

Notes

Methylaluminum Dichloride as a Cocatalyst for Ni(II) α -Diimine Complexes Catalyzed Ethylene Polymerization

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Introduction

Diimine Ni(II) catalysts have attained special interest due to their tunable polymerization activity and polymer microstructure by simple modification of the ligand architecture.^{1,2} Technical process for olefin polymerization requires the use of suitable cocatalysts to transform inactive but readily prepared and handled catalyst precursors into the active species. The activity of methylaluminumoxane (MAO) or its derivatives as cocatalysts is generally unmatched by other organoaluminum reagents. The ability of these substances to activate many kinds of catalytic precursors has been demonstrated for a wide range of transition metal catalyst precursors. However the practical use of MAO also poses some important drawbacks. For example, they are relatively expensive reagents that have to be used in large excess to achieve their optimum efficiency.

Recently we have reported the polymerization/oligomerization behavior of late transition metal catalysts in combination with common alkyl aluminums like ethylaluminum sesquichloride (EAS).^{3,4} In the present study we explore the use of methylaluminum dichloride (MADC) as a potential alternative for MAO towards the polymerization of ethylene with Ni(II) α -diimine catalysts.

Experimental

General Methods and Materials. All reactions were performed under inert atmosphere.^{5,6} Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOXTM catalyst and molecu-

lar sieve 5 Å/13X. Solvents were dried under nitrogen using standard reagents. All reagents used in this study were purchased from Aldrich Chemical Co. and used without further purification.

Characterization. ¹H NMR, ¹³C{H} NMR spectra of ligands were recorded on a Varian Gemini-2000 (300 MHz, 75 MHz) spectrometer. All chemical shifts were reported in parts per million (ppm) relative to residual CHCl₃ (δ 7.24) for ¹H and CDCl₃ (δ 77.00) for ¹³C{H}. ¹H and ¹³C{H} spectra of polyethylene (PE) were taken in C₆H₄Cl₂ at 135 °C on Inova-500 (500 MHz, 125 MHz) spectrometer. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60 F pre-coated aluminum plates with fluorescent indicator UV254. Purification of ligands was carried out with a Combi-Flash (Companion) auto-column machine. Elemental analysis was carried out using Vario EL analyzer and UV-visible spectra were recorded on a Shimadzu UV-1650PC UV-visible spectrophotometer. Mass spectra of catalysts were recorded using positive fast atom bombardment (FAB) methods on JEOL JMS-AX505WA, HP 5890 Series II spectrometer.

Molecular weight and molecular weight distribution of PE were determined by GPC (PL-GPC220/FTIR, 135 °C) in 1,2,4-trichlorobenzene using polystyrene columns as standard. Thermal analysis of PE was carried out by differential scanning calorimeter (Perkin-Elmer DSC, model: Pyris 1) at 10 °C/min heating rate under nitrogen atmosphere. The results of the second scan were reported to eliminate the difference in sample history. The branching numbers for PE were determined by ¹H NMR spectroscopy using the ratio of number of methyl groups to overall number of carbons and were reported as branches per thousand carbons.

Polymerization. Ethylene polymerizations were performed in a 250 mL round-bottom flask equipped with a magnetic stirrer and a thermometer outside.^{5,6}

When reactor was equilibrated with bath temperature, ethylene was introduced into the reactor after removing nitrogen gas under vacuum. When no more absorption of ethylene into toluene was observed, required amount of cocatalyst was injected into reactor and then polymerization was started. Polymerization rate was determined at every 0.01 s from the rate of consumption, measured by a hotwire flow meter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an A/D converter. Polymerization was quenched by the addition of methanol containing HCl (5 v/v %) and then unreacted monomer was vented. The polymer was washed with an excess amount of methanol and dried in vacuum at 50 °C. To make a worthy comparison of the effect of catalyst structure on catalytic activity and polymer structure and properties, all data were collected under similar conditions.

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Results and Discussion

We have reported the synthesis, characterization and ethylene polymerization activity of a series of sterically and electronically modulated Ni(II) α -diimine catalysts recently.⁴ The synthesis of α -diimine ligands involves the condensation of a diketone with 2 equivalent (eq.) of specially designed arylamine having electron withdrawing and donating substituents ($Y = \text{NO}_2, \text{H}, \text{OCH}_3$ in Figure 1). Brookhart and Svejda found the synthesis of α -diimine ligand derived from 4-nitroaniline and acenaphthenequinone unsuccessful due to the strong electron withdrawing nature of nitro group.⁷ Recently a tedious synthetic method was reported for α -diimine from 4-nitroaniline and 2,3 butanedione.⁸ Since the nitro group in our system lies in a considerable distance from imino moiety, the synthesis of ligand was much easier than expected. The ligands were treated with (DME)NiBr₂ to obtain the corresponding catalysts in good yields. All catalysts were highly active towards ethylene polymerization in combination with common alkylaluminums and MAO.

The choice of aluminum cocatalyst has a significant effect on ethylene polymerization reactions. Even though the effect of cocatalysts like MAO remains a 'black box', it was proved that the amount of alkyl aluminums or aluminoxane affects the molecular weight of polymers. Previously we compared the high polymerization activity of Ni(II) α -diimine catalysts in the presence of common alkyl aluminums such as EAS with MAO.⁴ In addition we found that MADC showed good catalytic activity towards ethylene polymerization. Interestingly the nitro substituted **1d**/MADC system showed 5 fold activity compared to other

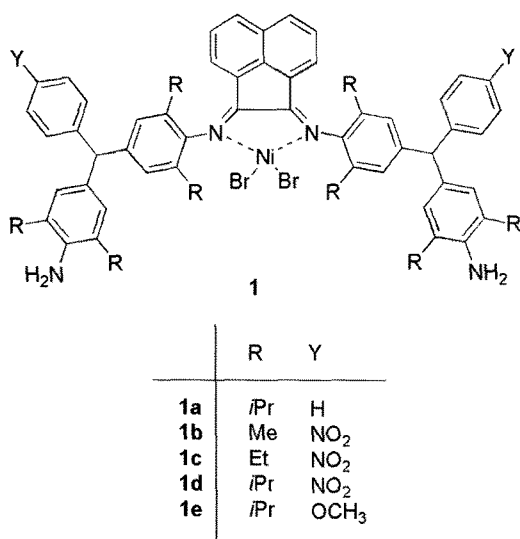


Figure 1. Ni(II) α -diimine complexes under investigation having general formula: $[\text{ZN} = \text{C}(\text{An})-\text{C}(\text{An}) = \text{NZ}]\text{NiBr}_2$, $\text{Z} = (4\text{-NH}_2\text{-3,5-C}_6\text{H}_2\text{-R}_2\text{CH}(4\text{-C}_6\text{H}_4\text{Y}))$; An = acenaphthenequinone; R = Me, Et, *i*Pr; Y = H, NO₂, OCH₃.

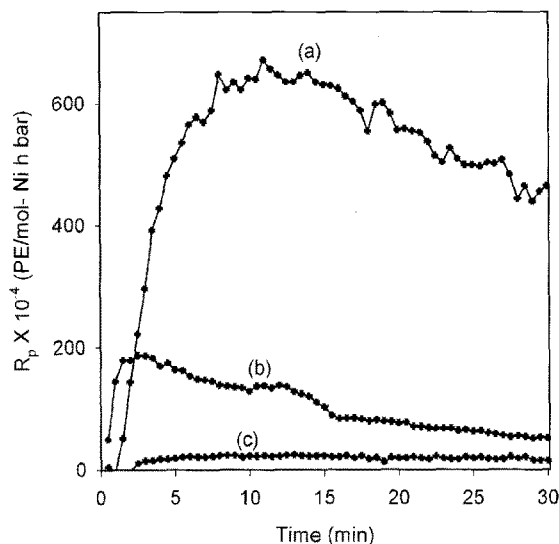


Figure 2. Rate of polymerization (R_p) versus time plot of ethylene polymerization by catalyst precursor having general formula: $[\text{ZN} = \text{C}(\text{An})-\text{C}(\text{An}) = \text{NZ}]\text{NiBr}_2$, $\text{Z} = (4\text{-NH}_2\text{-3,5-C}_6\text{H}_2\text{-}i\text{Pr}_2\text{CH}(4\text{-C}_6\text{H}_4\text{NO}_2))$; An = acenaphthenequinone; with various cocatalysts. (a) **1d**/MADC, (b) **1d**/EAS, (c) **1d**/MAO. Polymerization conditions: toluene solvent = 80 mL in a 250 mL glass reactor, temperature = 30 °C, catalyst = 2.5 μmol , Al/Ni = 300 and atmospheric pressure of monomer.

cocatalysts as shown in the Figure 2. Each catalyst gave extremely different behavior on varying the cocatalysts. With **1d**/MAO and **1d**/EAS activities were found to be 2.43 and 9.84×10^5 g-PE/ mol Ni h bar respectively when **1d**/MADC gave super activity of 51.5×10^5 g-PE/ mol Ni h bar (Entry 8, 9 and 7 in Table I). By earlier reports about metallocene catalysts, changes in cocatalyst greatly affected the catalyst's performance and properties of polymer obtained.⁹ The high activity of all our catalysts in MADC medium over EAS and MAO can be attributed to any type of catalyst-cocatalyst interactions which are still not clear. Even though MAO is a superior alkylating agent and has a greater capacity to produce and stabilize cation like complexes, its bulky structure along with the bulkiness of the catalyst may be one of the main reasons for the low activity with MAO. With TMA all the catalysts were found to be inactive.

The catalytic activity was changed by modifying the *ortho* substituents of *N*-aryl ring from methyl to isopropyl groups. A considerable drop in the activity of complexes bearing isopropyl groups was observed when compared to complexes bearing methyl groups. For example, catalyst **1b** (Entry 3, Table I) bearing *ortho* methyl substituents of the *N*-aryl ring showed an activity (as average rate of polymerization ($R_{p,avg}$) for 30 min) of 56.5×10^5 g-PE/ mol Ni h bar at 30 °C combined with 300 equivalents of MADC, catalyst **1c** bearing ethyl substituents showed an activity of 54.1×10^5 g-PE/ mol Ni h bar, and isopropyl group substituted **1d** showed an activity of 51.5×10^5 g-PE/ mol Ni h bar (Entry

Table I. Ethylene Polymerization Results Carried Out at Atmospheric Pressure of Ethylene in a 250 mL Glass Reactor Containing 80 mL of Toluene Solvent and 2.5 μ mol Catalyst

Entry	Catalyst/Cocatalyst (Al/Ni)	T_p (°C)	Activity ^a	M_n^b (10^{-3})	PDI ^b	T_m^c (°C)	Branches/1000 C ^d
1	1a/MADC (300)	30	178.87	46.6	3.8	117	98
2	1a/MAO (300)	30	22.06	59.0	2.6	120	53
3	1b/MADC (300)	30	564.73	48.2	3.9	125	12
4	1b/MAO (300)	30	36.25	46.2	4.3	127	10
5	1c/MADC (300)	30	541.26	51.6	3.8	122	18
6	1c/MAO (300)	30	28.46	50.46	4.2	120	15
7	1d/MADC (300)	30	515.48	57.8	3.8	116	121
8	1d/MAO (300)	30	24.25	54.6	4.6	115	81
9	1d/EAS (300)	30	98.36	52.2	3.6	119	130
10	1d/MADC(400)	30	286.4	n.d. ^e	n.d.	117	75
11	1d/MADC(200)	30	111.64	n.d.	n.d.	116	78
12	1d/MADC (100)	30	9.56	n.d.	n.d.	117	80
13	1d/MADC (75)	30	4.54	n.d.	n.d.	118	72
14	1d/MADC (300)	10	526.27	146.8	3.5	119	98
15	1d/MADC (300)	50	286.56	36.4	4.1	115	126
16	1e/MADC (300)	30	56.65	51.7	4.1	119	104
17	1e/MAO (300)	30	50.07	48.4	5.7	118	63

^aAverage rate of polymerization as 10^4 g-PE/mol Ni h bar. ^bDetermined by GPC, ^cDetermined by DSC (°C). ^dBranches per 1000 carbon atoms determined by ¹H NMR. ^eNot determined.

7, Table I) at similar conditions. Generally a threshold amount of cocatalyst is needed for the effective activation of catalyst, presumably to scavenge impurities that may poison the active catalyst. From our repeated experiments it was observed that the active species for ethylene polymerization were generated after 75 equivalents (eq.) of MADC. For MAO and EAS it was found to be 22 and 25 eq. respectively.⁴

We have established the influence of these remote substituents Y = OMe, H, NO₂ (Figure 1) on ethylene polymerization in combination with MAO and EAS.⁴ With MADC the polymerization activity of various substituted catalysts follows the order **1d** (Y = NO₂) \gg **1a** (Y = H) $>$ **1e** (Y = OMe) as shown in Figure 3. This can be explained with the known facts for a late transition metal catalyst bearing strong electron withdrawing/donating groups as general trend. For late transitional metal catalysts, lowering of electron density on the metal center through the addition of ligands with electron-withdrawing groups produces more active catalysts and vice versa.⁷ The same trend was observed with MADC as shown in the Figure 3. When the electron withdrawing NO₂ substituted catalyst **1d** gave activity of 51.5×10^5 g-PE/ mol Ni h bar (Entry 7, Table I), the electron donating OMe substituted catalyst **1e** gave 5.7×10^5 g-PE/ mol Ni h bar (Entry 16, Table I).

Comparing the molecular weight of PE obtained with various cocatalysts (Entry 7, 8 and 9 in Table I), it was found that **1d**/MADC gave highest and **1d**/EAS gave lowest val-

ues. All system produced PE with broad molecular weight distributions ranging PDI from 3.5-4.6. This may be attributed to the presence of any foreign active species by the interaction of cocatalyst with various substituents in catalysts. The free amino groups on the catalytic system may also interact with various co-catalysts used.¹⁰ However, we could not detect any bimodal feature by GPC. Branching of carbon atoms increased with temperature while polymer molecular weight and melting point decreased along with the diminished activity (Entry 7, 14 and 15 in Table I). This is due to the deactivation of active species at high temperature as expected. Highly branched PE was obtained when common alkyl aluminum was used when compared with MAO. From the Table I it is clear that the branching with MADC and EAS were 121 and 130 respectively than that with MAO which was 81 (Entry 7, 9 and 8).

Many early and late transition metal complexes were examined experimentally and theoretically to elucidate their active species formed during olefin polymerizations via UV/VIS spectroscopy.¹¹ In order to confirm the specific role of cocatalysts on polymerization rate through active species formed, a series of UV-visible spectroscopic analysis of catalytic system were implemented in toluene at 25 °C (Figure 4). Absorption spectrum of α -diimine ligand and corresponding nickel complex did not show any characteristic peak between 350 and 800 nm whereas addition of cocatalyst to

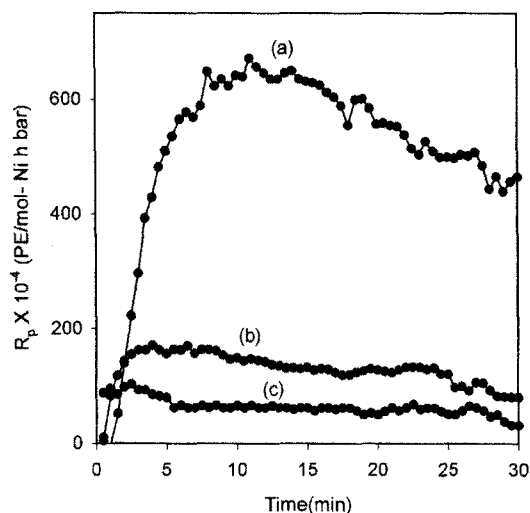


Figure 3. R_p versus time plot of ethylene polymerization catalyzed by various catalyst precursors having general formula: $[ZN = C(An)-C(An) = NZ]NiBr_2$, $Z = (4-NH_2-3,5-C_6H_2iPr_2)CH(4-C_6H_4Y)$; An = acenaphthenequinone; and (a) $Y = NO_2$ (**1d**), (b) $Y = H$ (**1a**), and (c) $Y = OCH_3$ (**1e**) with MADC (Al/Ni = 300). Polymerization conditions: toluene solvent = 80 mL in a 250 mL glass reactor, temperature = 30 °C, catalyst = 2.5 μ mol, and atmospheric pressure of monomer.

toluene solution of nickel complex resulted in the formation of new absorption bands, one centered at 700 nm whereas the others observed between 400–520 nm. The absorption maximum around 400–520 nm is of activated species and that around 700 nm is due to the dormant species.¹² UV spectra demonstrate the effect of MADC, MAO and EAS towards catalysts. Evidently MADC generates more active species than EAS and MAO, which is akin to our polymerization data. It is clear from Figure 4 (curve c) that the deactivated species were more than activated species when MAO was used as the cocatalyst, as indicated by the absorption at 700 nm.¹¹ Instead with MADC the dormant species are too less when compared to the active species (400–500 nm, curve d, Figure 4).

Conclusions

Sterically and electronically modulated Ni(II) α -diimine complexes were found to be highly active towards ethylene polymerization in the presence of MADC cocatalyst. Electron withdrawing nitro substituted catalysts showed unusual activity in combination with MADC when compared to MAO and EAS. The molecular weight and branching of PE was high when common alkyl aluminums such as MADC and EAS were used as cocatalysts. Since MAO is much more expensive than other common alkyl aluminum the search for more industrially viable cocatalysts has high significance.

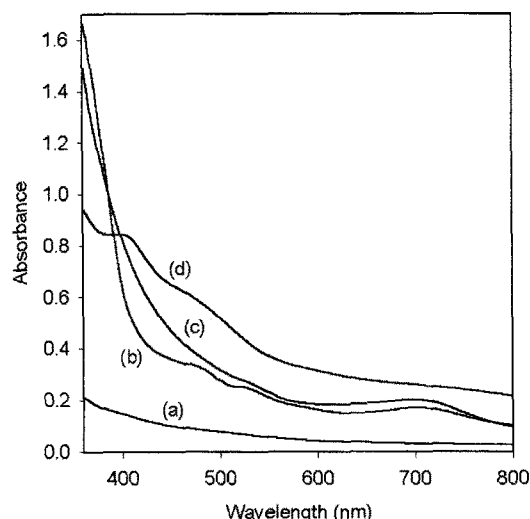


Figure 4. UV/VIS absorption spectra of (a) catalyst precursor having general formula: $[ZN = C(An)-C(An) = NZ]NiBr_2$, $Z = (4-NH_2-3,5-C_6H_2iPr_2)CH(4-C_6H_4NO_2)$; An = acenaphthene quinone (**1d**), (b) **1d**/EAS, (c) **1d**/MAO, and (d) **1d**/MADC in toluene at 25 °C and Al/Ni = 150.

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