Oligomerizations and Polymerizations of Olefins by Various Late Transition Metal Catalysts

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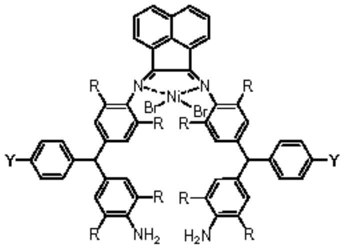
Introduction

Rapid advances after Ziegler and Natta's discovery in catalytic olefin polymerization, including metallocene revolution, gave an upward thrust to the polyolefin industry. Even though highly active homogeneous single site metallocene/methyl aluminoxane (MAO) system gave luxury of tailoring the microstructure of polymers, their high oxophilicity and inability to incorporate polar monomers paved the way for systems based on late transition metals, which is now flourishing to the best [1-3]. The most commercially advanced catalysts of this type are diimine complexes of Pd(II)/Ni(II), and Fe(II)/Co(II) complexes with bis(imino)pyridyl ligands [4].

In this presentation, effect of extremely bulky ligands with electron withdrawing/donating substituents at a remote position from the late transition metal center and of using homo- and multi-nuclear multi-metal on the ethylene polymerization is to be paged.

Results and discussion

Ni(II) catalysts bearing α-diimine ligands attained special interest due to their tunable activity and polymer microstructure by simple modification of the ligand architecture. Catalysts devoid of bulky substituents in *ortho* aryl positions have been found to oligomerize ethylene selectively to α–olefins and hence these substituents were recognized to be the key factor for late transition-metal catalysts to obtain high molecular weight (MW) polymers [4]. We synthesized a series of bulky diimine nickel catalysts with electron withdrawing/ donating groups at a remote position from the metal center (Fig. 1).



Cat.	**Y**	R
3a	H	Me
3b	H	Et
3c	H	*i*Pr
3d	NO_2	Me
3e	NO_2	Et
3f	NO_2	*i*Pr
3g	OMe	Me
3h	OMe	Et
3i	OMe	*i*Pr

Figure 1. Nickel(II) α-diimine catalysts bearing substituents at a remote position from the metal center

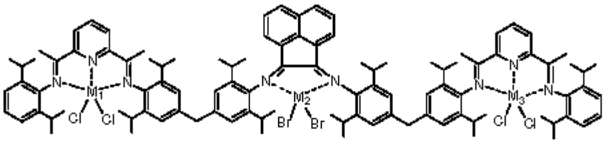
Table 1 summarizes ethylene polymerization results obtained by the catalysts shown in Fig. 1. By gaining advantages from existing technology we could design a catalytic system showing very high activity to yield polyethylene (PE) with high MW. Newly synthesized catalysts with bulky substituted α-diimine ligands polymerize ethylene with higher activity than reported system [4a] and the activity along with polymer properties was tuned according to different cocatalysts to yield high MW PE. Polymerization activity varied with substituents on the catalyst, even if they are at remote position from the metal center. Influence of such remote substituents was successfully investigated by cyclic voltammetry measurements. Catalytic active species resulting from the activation of nickel complex by cocatalysts were identified by UV-Vis spectroscopy and found that ethylaluminum sesquichloride (EAS) generates more active species which are stable for deactivation. EAS was found to be the best cocatalyst for our system under almost all conditions and good activity was also maintained with MAO. Polymers obtained by our catalysts were highly branched with MWD values of 2.6 to 5.7. Even though measured activities of these catalysts were affected by several variables and are often difficult to interpret, experimental evidences substantiate the remote substituent effect.

In our efforts to search for new late transition metal catalysts which can control the microstructure, MW, and MWD of PE in ethylene polymerization, we found that substituted bis-aniline compound could be utilized to prepare tri-nuclear homo- (Fe(II) or Ni(II)) or bimetallic [Fe(II)-Ni(II)] catalysts as shown in Fig. 2.

Table 1. Ethylene polymerization results carried out at P_{C2H4} = 1.3 bar in toluene solvent

Cat./cocat.	T_p (°C)	R_p[a]	M_n[b]x 10^{-3}	PDI[b]	T_m[c] (°C)	Branch[d]
3a/MAO	10	93.4	52.7	3.75	126	20
3a/MAO	30	100	26.1	3.58		44
3b/MAO	30	62.0			123	45
3c/MAO	30	43.3	48.9	2.99		96
3c/MAO	30	22.1	59.0	2.62	120	53
3c/EAS	30	91.2	56.9	2.73		103
3d/MAO	30	33.0			126	3
3e/MAO	30	25.4			122	12
3f/MAO	10	27.4	140	3.68	119	34
3f/MAO	30	24.3	54.6	4.63	115	81
3f/MAO	50	2.60				89
3f/EAS	30	98.4	52.2	3.57		130
3i/EAS	30	78.7	49.4	4.08		99
3i/MAO	30	50.1	48.4	5.70	116	63
3c/TEA	30	2.0				

[a] Average rate of polymerization as 10^7 g-PE/ mol Ni h atm. [b] Determined by GPC, [c] Determined by DSC (°C). [d] Branches per 1000 carbon atoms determined by ^{1}H NMR.



Cat 1: M_1, M_3 = None; M_2 = Ni; Cat 2: M_1, M_3 = Fe; M_2 = None; Cat 3: M_1, M_3 = Fe; M_2 = Ni

Figure 2. Tri-nuclear homo- or bimetallic [Fe(II)-Ni(II)] catalysts.

As shown in Table 2, Ni(II) catalyst (**Cat-1**) yields highly branched PE and Fe(II) catalyst (**Cat-2**) linear PE of high MW. Both catalysts produce PE of moderate PDI value. The tri-nuclear Fe(II)-Ni(II) based catalyst (**Cat-3**) yields PE of extremely broad MWD value. In addition the MWD values and degree of branching could be tuned by controlling parameters such as temperature, cocatalyst to catalyst ratio, and type of cocatalyst. It is interesting to note that **Cat-3** is more active than **Cat-1** or **Cat-2** at the same conditions. Detailed UV-Vis study showed that deactivating species present in homo-nuclear Ni catalyst were quenched in trinuclear bimetallic catalyst, resulting in synergistic activity effect.

Table 2 Results of ethylene polymerizations [a]

Cat/cocat.	R_p[b] x10^{-8}	M_n[c]	MWD [c]	T_m[d] (°C)	Branch[f]
Cat-1/MAO	1.2	36000	3.5	-	103.3
Cat-2/MAO	24.1	205700	4.9	133.3	2.62
Cat-3/MAO	28.3	1600	73.2	131.7	16.5
Cat-3/EAS	8.6	65000	3.0	-	134.2
Cat-3/TEA	9.9	700	144.	130.8	32.5

[a] Polymerization conditions: cat = 2 μmol, toluene solvent = 80 mL, temp = 30°C, P_{C2H4} = 1.3 bar, [cocat]/[cat] = 300. [b] Average rate of polymerization as g-E/mol-Ni h bar. [c] Determined by GPC. [d] Determined by DSC. [e] Branches per 1000 carbon atoms determined by ^{1}H NMR.

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