Steric hindrance effects of phenoxyimine nickel catalysts in ethylene/propylene polymerization

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Abstract. A new mononuclear phenoxyimine nickel (II) catalyst with a xanthene skeleton was synthesized and applied to polymerization of ethylene/propylene. Higher activities were achieved in comparison with the catalyst lacking the axial steric hindrance and the catalyst with a synergistic effect. Moreover, the synthetic method was easier than that for the bimetallic catalyst.

1. Introduction

In olefin polymerization catalysts, increasing attention was attracted by late-transition-metal catalysts because of their great potential for (co)polymerization [1,2]. In addition, late-transition-metal phenoxyimine catalysts can produce highly branched polyethylene or poly(α-olefins) with long linear region through a “chain walking” process [3-9]. Lots of efforts such as electronic and steric adjustments, bimetallic cooperative effects [10-13], and fluorine bonding [14-16] have been made to modify the catalytic properties [17-23]. Microstructure of the resulting polymer depends on ligands’ electronic nature. Steric hindrance of coordination sites promotes chain propagation over chain transfer, yielding (ultra)high molecular weight polymers [24]. Moreover, polyethylene with high molecular weight and low branching or low molecular weight and high branching can be produced through chain of substituent electronics [25, 26]. Chen et al. [27] synthesized dinuclear α-dimine nickel complexes bearing xanthene as the bridge, which enabled the formation of semicrystalline polyethylene with much lower branching density compared with the mononuclear analogue in ethylene polymerization (No.1 in figure 1). Wang et al. [28] prepared some xanthene-bridged dinuclear nickel complexes which showed high catalytic activities (No.2 in figure 1). Besides the nickel catalysts, the xanthene skeleton can also be used as steric hindrance in polymerization catalyst No.3 [29]. Brookhart et al. reported catalyst No.4 with hindrance and fluorine atom effects [30]. Weak attractive interactions between neighboring groups can strongly promote chain walking and chain transfer. Mecking et al. revealed that catalyst activities could be controlled by choice of substituents [31] (No.5 in figure 1).
In nickel catalysts, fluorine substituents on a suitable position can stabilize the active sites through C-H…F / M…F interactions, leading to enhanced molecular weight, improved thermal stability and decrease in branching [17-19]. In our previous investigation, binuclear nickel catalyst No.7 (figure 2) with steric hindrance and metal-metal synergistic effects showed higher catalytic activity and thermal stability in ethylene polymerization [32]. However, the synthesis of binuclear metal catalysts was more complex than that of the mononuclear catalyst, and the reported propylene polymerization by phenoxyimine nickel catalysts usually displayed low activities and poor regio- and stereo-selectivities. Herein, we simplified the synthetic method and obtained new mononuclear nickel catalyst No.8. This is
the first time to synthesize and use the mononuclear nickel catalyst with xanthene skeleton. The axial steric hindrance played an important role in polymerization efficiency.

The xanthene-based salicylaldehyde catalyst was synthesized by the route shown in figure 3. Catalyst 8.1 was synthesized according to [19]. The following imine ligand L8 and pre-catalyst No.8 were synthesized by precise control of reagents amounts.

2. Results and discussion

Ethylene homopolymerizations were performed and the results are shown in table 1 and figure 4.

| Ent. | Precat. | Temp. (°C) | Time (min) | Yield (g) | TOFb | Br. c | Tm d | Mn e | Mw/Mn e |
|------|---------|------------|------------|-----------|------|-------|------|------|----------|
| 1    | 6 (20)  | 25         | 40         | 2.93      | 220  | 14    | 120.8| 61.7 | 2.57     |
| 2    | 6 (20)  | 50         | 40         | 5.64      | 423  | 55    | 119.1| 6.4  | 2.16     |
| 3    | 7 (20)  | 25         | 40         | 8.05      | 302  | 36    | 125.9| 39.7 | 3.72     |
| 4    | 8 (20)  | 25         | 40         | 3.84      | 288  | 89    | 120.6| 93.6 | 2.10     |
| 5    | 8 (10)  | 25         | 10         | 0.55      | 330  | 22    | 121.5| 60.4 | 2.82     |
| 6    | 8 (10)  | 50         | 10         | 0.94      | 564  | 54    | 119.4| 52.8 | 2.75     |
| 7    | 8 (10)  | 70         | 10         | 0.23      | 138  | 78    | 118.7| 26.6 | 2.14     |

aCo-cat.: B(C6F5)3 (Ni:B = 1:2); Pressure of ethylene: 90 psig. bIn 103 g[PE]mol[Ni]h−1.

Higher activities were obtained with catalysts containing the rigid xanthene skeleton. Compared with catalyst 6, the activity of catalyst 8 and the corresponding product molecular weight under the same reaction temperature improved simultaneously (table 1, entries 1 and 3). The results indicated that with the presence of xanthene skeleton and the extra salicylaldehyde segment the steric hindrance of the nickel center increased and inactivation of the catalyst reduced. Product with a higher degree of branching (89 branches / 1000 carbons) was obtained after 40 min of reaction (table 1, entry 4). A possible reason for the branching increase was that after a while, the rate of chain transfer became higher than the monomer insertion rate. Although binuclear catalyst No.7 showed a higher activity due to the bimetallic cooperative effect, the branching was more catalyzed using catalyst 8. In addition, higher thermal stability was achieved by catalyst 8 compared to 6. The SEM spectra showed different micro morphologies for 6 and 8. The molecular weight and degree of branching change with reaction temperature (table 1, entries 5-7). With the increase of polymerization temperature, the rates of chain growth, chain transfer, and chain walking increased. The highest catalytic activity was found at 50°c.
(5.64×105 g [PE] mol [Ni]-1 h−1). The molecular weight of the polymer (53 kDa) did not significantly decrease compared with catalyst 6 because of faster monomer insertion. However, the rates of chain transfer and chain walking increased faster than the rate of chain growth at a too high temperature, leading to partial deactivation of the catalyst. As a result, the activity and the degree of branching decreased at 70°C.

Propylene polymerizations were performed using catalysts 6, 7 and 8 (table 2).

| Ent. | Precat. | Yield (g) | TOF | [mmmm] | \(M_n\) | \(M_w/M_n\) |
|------|---------|-----------|-----|---------|--------|-----------|
| 1    | 6       | 0.006     | 0.10 | 77      | 8.75   | 1.23      |
| 2    | 7       | 0.020     | 0.18 | 59      | 9.6    | 1.18      |
| 3    | 8       | 0.021     | 0.35 | 65      | 10.4   | 1.21      |

*Pre-cat. 20 µmol; Co-cat.: B(C₆F₅)₃(Ni:B 1:2); Solvent: 25 mL toluene; Temperature: 25 °C; Propylene pressure: 20 psig; Reaction time: 90 min.

The previously reported polymerization of propylene by phenoxyimine nickel catalysts usually displayed low activities and poor regio- and stereoselectivities. The reason was propensity to generate amorphous and atactic polymers. As a result, only poor stereoselectivities, poor regioselectivities, and fast chain-walking were reported [8, 33-36]. The data in table 2 suggested the catalyst 8 showed better performance than catalysts 6 and 7. It seems that the steric hindrance in catalyst 8 is more appropriate for propylene insertion. The PDI of polypropylene was narrow revealing efficient suppression of chain transfer.

3. Experimental

3.1. Synthesis of Mono-nickel catalyst 8 with xanthene skeleton (figure 5)

Preparation of L8: To a stirred toluene solution of compound 8. 1 (1 mmol) and 2,2\(^{\prime}\),3,3\(^{\prime}\),4,4\(^{\prime}\),5,5\(^{\prime}\),6,6\(^{\prime}\)-decafluoro-5\(^{\prime}\)-methyl-[1,1\(^{\prime}\),3,1\(^{\prime}\)-terphenyl]-2\(^{\prime}\)-amine (1 mmol), p-toluenesulfonic acid (0.05 mmol) was added. The flask was then equipped with a Dean-Stark trap and a condenser. Then the reaction was heated to 150°C and refluxed overnight. After cooling to room temperature, the mixture was washed with water and brine. The mixture was extracted with EtOAc, and dried over Na₂SO₄. The organic phase was concentrated and the crude product was purified by silica gel column chromatography (PE/DCM = 5:1) to afford yellow solid product L8 (72%).

\[\text{CHO} \quad \text{C₆F₅} \quad \text{NH₂} \quad \text{C₆F₅} \]
\[\text{CHO} \quad \text{OH} \quad \text{Bu} \quad \text{OH} \quad \text{p-TsOH, Toluene} \]

\[1) \text{KH, THF} \]
\[2) \text{NiNaph(PPh₃)₂Cl, Tol.} \]

**Figure 5.** Synthesis of Mono-nickel catalyst 3 with xanthene skeleton
116.7, 33.64, 33.63, 33.6, 28.0, 27.9, 25.9, 24.3, 21.6, 19.7, 19.2. HRMS (ESI, m/z): Calculated for C28H30F10NO4 [(M+H)+]: 848.3046, found 848.3048. Synthesis of complex 8: L8 (0.5 mmol), THF (3 mL) and KH (0.8 mmol) was added to a Schlenk flask under N2. After 5 h stirring, the mixture was condensed under vacuum. The toluene solution of the condensed potassium salt was added to a toluene (5 mL) solution of trans-[Ni(PPh3)2(Naph)Cl] (0.48 mmol) dropwisely at room temperature. After 20 h stirring, the mixture was filtered through celite and the solvent was evaporated by vacuum. The solid residue was recrystallized by toluene and hexane, 8 was obtained as yellow powder (79%). 1H NMR (400MHz, CDCl3): δ 12.41 (J = 8.7 Hz, 1H, d), 9.50 (J = 8.3 Hz, 1H, d), 8.94 – 8.66 (1H, m), 8.03 (J = 7.5 Hz, 1H, d), 7.74 – 6.71 (30H, m), 2.50 (3H, s), 1.73 (3H, s), 1.21 (9H, s), 1.20 (9H, s). 19F NMR (282MHz, CDCl3) δ -58.2, -58.7, -59.6, -77.1, -79.6, -83.4, -84.5, -86.3. 31P NMR (162MHz, CDCl3): δ 27.1. HRMS (ESI, m/z): Calculated for C64H50F10NNiO5P [(M+H)+]: 1430.3839, found 1430.3862.

3.2. Ethylene (propylene) polymerization
A 300 mL heavy-walled glass reactor was loaded with pre-catalyst, B(C6F5)3, and toluene (20 mL) in the glovebox. The glass reactor was then interfaced to a high-pressure line. Then the solution was heated to the appropriate temperature. Ethylene (or propylene) was injected to 90 (or 20) psig, and the reaction was carried out for a desired time. After the reaction, the solution was acidified by HCl / MeOH. The solution with precipitated white solid was stirred for 2 h. The polymer was then collected by filtration, washed with MeOH, and dried under vacuum at 80°C for 12 h.

4. Conclusion
In summary, a mononuclear nickel catalyst with the xanthene skeleton was synthesized and characterized. The catalyst showed higher ethylene polymerization activities than the catalyst without xanthene skeleton due to the axial steric hindrance caused by the adjacent salicylaldehyde segment. The regio- and stereo-selectivities obtained with the catalyst were better than with the bimetallic catalyst, illustrating that the effect of axial steric hindrance played a more important role than the synergistic effect. It also showed activities and narrow PDI s for propylene polymerization. Further studies on the improvement of propylene polymerization by catalysts with bulky steric substituents are currently underway.

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Declarations
The authors declare that they have no competing interests.

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