

Influence of type and positioning of N-aryl substituents on vinyl polymerization of norbornene by Ni(II) α -diimine complexes

Vinukrishnan Appukkuttan, Jin Hyuk Kim, Chang Sik Ha and Il Kim[†]

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

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Abstract—Effects of structural variations of the diimine ligand on catalyst activities for vinyl polymerization of norbornene (NB) have been investigated by a series of Ni(II) α -diimine catalysts of the general formula: [$\{ArN=C(Ac)-C(Ac)=NAr\}NiBr_2$ (Ac=acenaphthyl) (**Cat(H)**, Ar=C₆H₅; **Cat(2,6-Me)**, Ar=2,6-C₆H₃Me₂; **Cat(2,6-Et)**, Ar=2,6-C₆H₃Et₂; **Cat(2,6-*i*Pr)**, Ar=2,6-C₆H₃-*i*-Pr₂; **Cat(2,3-Me)**, Ar=2,3-C₆H₃Me₂; **Cat(2,4-Me)**, Ar=2,4-C₆H₃Me₂; **Cat(2,5-Me)**, Ar=2,5-C₆H₃Me₂; **Cat(3,5-Me)**, Ar=3,5-C₆H₃Me₂; **Cat(2,4,6-Me)**, Ar=2,4,6-C₆H₂Me₃). *In situ* reactions with methylaluminoxane generated the active catalysts, and they showed good activity towards NB polymerizations. As indicated by relatively higher activities of **Cat(H)** and **Cat(3,5-Me)**, it can be generalized that catalysts having 2,6-substituents are less active due to steric interaction between monomer and substituents. In addition, electron donating methyl groups at 2-, 4- or 6-position on the N-aryl have a *con* effect and that at 3,5-position has a *pro* effect.

Key words: Catalysis, Diimine Ligands, Late Transition Metal, Microstructure, Norbornene, Vinyl Polymerization

INTRODUCTION

Cycloolefin polymers based on norbornene and its derivatives have recently gained immense attraction owing to their unique physical properties such as high glass transition temperature, optical transparency and low birefringence [1-3]. Bicyclo[2.2.1]hept-2-ene, better known as norbornene (NB), is known to be polymerized by ring opening metathesis (ROMP), cationic or radical and also by vinylic addition methodologies resulting in polymers of different microstructure [4,5]. ROMP, the early explored method for NB polymerization, results in polymers with double bonds in their backbone and thus exhibiting poor thermal properties [6]. Vinyl type polymerization opens the double bond π -component leaving the bicyclic structural unit intact in a similar manner to olefin polymerization mechanistically. Zirconocenes exhibit low activity towards NB polymerization and polymers are generally characterized by its high crystallinity making it difficult to process [7,8]. But soluble norbornene addition polymers produced by half-titanocene have been recently reported [9].

There has been a great deal of interest in late-metal catalyst for NB polymerizations as it is highly active and produces high molecular weight (MW) polymers soluble in halogenated solvents making it easy to characterize and process. Cationic palladium complexes were the early explored [10]. Brookhart and coworkers' discovery of α -diimine system for olefin polymerization led to a number of reports based on complexes of late-transition metals for NB polymerizations [11-14]. In transition metal catalyzed olefin polymerization (metallocene and late-metal complexes) the tunable ligand structure makes them show stereo-electronic influence towards activity and polymer microstructure. There have been reports on the

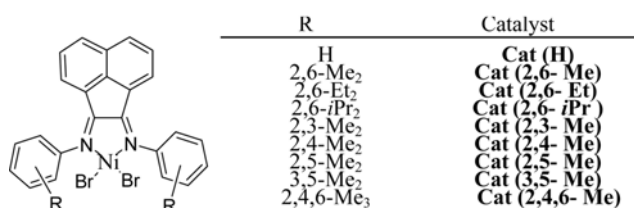


Fig. 1. Representation of various Ni (II) α -diimine catalysts used in the present study.

influence of nickel-based catalyst with different substituents for linear α -olefin and MMA polymerization [15,16]. In the present work we report the effect of different type and positioning of alkyl substitution on the N-aryl ring of Ni(II) α -diimine complex (Fig. 1) with its varied steric and electronic environment towards the polymerization of a bulky cycloolefin NB.

EXPERIMENTAL

All reactions involving air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere using a standard glove box and the Schlenk technique. Toluene was distilled over Na/benzophenone and stored over molecular sieves. NB (Aldrich) was dried over CaH₂, distilled and stored as a solution in toluene. All other chemicals including methylaluminoxane (MAO, as a 10 wt% total Al solution in toluene) were obtained from Aldrich Chemical Co. and used without further purification. Catalysts were synthesized according to procedure reported elsewhere [17]. Solution polymerizations of norbornene were carried out according to previous reports [13]. Molecular weights (MW) and its distribution (MWD) of polynorbornene (PNB) samples were determined by gel permeation chromatography (PL-GPC220/FTIR, 135 °C) in 1,2,4-trichlorobenzene using polystyrene standards. Thermal analyses of polymers were done by differential scanning calorimetry (PL-DSC, Polymer Lab-

[†]To whom correspondence should be addressed.

E-mail: ilkim@pusan.ac.kr

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Table 1. Norbornene polymerization results using various Ni (II) α -diimine catalysts. Polymerization conditions: toluene=20 mL; [Cat.] = 2.0×10^{-4} M; cocatalyst=MAO, [Al]/[Ni]=2,000; T_p =30 °C, Time=30 min, [NB]=1.59 M

| No | Catalyst | Yield (g) | Conversion (%) | Activity 10^5 g/mol-Ni h | $M_n \times 10^{-4}$ | MWD |
|----|----------------------|-----------|----------------|----------------------------|----------------------|------|
| 1 | Cat(H) | 1.95 | 65.0 | 4.86 | 16.2 | 3.26 |
| 2 | Cat(2,6-Me) | 1.17 | 39.0 | 2.92 | 12.6 | 3.27 |
| 3 | Cat(2,6-Et) | 1.01 | 33.7 | 2.52 | 8.6 | 2.61 |
| 4 | Cat(2,6-iPr) | 0.41 | 13.7 | 1.02 | 11.0 | 1.87 |
| 5 | Cat(2,3-Me) | 1.91 | 63.7 | 4.76 | 19.5 | 2.37 |
| 6 | Cat(2,4-Me) | 1.19 | 39.7 | 2.97 | 20.2 | 3.17 |
| 7 | Cat(2,5-Me) | 1.97 | 65.7 | 4.91 | 19.8 | 2.78 |
| 8 | Cat(3,5-Me) | 2.15 | 71.7 | 5.36 | 20.7 | 3.04 |
| 9 | Cat(2,4,6-Me) | 0.46 | 15.3 | 1.12 | 9.3 | 3.19 |

oratories) analysis and thermogravimetric analysis (TGA, TA Instruments). ^1H NMR at 120 °C was recorded on a JNM-ECP400 (400 MHz) instrument by using $\text{C}_6\text{D}_4\text{Cl}_2$ as solvent.

RESULTS AND DISCUSSION

Nickel(II) α -diimine catalysts (Fig. 1) with different ligand structure having varied stereo-electronic influence towards the metal center were synthesized by condensation between diketone and aryl amines with appropriate alkyl substituents at specified positions. The results of vinyl polymerization of NB by these catalysts in combination with MAO as cocatalyst are summarized in Table 1. The general trend for polymerization is that catalysts with no or less bulky substituent at the *ortho* (2,6) positions of N-aryl ring showed higher activity as evidenced by high activity of **Cat(3,5-Me)** and **Cat(H)**. As shown in Fig. 2 there is a sharp decrease in activity as the *ortho* substituent goes from proton to isopropyl through methyl and ethyl

as 2,6-substituents, which is somewhat contrary to observed results in ethylene polymerization [18]. This result may be caused by the structural difference of monomer-active site. Bulky substituents hinder bulky NB from facile coordination to active site, resulting in sharp decrease of activity. This trend happens in ethylene polymerizations but at a less degree due to the negligible steric hindrance. **Cat(H)** with no substituents shows 65% conversion, while **Cat(2,6-iPr)** shows only 13.7% conversion. Kaminsky and Noll [19] reported that $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ catalyst with its open structure was more active than $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$, and the latter was 100 times more active than unbridged Cp_2ZrCl_2 with its narrow opening at metal center. Further, in another study involving NB-ethylene copolymerization by *ansa*-metallocene of C_2 - and C_s -symmetries, C_2 -symmetric compound was characterized by a decrease in activity as NB-ethylene ratio increased, whereas the C_s -type one showed steady activity at higher monomer ratio. This is due to the fact that shorter bridges of ligands surrounding the metal opens up the coordination site making the access of bulkier monomer much easier [4,19,20]. Song and coworkers have shown similar results with methyl and ethyl bridged zirconocene for NB-ethylene copolymerization [21]. Much the same way in the present study catalyst was either devoid of any *ortho* substituents, **Cat(H)**, and that with substituents much away from active center, **Cat(3,5-Me)**, with its wider cone coordination site was more active.

It is quite astonishing to note that **Cat(3,5-Me)** of its steric environment similar to **Cat(H)** is more active than **Cat(H)** (Table 1). Moreover, comparing the activities of **Cat(2,3-Me)**, **Cat(2,4-Me)** and **Cat(2,5-Me)** catalysts, all having similar structural feature, **Cat(2,3-Me)** and **Cat(2,5-Me)** catalysts show similar activity with unsubstituted **Cat(H)**, while **Cat(2,4-Me)** catalyst shows much less activity. In the case of Ni α -diimine catalysts, nickel metal is coordinated to diimine ligands through lone pairs of electrons in nitrogen. Thus the ease of availability of a lone pair electron from nitrogen determines the net positive charge on the metal center, that is, if the electron is quite easily available, the stronger will be the Ni-N bond and hence metal is less electro-positive, and vice versa. The basicity of aniline molecules is significantly increased by the presence of electron donating groups at *ortho* and *para* (2, 4 and 6) positions as they inhibit the participation of lone pair electrons on nitrogen in resonance [22]. But the groups at *meta* (3 and 5) positions did not significantly affect the basicity compared to *ortho* and *para*. Thus the methyl groups at *ortho* and *para* positions have a *con* effect to-

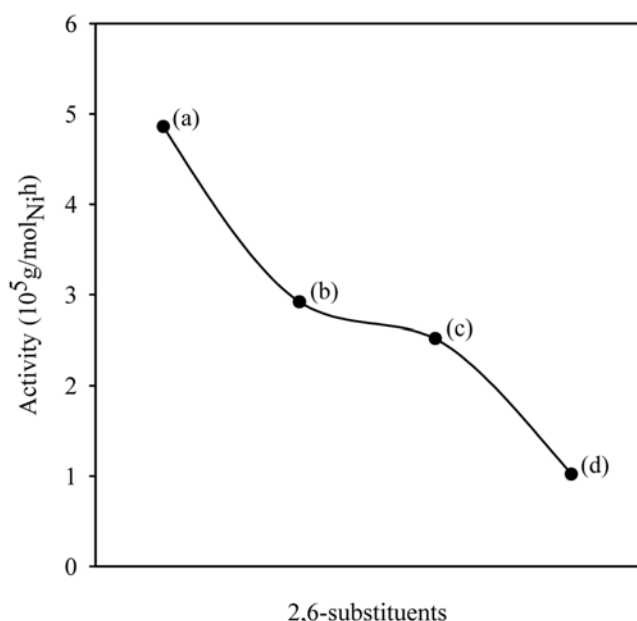


Fig. 2. Variation of activity according to the size of 2,6-substituents on diimine ligands: (a) **Cat(H)**, (b) **Cat(2,6-Me)**, (c) **Cat(2,6-Et)**, and (d) **Cat(2,6-iPr)**. Toluene solvent=20 mL; [MAO]/[Ni]=2,000; [Cat.] = 2.0×10^{-4} M, Temperature=30 °C.

wards polymerization activity, and those at *meta* positions have a *pro* effect. This *pro* effect of methyl groups at 3- and 5-positions makes **Cat(3,5-Me)** more active than **Cat(H)**. In the case of **Cat(2,3-Me)**, **Cat(2,4-Me)** and **Cat(2,5-Me)**, the *con* effect of methyl groups at 2- and 4-positions makes it less active, and for other two catalysts the *con* effect of *ortho* substituent is nullified by the *pro* effect of *meta* substituent making it show similar activities with unsubstituted catalyst. The *con* effect of 2,6-dimethyl groups of **Cat(2,6-Me)**, apart from the sterical consideration, significantly reduces the activity compared to **Cat(H)**. To check the *pro-con* effect of the methyl group we carried out NB polymerizations with **Cat(2,4,6-Me)** and compared with that of **Cat(2,6-Me)** of which both catalysts have same structural features at *ortho* position but have different electronic nature due to an additional methyl group at *para* position of the former. **Cat(2,4,6-Me)**, with its enhanced *con* effect by a third methyl group at 6-position, was considerably less active than **Cat(2,6-Me)**, clarifying the above explanation.

GPC characterization (Table 1) showed that all polymers are of high molecular weight and narrow MWD ranging 1.87 to 3.27. It is interesting to note that the MW value of PNB produced by catalyst with less *ortho* substituent is almost two times of that of PNBs produced by catalysts with 2,6-substituents that give high MW polymer in ethylene polymerizations. As the average degree of polymerization depends directly on the rate of propagation and conversely on termination, the open structure of the active center of less *ortho* substituted catalyst may enhance the rate of insertion compared to termination resulting in high molecular weight polymers [23]. ^1H and ^{13}C NMR analyses of resulting PNBs confirmed vinyl type polymerization as there is an absence of vinylic peaks in the spectrum. TGA analysis under nitrogen atmosphere showed that PNBs were stable up to 450 °C. DSC analyses of polymers were inconclusive since there were no detectable T_g values, and T_m values of PNBs are very close to their decomposition temperatures [24].

CONCLUSIONS

Vinylic polymerizations of NB were performed with a series of Ni(II) α -diimine complexes, modifying the size and position of the alkyl substituents on the N-aryl rings. As the size of the alkyl groups at 2,6-position increases, the activity decreases sharply. In general, catalysts with no 2,6-substituents or with only remote substituents showed high activity due to a reduced steric interaction between bulky NB and active sites. While catalysts with methyl groups at 2-, 4- or 6-position of the N-aryl ring have a *con* effect to activity owing to their enhanced basicity of nitrogen atom making Ni less electro-positive, catalysts with methyl groups at 3,5-position show a *pro* effect, resulting in **Cat(3,5-Me)** being the most active catalyst. Thus, the design of ligand microstructure is an essential tool to tune the activity of such catalysts by regulating the structural and electronic influence on the metal center.

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