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### Binuclear late transition metal catalysts for $\alpha$ -olefin polymerization

**Mostafa Khoshsefat,<sup>1</sup> Saeid Ahmadjo,<sup>\*1</sup> Mohammad Mahdi Mortazavi,<sup>1</sup> Gholam Hossein Zohuri,<sup>2</sup> Abbas Dechal<sup>1</sup>**

**1. Department of Catalyst, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran**

**2. Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, P.O. Box: 91775, Mashhad, Iran**

#### Abstract

Two binuclear  $\alpha$ -diimine nickel (II) catalyst (A) {2,6-diisopropyl-C<sub>6</sub>H<sub>4</sub>-N=C-(C<sub>10</sub>H<sub>6</sub>)-C=N-C<sub>6</sub>(CH<sub>3</sub>)<sub>4</sub>-N=C-(C<sub>10</sub>H<sub>6</sub>)-C=N-2,6-diisopropyl-C<sub>6</sub>H<sub>4</sub>} {NiBr<sub>2</sub>} and {2,6-diisopropyl-C<sub>6</sub>H<sub>4</sub>-N=C-(C<sub>10</sub>H<sub>6</sub>)-C=N-C<sub>6</sub>H<sub>4</sub>-N=C-(C<sub>10</sub>H<sub>6</sub>)-C=N-2,6-diisopropyl-C<sub>6</sub>H<sub>4</sub>} {NiBr<sub>2</sub>} (B) were prepared under controlled conditions and used in 1-hexene homopolymerization. The catalysts have a rigid bridge which catalyst A has four methyl groups on center ring while in catalyst B hydrogen atoms cause less steric effects. To investigate ortho-substituent impact (methyl) on catalyst behavior, the experiments were performed under similar condition and diethylaluminum chloride (DEAC) was used as cocatalyst. The binuclear complexes were compared in catalytic performance which catalyst A showed higher activity versus catalyst B. The highest activities for catalyst A were at lower [Al]/[Ni] molar ratio in comparison to catalyst B.

**Keywords:** Catalytic polymerization -Binuclear  $\alpha$ -diimine complex -Poly(1-hexene) -Ortho substituent- Structure-Property relation.

#### Introduction

In plastic and polyolefin industry, homo- and copolymerization of olefins using the catalytic polymerization system have a huge contribution [1,2]. Polyolefins with their vast application play an important role in our life from artificial limbs and food/medical packaging to automotive and electrical components and lubricants [3]. Not only polymerization condition has effect on the polymerization behavior and properties of the manufactured polymer, but also structure of catalysts have a dramatically impact on final products [4,5]. Microstructure control has an important role in polymer properties which the  $\alpha$ -diimine nickel catalysts for olefin polymerization has attracted the researchers' attention due to their unique reactivity patterns and unusual catalytic properties such as producing branched polyethylene without any  $\alpha$ -olefin comonomers and chemical stability through less oxophilic properties [4,6]. Modification of the  $\alpha$ -diimine framework is an approach to achieve living polymerization, including  $\alpha$ -diimine backbone and substituents on the side

groups. The steric bulk groups of ligands especially ortho-substituents above and below the metal active centers are critical to the catalyst behavior and resulting polymer which are a key to retarding chain transfer reaction and manipulation kinetics parameters to obtain higher or lower catalyst activity and polymer properties [4,7].

In this work, two binuclear late transition metal catalyst were synthesized under controlled condition and used in homo-polymerization of 1-hexene. Ortho-substituent effect of ligand structure on catalyst productivity was investigated.

#### Experimental

The A and B complexes (Scheme 1) were prepared according to our recently work [8]. The bulk polymerization 1-Hexene monomer (purified prior to use) was carried out in a round bottom flask. The monomer (10 ml) was injected to the round bottom flask containing 35 ml toluene which was conducted under schlenk system. Afterward, the co-catalyst and catalyst were introduced to the flask, respectively. This system was stirred to reach completely gelation.

\* Correspondence to: S. Ahmadjo (E-mail: S.ahmadjo@ippi.ac.ir)



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The poly (1-hexene) was precipitated and purified by acidic Methanol (5%).

### Results and Discussion

Polymerization of 1-hexene in presence of the binuclear catalysts at different [Al]/[Ni] molar ratios illustrated in the Figure 1 which the catalysts activity increased with the [Al]/[Ni] ratio to a maximum value followed by a decreasing for both complex. Increasing of cocatalyst concentration can cause enhancing the activation of centers (through the alkylation) to reach optimum value, however, decreasing may due to inhibition of the monomer coordination with active sites by the excess amount of the DEAC [9]. Catalyst A has reached to optimum condition at lower [Al]/[Ni] molar ratio in comparison to catalyst B. We recently also reported polymerization of ethylene using these catalyst (A and B) which the Catalyst A showed higher activity than Catalyst B [10]. This observation can be devoted to presence of methyl groups which increase the electronic and steric effects on the center and mechanism of catalyst activation.

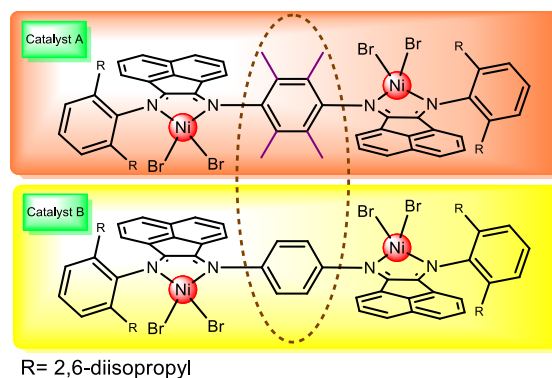
### Conclusion

Two binuclear  $\alpha$ -diimine Ni(II)-based catalysts (A and B) were prepared under controlled conditions and used in 1-hexene homopolymerization. *Ortho*-substituent effect of ligand structure showed an impact on catalyst productivity which catalyst A with methyl groups on center ring exhibited higher catalyst activity at lower [Al]/[Ni] molar ratio in comparison to catalyst B. This phenomenon attributed to the more dinuclearity and cooperative effect between the proximate centers in catalyst A by presence of the methyl groups to be more stable and active for propagation reactions versus the deactivation and chain transfer reactions.

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Scheme 1. Representation of catalyst A and B structures.

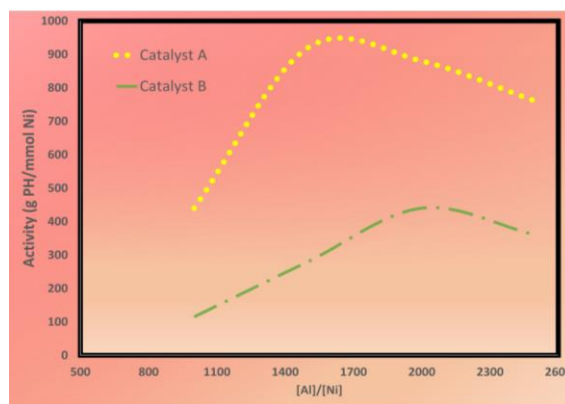


Fig 1. Polymerization of 1-hexene using catalyst A and B in presence of DEAC as cocatalyst.