANa produced a polymer with an $[\alpha]_D$ of opposite sign to that obtained with DTANa (Table 2, run 1). In order to optimize the reaction conditions, the AOCF with the VO(stearate)₂–TANa catalyst system was carried out under various conditions (runs 2–4). The AOCF in the presence of 2 equiv. of DTANa to VO(stearate)₂ gave a polymer in a 48% yield, however, the optical activity of the obtained polymer decreased to –172 (run 2). Accordingly, the catalyst system composed of a 1:1 ratio of VO(stearate)₂ and TANa should be appropriate. The monomer concentration and polymerization temperature (60 °C) also affected the

catalyst performance. The polymers were obtained in a much higher yield, and the latter polymer contained a small amount of the THF-insoluble fraction. These THF-soluble fractions, however, showed a lower specific rotation value (runs 3 and 4).

The CD spectra of the polymers obtained using the VO(stearate)₂–L(or D)TANa catalyst are depicted in Fig. 3. The mirror-image spectral patterns were observed between the polymers obtained with LTANa and DTANa, that is, the polymer with an (*R*)-structure was selectively produced by the former catalyst during the polymerization. The absorption intensities at 230 nm are in good agreement with

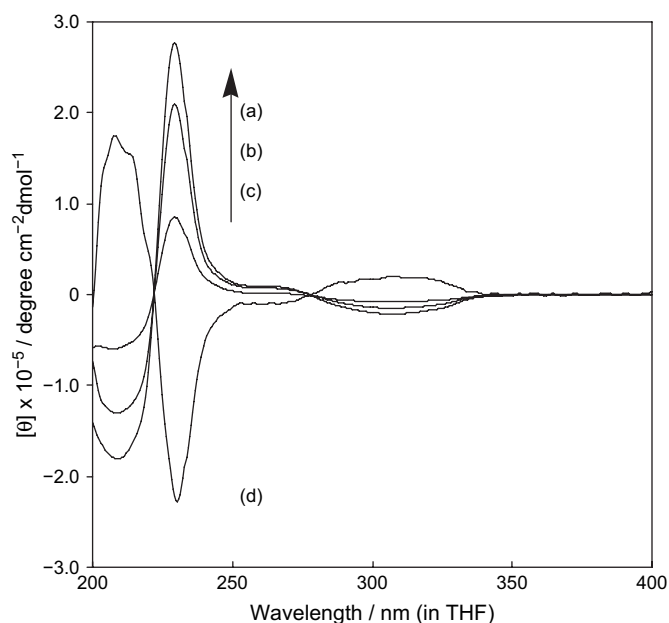


Fig. 3. CD spectra of poly(DHN')s obtained with (a) VO(stearate)₂–DTANa for 48 h (Table 1, run 4), (b) VO(stearate)₂–2DTANa for 48 h (Table 2, run 2), (c) VO(stearate)₂–DTANa for 48 h (60 °C) (Table 2, run 4), and (d) VO(stearate)₂–LTANa for 48 h (Table 2, run 1).

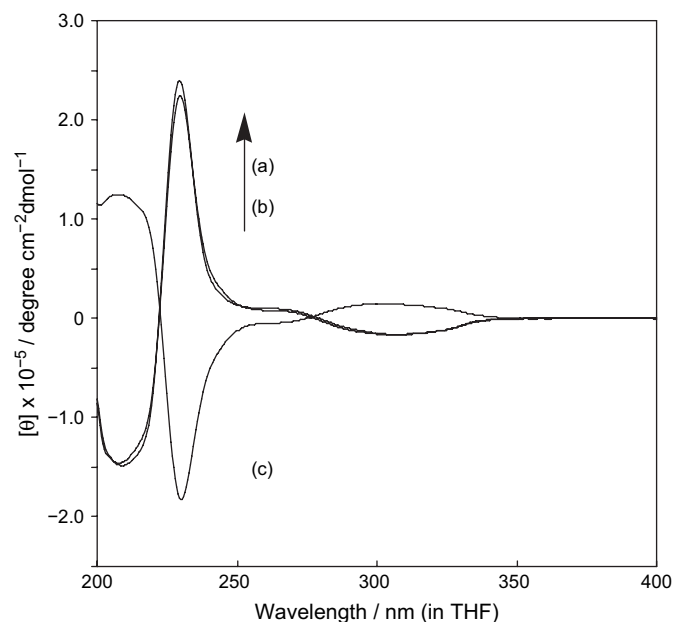
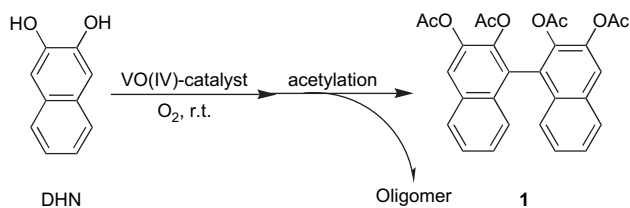


Fig. 4. CD spectra of poly(DHN')s obtained with (a) VO(stearate)₂–DTALi for 48 h (Table 2, run 6), (b) VO(stearate)₂–DTALi for 96 h (Table 2, run 7), and (c) VO(stearate)₂–LTALi for 48 h (Table 2, run 5).



Scheme 5.

the absolute value of the specific rotation ($[\alpha]_D$) of the obtained polymers.

The AOC of DHN with the tartaric acid and its lithium salt was carried out (runs 5–9). The polymerization using $\text{VO}(\text{stearate})_2\text{-L(or D)TALi}$ in THF for 48 h afforded a polymer with a specific rotation ($[\alpha]_D$) being almost equal to that of the polymer obtained using the sodium salts, although the polymer yield was low (runs 5–7). The polymerization in $\text{CH}_2\text{Cl}_2\text{-MeOH}$ [7/1 (v/v)] gave a polymer in quantitative yield, which did not show any optical activity, similar to that of the polymerization using the $\text{VO}(\text{stearate})_2\text{-DTANa}$ catalyst (run 8). The polymerization in the presence of LTAH or LMANa (Scheme 3) resulted in no yield, suggesting that the tartaric acid salt structure is important for the polymerization (runs 9 and 10).

The CD spectra of $\text{poly}(\text{DHN}')$ obtained in the presence of TALi are shown in Fig. 4. The spectral patterns are quite similar to those of the polymers obtained using the $\text{VO}(\text{stearate})_2\text{-TANa}$ catalyst, and the CD absorption intensities at around 230 nm were almost equal to that of the polymer obtained with the TANa system.

Model reactions, that is, the oxidative coupling of 2-naphthol and its derivatives, such as 3-benzyloxy-2-naphthol and methyl 3-hydroxy-2-naphthoate, with $\text{VO}(\text{stearate})_2\text{-L(or D)-TAM}$ were performed. However, the coupling product was not obtained in every case. Therefore, the adjacent dihydroxyl structure should be required for the coupling reaction. The OCP of DHN with the $\text{VO}(\text{stearate})_2\text{-DTAM}$ ($M = \text{Na, Li}$) catalyst in THF at room temperature for a relatively short time (13–24 h) under an O_2 atmosphere was then conducted (Scheme 5). After acetylation of the product mixture, the dimeric product (**1**) was isolated by silica gel column chromatography and obtained in 29–45% yields with an enantiomeric excess of 88% (*S*) for DTANa (reaction time: 13 h) and 89% (*S*) for DTALi (24 h). The (*S*)-configuration of the obtained **1** is identical with the observed selectivity for the polymerization with DTAM. Accordingly, the polymerization should

progress with the enantioselectivity estimated from these model reactions.

The AOC of 2,6-DHN or racemic HMBN (Scheme 4) using $\text{VO}(\text{stearate})_2\text{-DTANa}$ (10 mol%) in THF was also examined. However, the MeOH-insoluble polymer was not obtained. The AOC of dodec-DHN with $\text{VO}(\text{stearate})_2\text{-LTANa}$ in THF gave a polymer in an 81% yield with the much higher specific rotation ($[\alpha]_D$) of +190 than that of the polymer obtained with $\text{VOSO}_4\text{-(S)Phbox}$ ($[\alpha]_D = +60$) [16], and the polymer showed an M_n of 11×10^3 . These results again support the fact that the hydroxyl group at the 3-position of the monomer plays an important role in the coupling reaction and the 2,3-dihydroxynaphthalene structure as a monomer should be essential for the oxidative coupling polymerization with the $\text{VO}(\text{stearate})_2\text{-TAM}$ ($M = \text{Na, Li}$) catalyst system.

A mechanism for the catalytic oxidative coupling with the oxovanadium complex was postulated as follows [10,27]: the one-electron oxidation should be promoted on the 2-naphthol derivatives by the in situ generated vanadium(V) species that affords a radical intermediate, which concertedly couples with each other. The released vanadium species are oxidized by a molecular oxygen to regenerate the vanadium(V) species.

Despite of our efforts on isolation of the complex generated from $\text{VO}(\text{stearate})_2$ and TANa, the experiments were in unsuccessful. Accordingly, the detailed catalyst structure is not clear at present. After the reaction of $\text{VO}(\text{stearate})_2$ with 4 equiv. of LTANa in MeOH for 3 h at room temperature and filtration of the reaction mixture, 37% of the stearic acid was recovered in the filtrate, while the stirring of $\text{VO}(\text{stearate})_2$ alone in MeOH gave the stearic acid in a 3% yield. These results suggest that the counter anion exchange reaction between stearate and tartarate should occur and generate an oxovanadium tartarate complex. The vanadyl(IV) tartrate prepared by the reduction of V_2O_5 with an excess of either the optically active or the racemic tartaric acid, followed by the addition of the base, ($M_4[(\text{VO})_2(\text{tartarate})_2] \cdot x\text{H}_2\text{O}$) was reported, in which a binuclear oxovanadium complex structure was proposed for it [28,29]. Various chiral binuclear metal complexes as oxidative coupling catalysts having a good catalytic activity and stereocontrolled ability are available [5,8,10,26]. Therefore, the $\text{VO}(\text{stearate})_2\text{-TAM}$ system may generate a binuclear-type vanadyl-tartarate complex in situ leading to the coupling with a high stereoselectivity during the AOC of DHN as shown in Fig. 5.

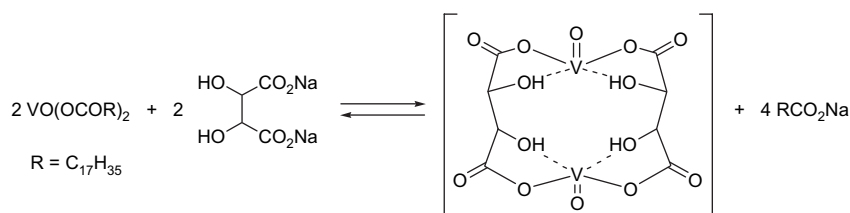


Fig. 5. Plausible binuclear oxovanadium complex formation.

4. Conclusions

Novel VO(stearate)₂-L(or D)TAM (M = Na, Li) catalysts for the AOCPP were developed. The polymerization proceeded under mild conditions, and the obtained polymer showed the highest stereoselectivity among the polymers obtained using the previously reported CuCl–bisoxazoline or VOSO₄–bisoxazoline catalyst system. The catalytic activity and stereocontrol ability were significantly affected by the monomer and catalyst structures and the reaction conditions. It is noteworthy that this catalyst system does not only possess novelty, but also cheap and convenient, that is, the catalyst can be simply prepared by mixing VO(stearate)₂ with the tartaric acid salt without isolation just before the polymerization.

Acknowledgements

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