

# Dinuclear catalysts with two adjacent Ni centers for ethylene polymerization

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## Abstract

A series of mono- (M1 and M2) and dinuclear (C1-C6) Ni  $\alpha$ -diimine catalysts activated by modified methylaluminoxane (MMAO) were used in polymerization of ethylene. The behavior of catalysts and polymer properties regarding ligand architecture from ortho-substituent and backbone to rigidity/flexibility of the linker between the active centers were investigated. Catalyst C2 bearing the optimum bulkiness and dinuclearity showed the highest activity (1.6 $\times$ 10<sup>6</sup> gr. PE/mol Ni.h), lower short chain branching (32.5/1000 C) in comparison to dinuclear and mononuclear analogues. Although, the mononuclear catalysts M1 and M2 polymerized ethylene to a branched amorphous polymer, the dinuclear catalysts made different branched semicrystalline PE. Kinetic profiles of polymerization showed the relation between the structure and monomer uptake where the monomer uptakes were too fast for mononuclears but higher stability of C2 led to greater consumption at prolonged polymerization.

**Keywords:** polyethylene, synergistic effect, dinuclear catalyst, late transition metal, structure-property relation

## Introduction

The effective distance between two center is basically depends on the nature of centers and ligand structure. The possible interactions between the monomer/polymeryl-chain and second center are in regard to the presence of weakly basic substituents such as hydrogen or phenyl on monomer and monomer length, as well. On the other hand, the nature and length of linker between two center are crucial. As a rigid bridge can pose the centers in a consistent distance, a flexible one could be variable. Different structure of bridges (polymethylene, phenylene, silane, siloxane and rigid/flexible) in the multinuclear metallocene and CGC based catalysts have been used and reported, although in the field of late transition metal catalysts, there are some sporadic reports [1].

Chen et al. reported a rigid conjugated  $\alpha$ -diimine backbone in dinuclear Ni and Pd catalysts and unimodal to bimodal molecular weight distribution of polyethylene were observed, respectively [2]. A series of symmetrical to unsymmetrical bimetallic nickel complexes bearing aryl-linked iminopyridines affording mixtures of waxes and low molecular weight solid polyethylene were reported by Solan [3]. A virtually structure of flexible/rigid bridges by Schumann et al. were active in ethylene polymerization but microstructure properties of product not mentioned [4]. In addition, we reported a series of dinuclear  $\alpha$ -diimine Ni based catalysts which the structure bearing higher

electronic and steric effect showed higher activity, although MWD was broad [5].

Altogether, by considering all previous reports on dinuclear Ni-based catalysts, the structural properties of bridge need more investigations. Based on this, we studied on the effect of nature and length of spacer between two nickel centers on the dinuclear  $\alpha$ -diimine based catalysts using MMAO as cocatalyst.

## Experimental

The ligand and complexes were synthesized according to our recent report [6]. Ethylene polymerizations were conducted in a 200 mL stainless steel Bucci reactor, using toluene as the solvent. Dried toluene was introduced under nitrogen atmosphere, MMAO and catalyst, respectively. Ethylene consumption was compensated using a mass flow meter to keep the pressure constant. Finally, the reactor was evacuated and the product was washed with acidic methanol (5%) and dried under reduced pressure.

## Results and Discussion

The results of ethylene polymerization showed the highest catalyst activity of C2 in comparison to the dinuclear and mononuclear catalysts in order of C2>M2>M1>C4>C3>C1>C6>C5. Catalyst C2 is bearing the optimum bulkiness around the active center (Me and iso-Pr) which called "ortho-aryl effect". This effect implies

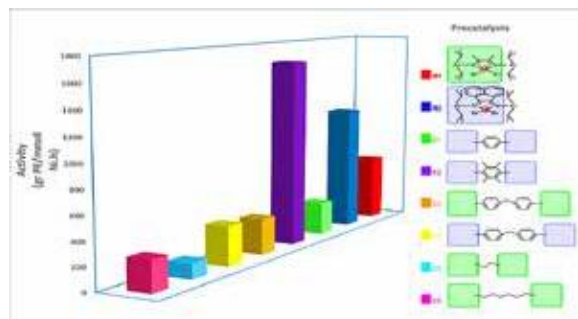


Fig. 1. Bar chart of activity of the mono- (M1 and M2) and dinuclear (C1-C6) catalysts

the steric and electronic impacts of ligand architecture and metal center, as well. According to the kinetic profiles of polymerization, it demonstrates the ethylene consumption for dinuclear complexes, and the structures with more electron rich groups and substituents (phenyl and -CH<sub>2</sub>-units) as a bridge represented greater ethylene uptake. The effect of backbone was observed in the catalysts M2 and C4 in comparison to M1 and C3, respectively. Higher activity of M2 than M1 is consistent on our previous results on high  $\alpha$ -olefin polymerization [6]. It suggested that the presence of acenaphthene can make the active center to be a better  $\pi$ -acceptor. This trend along with the ortho- aryl effect in catalyst C2, made it to be the most effective and stable catalyst.

Activation of the complexes is too fast following by reach to high values of ethylene uptake, propagation, chain transfers, termination and deactivation reactions (Fig. 2). It also disclosed that the rate determining step in polymerization of ethylene is the chain growth while for the higher  $\alpha$ -olefins is the monomer trapping [7]. The rate of each step depends on the catalyst structure and polymerization condition. Although the steep slope at beginning of the kinetic profile is representing a fast activation and strong monomer coordination, but the trend of the profile highlights the activity as time goes by.

Since the reactions were carried out at similar conditions, the effects of structure on polymerization kinetics revealed that optimum bulkiness in architecture of catalyst leads to efficient shielding of axial sites of active centers against

deactivation and chain transfer reactions.

## Conclusion

Catalyst C2 bearing the optimum bulkiness, dinuclearity and proximity of centers showed the highest activity, lower SCB in comparison to dinuclear and mononuclear analogues. Although, the mononuclear catalysts M1 and M2 polymerized ethylene to a branched amorphous polymer, the dinuclear catalysts made different branched semicrystalline PE. Kinetic profiles of polymerization showed the relation between the structure and monomer uptake where the monomer uptakes were too fast for mononuclears but higher stability of C2 led to greater consumption at prolonged polymerization. As a result, proximity of Ni centers in dinuclear catalyst structure with shielded axial sites could increase the performance of catalyst.

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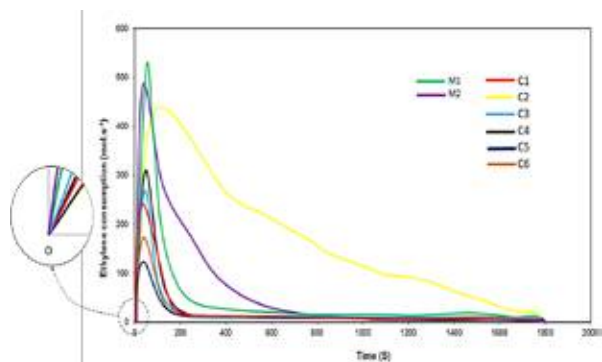


Fig. 2. Kinetic profile of ethylene polymerization using mono- (M1 and M2) and dinuclear (C1-C6) catalysts