SYNTHESIS AND CHARACTERIZATION OF POLYETHYLENES BY NICKEL-DIIMINE AND METALLOCENE CATALYSTS

By

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ABSTRACT

Polyethylene (PE) synthesis has shown tremendous progress towards the production of polymers with innovative chemical and physical properties as a consequence of the development of new classes of single-site catalysts, including metallocene and the more recently developed nickel-diimine catalysts. This thesis describes the synthesis and characterization of a series of PE materials using a variety of metallocene and nickel-diimine catalysts. The main objective of this thesis work is to develop a better understanding of the influences of polymerization conditions and catalyst systems on polymer properties.

A detailed investigation of the polymerization of ethylene by (α-diimine)nickel(II) catalysts was first carried out. The catalysts used were ((ArN=C(An)-C(An)=NAr)$NiBr_2$, (ArN=C(CH_3)-C(CH_3)=NAr)$NiBr_2$ and (ArN=C(H)-C(H)=NAr)$NiBr_2$; where An = acenaphthene and Ar = 2,6-(i-Pr)$_2C_6H_3$). Changes in the α-diimine backbone structure showed remarkable effects on the polymer microstructure as well as catalyst activity. For all the three catalysts, increasing ethylene pressure or reducing polymerization temperature led to a reduction in the chain walking rates, and thus reduced the melting temperature and crystallinity of the polymer produced.

A Ni/α-diimine catalyst, 1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide was then supported on MMAO-treated silica to produce short chain branched PEs by ethylene polymerization. The supported catalyst gave far lower activity than the homogeneous catalyst. Depending on polymerization conditions, two active site populations were observed during polymerization using supported catalyst; one remained

fixed on the surface of the support, and the other was extracted from the support exhibiting the same polymerization behavior as the homogeneous catalyst.

A tandem homogeneous catalytic system was also used for the synthesis of ethylene-1-hexene copolymers from ethylene as the sole monomer. The catalytic system employed the tandem action between an ethylene trimerization catalyst, $(\eta^5\text{-}C_5H_4CMe_2C_6H_5)TiCl_3$(**1**)/MMAO, and a copolymerization metallocene catalyst, $[(\eta^5\text{-}C_5Me_4)SiMe_2(^tBuN)]TiCl_2$(**2**)/MMAO. During the reaction, **1**/MMAO *in situ* generated 1-hexene with high activity and high selectivity and simultaneously **2**/MMAO copolymerized ethylene with the produced 1-hexene to generate butyl branched PE. By simple manipulation of the catalyst molar ratio and polymerization condition, a series of branched PE samples were efficiently produced.

A binary catalyst system, consisting of a Ni/α-diimine catalyst, 1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide(**1**) and a zirconocene catalyst, rac-ethylenebis(indenyl) zirconium dichloride](**2**), was developed to synthesize a series of reactor blends of linear and branched PEs. The nickel diimine catalyst generated branched PE, while the zirconium catalyst produced linear PE. At various levels of temperature, ethylene pressure, and Catalyst **2** fraction, PE blends with different melting behaviors were produced. GPC-V analysis of the PE samples showed monomodal molecular weight distributions with narrow polydispersities.

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PUBLICATIONS

This Ph.D. thesis is organized in a sandwich style based on the following published / submitted papers:

1. **F. AlObaidi**, S. Zhu, "Synthesis of Reactor Blend of linear and branched Polyethylene Using Metallocene/Ni-Diimine Binary Catalyst System in a Single Reactor", *Journal of Applied Polymer Science*, submitted.
2. **F. AlObaidi**, Z. Ye, S. Zhu, "Ethylene Polymerization with Homogeneous Nickel-Diimine Catalyst: Effect of Catalyst Structure and Polymerization Conditions on Catalyst Activity and Polymer Properties", *Polymer*, **2004,** *45, 6823-6829.*
3. Z. Ye, **F. AlObaidi**, S. Zhu, "A tandem catalytic system for synthesis of ethylene-1-hexene copolymers from ethylene stock", *Macromolecular Rapid Communication*, **2004**, *25, 647-652.*
4. **F. AlObaidi**, Z. Ye, S. Zhu, "Synthesis of Linear Low-Density Polyethylene of Ethylene/1-Hexene Directly from Ethylene Using Tandem Catalytic System in Single Reactor", *Journal of Polymer Science, Part A, Polymer Chemistry,* **2004**, *42, 4327-4336.*
5. **F. AlObaidi**, Z. Ye, S. Zhu, "Ethylene Polymerization with Silica-Supported Nickel Diimine Catalyst: Effect of Support and Polymerization Conditions on Catalyst Activity and Polymer Properties", *Macromolecular Chemistry and Physics*, **2003**, *204, 1653-1659.*

TABLE OF CONTENTS

LIST OF FIGURES

Chapter 3 Page

Chapter 4 Page

Chapter 5 Page

Chapter 6 Page

LIST OF SCHEMES

Chapter 1 Page

Chapter 3 Page

Chapter 5 Page

Chapter 6 Page

LIST OF TABLES

Chapter 3 Page

Chapter 4 Page

Chapter 5 Page

Chapter 6 Page

NOMENCLATURE

Atm	Atmosphere (s)
CCD	Chemical Composition Distribution
CGC	Constrained Geometry Catalyst
Cp	Cyclopentadienyl
Cp*	Tetramethylcyclopentadienyl
DSC	Differential Scanning Calorimeter
DRI	Differential Refractive Index
GPC	Gel Permeation Chromatography
GPC-VIS	Gel Permeation Chromatography coupled with on-line Viscometer
HDPE	High Density Polyethylene
ICP-MS	Inductively Coupled Plasma- Mass Spectroscopy
LCB	Long Chain Branching
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MAO	Methylaluminoxane
MMAO	Modified Methylaluminoxane
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
MW	Molecular Weight
MWD	Molecular Weight Distribution
^{13}C NMR	Carbon-13 Neutron Magnetic Resonance
PDI	Polydispersity Index
PE	Polyethylene
SCB	Short Chain Branching
SEC	Size Exclusion Chromatography
T_m	Melting temperature

TCB	1,2,4-trichlorobenzene
TMA	Trimethylaluminum
Z-N	Ziegler-Natta

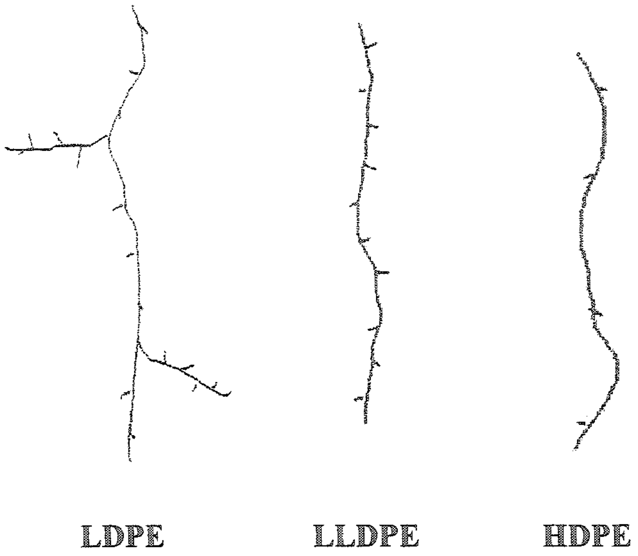
Chapter 1

Introduction and Research Background

1.1 Background Overview of Polyethylene

Since its discovery in 1933, polyethylene has become one of the most important commodity polymers in the world. The worldwide consumption of polyethylene was around 47 million tones in 1999, and it is estimated to reach 59 million tones by 2004.[1] A key factor for this growth is the overall increase in demand due to the economic development as well as the continuing improvement in polyethylene properties and production technologies.[2]

Polyethylene has traditionally been classified, based on its density and linearity, into three major groups: low density PE (LDPE), high density PE (HDPE), and linear low density PE (LLDPE). The generic structure of LDPE, LLDPE, and HDPE are illustrated in Scheme 1.1. Various types of polyethylene exhibit a wide range of properties with specific attributes depending on physical and chemical characteristics of the polyethylene resins.[2] Generally, the molecular characteristics of a polyethylene resin control its chemical and physical properties. Due to its broad range of properties, polyethylene is usually used for a wide range of applications, ranging from simple plastic bags to high strength fibers.[3] In general, polyethylenes are noted for their desirable balance of physical properties in the solid state and their chemical inertness.



Scheme 1.1 Chain structures of polyethylene (LDPE – low density polyethylene; LLDPE – linear low density polyethylene; HDPE – high density polyethylene).

LDPE has a typical density range of 0.910-0.935 g/ml. It was first produced in 1933 by Imperial Chemical Industries (ICI) using a high pressure (200~300 bar), high temperature (150~260 °C) free radical process. Two types of reactors are used for the production of LDPE: autoclave and tubular reactor. The difference between the efficient mixing in autoclave reactor and the lack of mixing in tubular reactor presents distinct flexibilities in the control of process conditions and hence the molecular structure of the product.[4]

Due to the nature of free radical polymerization mechanism, LDPE is mainly a branched polymer with both long chain branches (LCB) resulting from transfer to polymer and short chain branches (SCB) resulting from intramolecular backbiting reactions.[5] The SCBs found in LDPE reduce its degree of crystallinity, resulting in a flexible product with low density, high clarity, and impact resistance.[6] On the other hand, the LCBs give desirable processing characteristics such as high melt strength and low viscosities.[2]

LDPE is mainly used in packaging applications such as consumer bags, liners, overwraps, heavy duty sacks, agricultural films, and food packaging.[2,6] Other applications include power cables, toys, caps, and closures.[2] Despite its unique molecular structure, the commercial expansion of LDPE production has been limited over the years mainly due to its high construction and operation costs and to the development of new competitive polyethylene production catalysis and processes.[1]

The discovery of Ziegler-Natta and Phillips catalysts in the 1950s had a remarkable impact on the development of olefin polymerization catalysis. These discoveries laid the basis for the coordination catalysis of ethylene polymerization, which has continued to develop. In contrast to high pressure free radical process, these catalysts allowed the production of essentially linear polyethylene at low pressure and temperature. Nowadays, these catalysts are widely used in the polyethylene industry.[4]

Generally, Phillips catalysts are based on chromium trioxide supported on silica (CrO3/SiO2).[8] However, Ziegler-Natta catalyst, in its broad definition, is composed of two components: a transition metal salt from groups IV-VIII as a catalyst and a metal alkyl from group I-III as a cocatalyst. Most of the Ziegler-Natta catalysts used in industry are based on titanium salts and aluminum alkyls.[7] The main applications of Ziegler-Natta catalysis are the polymerization of ethylene, α-olefins, and dienes.[7] By far, the two most important operations are the polymerization of ethylene and propylene.

Both Z-N and Phillips catalysts possess more than one active site type with each site type having a distinct ratio of chain transfer to propagation rates and comonomer reactivity ratios. Due to this multi-site feature, these catalysts yield polymer with broad molecular weight distribution (MWD), and in case of copolymerization, broad chemical composition distribution (CCD). Such product heterogeneity is responsible for the differences in thermal and mechanical properties between different polyethylenes having the same average MW and composition.[2] Phillips catalysts produce only HDPE with broad MWD (PDI~15-30).[8] Ziegler-Natta catalysts can produce both LLDPE and HDPE with narrower MWD (PDI~3-7).

The discovery of Z-N and Phillips catalysts has imposed an enormous pressure for companies to develop low pressure commercial technologies for the production of polyethylene. Nowadays, polyethylene is commercially produced by several low pressure continuous processes. Depending on the polymerization mechanisms and reactor operating conditions, polyethylene production processes can be classified into three main types. Gas phase, slurry, and solution processes are all used for the production of polyethylene, but the gas phase and slurry are the most widely used ones in industry.[4] All these processes normally operate in the temperature range of 80-120 °C and at pressures of 20-30 bars. They differ significantly in operation and in production capabilities for specific product ranges. These processes are used for the production of polyethylene using several proprietary catalysts such as conventional Ziegler-Natta, Phillips, or the recently developed metallocene catalysts.

LLDPE is a copolymer of ethylene and a small amount of α-olefin, such as 1-butene, 1-hexene, and 1-octene. LLDPE has a typical density range of 0.910-0.925 g/ml. Copolymerization of ethylene with α-olefins disrupts the order of linear polyethylene chain by introducing short chain branches. As a consequence, the density, crystallinity, and rigidity of the polymer materials are decreased.[2] By varying the amount and type of α-olefin, type of catalyst, and polymerization conditions, one can produce various grades of copolymers to meet specific market needs.

The majority of LLDPE resins fall within the density range encompassed by LDPE polyethylene, and thus they share many of the same markets and applications. LLDPE makes around 25 % of share in the polyethylene market and is mainly used for film applications (66 %).[2] In the film applications, LLDPE distinguishes itself by superior toughness, as measured by tear strength, impact resistance, and puncture resistance. LLDPE can also be used for injection molding applications, such as food container lids and toys, where flexibility combined with toughness is needed.[2]

HDPE had been produced for the first time by both Ziegler-Natta and Phillips catalysts in the mid 1950's. HDPE has a typical density range of 0.940-0.965 g/ml. HDPE is linear in nature with none or very low level of short chain branching.[1] Compared to LDPE and LLDPE, HDPE is far more crystalline and consequently has higher density and higher thermal stability. It also has increased tensile strength, stiffness, and chemical resistance. However, HDPE has reduced low-temperature impact strength, elongation, permeability, and resistance to stress cracking.[9] HDPE has a market share of 45 % among all the polyethylenes and is primarily used in blow molding of bottles and toys (35 %), injection molding of household goods (18 %), and film applications (19 %).[6]

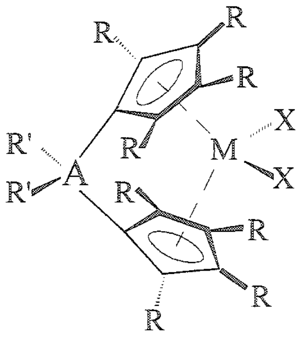
1.2 Single-Site Ethylene Polymerization Catalysts

1.2.1 Metallocene Catalysts

Metallocenes are relatively old organometallic complexes that were discovered as early as 1950. In the late 1950s, Giulio Natta reported the polymerization of ethylene with bis(cyclopentadienyl) titanium derivatives and alkylaluminum under mild reaction conditions. The activity of these metallocenes was found to be very low and there was little promise for commercial use at that time. Since then, the potential of metallocenes as commercial catalysts remained unrealized until 1980, when Kaminsky and coworkers discovered accidentally that adding a trace amount of water to the polymerization reactor improved their catalytic activity dramatically.[3]

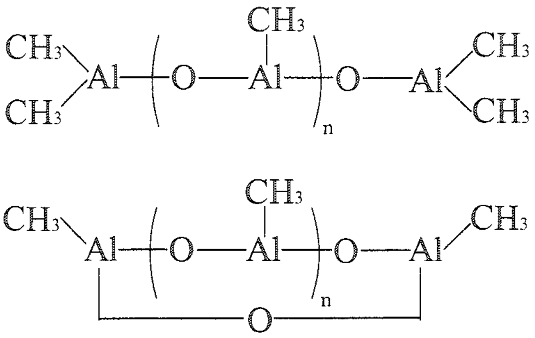
After further research, it was found that the high activity was a result of the hydrolysis of the cocatalyst alkylaluminum to form alkylaluminoxane, which is an effective cocatalyst for metallocene catalysts. Since then, intensive research efforts in both academia and industry have been undertaken to bring metallocene products to commercial use.[3] The development of these catalysts has been described as a major milestone in the history of polyolefin technology development. The main reason for this enormous interest lies in the ability of metallocene catalysts to produce well defined polymer products with properties tailored to the precise needs of the end application.

In their general form, metallocene catalysts comprise a metal atom from group IV (Ti, Zr, Hf) sandwiched between π-carbocyclic ligands such as cyclopentadienyl, fluorenyl, indenyl, or their substituted structures. Scheme 1.2 shows the generic structure of metallocene catalysts. There are a very large number of metallocene catalyst systems. The effect of the substituents on the metallocene ligands is one of the most important aspects of these catalyst systems. A limitless number of metallocenes with different capabilities toward olefin polymerization can be generated by varying the number of rings and substituents (R); the type of transition metal (M); and its substituents (X); the type of the bridge (R'), if present, and the type of cocatalyst.[10] The variations in the metallocene structure define the electronic and steric environment of the active site, which in turn establishes the catalyst's regulation of processes of monomer/comonomer insertion and chain transfer mechanisms.[11]



Scheme 1.2 Generic structure of metallocene catalysts.

The cocatalysts are the key to the metallocene's activity. Methylaluminoxane (MAO) is mostly used and is synthesized by the controlled hydrolysis of trimethyl aluminium (TMA).[12] Other bulky anionic complexes which show weak co-ordination, such as borates, play an increasing role too.[12] While the structure of MAO is complex, it is generally accepted that it is a mixture of linear and cyclic oligomers with a molecular weight between 1000 and 1500 g/mol.[11] MAO are also believed to form cage-like cluster of structures.[11] The structures of MAO are shown in Scheme 1.3.



Scheme 1.3 Proposed structures of MAO.

The exact details of the metallocene reaction mechanism including the role of the cocatalyst are the current topics of intense research and debate. The MAO cocatalyst is believed to: i) alkylate metallocene, forming an active complex, ii) scavenge for impurities, iii) stabilize the cationic center in an ion-pair interaction, and iv) possibly prevent bimetallic deactivation processes from occurring.[11]

A new form of MAO known as modified methylaluminoxane (MMAO) can be formed by the reaction of TMA with tetraalkyldialuminoxane containing ethyl or higher alkyl groups with the optional presence of water.[13] Unlike conventional MAO, MMAO contains alkyl substituents derived from tetraalkyldialuminoxane and gives isobutyl groups upon hydrolysis. Due to the isobutyl groups, MMAO exhibits high solubility in both aliphatic and aromatic solvents, whereas MAOs exhibit limited solubility in aliphatic solvents. Moreover, MMAO has the additional advantage of having longer shelf-life than conventional MAO, which tends to gel over time and hence lose its cocatalyst activity.[13]

Metallocene catalysts have revolutionized the polyolefins industry in general, and polyethylene's in specific.[2] Due to their unique properties, metallocene polyolefins are expected to penetrate a broad range of polymer markets. Metallocene catalyst systems are now used commercially in the manufacture of several families of new and improved polymers for both specialty and commodity polyolefin markets.[1] It is expected that metallocene products will reach a market volume of around 5 million tons by 2004, representing 9% of the overall polyethylene market.[1] The primary reason for the great interest in this catalyst is that compared to conventional Ziegler-Natta and Phillips type catalysts, metallocenes offer significant process advantages and produce polymers with very favorable properties.

The main advantages of metallocene catalysts are that they offer extremely high productivity, better flexibility and versatility for the synthesis and control of polyolefin structure.[10] The major difference of metallocene catalysts, when compared to Ziegler-Natta or chromium catalysts, is their structure, often referred to as single site, produce a uniform polymeric product that has a most probable molecular weight distribution (PDI $\approx$ 2) and homogeneous chemical composition distribution (CCD).

One of the major and growing uses of metallocene catalyst systems is the production of linear low density polyethylene (LLDPE).[1,2] Metallocene based LLDPE resins have many advantages over those produced with the conventional Ziegler-Natta catalyst systems. Because of the narrow CCD, the metallocene produced LLDPE copolymers exhibit many improved properties such as high clarity, strength, and lower hexane-extractables.[2,6] These properties are very important for film and other packaging applications where low haze and good clarity are required.[2]

On the other hand, metallocene catalyzed PE resins are not as readily processed as those produced with conventional Z-N catalyst. Because of the narrow MWD, metallocene PE resins suffer from poor processability, low melt strength and high melt fracture. These deficiencies in metallocene resins are overcome by either broadening their MWD or incorporating long chain branches (LCB). Metallocenes have proved to be very efficient catalysts for the production of long chain branched polyethylene.[3,10,11,14] The frequency of LCBs is believed to be controlled by the variation of metallocene structure and the manipulation of reaction conditions.[15]

Despite their many advantages, one important disadvantage needs to be solved before homogeneous metallocene catalysts can be used widely in industry. This is based on the fact that most of the commercial olefin polymerization units, such as gas and slurry phase processes, are designed to handle heterogeneous catalysts. Running homogeneous catalysts in these processes imposes two major problems; difficulty to control polymer particle morphology and severe reactor fouling; making process operation and polymer recovery impractical for a large scale production. To overcome these drawbacks, homogeneous catalysts ought to be supported on inert carriers, without losing much of the homogeneous catalyst advantages of high catalyst activity and desired polymer properties.

Supporting metallocene catalysts has been extensively investigated from both academic and industrial sectors due to the advantages in control of polymer particle morphology and applicability in gas and slurry phase commercial technologies.[16-19] Metallocene catalysts can be effectively supported on different types of inorganic carriers; the mostly used supports are spherical silica, $MgCl_2$ and Al_2O_3.[17-26] Spherical silica is one of the most commonly used catalyst carriers, since it leads to good polymer particle morphology.[19,20] Different supporting techniques are usually employed to optimize and control the final characteristics of the catalyst.[19,26] One of the techniques, which proved to be efficient and is commonly used in the literature, is to impregnate the catalyst on MAO-treated silica.[19,26]

Until recently, most activity in the metallocene field has focused on polyethylene but there have been significant developments in polypropylene as well. By using stereospecific metallocenes, various polypropylene types, such as atactic, isotactic, and syndiotactic, can be efficiently synthesized.[27] Metallocene catalysts have also been used for the synthesis of isotactic polymers of higher α-olefins, cyclic olefins and dienes.[27]

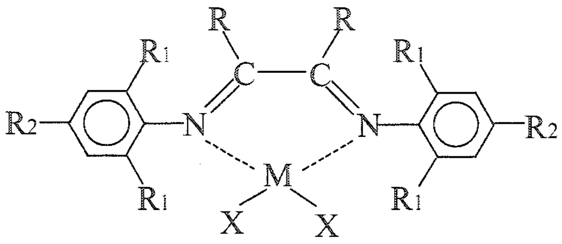
1.2.2 Late Transitional Metal Catalysts

Olefin polymerization catalysis is one of the most important research activities in the chemical industry. For the past 15 years, much of this research has been focused in the area of early transition metal (Ti, Zr or Cr) based metallocene catalysis, which has been a driving force for technology renewal in the polyolefins industry. Although, metallocene catalysts are extensively used for the coordination polymerization of nonpolar olefins such as ethylene and propylene, the use of these catalysts in the copolymerization of functionalized olefins has been limited. Most functionalized olefins, particularly commercially available polar monomers, poison metal catalysts based on early transition metals, which are highly oxophilic. For this reason, copolymers containing functionalized olefins with ethylene are still produced industrially by the free radical polymerization technology. Copolymers of ethylene with functionalized olefins such as methyl methacrylate, and vinyl acetate are very important commercial polymers.

Late transition metal catalysts have both low oxophilicity and greater tolerance towards functional groups than early transition metals.[28] Driven by this advantage, both academic and industrial institutions have undertaken massive and intensive research programs to develop a new generation of late transitional metal catalysts and explore their potential for olefin polymerization.[28-30]

The area of ethylene polymerization with late transition metal catalysts was extensively stimulated when Brookhart and his group reported a family of highly active α-diimine based Ni(II) and Pd(II) catalysts.[28,31] Similar to metallocenes, these catalysts are single-site type catalysts and usually activated using MAO as a cocatalyst. Scheme 1.4 shows the generic structure of these catalysts.

These catalysts were shown to afford polymerizing ethylene and α-olefins to high molecular weight polymers with activities comparable to those of metallocene catalyst systems. However, significant differences in microstructure and polymer properties were observed between polymers made with the Ni/Pd-based catalysts and those made with conventional Z-N and metallocene technologies. The property of polyethylene produced with Ni(II)- or Pd(II)-based catalysts cover a wide range of grades from highly branched, completely amorphous to linear semi-crystalline material.

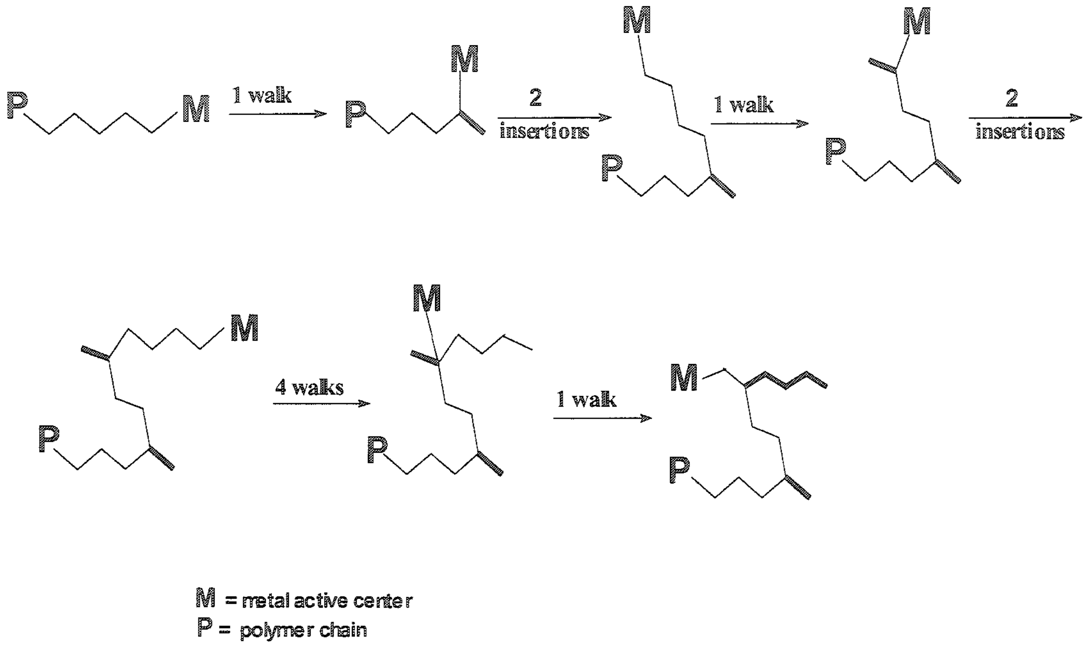


M = Ni, Pd;
R, R_1, R_2 = alkyl;
X = Br, alkyl.

Scheme 1.4 Generic structure of Ni(II)/Pd(II) α-Diimine catalysts.

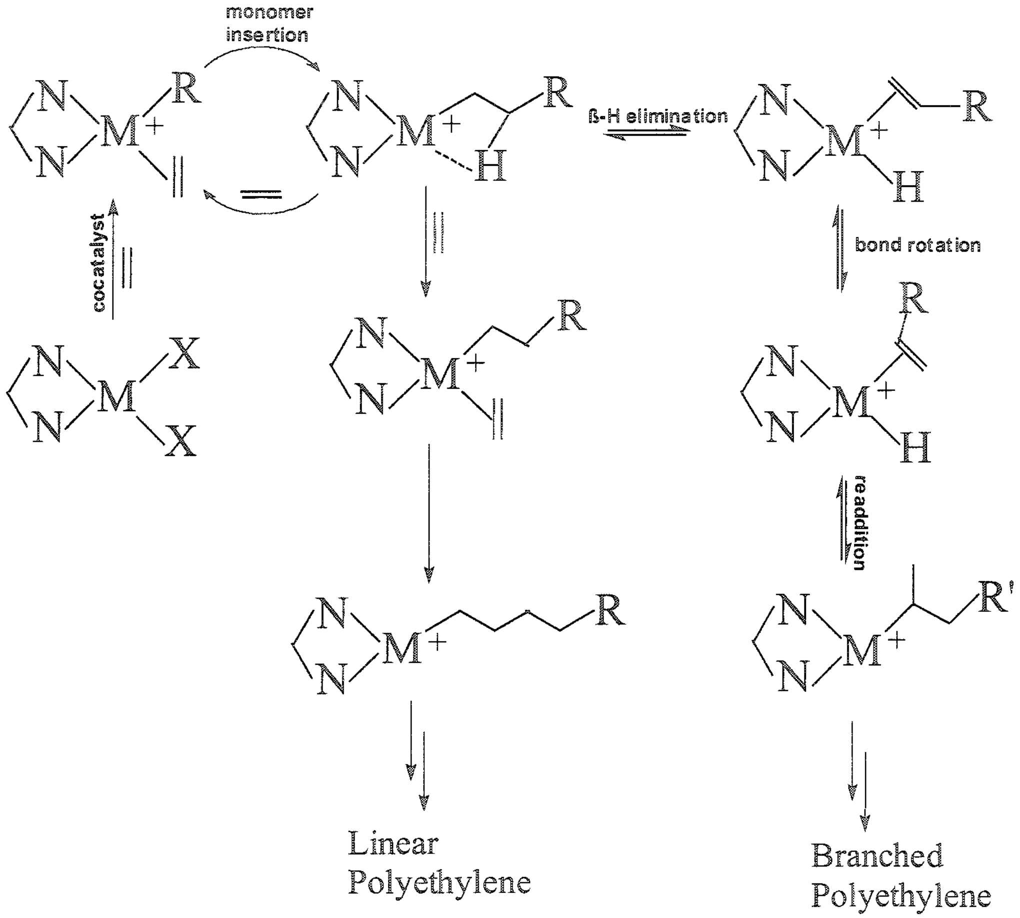
The polymer properties observed are greatly dependent on catalyst structure (metal and diimine ligand types) and polymerization conditions, such as ethylene pressure and reaction temperature.[28,30,31] Branching increases with an increase of temperature and decreases with an increase of ethylene pressure. Reducing the steric bulk of the diimine ligand results in less branched, more linear polymers with decreased molecular weight.[31]

The mechanistic details of Ni(II) and Pd(II) diimine catalyzed ethylene polymerization have been extensively studied in the literature. The main feature of these catalysts is the chain walking mechanism.[28,31] Different from metallocenes, this feature enables these catalysts to produce branched polyethylenes without the use of α-olefins comonomers.[28,31] In the chain walking mechanism, the catalytic active site is not fixed at the end of the polymer chain, but it moves rather along the growing polymer chain. Scheme 1.5 illustrates a simplified scheme of the chain walking mechanism to form methyl and butyl branches.



Scheme 1.5 Chain walking mechanism to form methyl and butyl branches.

Unlike Ni(II) based catalysts, with Pd(II) α-diimine catalyst systems, the chain walking mechanism has a drastic impact on the polymer chain topologies. Under a given set of conditions, polyethylenes derived from the Ni(II) α-diimine catalysts are generally less branched than polyethylenes derived from their Pd(II) analogues.[34] In addition, when polymerizing ethylene with Pd α-diimine catalysts, the polyethylene topology can effectively be controlled from linear structure with moderate branching to hyberbranched oils, by simply changing polymerization temperature and pressure.[34]



Scheme 1.6 Mechanism for ethylene polymerization and polymer branching formation with Ni/Pd α-Diimine complexes.

This simplicity in the control of polymer chain topology, makes Pd(II) catalyzed ethylene polymerization, an attractive subject for further research to develop new polymeric materials with novel properties.

Generally, the proposed mechanism for Ni(II) and Pd(II) catalysts, shown in Scheme 1.6, includes the initiation step via the coordination of olefin to the metal alkyl complex followed by a migratory insertion into the metal alkyl bond and formation of new alkyl complex.[28,31] Further insertions of olefins lead to chain growth and the formation of linear polyethylenes. Alternatively, the metal alkyl complex can go through an isomerization process to eliminate β-hydride to yield 1-alkene hydride complex. This species can undergo reinsertion with bond rotation resulting in the production of a branched alkyl metal complex. Changing polymerization conditions, ligand structure and metal type can adjust the competition between chain walking and monomer insertion processes to tailor polymer chain topology and branching density.[33-36]

Another key feature of these late transition metal catalysts is their exceptional functional group tolerance. This feature is mainly seen in the cationic Pd-diimine catalysts, which are considered far more functional group tolerant than Ni diimine catalysts. The cationic Pd-diimine catalysts allow ethylene polymerization in the presence of ethers, organic esters, and acids.[28] These catalysts have also been used for ethylene polymerization in aqueous medium and in supercritical CO_2 [28] The most interesting feature of these catalysts is their capability to copolymerize ethylene with polar monomers such as acrylates in an efficient manner.[37]

Due to their unique features, late transitional metal catalysts are likely to dominate the future research activities in the polyolefins area. These catalysts have exceptional capabilities, allowing for the development of new class of polymers with properties never thought about before in the polyolefin area.

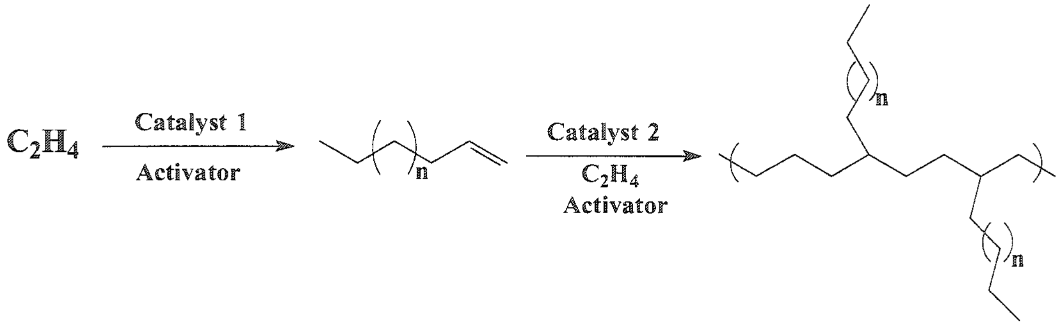
1.3 Ethylene Polymerization Using Binary Catalyst Systems

1.3.1 Synthesis of LLDPE from ethylene by Tandem Catalysis

Ethylene-based copolymers are industrially important materials. Linear low density polyethylene (LLDPE), a copolymer of ethylene and α-olefin, is an important class of ethylene-based copolymers. Copolymerization of ethylene with α-olefin introduces short chain branching (SCB) into chain backbone and modifies the physical properties of the polymer.[2] As a consequence, the density, crystallinity and rigidity of the polymer are decreased, and other properties such as clarity and impact strength are improved.[2]

LLDPE is most commonly produced by copolymerization of ethylene with α-olefin using transition metal catalysts such as the classical Ziegler-Natta catalysts and/or recently developed single-sited metallocene catalysts. In industry, the most commonly used co-monomer is 1-butene due to its low cost; however, it has been shown that using 1-hexene or 1-octene improves mechanical properties of the copolymer.[38] The production of LLDPE using this common route requires an integration of two different processes operated at different conditions; one for oligomerization of ethylene to produce α-olefin, and the other for the copolymerization of ethylene with the produced α-olefin. Recently, there have been considerable efforts to search for alternative processes that promote the synthesis of LLDPE from ethylene as the sole monomer.[39,40] In contrast to the commonly used two-stage process, these single-step processes certainly add a big advantage due to the savings in the costs of plant investment and operation.

An efficient approach employs a binary tandem action catalyst system for ethylene polymerization.[39,40] One catalyst produces short and long chain 1-alkenes through ethylene oligomerization/polymerization. For better control of branching length in the copolymer, a suitable catalyst for generating 1-alkene should be selected. The second catalyst is responsible for polymerizing ethylene and for incorporating the in situ produced 1-alkene into the polyethylene chain. The amount of branching produced by the binary catalyst system is controlled by simple adjustment of the ratio of the two catalysts.[39,40]



Scheme 1.7 General process for ethylene polymerization using binary tandem catalytic system

The simplicity and effectiveness of this approach makes it a promising alternative route to produce LLDPE from ethylene as the only monomer. Scheme 1.7 shows the polymerization process for ethylene polymerization using binary tandem catalytic system.

The oligomerization of ethylene typically affords a distribution of 1-olefins which must then be separated to give the product with desired carbon number.[41] One of the most useful components of this mixture is 1-hexene, which is used predominantly as a comonomer for linear low density polyethylene. Recently, there have been a few studies investigating the performance of various catalysts for the trimerization of ethylene to 1-hexene with high selectivity and activity.[42-44] The performance of these catalysts was remarkable making them very suitable for use in tandem with olefin polymerization catalysts to produce LLDPE from ethylene only.

In order to design a successful binary tandem catalytic system, it is necessary to consider a number of factors in selecting the individual catalysts.[39] One of the main factors is the catalyst compatibility; that is, to avoid interference between catalytic species. Furthermore, due to the cooperative action between the binary catalysts, it is necessary that the reactivity of both catalysts be well matched at the same reaction condition. Fortunately, the advent of homogeneous single-sited metallocene has permitted an unprecedented freedom in selecting the suitable combinations of binary tandem catalytic systems. Recent studies have shown great interest in the use of tandem catalyst systems as an alternative route for ethylene polymerization to control the polymer properties.

Bazan and coworkers have recently disclosed a number of reports describing ethylene polymerization with different tandem catalytic systems for the synthesis of branched polyethylene with various branching lengths. In one report, they synthesized butene-ethylene copolymers by the tandem action of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(^tBuN)]TiMe\}\{MeB(C_6F_5)_3\}$ as an ethylene polymerization catalyst, and $[(C_6H_5)_2PC_6H_4C(OB(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ as an oligomerization catalyst.[45] In the same report, through adjusting reaction conditions and catalyst ratio, they were able to produce hexene-butene-ethylene copolymers using the same tandem catalytic system.[45] In another report, they combined, $(C_5H_5BOEt)_2ZrCl_2$/MAO as a catalyst to produce 1-alkene from ethylene, with $[(\eta^5\text{-}C_5Me_4)SiMe_2(^tBuN)]TiCl_2$/MAO as an ethylene polymerization catalyst, for the synthesis of branched polyethylene with various branch lengths from ethylene as the only monomer.[46]

Bazan and coworkers also demonstrated the synthesis of branched polyethylene with various branch lengths from ethylene only, by using tandem catalytic systems comprising Fe-based catalyst for producing 1-alkene, and zirconium-based metallocene for ethylene copolymerization with the in situ produced 1-alkene.[47] In a recent work, they used a triple tandem catalytic system to produce a wide range of branched polyethylenes from a single ethylene monomer.[48] Phillips Petroleum synthesized branched polyethylene using a tandem catalytic system comprised of chromium compound and pyrrole derivatives with alkylaluminium as an activating agent.[49] In this system, adding a stoichiometric amount of the pyrrole derivative modifies the chromium site to generate the oligomerization component. Tandem catalytic systems were also reported for the production of long chain branched polymers.[50,51]

1.3.2 Synthesis of Polyethylene Reactor blends with Binary Catalyst system

Single site olefin polymerization catalysis has evolved considerably since the discovery of metallocene catalysts in the 1980s. Metallocene catalysts have been well known for their excellent flexibility and versatility for the synthesis and control of polyolefin structure.[3] In addition to metallocene catalysts, another milestone in the area of olefins polymerization catalysis was the discovery of the homogeneous single site α-diimine based late transition metal catalysts (Ni and Pd) in 1995.[28]

A great interest in these single site olefin polymerization catalysts has been driven by their ability to produce polyolefinic materials with new or improved performance parameters. In this context, there have been many studies focusing on utilizing these catalysts for the production of new polyolefinic materials or tailoring the characteristics of a specific polymer by employing different polymer blending methods. One method, which is widely used to enhance polymer processibility, involves the production of new polyolefins with broad molecular weight distribution by physical blending of two or more polymers with different molecular weights.[40,55] Another method involves the use of a series of multi-stage reactors, each running under different polymerization conditions, and thus producing polymers with different properties.[40,56]

The third method utilized to produce polymer blends, known as reactor blending, involves combining two or more types of catalysts to produce polymers with different and controlled properties in a single reactor.[40] In this method, each catalyst polymerizes ethylene independently generating different polyethylenes during the polymerization reaction, and thus forming a typical reactor blends.[40] The simplicity of this method allows the polymer properties to be tailored by simple adjustment of the catalyst ratios and the polymerization conditions. Recently, few studies have shown that ethylene polymerization with the combination of metallocene and nickel or iron diimine catalysts produces reactor blends of branched and linear polyethylene.[57-59] The combination of these catalysts shows high activity and can give materials with new properties.

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Chapter 2

Research Objectives and Thesis Outlines

2.1 Research Objectives

In the last decade, polyethylene chemistry has shown tremendous progress in the production of polyolefins with innovative chemical and physical properties as a consequence of the development of new classes of catalysts, including metallocene catalysts, and more recently, Ni(II) and Pd(II) diimine based complexes. Following this progress and utilizing the newly discovered single-site catalyst systems, the overall objective of this thesis are: (1) to synthesize and characterize a wide range of polyethylene products utilizing metallocene and Ni-diimine catalysts; and (2) to study the effects of the catalyst structure and polymerization conditions on catalyst activity and polymer microstructure and properties.

2.2 Thesis Outlines

This thesis has been divided into seven separate chapters. The first two chapters cover the introduction and research objectives, respectively. The seventh chapter covers the significant research contributions and recommendations for future work. Chapters 3-6 are based on four papers that have been published or submitted to various academic journals. This is a thesis of sandwich type that follows McMaster's guideline for thesis writing.

Chapter 3 investigates ethylene polymerization in a slurry semi-batch reactor using a series of MMAO-activated nickel α-diimine catalysts. This study investigates the effects of ethylene pressure, reaction temperature, and α-diimine backbone structure variation on the catalyst activity and polymer properties, such as branch content, molecular weight and distribution, and thermal characteristics of the final polymer. Different from previous studies, this work explores a wide range of polymerization conditions to understand the broadest effect on the final polymer properties.

Chapter 4 explores the polymerization of ethylene using silica supported nickel diimine catalyst in a slurry semi-batch reactor. The effects of catalyst supporting and polymerization conditions on catalyst activity and polymer properties, such as the branching content and distribution, molecular weight and distribution, and thermal characteristics of the final polymer, are systematically investigated. This study compares the performance of homogenous and supported catalysts for ethylene polymerization.

Chapter 5 develops a binary tandem catalytic system for the synthesis of ethylene-1-hexene copolymers directly with ethylene as the sole monomer. A systematic investigation is performed studying the effects of reaction conditions and catalyst ratio on the performance of the tandem catalytic system and the properties of produced copolymers. The molecular structure of produced copolymers is investigated using ^{13}C NMR, DSC, and GPC.

Chapter 6 studies the synthesis of a series of reactor blends of linear and branched ethylene homopolymers using combinations of nickel diimine and zirconocene catalysts in a semi-batch ethylene polymerization reaction. The study explores the effect of catalyst fraction and reaction conditions on the properties of the produced reactor blends. The effect of these variables on catalysts compatibility has also been investigated. The characteristics of the produced reactor blends are investigated using DSC and GPC.

Chapter 3

Ethylene polymerization with Homogeneous Nickel-Diimine Catalysts: Effects of Catalyst Structure and Polymerization Conditions on Catalyst Activity and Polymer Properties

This chapter is based on the paper published in *Polymer,* **2004**, *45, 6823-6829* by F. AlObaidi, Z. Ye, and S. Zhu.

3.1 Abstract

Ethylene polymerization was carried out using three nickel α-diimine catalysts ((ArN=C(An)-C(An)=NAr)$NiBr_2$ (**1**), (ArN=C(CH_3)-C(CH_3)=NAr)$NiBr_2$ (**2**) and (ArN=C(H)-C(H)=NAr)$NiBr_2$ (**3**); where An = acenaphthene and Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$) activated with MMAO in a slurry semi-batch reactor. We investigated the effects of ethylene pressure, reaction temperature, and α-diimine backbone structure variation on the catalyst activity and polymer properties. Changes in the α-diimine backbone structure had remarkable effect on the polymer microstructure as well as the catalyst activity. Catalyst **2** produced polymer with the highest molecular weight, while Catalyst **3** produced polymer with the lowest molecular weight. In addition, Catalyst **2** produced polymer with the highest branching level, while Catalyst **3** produced the lowest branching level exhibiting a melting behavior typical of high-density polyethylene (HDPE). With all the three catalysts, polymer molecular weight tended to decrease with increasing polymerization temperature due to the increase in chain transfer rates. In general, there was no clear and consistent trend observed for the effects of ethylene pressure on the polymer molecular weight. However, in polyethylene produced with Catalyst **2**, the molecular weight was independent of ethylene pressure suggesting that chain transfer to ethylene was a dominant mechanism for this catalyst.

Keywords: ethylene polymerization, nickel-diimine, catalyst activity, chain walking, molecular weight, short chain branching.

3.2 Introduction

Since the first commercial production of polyolefin products, there have been many advances in the area of olefins polymerization catalysis. One of the recent advances in the polyolefin technology was the use of homogeneous single-site metallocene catalysts. Compared to conventional olefins polymerization catalysts, metallocene catalysts offer better flexibility and versatility for the synthesis and control of polyolefin structure.[1] Another major advancement in the area of olefin polymerization catalysis was the discovery of the homogeneous α-diimine based late transition metal catalysts (Ni and Pd) in 1995.[2] These catalysts were shown to afford polymerizing ethylene to highly branched, high molecular weight homopolymers at remarkable polymerization activity.[2-5] These new catalysts have stimulated considerable academic and industrial research efforts in the polyolefins area.

Different from metallocene, these catalysts can produce polyethylene with branch structures without the use of α-olefin comonomers, attributing that to a catalytic mechanism referred to as "chain walking".[2-4] The properties of polyethylene produced with these catalysts cover a wide range of grades from highly branched completely amorphous to linear semi-crystalline materials.[2-10] The polymer properties observed are greatly dependent on catalyst structure (metal and diimine ligand types) and polymerization conditions, such as ethylene pressure and reaction temperature.[2-4] For example, for a specific catalyst structure, increasing ethylene pressure decreases the branch content, while increasing polymerization temperature increases the branch content. This effect is usually related to the competition between the chain walking and chain propagation processes.[2,3] There were numerous theoretical and experimental studies on ethylene polymerization using homogeneous nickel-diimine catalysts.[9-16] Many of these studies have been done to understand the effects of catalyst structure and polymerization conditions on the chain walking mechanism.[11-16]

In this chapter, we report a systematic comparative study concerning the performances in polyethylene synthesis of three nickel α-diimine catalysts activated with MMAO. We show the effects of changing the α-diimine backbone structure and polymerization conditions (ethylene pressure and temperature) on catalyst activity and polymer properties such as branch content, molecular weight and distribution, and thermal characteristics of the final polymer. Different from previous studies, our work explores a wide range of polymerization conditions to understand the broadest effect on the final polymer properties.

3.3 Experimental Part

3.3.1 Materials

All manipulation involving air and/or moisture sensitive compounds were performed in a dry nitrogen glove box or under ultra pure nitrogen protection. The α-diimine ligands [(ArN=C(An)-C(An)=NAr, An = acenaphthene; (ArN=C(CH_3)-C(CH_3)=NAr); and (ArN=C(H)-C(H)=NAr), Ar = 2,6-(i-Pr)$_2$$C_6H_3$)] and the corresponding dibromide nickel-diimine catalysts [(ArN=C(An)-C(An)=NAr)NiBr_2 (**1**), (ArN=C(CH_3)-C(CH_3)=NAr)NiBr_2 (**2**) and (ArN=C(H)-C(H)=NAr)NiBr_2 (**3**)] were synthesized following the procedures reported in the literature.[2] The cocatalyst, modified methylaluminoxane (MMAO: with 65.9 mol% methane and 31.7 mol% isobutane) was purchased from Akzo-Nobel Corporation as 7.25 wt% aluminum in toluene. Polymerization-grade ethylene (99.9% purity) was purchased from Matheson Gas and further purified by passing it through CuO, ascarite, and molecular sieves. Anhydrous toluene from Aldrich was refluxed over sodium with benzophenone as indicator and distilled under ultra pure nitrogen atmosphere prior to use.

3.3.2 Polymerization Runs

(a) Ethylene polymerization with 1/MMAO and 2/MMAO at 3 psig ethylene pressure

The polymerization was carried out in a 500 mL glass reactor equipped with a magnetic stirrer under 3 psig ethylene pressure. Toluene and MMAO were introduced into the reactor under nitrogen atmosphere. The reactor was evacuated, pressurized with ethylene, and then placed into an oil bath set at the operating temperature. After equilibrium for 15 minutes, a prescribed amount of catalyst solution was injected to start the polymerization. The reaction temperature and ethylene pressure were kept constant throughout the reaction. Magnetic stirring was applied. After 15 minutes, the reactor was vented and quenched by injecting methanol. The polymer produced was collected, washed with acidic methanol, and then dried under vacuum for 16 hours.

(b) Ethylene polymerization with 1/MMAO, 2/MMAO, and 3/MMAO at higher ethylene pressure

The polymerization was carried out in a 1-liter Autoclave stainless steel reactor operated in a semi-batch mode. The reactor was carefully cleaned with acetone, vacuumed at 150 °C for 3 hours, and then purged four times with ultra pure nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The required amount of co-catalyst, MMAO, solution was injected to the reactor under nitrogen atmosphere using gas-tight syringes. The mixture was kept under stirring while the reactor was heated up to establish the desired polymerization temperature. Once the desired temperature was established, a prescribed amount of catalyst solution or slurry was added to the reactor under pure nitrogen atmosphere using gas-tight syringes. To start polymerization, the reactor was pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuous feeding of gaseous ethylene to the reactor. The reactor temperature was maintained within ±1 °C of desired temperature by water/ethylene glycol cooling circulation. The reaction was stopped by rapid depressurization of the reactor followed by quenching with methanol. The polymer produced was washed with acidic methanol, then filtered and dried under vacuum at 60 °C for 16 hours.

3.3.3 Polymer characterization

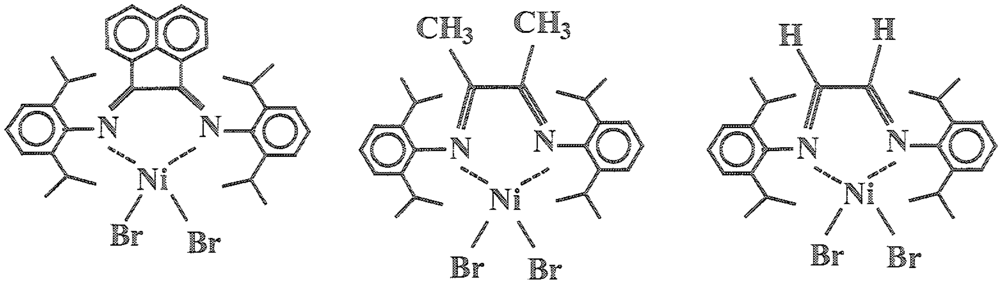
Polymer molecular weight (MW) and molecular weight distribution (MWD) were measured at 140 °C in 1,2,4-trichlorobenzene using Waters Alliance GPCV 2000 with DRI detector coupled with an on-line capillary viscometer. A calibration curve was established using monodisperse polystyrene standards. ^{13}C NMR analysis was conducted on a 75.4 MHz Bruker AV300 pulsed NMR spectrometer with waltz-supercycle proton decoupling at 120 °C. The polymer sample was dissolved in 1,2,4-trichlorobenzene and deuterated o-dichlorobenzene mixture in a 10 mm NMR tubes with concentration of about 18 wt%. The spectra required more than 5000 scans to obtain an acceptable signal-to-noise ratio. Polymer chemical shift assignments and calculations followed the procedure published in the literature.[13] The DSC analysis was carried out using Thermal

Analysis 2910 instrument from TA Inc. in the standard DSC run mode. A 30 ml/min of ultra pure nitrogen gas was fed continuously to purge the calorimeter. Sample cooling was done using a refrigeration cooling unit attached to the DSC cell. The instrument was initially calibrated for melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample, about 5 mg, was first equilibrated at -30 °C, then heated to 180 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled down to -30 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10 °C/min. The peak temperature with the highest endotherm was chosen as the melting point.

3.4 Results and Discussion

3.4.1 Effect of Catalyst Structure on Catalyst Activity and Polymer Properties

It has been reported previously that changes to the α-diimine structure can have remarkable effects on polymer structure and catalyst activity.[2,11] One of the main objectives of this work is to study the effect of changing substitution at the backbone carbon atoms of the α-diimine ligand on the catalyst activity and polymer properties. We investigated the backbone structure effects using Catalysts **1**, **2**, and **3**, where all contain the same bulky 2,6-di(isopropyl)phenyl groups as imine substituents. Table 3.1 shows the results of polymerization runs and polymer properties. The nickel α-diimine catalysts investigated are shown in *Scheme 3.1*.



1 **2** **3**

Scheme 3.1 Chemical structures of the Ni-diimine catalysts used in this work

All three catalysts exhibited high activity for ethylene polymerization with activities in the order of 10^6 gram PE/ (mol Ni × hr) at low and high pressure runs, which are comparable to those of metallocene catalysts.[17] The catalysts gave the activities in the order of:

Catalyst **1** > Catalyst **3** > Catalyst **2**.

This difference in activity can be seen by referring to Runs 6, 11, and 21 for polymerization at 30 °C and 200 psig and Runs 7, 12, and 19 for polymerization at 50 °C and 200 psig for the three catalysts, respectively.

As shown in Table 3.1, a remarkable effect of the α-diimine backbone structure on the polymer molecular weight and chain walking capability was observed. The catalysts yielded the molecular weight in the order of:

Catalyst **2** > Catalyst **1** > Catalyst **3**.

Table 3.1 Ethylene polymerization with homogeneous catalysts, **1**/MMAO, **2**/MMAO and **3**/MMAO.^{a}

Run	Cat.	Cat. (μmol)	T (°C)	P (psig)	Activity^b ($x10^{-3}$)	Mn^c (kg/mol)	PDI^c	Tm^d (°C)	$\Delta H_m{}^d$ (J/g)	$X_c{}^e$ (%)
1	1	1.6	35	3	3.35	118	2.02	-	-	-
2	1	2.38	40	50	9.53	117	2.74	76	35.6	12.2
3	1	1.78	40	150	12.6	138	2.81	98	61.8	21.0
4	1	1.78	40	200	36.2	196	2.24	102	73.3	25.5
5	1	1.78	40	350	40.7	178	2.57	111	83.5	28.5
6	1	1.78	30	200	32.4	259	3.28	108	80.7	27.5
7	1	1.78	50	200	26.5	172	2.60	89	48.6	16.6
8	1	1.78	60	200	4.2	145	2.14	73	42.7	14.2
9	1	0.5	10	200	16.4	-	-	127	95.6	33.0
10	2	3.5	25	3	2.1	210	1.80	-	-	-
11	2	2.0	30	200	13.8	704	2.50	103	63.8	21.8
12	2	2.0	50	200	10.2	350	2.23	61	29.0	9.9
13	2	4.0	70	200	1.8	248	2.16	21	25.8	8.7
14	2	2.0	50	100	6.2	362	2.10	40	27.2	9.2
15	2	2.0	50	300	12.2	405	2.53	78	33.0	11.1
16	2	2.0	30	400	15.3	727	2.35	116	79.1	27.2
17	2	2.0	50	400	13.5	403	2.02	88	35.1	12.0
18	3	2.0	50	25	3.1	19	2.9	120	144	49
19	3	2.0	50	200	18.7	21	3.3	128	167	57
20	3	2.0	50	400	22.3	23	3.2	133	184	63
21	3	2.0	30	200	28.5	29	2.8	132	176	60
22	3	4.0	70	200	2.6	14	2.9	125	162	55

a: Al(MMAO)/Ni molar ratio: 3000, Solvent: 250 ml for 3 psig runs and 400 ml toluene for all higher pressure runs, Stirring: 1500 rpm; Reaction time: 15 min for runs 1 and 10; 20 min for run 9; 10 min for all other runs; b: Activity in kgPE/(mol Ni x hr); c: Determined from GPCV measurement at 140 °C in 1,2,4-trichlorobenzene; d: Determined from DSC measurement; e: Crystallinity based on ΔH_m = 293 J/g for a 100% crystalline PE.

The effect on molecular weight can be seen, for instance, by comparing Run 11 (Catalyst **2** with M_n= 704000 g/mol), Run 6 (Catalyst **1** with M_n= 259000 g/mol) and Run 21 (Catalyst **3** with M_n= 29000 g/mol), which were conducted at the same conditions. It is significant to note that Catalyst **3** produced polymer with far lower molecular weight than Catalysts **1** and **2**.

In addition, a strong correlation was observed between the steric bulk of α-diimine backbone structure and the degree of branching in polymer produced as evident in the DSC thermal analysis. We reported the DSC thermal analysis in terms of melting temperature (T_m), heat of fusion (ΔH_m) and degree of crystallinity (X_c). The melting behavior of polyethylene is mainly related to the short chain branching density. Increasing short chain branching density decreases lamellar thickness of the crystal structure and thus lowers melting temperature of the polymer. The short chain branching also affects the degree of crystallinity which is proportional to the fractional amount of crystalline phase in polymer sample. The catalysts produced the branching level in the order of:

Catalyst **2** > Catalyst **1** > Catalyst **3**

Catalyst **3** produced polymer exhibiting melting behavior typical of high-density polyethylene (HDPE). For example, comparing Runs 7, 12 and 19 where polymerization conditions were identical at 50 °C and 200 psig, Catalyst **1** produced polymer with T_m= 89 °C and X_c = 16.6, Catalyst **2** produced polymer with T_m= 61 °C and X_c = 9.9, while Catalyst **3** produced polymer with T_m= 128 °C and X_c = 57. Figure 3.1 shows the DSC thermograms for polyethylene prepared using Catalysts **1**, **2** and **3** at 50 °C and 200 psig.

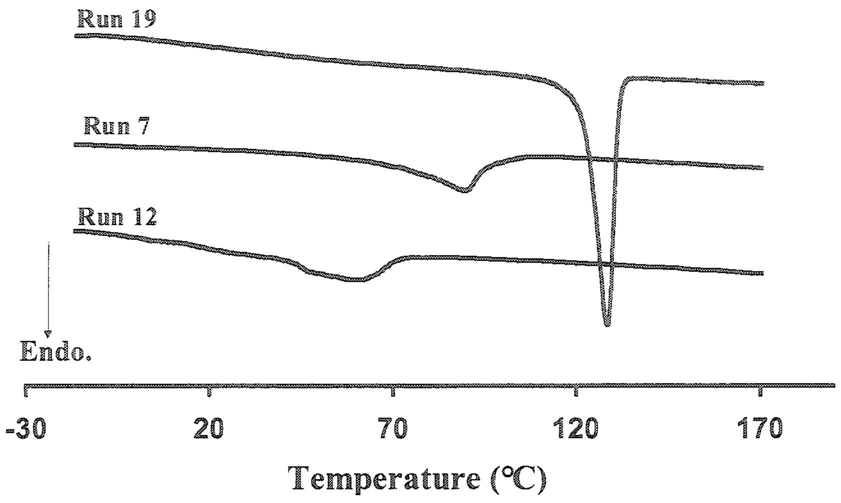


Figure 3.1 DSC thermograms for polymers produced with Catalysts **1** (run 7), **2** (run 12) and **3** (run 19) at 50 °C and 200 psig: the effect of catalyst structure on polymer melting behavior.

It is significant to note that there was no clear and consistent trend for the effects of changing the α-diimine backbone structure on the polymer properties such as the molecular weight and the melting behavior. Changing the α-diimine backbone structure from acenaphthyl (catalyst **1**) to methyl (catalyst **2**) substituents, increased the polymer molecular weight, however changing the α-diimine backbone structure to hydrogen (catalyst **3**) substituent, reduced the molecular weight drastically. Similarly, changing the α-diimine backbone structure from acenaphthyl (catalyst **1**) to methyl (catalyst **2**) substituents, reduced the polymer melting point, however changing the α-diimine backbone structure to hydrogen (catalyst **3**) substituent, increased the melting point drastically. This change on the polymer structure could be attributed to the steric as well as electronic effects imposed on the catalyst as we change the α-diimine backbone structure.

3.4.2 Effect of Polymerization Conditions on Catalyst Activity and Polymer Properties

The chain walking mechanism appeared to be present for all the three catalyst systems. Increasing ethylene pressure or decreasing reactor temperature led to an increase in the polymer melting point. This trend showed a reduction in the short chain branch content due to the dominance of chain propagation over chain walking reactions at such conditions. However, depending on the catalyst structure, the response effect differed from one catalyst to another. As shown in Table 3.1, we investigated the performance of the three catalysts at a wide range of temperatures and ethylene pressures to understand the broadest effect on polymer properties and catalyst activity.

For all the three catalysts, the effects of reaction temperature and ethylene pressure on catalyst activity were very clear from the experimental data. As we reported previously,[18] Catalyst 1 activity increased with polymerization temperature reaching a maximum at 40 °C, but at higher temperature activity was reduced due to the increase in catalyst deactivation rate as known for most olefin polymerization catalysts. This temperature effect on activity was observed when comparing Runs 4, 6, 7 and 8, where ethylene pressure was held at 200 psig and reaction temperature was changed as shown in

Table 3.1. A similar trend was observed for both Catalysts **2** and **3** when tested at similar conditions, with ethylene pressure kept at 200 psig. The activity was high when running at 30 °C and the catalyst deactivation was seen as we run at 50 °C, with more severe deactivation at polymerization temperature of 70 °C. This trend can be seen clearly by referring to Table 3.1, Runs 11, 12 and 13 for Catalyst **2**, and Run 21, 19, and 22 for Catalyst **3**.

The effect of ethylene pressure on catalyst activity followed the same trend for all the three catalysts. This trend shows that catalyst activity increased with ethylene pressure which can be explained since catalyst active sites were exposed to higher ethylene concentration at higher pressure. This trend is observed by comparing Runs 3, 4 and 5 for Catalyst **1**, Runs 12, 14, 15 and 17 for Catalyst **2**, and Runs 18, 19 and 20 for Catalyst **3**.

The molecular weights of the polyethylene samples produced by each of the three catalysts were found to decrease as the polymerization temperature was increased. For example, running Catalyst **2** at 200 psig, the molecular weight dropped from M_n = 704000 when the polymerization was carried out at 30 °C to M_n = 350000 at 50 °C and M_n = 248000 at 70 °C. Similar effects were also observed with the other two catalysts; comparing Runs 6, 7 and 8 for Catalyst **1**, and Runs 21, 19, and 22 for Catalyst **3**. These observations suggest that for all the three catalysts, increasing polymerization temperature increases the rate of chain transfer.

With all three catalysts, there was no clear and consistent trend of the effect of ethylene pressure on the molecular weight of the polymer produced. For example, for Catalyst **1**, the polymer molecular weight slightly increased with ethylene pressure up to a certain pressure; as seen from Runs 2, 3 and 4. However the trend was reversed when ethylene pressure was increased from 200 psig to 350 psig as seen from Runs 4 and 5. This shows that the competition between propagation and termination rates was affected by the level of ethylene pressure. However, for Catalyst **2**, changing ethylene pressure did not show an appreciable effect on the molecular weight of the polymer produced. This observation has been confirmed at both low and high pressure levels. For example, running Catalyst **2** at 30 °C, the molecular weight changed from $M_n = 704000$ when the polymerization was carried out at 200 psig to $M_n = 727000$ at 400 psig. Similar effects were also observed when running Catalyst **2** at 50 °C; for example, comparing Run 12 with 14 and Run 15 with 17. This observation probably suggests that chain transfer to ethylene is a dominant mechanism for Catalyst **2**.

The differences in the properties of the polyethylenes produced by all the three catalysts are mostly due to variations in the degree of short chain branching caused by changes in polymerization parameters (temperature and pressure) for each catalyst. Short chain branches affect polymer properties, such as crystallinity and melting temperature, and are important in controlling the polymer application. For both Catalysts **1** and **2**, there was a very strong correlation between reaction parameters and polymer properties. For example, when running Catalyst **1** at 200 psig, polymer melting temperature and crystallinity increased from T_m= 73 °C and X_c = 14.2 when the polymerization was carried out at 60 °C to T_m= 127 °C and X_c = 33 when the polymerization was carried out at 10 °C. Similarly, running Catalyst **1** at the fixed temperature of 40 °C, the polymer melting point increased as we increased the reactor pressure. This trend was observed by referring to Table 3.1, Runs 2, 3, 4, and 5. These T_m and X_c variations are associated with the enhancement of branching in the polymer chains. Table 3.2 shows the SCB distribution measured by ^{13}C NMR of some selected polyethylene samples produced by Catalyst **1** at selected polymerization conditions.

Table 3.2 Short chain branching distribution of polyethylene produced with 1/MMAO.[a]

Run	Methyl	Ethyl	Propyl	Butyl	Pentyl	Hexyl and longer	Total	Tm (°C)
2	44.2	4.1	2.5	2.8	3.0	6.9	63.5	76
3	24.6	2.9	1.4	1.2	1.9	3.0	35.0	98
6	17.7	1.5	0.8	0.9	1.3	2.6	24.8	109
7	32.5	2.5	1.5	1.4	1.2	2.5	41.6	89

a: Short chain branching distribution measured by ^{13}C NMR as Branch/1000 Carbons

It is worth noting that methyl branches were always predominant as was usual with this type of catalyst system. Figures 3.2 and 3.3 show the DSC thermograms for polymers produced with Catalyst **1** at selected polymerization conditions. The effect of temperature and pressure on the melting behavior of the polymer produced by Catalyst **2** followed a similar trend as Catalyst **1**. Figures 3.4 and 3.5 show the DSC thermograms for the polymers produced with Catalyst **2** at selected polymerization conditions.

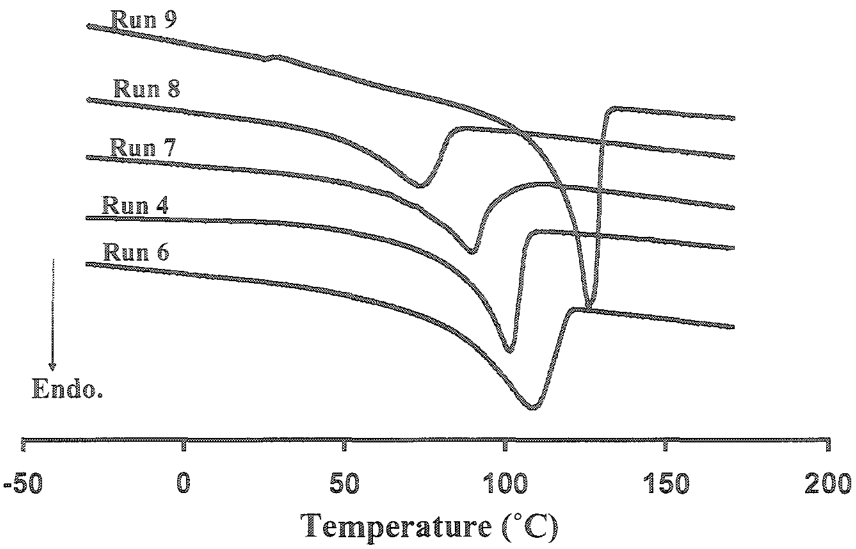


Figure 3.2 DSC thermograms for the polymers produced with Catalyst 1 at 200 psig: the effect of polymerization temperature on polymer melting behavior.

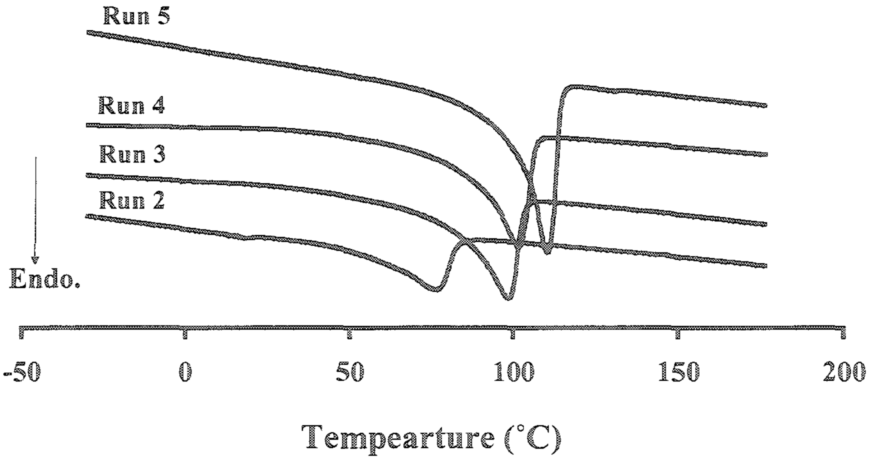


Figure 3.3 DSC thermograms for the polymers produced with Catalyst 1 at 40 °C: the effect of ethylene pressure on polymer melting behavior.

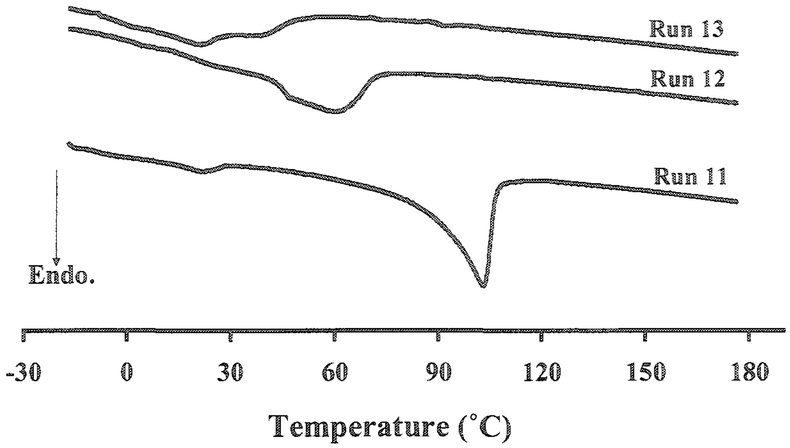


Figure 3.4 DSC thermograms for the polymers produced with Catalyst 2 at 200 psig: the effect of polymerization temperature on polymer melting behavior.

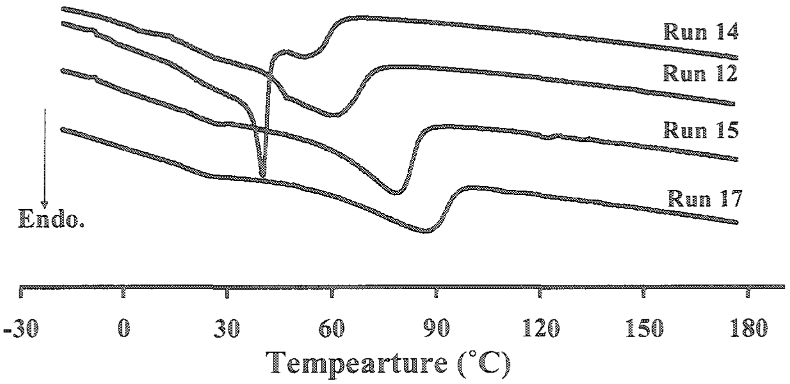


Figure 3.5 DSC thermograms for the polymers produced with Catalyst 2 at 50 °C: the effect of ethylene pressure on polymer melting behavior.

The effect of temperature and pressure on the melting behavior of the polymer produced by Catalyst 2 followed a similar trend as Catalyst 1. Figures 3.4 and 3.5 show the DSC thermograms for the polymers produced with Catalyst 2 at selected polymerization conditions. However, as shown in the DCS thermograms, the polyethylenes produced by Catalyst 2 exhibited broad melting peaks especially for the highly branched samples, with low melting point and crystallinities. This observation could be attributed to more irregularity of the chain structure of the polyethylene produced by Catalyst 2. In addition, Catalyst 2 shows a stronger response to changes in polymerization temperature. For example, for an increase of 20 °C in polymerization temperature while ethylene pressure was kept at 200 psig, melting temperature of the polymer produced by Catalyst 2 was reduced by 42 °C (Runs 11 and 12), but for the polymer produced by Catalyst 1, melting temperature was reduced by 19 °C (Runs 6 and 7). This reflects that the effect of polymerization temperature on chain walking rate was more pronounced in Catalyst 2 than Catalyst 1.

Surprisingly, the polymers produced by Catalyst 3 exhibited melting behavior which was totally different from either Catalyst 1 or 2. Figures 3.6 shows the DSC thermograms for polymers produced with Catalyst 3 at selected polymerization conditions. Relatively, these polymers showed very sharp melting peaks with high melting temperatures and crystallinities, typical of high-density polyethylene (HDPE).

Moreover, comparing to Catalyst 1 and 2, the response of the polymer melting behavior to polymerization temperature and pressure was very low for Catalyst 3.

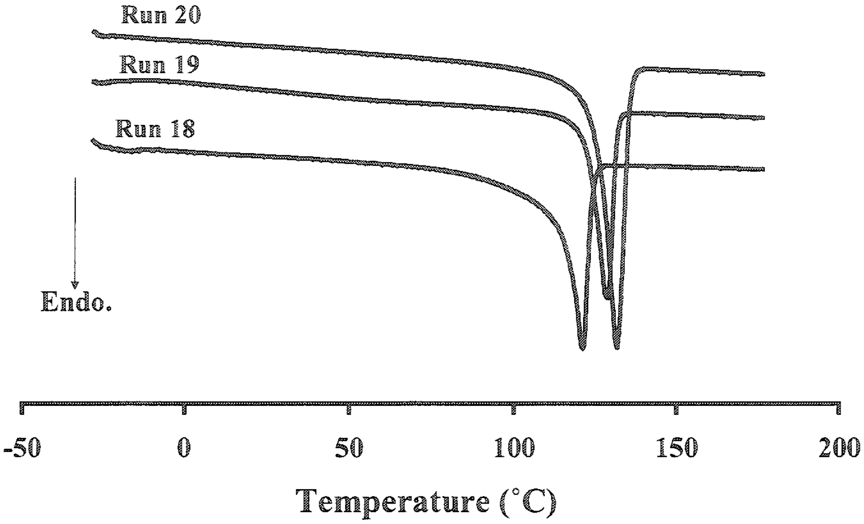


Figure 3.6 DSC thermograms for the polymers produced with Catalyst 3 at 50 °C: the effect of ethylene pressure on polymer melting behavior.

For example, for an increase of 20 °C in polymerization temperature while ethylene pressure was kept at 200 psig, melting temperature of polymer produced by Catalyst 3 was reduced by 4 °C (Runs 19 and 21). In addition, doubling ethylene pressure while keeping polymerization temperature at 50 °C, the melting temperature was increased by 5 °C (Runs 19 and 20).

3.5 Conclusion

Ethylene polymerization was carried out using three nickel α-diimine catalysts activated with MMAO in a slurry semi-batch reactor. We investigated the effects of ethylene pressure, reaction temperature, and the variations of α-diimine backbone structure on the catalyst activity and polymer properties. For all the three catalysts, increasing ethylene pressure or reducing polymerization temperature led to a reduction in the extent of branching, and thus reduced the melting temperature and crystallinity of the polymer produced. Changes to the α-diimine backbone structure showed remarkable effects on the polymer microstructure as well as catalyst activity. However, there was no clear and consistent trend for the effects of changing the α-diimine backbone structure on polymer properties such as the molecular weight and the melting behavior. With all three catalysts, polymer molecular weight tended to decrease with increasing polymerization temperature due to the increase in chain transfer rates at high temperature. However, there was no clear and consistent trend of the effect of ethylene pressure on the molecular weight of the polymer produced with the three catalysts. In the polyethylene produced with Catalyst **2**, the molecular weight was independent of ethylene pressure suggesting that chain transfer to ethylene was a dominant mechanism for this catalyst.

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Chapter 4

Ethylene Polymerization with Silica-Supported Nickel Diimine Catalyst: Effect of Support and Polymerization Conditions on Catalyst Activity and Polymer Properties

This chapter is organized based on the paper published in *Macromol. Chem. Phys.* **2003**, *204*, 1653-1659 by Fahad AlObaidi, Zhibin Ye, and Shiping Zhu.

4.1 Abstract

Ethylene was polymerized using both homogeneous and modified methylaluminoxane (MMAO)-treated silica supported nickel-diimine catalyst (1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide) in a slurry semi-batch reactor. The effects of catalyst supporting and polymerization conditions (ethylene pressure and reaction temperature) on catalyst activity and polymer properties were systematically investigated. The supported catalyst gave far lower activity than the homogeneous catalyst. The activities of both catalyst systems increased with polymerization temperature with a maximum at 40 °C. Compared with the homogeneous catalyst, the supported catalyst system produced polyethylene with a different microstructure. Due to steric effects, the supported catalyst system exhibited lower chain walking rates than the homogeneous catalyst, producing polymers with less branching content and, thus higher melting points. Depending on polymerization conditions, two active site populations were observed during polymerization using supported catalyst;

one population remained fixed on the surface of the support, and the other was extracted from the support, exhibiting the same polymerization behavior as the homogeneous catalyst.

Keywords: ethylene polymerization, catalyst , silica support, Ni-Diimine catalyst, short chain branch, chain walking mechanism.

4.2 Introduction

The discovery of homogeneous metallocene catalysts has had major technological advantages for the polyolefin industry. In comparison with conventional Ziegler-Natta catalysts, metallocene-based catalysts are of the single site type, offering better flexibility and versatility for the synthesis and control of polyolefin structure.[1] In addition to metallocene catalysts, another major advancement in the area of olefin polymerization was the discovery of homogeneous α-diimine based late transition metal catalysts (Ni and Pd) in 1995.[2] These new catalysts have stimulated considerable research efforts in the polyolefins area. Different from metallocenes, these catalysts can produce polyethylene with branched structures without the use of α-olefin comonomers and display a catalytic mechanism referred to as "chain walking".[2-8] The properties of polyethylene produced with these catalysts cover a wide range of grades from highly branched, completely amorphous, to linear, semi-crystalline materials.[2-4] The polymer properties observed are greatly dependent on catalyst structure (metal and diimine ligand types) and polymerization conditions, such as ethylene pressure and reaction temperature.[2,3] For example, for a specific catalyst structure, increasing ethylene pressure decreases the short chain branching (SCB) content, while increasing polymerization temperature increases the SCB content. This effect is usually related to the competition between the chain walking and chain propagation processes.[2,3]

Despite their many advantages, one important disadvantage needs to be solved before homogeneous catalysts can be used widely in industry. This is based on the fact that most of the commercial olefin polymerization units, such as gas and slurry phase processes, are designed to handle heterogeneous catalysts. Running homogeneous catalysts in these processes imposes two main problems: difficulty controlling polymer particle morphology and severe reactor fouling, making process operation and polymer recovery impractical for a large-scale production. To overcome these drawbacks, homogeneous catalysts should be supported on inert carries, without losing much of the homogeneous catalyst advantages of high catalyst activity and desired polymer properties.

Supporting metallocene catalysts has been extensively investigated from both academic and industrial sectors due to the advantages of control of polymer particle morphology and applicability in gas and slurry phase commercial technologies.[9-12] Metallocene catalysts can be effectively supported on different types of inorganic carriers, the most frequently used are spherical silica, $MgCl_2$ and Al_2O_3.[10-19] Metallocene catalysts have also been supported on polymeric carriers such as polystyrene particles.[17] Spherical silica is one of the most commonly used catalyst carriers, since it leads to good polymer particle morphology.[12,13] Different supporting techniques are usually employed to optimize and control the final characteristics of the catalyst.[12,19] One of the techniques, which proved to be efficient and is commonly used in the literature, is to impregnate the catalyst on MAO-treated silica.[11,19]

Nickel diimine catalysts have been supported on different types of inorganic supports, such as silica,[20-24] and polymeric supports.[25] Exxon chemical has synthesized polyethylene in slurry and fluidized bed gas phase reactors using nickel-diimine catalyst supported on MAO-treated silica.[20] An in situ supported nickel-diimine catalyst system has been used by Soares et al.,[22] for ethylene polymerization, to investigate the effect of polymerization conditions on polymer microstructure and morphology. To enhance catalyst activity, Brookhart et al. have polymerized ethylene using nickel-diimine catalyst covalently attached to silica particles.[23]

In this chapter, we describe the use of nickel diimine catalyst (1,4-bis(2,6-diisoprpylphenyl) acenaphthene diimine nickel(II) dibromide) supported on MMAO-treated silica for ethylene polymerization in a slurry reactor. We show the effect of supporting, and polymerization conditions (ethylene pressure and temperature) on the branching content and distribution, molecular weight and distribution, and thermal characteristics of the final polymer. This study is done based on a comparison between homogenous and supported catalysts for ethylene polymerization.

4.3 Experimental Part

4.3.1 Materials

All manipulation involving air and/or moisture sensitive compounds were performed in a dry nitrogen glove box or under ultra pure nitrogen protection. The α-diimine ligand (ArN=C(An)-C(An)=NAr, An=acenaphthene, Ar=2,6-(i-Pr)$_2$C$_6$H$_3$) and the dibromide nickel-diimine catalyst (ArN=C(An)-C(An)=NAr)NiBr$_2$ were synthesized following the procedures reported in the literatures.[2] The cocatalyst, modified methylaluminoxane (MMAO: with 65.9 mol-% methane and 31.7 mol-% isobutane) was purchased from Akzo-Nobel Corporation as 7.25 wt% aluminum in toluene. Polymerization-grade ethylene (99.9% purity) was purchased from Matheson Gas and further purified by passing it through CuO, ascarite, and molecular sieves. Anhydrous toluene from Aldrich was refluxed over sodium with benzophenone as indicator and distilled under ultra pure nitrogen atmosphere prior to use. Silica particles (Grade 948) were kindly supplied by Grace Davison.

4.3.2 Preparation of Nickel-Diimine Supported Catalyst

Silica particles were calcinated at 600 °C under ultra pure nitrogen for 4 hours and then stored in a dry nitrogen glove box. One gram of the calcinated silica was heated at 180 °C under vacuum for 12 hours prior to use. The calcinated silica was added, under nitrogen atmosphere, to 60 ml toluene solution of 7 mmol Al of MMAO. The mixture was vigorously stirred for 16 hours at room temperature. The solid was filtered, washed

5 times with 80 ml toluene, and then dried under vacuum at room temperature. The MMAO-treated silica was then mixed with 60 ml solution of 0.5 mmol of nickel diimine catalyst. The mixture was stirred vigorously for 14 hours at room temperature. The solid was filtered, washed 6 times with 60 ml of toluene, and then dried under vacuum at room temperature.

The contents of Al and Ni in the supported catalyst were measured by ICP-MS analytical technique. About 10 mg of the supported catalyst was completely dissolved in a mixture of 5 ml hydrofluoric acid (HF) and 2 ml nitric acid (HNO_3) on a hotplate. Then the solution was diluted with distilled water prior to ICP-MS analysis. Table 4.1 shows the physical properties of the silica particles and Al and Ni contents in the supported catalyst.

Table 4.1 Physical properties of silica support and Al & Ni loading on the supported catalyst.

Silica Support	Average Particle Diameter (μm)	55
	Surface Area (m^2/g)	309
	Pore Volume (cc/g)	1.6
Supported Catalyst	Ni wt% [a]	0.86
	Al wt% [b]	13.3

a: weight percent of Ni in supported catalyst (catalyst + support)
b: weight percent of Al in supported catalyst

4.3.3 Polymerization Runs

All polymerization runs, with homogeneous and heterogeneous catalysts, were carried out in a 1-liter Autoclave stainless steel reactor operated in a semi-batch mode.

The reactor was carefully cleaned with acetone, vacuumed at 150 °C for 3 hours, and then purged four times with ultra pure nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The required amounts of co-catalyst, MMAO, and solution were injected to the reactor under nitrogen atmosphere using gas-tight syringes. The mixture was stirred continuously while the reactor was heated up to establish the desired polymerization temperature. Once the desired temperature was established, the catalyst solution or slurry was added to the reactor under pure nitrogen using gas-tight syringes. To start polymerization, the reactor was pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuous feeding of gaseous ethylene to the reactor.

The reactor temperature was maintained within ±1 °C of the desired temperature by water/ethylene glycol cooling circulation. The reaction was stopped by rapid depressurization of the reactor followed by quenching with methanol. The polymer produced was washed with acidic methanol to remove MMAO residue, then filtered, and dried under vacuum at 60 °C for 16 hours.

4.3.4 Polymer Characterization

Polymer molecular weight (MW) and molecular weight distribution (MWD) were measured at 140 °C in 1,2,4-trichlorobenzene using Waters Alliance GPCV 2000 with DRI detector coupled with an on-line capillary viscometer. A calibration curve was established using monodisperse polystyrene standards. ^{13}C NMR analysis was conducted on a 75.4 MHz Bruker AV300 pulsed NMR spectrometer with waltz-supercycle proton decoupling at 120 °C. The polymer sample was dissolved in 1,2,4-trichlorobenzene and deuterated o-dichlorobenzene mixture in a 10 mm NMR tubes with concentration of about 18 wt-%. The spectra required more than 5000 scans to obtain an acceptable signal-to-noise ratio. Polymer chemical shift assignments and calculations followed the procedure published in the literature.[5]

The DSC analysis was carried out using Thermal Analysis 2910 instrument from TA Inc. in the standard DSC run mode. A 30 ml/min of ultra pure nitrogen gas was fed continuously to purge the calorimeter. Sample cooling was done using a refrigeration cooling unit attached to the DSC cell. The instrument was initially calibrated for melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample, about 5 mg, was first equilibrated at -30 °C, then heated to 180 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled down to -30 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10 °C/min.

4.4 Results and Discussion

4.4.1 Effect of Catalyst Support on Catalyst Activity

The objective of this work is to study the effect of support on catalyst performance with regard to activity and polymer properties. Therefore, ethylene polymerization runs using homogeneous nickel-diimine catalyst were initially conducted under various reaction conditions to set a base line reference. Table 4.2 shows the results of homogeneous polymerizations and polymer properties. Two of the runs, H1 and H3, were conducted at the same conditions as reported in the literature for comparison purposes.

Table 4.2 Ethylene polymerization using homogeneous nickel-diimine catalyst.[a]

Run	Catalyst (Ni-μmol)	Temp (°C)	Pressure (psig)	Time (min)	Activity [b] $x10^{-3}$	Mn, g/mol $x10^{-3}$	PDI	Tm (°C)
H1	1.6	35	3	15	2.75	124	1.96	-
H2	1.6	35	3	15	3.35	118	2.02	-
H3	1.0	35	200	10	12.0	238	2.62	108
H4	2.38	40	50	10	9.53	117	2.74	76
H5	1.78	40	150	10	12.6	138	2.81	98
H6	1.78	40	200	10	36.2	196	2.24	102
H7	1.78	40	350	10	40.7	178	2.57	111
H8	1.78	30	200	10	32.4	259	3.28	109
H9	1.78	50	200	10	26.5	172	2.60	89
H10	1.78	60	200	10	4.2	145	2.14	73

a: Al(MMAO)/Ni molar ratio: 3000, Solvent: 400 ml toluene, Stirring: 1300 rpm
b: Activity in kgPE/(mol Ni x hr)

The data shows similar performance trends as reported for homogeneous catalyst in the literature.[3] The catalyst activity at low pressure, Run H1, gave activity higher than what was reported in the literature.[3] However, at high pressure, Run H3, the activity was lower than the literature value.[3] The effect of polymerization conditions on polymer properties followed the usual trend reported for this catalyst.[2-3] Increasing reactor ethylene pressure or decreasing reactor temperature led to an increase in the polymer melting point. This trend showed a reduction in the short chain branch content in the polymer due to the dominance of chain propagation over chain walking reactions under such conditions.

The polymer molecular weight increased with ethylene pressure up to a certain pressure; as seen from Runs H4, H5 and H6. However the trend was reversed when ethylene pressure was increased from 200 psig to 350 psig as seen from Runs H6 and H7. This shows that the competition between propagation and termination rates was affected by the level of ethylene pressure. The polymer molecular weight was also decreased with increasing polymerization temperature due to higher chain transfer rates. The catalyst activity increased with polymerization temperature reaching a maximum at 40 °C, but at higher temperature activity was reduced due to the increase in catalyst deactivation rate as reported in the literature.[3] The catalyst activity also increased with ethylene pressure since catalyst active sites were exposed to higher ethylene concentration at higher pressure.

Table 4.3 shows the results of polymerization and polymer properties of polyethylene synthesized using nickel-diimine supported on MMAO-treated silica. Compared with the homogeneous catalyst, a drastic reduction in the activity of the supported catalyst was observed under the same reaction conditions. This reduction in catalyst activity is a well-known phenomenon in olefin polymerization using supported catalyst. This phenomenon is mainly attributed to the damage of some active sites due to the interaction of the catalyst and support during adsorption process and the steric hindrance physically imposed by the support limiting the accessibility of catalyst active sites.[16,26]

Table 4.3 Ethylene polymerization using nickel-diimine catalyst supported on MMAO-treated silica[a]

Run	Catalyst (mg)	Temp (°C)	Pressure (psig)	Time (min)	Activity [b] $x10^{-3}$	Mn, g/mol $x10^{-3}$	PDI	Tm (°C)
S1	30	30	200	30	0.592	477	2.41	122
S2	55	50	200	30	0.869	118	4.31	89, 115
S3	60	40	50	30	0.528	238	4.79	75, 114
S4	60	40	150	30	0.113	117	3.63	99, 115
S5	60	40	350	30	0.215	138	4.99	119

a Al(MMAO)/Ni molar ratio: 3000, Solvent: 400 ml toluene, Stirring: 1300 rpm

b Activity in kgPE/(mol Ni x hr)

Similar to the homogeneous system, the supported catalyst activity followed the same trend; it decreased with increasing temperature and increased with increasing ethylene pressure.

4.4.2 Effect of Catalyst Support on Polymer Properties

Compared with the homogeneous catalyst, the supported catalyst system produced polyethylene with different microstructure. Table 4.4 shows the SCB distribution measured by ^{13}C NMR of some selected polyethylene samples produced by homogeneous and supported catalysts. The supported catalyst produced polyethylene with slightly less total branching than the homogeneous catalyst. For both catalyst systems, methyl branches were always predominant as was usual with this type of catalysts.

Table 4.4 Short chain branching distribution of polyethylene made with homogeneous and supported Ni-diimine catalyst.[a]

Run	Methyl	Ethyl	Propyl	Butyl	8	Hexyl and longer	Total	Tm (°C)
H8	17.7	1.5	0.8	0.9	1.3	2.6	24.8	109
H9	32.5	2.5	1.5	1.4	1.2	2.5	41.6	89
H4	44.2	4.1	2.5	2.8	3.0	6.9	63.5	76
H5	24.6	2.9	1.4	1.2	1.9	3.0	35.0	98
S1	12.6	1.1	0.7	0.8	1.0	1.3	17.5	122
S2	27.6	2.1	1.2	1.1	2.4	4.3	38.7	89, 115
S3	40.6	3.7	3.0	2.3	2.8	5.2	57.6	75, 114
S4	19.3	2.6	1.9	1.7	1.0	3.0	29.5	99, 114

a: Short chain branching distribution measured by ^{13}C NMR as Branch/1000 Carbons

As shown in Table 4.3, the effect of polymerization conditions on the properties of the polymers synthesized by the supported catalyst followed the same trend as seen for the homogeneous catalyst. The supported system showed a reduction in molecular weight as polymerization temperature increased due to the increase in chain transfer rates.

There was no clear trend of the effect of supporting on polymer molecular weight as compared with the results seen from the homogeneous catalyst. However, the effect of temperature on molecular weight for the supported system was greater than for the homogeneous system. This can be seen by referring to Runs H8, H9, S1 and S2, and comparing the changes in molecular weight with polymerization temperature, 87,000 g/mol for the homogeneous system versus 359,000 g/mol for the supported system.

There was no clear trend of the effect of ethylene pressure on the molecular weight of the polymer produced by the supported catalyst.

Compared with the homogeneous system, the supported catalyst produced polymer with a broader molecular distribution. For example, Run H4 had PDI of 2.74 while Run S3 had PDI of 4.79; and Run H7 had PDI of 2.57 while Run S5 had PDI of 4.99. The molecular weight broadening due to supporting is a known phenomenon and likely results from the interactions between catalyst and support, which leads to formation of multi-active sites having slightly different chain transfer rates.[12]

Similar to the homogeneous system, the chain walking mechanism appeared to be pronounced in the supported catalyst system. An increase in ethylene pressure or a decrease in polymerization temperature lowered the rate of chain walking, leading to the formation of linear polyethylene that gave high melting point. However, depending on the polymerization conditions, the melting behavior of polymers produced by the supported system differed greatly from those produced by the homogeneous system. Figures 4.1-4.5 compare the DSC thermograms of the polyethylene samples synthesized by the homogeneous and the supported catalyst under various polymerization conditions.

The melting behavior is related to the short chain branching content that was controlled by polymerization conditions: temperature and pressure. The high level of branching inhibits polymer chains from crystallization very effectively, resulting in a morphology that is predominantly non-crystalline and has a low melting temperature.

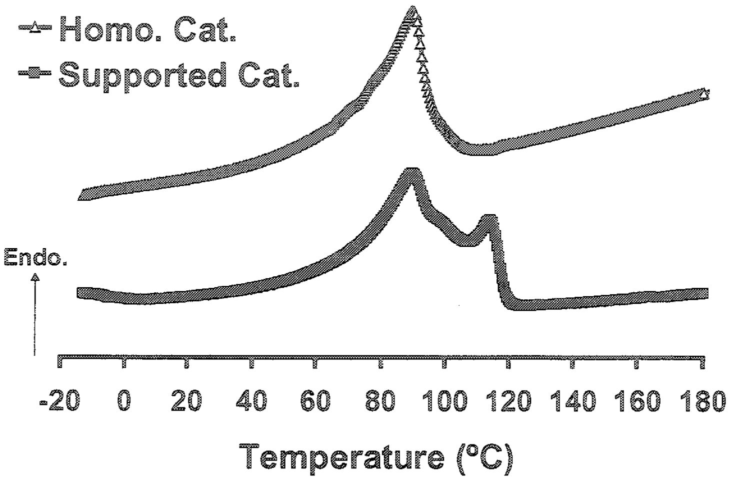

Figure 4.1 DSC thermograms for the polyethylene produced with homogeneous and supported catalysts at ethylene pressure of 200 psig and reaction temperature of 50 °C.

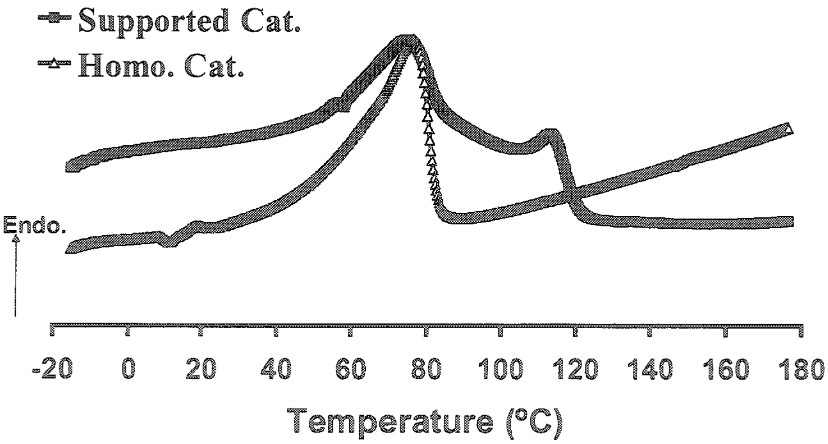

Figure 4.2 DSC thermograms for the polyethylene produced with homogeneous and supported catalysts at ethylene pressure of 50 psig and reaction temperature of 40 °C.

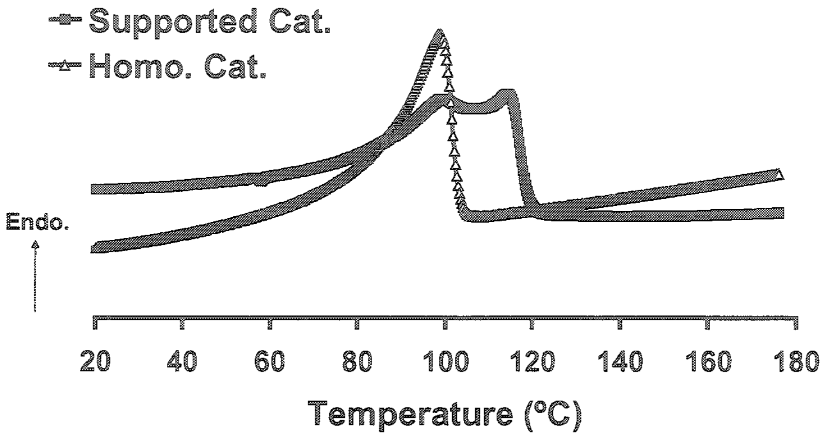

Figure 4.3 DSC thermograms for the polyethylene produced with homogeneous and supported catalysts at ethylene pressure of 150 psig and reaction temperature of 40 °C.

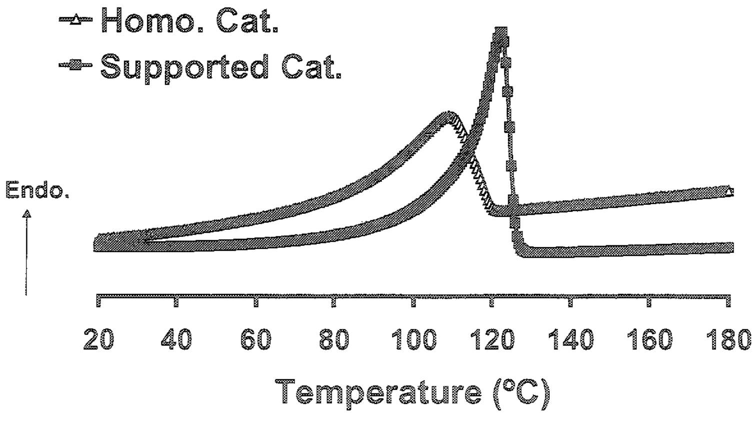

Figure 4.4 DSC thermograms for the polyethylene produced with homogeneous and supported catalysts at ethylene pressure of 200 psig and reaction temperature of 30 °C.

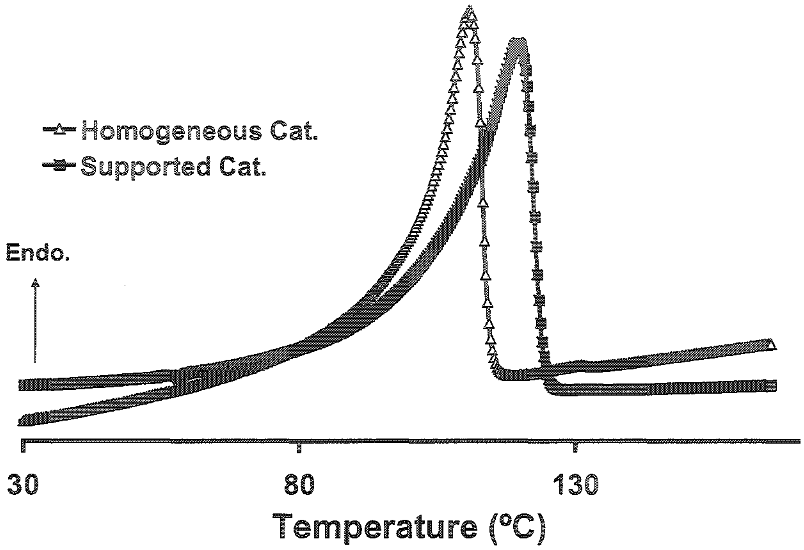

Figure 4.5 DSC thermograms for the polyethylene produced with homogeneous and supported catalysts at ethylene pressure of 350 psig and reaction temperature of 40 °C.

Interestingly, bimodal DSC thermograms were observed for highly branched samples, Runs S2, S3 and S4, but not for less branched linear samples, Runs S1 and S5. The bimodal melting behavior shows that the polymer produced was a mixture of two chain populations having different chain walking rates and, as a result, different short chain branching contents.

As shown in Figures 4.1-4.3, in all the samples showing bimodal melting behavior, an interesting phenomenon was that the lower melting temperature peak was centered at a value very close to the melting temperature produced with the homogeneous catalyst at the same polymerization conditions. This can be seen by comparing Runs S2, S3 and S4 with Runs H9, H4 and H5, respectively. Moreover, the lower melting temperature peaks show a clear dependence on polymerization conditions similar to the homogeneous catalyst. For example, increasing reactor pressure from 50 psig (Run S3) to 150 psig (Run S4) increased the lower melting temperature peak value from 75 °C to 99 °C.

Surprisingly, on the other hand, the high melting temperature peaks were fixed at similar values without responding to the changes in the polymerization conditions. Comparing Runs S2, S3 and S4 revealed that all the high melting temperature peaks were centered at 115 °C regardless of the changes in the reaction conditions.

The chain populations were probably produced from two types of active sites: those extracted from the support during polymerization and those unleached or kept fixed on the surface of the support. The extracted sites dissolved in the reaction solvent and followed the same polymerization behavior as the homogeneous catalyst, producing polyethylene with similar branching content. However, due to the strong steric effects exerted by the support, the unleached sites had lower chain walking rates and therefore produced polymer chains having lower branching content and thus higher melting point.

On the other hand, as shown in Figures 4.4 and 4.5, at the polymerization conditions where linear polymer was produced, Runs S1 and S5, the supported catalyst yielded polymer with one single DSC peak reflecting a single site catalyst system. This behavior reveals that at these conditions all active sites were kept attached (unleached) to the surface of the support, experiencing the same steric limitations from the support and, as a result, exhibiting lower chain walking rates, and thus produce polyethylene with a lower branching content is produced. Even though, the bimodal behavior was seen for polyethylene melting, it was not seen for molecular weight distribution, indicating that the two active sites had similar chain transfer and/or termination rates relative to monomer propagation. Similar bimodal melting behavior was also observed for ethylene polymerization using in situ silica supported nickel-diimine system [22] and nickel-diimine supported on mesoporous silica particles.[24]

4.5 Conclusion

Ethylene polymerization was carried out using MMAO-treated silica supported nickel diimine catalyst (1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide) in a slurry semi-batch reactor. Compared with the homogeneous catalyst, the catalyst activity of the supported catalyst was reduced significantly. The supported catalyst system exhibited lower chain walking rates than their homogeneous counterpart, and therefore produced polyethylene with less short chain branching content and, thus higher melting point. Depending on polymerization conditions, the polyethylene produced using the supported catalyst exhibited bimodal melting behavior, indicating the presence of two types of active sites having different chain walking rates. However, such bimodality was not seen for molecular weight distribution, indicating that the two sites had similar chain termination rates relative to chain propagation. In general, the supported catalyst produced polymers with slightly broader molecular weight distribution than the polymers produced with the homogeneous catalysts.

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Chapter 5

Synthesis of Linear Low-Density Polyethylene of Ethylene/1-Hexene Directly from Ethylene Using Tandem Catalytic System in Single Reactor

This chapter is organized based on the paper published in *Journal of Polymer Science, Part A: Polymer Chemistry,* **2004**, *42*, *4327-4336* by F. AlObaidi, Z. Ye, and S. Zhu, and on the paper published in *Macromol. Rapid Commun.*, **2004**, *25*, 647-652 by Z. Ye, F. AlObaidi, and S. Zhu.

5.1 Abstract

Tandem catalysis offers a promising synthetic route to the production of linear low density polyethylene (LLDPE). This chapter reports the use of a homogeneous tandem catalytic system for the synthesis of ethylene-1-hexene copolymers from ethylene stock as the sole monomer. The reported catalytic system employs the tandem action between an ethylene trimerization catalyst, $(\eta^5\text{-}C_5H_4CMe_2C_6H_5)TiCl_3(\mathbf{1})$/MMAO, and a copolymerization metallocene catalyst, $[(\eta^5\text{-}C_5Me_4)SiMe_2(^tBuN)]TiCl_2(\mathbf{2})$/MMAO. During the reaction, **1**/MMAO *in situ* generates 1-hexene with high activity and high selectivity and simultaneously **2**/MMAO copolymerizes ethylene with the produced 1-hexene to generate butyl branched polyethylene. We have demonstrated that, by simple manipulation of the catalyst molar ratio and polymerization condition, a series of branched polyethylene samples with melting temperature ranging from 96 °C to 128 °C, crystallinity from 5.4% to 53%, and hexene percentage from 0.3 to 14.2 can be efficiently produced.

Keywords: linear low density polyethylene (LLDPE), tandem catalytic system, ethylene trimerization, ethylene copolymerization, metallocene catalyst.

5.2 Introduction

Ethylene-based copolymers are industrially important materials. Linear low density polyethylene (LLDPE), a copolymer of ethylene and α-olefin, is an important class of ethylene-based copolymers. Copolymerization of ethylene with α-olefin introduces short chain branching (SCB) into chain backbone and modifies physical properties of the polymer.[1] As a consequence, the density, crystallinity and rigidity of the polymer are decreased, and other properties such as clarity and impact strength are improved.[1]

LLDPE is most commonly produced by copolymerization of ethylene with α-olefin using transition metal catalysts such as the classical Ziegler-Natta catalysts and/or recently developed single-sited metallocene catalysts. In industry, the most commonly used co-monomer is 1-butene due to its low cost; however, it has been shown that using 1-hexene or 1-octene improves mechanical properties of the copolymer.[2] The production of LLDPE using this common route requires integrating two different processes operating at different conditions; one for oligomerization of ethylene to produce α-olefin, and the other for the copolymerization of ethylene with the produced α-olefin. Recently, there have been considerable efforts to search for alternative processes that promote the synthesis of LLDPE from ethylene as the sole monomer.[3,4] In contrast to the commonly used two-stage process, these single-step processes certainly add a big advantage due to the savings in the costs of plant investment and operation.

In one approach, the recently developed Ni-diimine complexes have proven to be efficient in producing LLDPE with ethylene as the sole monomer in a single reactor.[5,6] Ni-diimine catalysts can produce polyethylene with short chain branching structures with ethylene as the only monomer through a catalytic mechanism referred to as "chain walking".[6,7] The overall branching content is controlled by simple changes in the catalyst structure and polymerization conditions.[7-9] As a drawback, these catalysts produce polyethylene with uncontrolled randomly distributed SCB with predominantly methyl branches,[10] making it unsuitable to replace the conventional high α-olefin LLDPE.

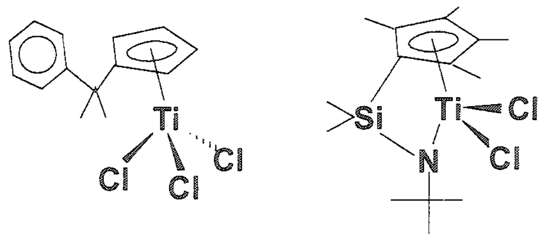
Another alternative approach employs a binary tandem action catalyst system for ethylene polymerization.[3,4] One catalyst produces short and long chain 1-alkenes through ethylene oligomerization/polymerization. For better control of branching length in the copolymer, a suitable catalyst for generating 1-alkene should be selected. The second catalyst is responsible for polymerizing ethylene and incorporating the *in situ* produced 1-alkene into the polyethylene chain. The amount of branching produced by the binary catalyst system is controlled by simple adjustment of the ratio of the two catalysts.[3,4] The simplicity and effectiveness of this approach makes it a promising alternative route to produce LLDPE from ethylene as the only monomer.

The oligomerization of ethylene typically affords a distribution of 1-olefins which must then be separated to give the product with desired carbon number.[11] One of the most useful components of this mixture is 1-hexene, which is used predominantly as a comonomer for linear low density polyethylene. Recently, there have been a few studies investigating the performance of various catalysts for the trimerization of ethylene to 1-hexene with high selectivity and activity.[12-14] The performance of these catalysts was remarkable making them very suitable for use in tandem with olefin polymerization catalysts to produce LLDPE from ethylene only.

In order to design a successful binary tandem catalytic system, it is necessary to consider a number of factors in selecting the individual catalysts.[3] One of the main factors is the catalyst compatibility; that is, to avoid interference between catalytic species.[3] Furthermore, due to the cooperative action between the binary catalysts, it is necessary that the reactivity of both catalysts be well matched at the same reaction condition.[3] Fortunately, the advent of homogeneous single-sited metallocene and late transitional metal catalysts has permitted an unprecedented freedom in selecting the suitable combinations of binary tandem catalytic systems. Recent studies have shown great interest in the use of tandem catalyst systems as an alternative route for ethylene polymerization to control the polymer properties.

Bazan and coworkers have recently disclosed a number of reports describing ethylene polymerization with different tandem catalytic systems for the synthesis of branched polyethylene with various branching lengths. In one report, they synthesized butene-ethylene copolymers by the tandem action of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2({}^tBuN)]TiMe\}\{MeB(C_6F_5)_3\}$ as an ethylene polymerization catalyst, and $[(C_6H_5)_2PC_6H_4C(OB(C_6F_5)_3)O\text{-}\kappa^2P,O]Ni(\eta^3\text{-}CH_2CMeCH_2)$ as an oligomerization catalyst.[15] In the same report, through adjusting reaction conditions and catalyst ratio, they were able to produce hexene-butene-ethylene copolymers using the same tandem catalytic system.[15] In another report, they combined, $(C_5H_5BOEt)_2ZrCl_2$/MAO as a catalyst to produce 1-alkene from ethylene, with $[(\eta^5\text{-}C_5Me_4)SiMe_2({}^tBuN)]TiCl_2$/MAO as an ethylene polymerization catalyst, for the synthesis of branched polyethylene with various branch lengths from ethylene as the only monomer.[16] They also demonstrated the synthesis of branched polyethylene with various branch lengths from ethylene only, by using tandem catalytic systems comprising Fe-based catalyst for producing 1-alkene, and zirconium-based metallocene for ethylene copolymerization with the in situ produced 1-alkene.[17] In a recent work, they used a triple tandem catalytic system to produce a wide range of branched polyethylenes from a single ethylene monomer.[18] Phillips Petroleum synthesized branched polyethylene using a tandem catalytic system comprised of chromium compound and pyrrole derivatives with alkylaluminium as an activating agent.[19] In this system, adding a stoichiometric amount of the pyrrole derivative modifies the chromium site to generate the oligomerization component.[19] Tandem catalytic systems were also reported for the production of long chain branched polymers.[20,21]

In this chapter, we reported our results for the synthesis of ethylene-1-hexene copolymers with the tandem catalytic system, which comprised of a cyclopentadienyl-arene titanium catalyst, $[(\eta^5\text{-}C_5H_4CMe_2C_6H_5)]TiCl_3$ (**1**)/MMAO, and a metallocene catalyst, $[(\eta^5\text{-}C_5Me_4)SiMe_2(^tBuN)]TiCl_2$ (**2**)/MMAO.(Scheme 5.1). Our work is focused on evaluating the performance of this tandem catalytic system at high ethylene pressures.



1 **2**

Scheme 5.1 Chemical structures of the catalysts used in this work.

5.3 Experimental Part

5.3.1 Materials

All manipulation involving air and/or moisture sensitive compounds were performed in a dry nitrogen glove box or under ultra pure nitrogen protection. The cyclopentadienyl-arene titanium catalyst precursor (**1**), was synthesized according to the literature procedure.[12,13] The constrained geometry catalyst precursor, $[(\eta^5\text{-}$

$C_5Me_4)SiMe_2(^tBuN)]TiCl_3$ (2), was purchased from Boulder Scientific Company and was used as received. The cocatalyst, modified methylaluminoxane (MMAO: with 65.9 mol% methane and 31.7 mol% isobutane) was purchased from Akzo-Nobel Corporation as 7.25 wt% aluminum in toluene. Polymerization-grade ethylene (99.9% purity) was purchased from Matheson Gas and further purified by passing it through CuO, ascarite, and molecular sieves. Anhydrous toluene from Aldrich was refluxed over sodium with benzophenone as indicator and distilled under ultra pure nitrogen atmosphere prior to use.

5.3.2 Trimerization and Polymerization Runs

(a) Ethylene trimerization with 1/MMAO

The trimerization was carried out in a 1-liter Autoclave stainless steel reactor operated in a semi-batch mode. The reactor was carefully cleaned with acetone, vacuumed at 150 °C for 3 hours, and then purged four times with ultra pure nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The required amount of co-catalyst, MMAO, solution was injected to the reactor under nitrogen atmosphere using gas-tight syringes. The mixture was kept under stirring while the reactor was heated up to establish the desired polymerization temperature. Once the desired temperature is established, a prescribed amount of catalyst solution was added to the reactor under pure nitrogen atmosphere using gas-tight syringes. To start trimerization, the reactor is pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuously feed gaseous ethylene to the reactor. The reactor temperature was maintained within ±1 °C of desired temperature by water/ethylene glycol cooling circulation. Mechanical stirrer was set at 1500 RPM. After 1 hour, the reactor was vented. The trimerization product was collected for GC-MS analysis. Polymer byproduct was collected, washed with acidic methanol, and then dried under vacuum for 16 hours.

(b) Ethylene polymerization with tandem 1/2/MMAO

The procedure similar to the trimerization process at high pressure was applied. The solutions of **1** and **2** were simultaneously added into the reactor to start the concurrent ethylene trimerization and polymerization process. After 1 hour, the reactor was vented and quenched by injecting methanol. The polymer produced was collected, washed with acidic methanol, and then dried under vacuum for 16 hours.

(c) Ethylene copolymerization with trimerization product directly prepared with 1/MMAO at 10 atm ethylene pressure

The trimerization was carried out in a 1 L Autoclave stainless steel reactor as described above. The solution of catalyst **1** was injected and then the reactor was pressurized to the desired ethylene pressure to start the trimerization. After 1 hour of trimerization reaction, the reactor pressure was vented slowly to 0 pressure, the reactor temperature was stabilized for 2 minutes, and then a solution of catalyst **2** was injected into the reactor to initiate the copolymerization process. In the whole process, desired ethylene pressure and reaction temperature were kept constant. After 1 hour, the reactor was vented and quenched by injecting methanol. The polymer produced was collected, washed with acidic methanol, and then dried under vacuum for 16 hours.

5.3.3 Polymer Characterizations

The GC-MS analysis was conducted on Micromass GCT time of flight mass spectrometer attached to Agilent HP6890 GC to determine the 1-hexene and C10 alkene concentrations in the trimerization product. Polymer molecular weight (MW) and molecular weight distribution (MWD) were measured at 140 °C in 1,2,4-trichlorobenzene using Waters Alliance GPCV 2000 with DRI detector coupled with an on-line capillary viscometer. A calibration curve was established using monodisperse polystyrene standards. ^{13}C NMR analysis was conducted on a 75.4 MHz Bruker AV300 pulsed NMR spectrometer with waltz-supercycle proton decoupling at 120 °C. The polymer sample was dissolved in 1,2,4-trichlorobenzene and deuterated o-dichlorobenzene mixture in a 10 mm NMR tube with concentration of about 18 wt%. The spectra required more than 4000 scans to obtain an acceptable signal-to-noise ratio. Polymer chemical shift assignments and calculations followed ASTM D5017-91 method.[23]

The DSC analysis was carried out using Thermal Analysis 2910 instrument from TA Inc. in the standard DSC run mode. A 30 ml/min of ultra pure nitrogen gas was fed continuously to purge the calorimeter. Sample cooling was done using a refrigeration cooling unit attached to the DSC cell. The instrument was initially calibrated for melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample, about 5 mg, was first equilibrated at 20 °C, then heated to 180 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled down to 20 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10 °C/min. The peak temperature with the highest endotherm was chosen as the melting point.

5.4 Results and Discussion

5.4.1 Performance of Individual Catalyst Systems

The approach of tandem catalysis to LLDPE production typically uses a single feed of ethylene and two different catalysts. The determination of reactivities of the individual catalysts is very crucial for designing an optimum tandem catalytic system. These measurements provide a base line to evaluate the performance of the binary catalyst system. The detailed investigation of ethylene trimerization with catalyst **1**,[12,13] and that of ethylene polymerization with catalysts **2** ,[24] have already been reported in the literature. However, in this work we report the performance of the individual catalysts conducted under our experimental conditions.

In a recent work, **1**/MAO was found to be very active for ethylene trimerization and to be one of the most selective catalysts for 1-hexene production.[12,13] Table 5.1 shows the experimental results of ethylene trimerization at various reaction conditions.

Our analysis of the liquid fraction by GC-MS revealed that the ethylene trimerization with 1/MMAO at different reaction conditions yielded products with high selectivity. The product fractions consisted of two main components: 1-hexene and C10 alkene. It is believed that the C10 alkene fraction mainly consists of 5-methyl-non-1-ene as reported in the literature.[12,13] In addition, small amount of high molecular weight polyethylene was produced as byproduct from the trimerization reaction. These PE byproducts had high melting points and melting enthalpies typical of high density polyethylene. It is worth noting that the PE byproducts exhibited broad molecular weight distribution, suggesting that this catalyst may behaved as a multiple site type towards ethylene polymerization.

Table 5.1 Ethylene trimerization with 1/MMAO[a]

							PE Properties			
Run	T (°C)	P (atm)	1-Hex[b] (g)(wt%)	C10[b] (g)(wt%)	PE (g)(wt%)	Prod.[c]	M_w (kg/mol)[d]	PDI[d]	T_m (°C)[e]	ΔH (J/g)[e]
1	30	4	11.9 (85)	1.6 (12)	0.4 (3)	1488	918	3.4	126.0	138.6
2	50	4	6.0 (80)	0.7 (9)	0.8 (11)	750	713	8.3	126.7	125.3
3	50	10	19.7 (86)	2.3 (10)	1.0 (4)	2463	823	7.2	126.1	131.0

[a] Other reaction conditions: solvent 450 ml toluene; Al/Ti = 1000 (molar); reaction time, 1hr; [b] Determined from GC-MS; [c] 1-Hexene productivity In (kg C_6 / mol Ti * hr); [d] Determined from GPCV measurement at 140 °C in 1,2,4-trichlorobenzene;[e] Determined from DSC measurement.

The activity and selectivity of this catalyst greatly depended on reaction conditions: ethylene pressure and reaction temperature. The 1-hexene productivity increased with increasing ethylene pressure. For example, when the trimerization was carried out at 50 °C, the 1-hexene productivity increased from 750 kg C_6/(mol Ti hr) at 4 atm to 2463 kg C_6/(mol Ti hr) at 10 atm. The effect of reaction temperature on the 1-hexene productivity was also very clear from the experimental data. In general, at 50 °C and above, the catalyst deactivation rate was sufficiently high and thus the 1-hexene productivity decreased significantly. This effect of temperature can be clearly seen for trimerizations held at 4 atm pressure, when the 1-hexene productivity at 30 °C (Run 1) was compared with that at 50 °C (Run 2).

Table 5.2 Ethylene polymerization with **2**/MMAO catalyst.[a]

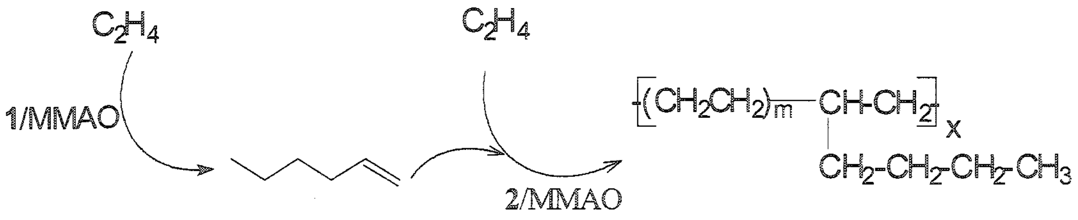
Run	Reaction conditions				Polymer properties				
	Temp (°C)	Press. (atm)	PE (g)	Prod.[b]	M_w[c] (K)	PDI[c]	T_m[d] (°C)	ΔH_m[d] (J/g)	χ_c[e] (%)
4	30	4	6.1	60	1267	17.4	132.3	120.0	40.9
5	50	10	24.3	60	749	18.7	134.9	164.1	56.0
6	30	10	22.7	20	1020	11.1	134.2	134.1	46.0

[a] Other reaction conditions. Solvent, toluene; total volume, 450 ml; Catalyst: 8 µmol.
[b] Polymer productivity in (kilograms of PE produced)/(mmol M hr).
[c] From GPCV measurement in 1,2,4-trichlorobenzene at 140 °C.
[d] From DSC measurement.
[e] Crystallinity based on ΔH_m = 290 J/g for a perfect PE crystal.

The catalyst system **2**/MMAO, known as constraint geometry catalyst (CGC), has an open structure that permits an easy incorporation of high α-olefins and ethylene macromonomers.[16,24] The results of ethylene polymerization with **2**/MMAO under various conditions are listed in Table 5.2. **2**/MMAO appeared to be a very stable system for ethylene polymerization and it remained to be active throughout the 1-hour reaction time. All the polymers produced with **2**/MMAO exhibited typical thermal properties for homo-polyethylene, such as high melting temperature (132~135 °C) and high crystallinity (41~56%). The molecular weight distributions of these polymers were broad. The reason for this broadening in MWD is not clear, however, it is believed to be caused by the heterogeneity of the physical states in the polymerization system due to PE precipitation, instead of by the heterogeneity of the active site types.

5.4.2 Ethylene Polymerization with Tandem 1/2/MMAO System

A successful tandem action of the 1-hexene generating catalyst, **1**, and the copolymerizing catalyst, **2** , in a single reactor should lead to the production of butyl branched ethylene-1-hexene copolymer from ethylene. Ethylene polymerization with the tandem **1**/**2**/MMAO catalyst system was conducted at various conditions with different catalyst ratios. The overall strategy of the tandem catalyst system is presented in Scheme 5.2.



Scheme 5.2 The strategy for the tandem catalyst system for producing ethylene-1-hexene copolymers.

The two catalysts were simultaneously added into the reactor to start the concurrent trimerization and copolymerization processes. For the reactions conducted under the same conditions, the amount of **2** was fixed, while the amount of **1** was varied to examine its effects on the polymer properties. Since the reactivities of the individual catalysts were sensitive to polymerization conditions, we designed our experiments to investigate the performance of the binary catalyst system at different levels of polymerization temperature and pressure. Table 5.3 summarizes the polymerization conditions and resulting polymer properties.

Table 5.3 Ethylene polymerization with the tandem **1**/**2**/MMAO system.[a]

Run	Reaction conditions				Polymer properties					
	1:**2**	Temp (°C)	Press. (atm)	Polymer (g)	M_w[b] (K)	PDI[b]	hexene[c] (%)	T_m[d] (°C)	ΔH_m[d] (J/g)	X_c[e] (%)
7	0.1:1	30	4	4.8	380	4.5	0.3	128.7	120.0	41.0
8	0.25:1	30	4	7.9	351	3.9	3.5	96.0	76.1	26.0
9	2:1	30	4	6.5	568	5.7	12.9	119.7[g]	29.3	9.9
10	0.25:1	50	4	20.5	266	3.3	0.8	120.8	105.7	36.1
11	0.1:1	50	4	19.7	270	2.5	-	129.0	147.0	50.2
12	0.25:1	70	4	46.0	180	3.2	-	133.6	155.2	53.0
13	0.1:1	50	10	28.3	216	2.7	-	129.2	151.4	51.7
14	0.25:1	50	10	24.7	236	4.8	-	120.4	107.4	36.7
15	1:1	50	10	26.0	245	2.9	1.1	119.0	88.3	30.1
16	1:1	50	2.5	13.2	188	5.8	0.84	121.7	83.0	28.5
17	2:1	30	10	19.8	217	4.1	13.4	125.0[g]	19.7	6.7
18[f]	2:1	30	10	23.3	197	2.8	14.2	124.0[g]	15.8	5.4

[a] Other reaction conditions. Solvent, toluene; total volume, 450 ml; catalyst 2: 8 μmol; time, 1 hr
[b] From GPCV measurement.
[c] Molar percentage of 1-hexene in the copolymer determined from ^{13}C NMR.
[d] From DSC measurement.
[e] Crystallinity based on ΔH_m = 290 J/g for a perfect PE crystal.
[f] Catalyst 2 was added after 1 hr reaction of catalyst 1. (polymerization runs procedure b)
[g] Melting peak was from a small amount of polymer byproduct produced by **1**/MMAO

Figure 5.1 shows the DSC thermogram for a series of copolymers produced at 4 atm and 30 °C with different catalyst ratios. By changing the catalyst ratio and polymerization conditions, copolymer grades with a wide range of melting temperatures and crystallinities were efficiently produced with the tandem catalytic system. At a fixed amount of **2**, an increase in **1** led to a significant decrease in the polymer melting temperature and in the degree of crystallinity due to the higher amount of 1-hexene produced and incorporated. For example, for the copolymerization runs at 4 atm and 30 °C, increasing **1**/**2** ratio from 0 to 2 effectively decreased the polymer crystallinity from 40.9 % (T_m = 132.3 °C, Run 4) to 9.9% (Run 9). The copolymer produced in Run 9 was mainly amorphous and the melting peak centered at 119.7 °C was from the polymeric by-product generated by **1**/MMAO.

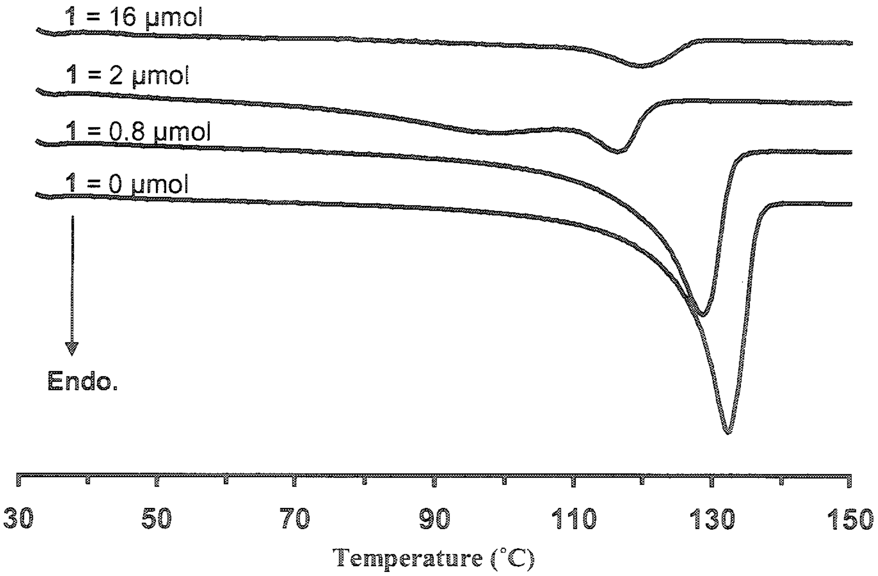


Figure 5.1 DSC thermograms for the polymers produced with **1**/**2**/MMAO system at 30 °C and 4 atm with moles of catalyst **2** fixed at 8 µmol: effect of varying the amount of catalyst **1** on the polymer melting behavior.

Figure 5.2 shows the effect of polymerization temperature on the melting behavior of the copolymers produced with **1**/**2**/MMAO at 4 atm. The **1**/**2** catalyst molar ratio was fixed at 0.25. At higher polymerization temperatures (50 °C), due to the deactivation of **1**/MMAO and, as a result, the reduction in 1-hexene productivity, the produced copolymers gave higher melting temperatures and crystallinities. This temperature effect can be clearly seen by comparing Runs 7 and 8 (4 atm and 30 °C) to Runs 10 and 11 (4 atm and 50 °C). It is worth noting that the effect of temperature increase on the copolymer melting behavior was not only attributed to the deactivation of the trimerization catalyst, but also to the increase in the ethylene propagation rate of catalyst **2**. For example, for the copolymerization at 4 atm, the polymer yield increased drastically from 7.9 g at 30 °C (T_m = 96 °C and X_C = 26%) to 46 g at 70 °C (T_m = 133.6 °C and X_C = 53%).

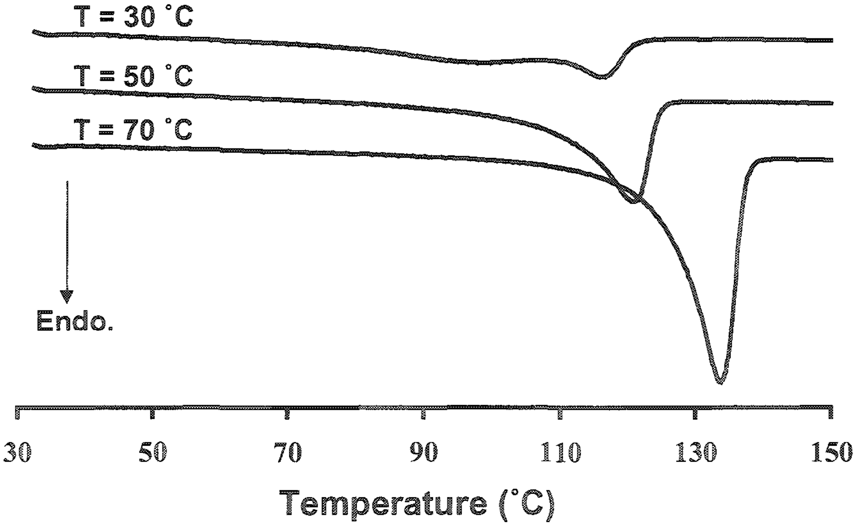


Figure 5.2 DSC thermograms for the polymers produced with **1**/**2**/MMAO system at 4 atm with **1**/**2** catalyst molar ratio fixed at 0.25: the effect of reaction temperature on the polymer melting behavior.

The ethylene pressure had a profound effect on the performance of the individual catalysts, **1**/MMAO and **2**/MMAO. However, it is very interesting to note that the effect of ethylene pressure on the melting behavior of the copolymer produced with the binary catalyst **1**/**2**/MMAO was minor. For example, running the binary catalyst **1**/**2**/MMAO at 50 °C with a fixed **1**/**2** catalyst ratio at 0.25, the copolymer melting properties changed from $T_m = 120.8$ °C and $X_C = 36.1\%$ at 4 atm to $T_m = 120.4$ °C and $X_C = 36.7\%$ at 10 atm. Similar observation was also seen for a different catalyst ratio: Run 11 versus Run 13. This observation suggests that increasing ethylene pressure increases the reaction rates of both **1**/MMAO and **2**/MMAO at comparable rates, resulting in a minimal effect on the polymer melting behavior.

Figure 5.3 shows ^{13}C NMR spectra for the copolymer produced in Run 9. By a simple adjustment of reaction conditions and catalyst ratio, the ethylene-1-hexene copolymers with 1-hexene molar percentages ranging from 0.3% to 14.2% were produced with the tandem catalytic system.

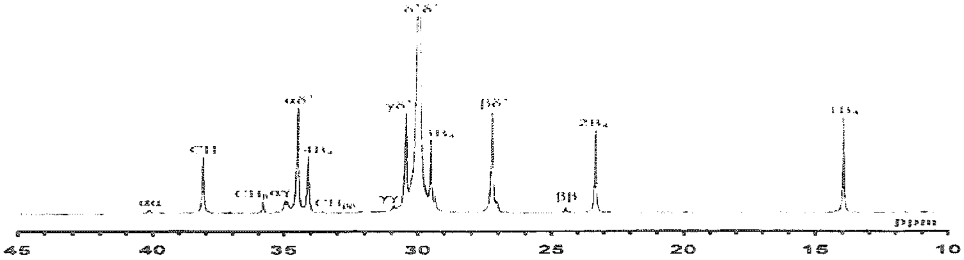


Figure 5.3 ^{13}C NMR spectra of the polymers produced in Run 9.

The ^{13}C NMR analysis revealed that all the copolymers produced with **1**/**2**/MMAO system exhibited a typical chain structure of ethylene-1-hexene copolymer with dominant butyl branches. However, in addition to butyl branches, the 5-methyl-heptyl branches resulted from the incorporation of 5-methyl-non-1-ene were also present in the copolymers when catalyst **2** was added an hour later than catalyst **1** (Run 18). The 5-methyl-heptyl branches, as identified from the methyl branch resonance centered at 20.0 ppm, counted for ~11 % of the total branches in the copolymer. On the other hand, for all the copolymers produced in the concurrent trimerization and polymerization reactions with the tandem catalytic system, the butyl branches were dominant and represented > 98% of the total branches and the amount of 5-methyl-heptyl branches was minimal.

A possible explanation for this difference in branching structure is related to the rates of 1-hexene generation and consumption. Deckers et al.[12,13] reported that during ethylene trimerization with **1**/MAO, a small amount of vinyl-ended byproduct, 5-methyl-non-1-ene, was formed from the cotrimerization of ethylene and 1-hexene. However, in the polymerization runs with the tandem catalytic system, 1-hexene was *in situ* generated and simultaneously consumed. Therefore, the 1-hexene concentration was lower than that in the trimerization-only reaction at the same condition, where the 1-hexene content was accumulated. This reduced 1-hexene concentration minimized the product of ethylene/1-hexene cotrimerization and thus resulted in a lower 5-methyl-heptyl branch content in the copolymer.

Figure 5.4 compares the molecular weight distribution curves for the copolymer and homopolymer produced at 50 °C and 10 atm. The GPCV analysis showed that the copolymers had lower weight average molecular weight owing to the incorporation of 1-hexene compared to the homo polyethylene produced with **2**/MMAO at the same reaction conditions. In addition, the MWDs of the copolymers were far narrower than those of the homo polymers. This narrow MWD can be attributed to the increase in the system homogeneity due to the increase of the copolymer solubility in the reaction medium.

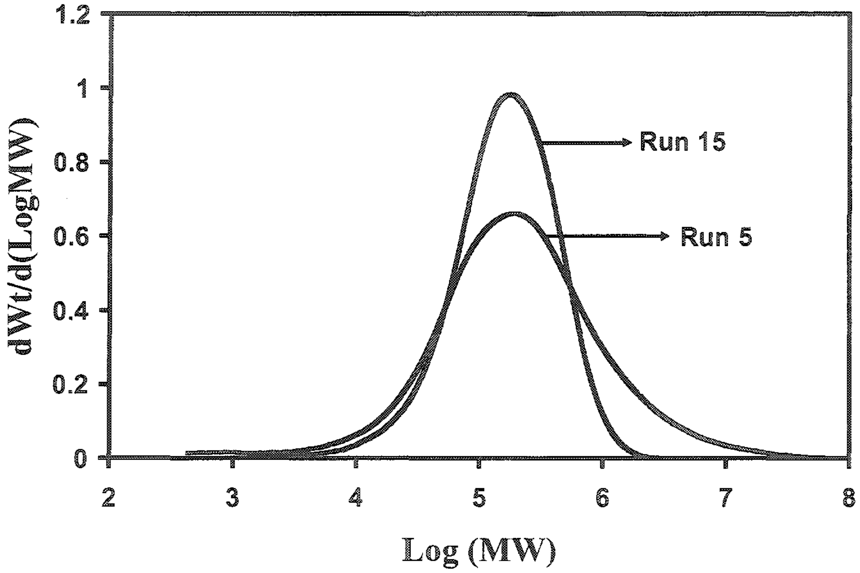


Figure 5.4 Molecular weight distribution of the polymers produced in Runs 5 and 15.

5.5 Conclusion

Tandem catalytic systems, **1**/**2**/MMAO, was investigated to synthesize ethylene-1-hexene copolymers from ethylene in a single reactor. It is clear from the results reported that simple manipulation of the catalyst molar ratios and polymerization conditions can be used to efficiently produce a wide range of polyethylene materials with different melting points and crystallinities from ethylene as the only monomer. ^{13}C NMR analyses of the polymer produced by catalyst **1**/**2**/MMAO showed that butyl branches are dominant representing > 98% of the total branches. Increasing ethylene pressure increases the reactivities of both **1**/MMAO and **2**/MMAO at comparable rates, resulting in a minimal effect on the polymer melting behavior. In addition, the effect of temperature increase on the copolymer melting behavior was not only attributed to the deactivation of the trimerization catalyst, but also to the increase in the ethylene propagation rate of catalyst **2**.

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Chapter 6

Synthesis of Reactor Blend of linear and branched Polyethylene Using Metallocene/Ni-Diimine Binary Catalyst System in a Single Reactor

This chapter is organized based on the paper submitted to *Journal of Applied Polymer Science* by Fahad AlObaidi, and S. Zhu.

6.1 Abstract

This work reports the synthesis of a series of reactor blends of linear and branched polyethylene materials using a combination of [1,4-bis(2,6-diisoprpylphenyl) acenaphthene diimine nickel(II) dibromide](**1**)/MMAO, known as active catalyst for the production of branched polyethylene, and [rac-ethylenebis(indenyl) zirconium dichloride](**2**)/MMAO, which is active for the production of linear polyethylene. The polymerization runs were performed at various levels of temperature, pressure, and catalyst **2** molar fractions. At 5 °C, there was very low influence of catalyst **2** molar fraction on the overall catalyst activity. However, at 30 °C and 50 °C, the overall catalyst activity increased linearly with catalyst **2** molar fraction. The same linear dependency was also found for the polymerization reactions carried out at 60 °C and 100 °C. At various levels of temperature and ethylene pressure, higher melting temperature and crystallinity were observed with an increase in catalyst **2** molar fraction. At 60 °C and 100 psig, the DSC thermograms of the polymers produced with **1**/**2**/MMAO exhibited two distinct peaks with melting temperatures closely corresponding to the melting temperatures of the polymers produced with the individual catalysts; 1/MMAO and 2/MMAO. The GPCV analysis of all polyethylene samples showed monomodal molecular weight distributions with low polydispersities.

Keywords: Reactor blends, ethylene homopolymers, Ni-diimine, metallocene catalysts.

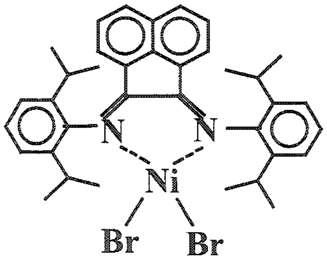
6.2 Introduction

Single site olefin polymerization catalysis has evolved considerably since the discovery of metallocene catalysts in the early 1980s. Metallocene catalysts have been well known for their excellent flexibility and versatility for the synthesis and control of polyolefin structure.[1] Compared to the conventional Ziegler Natta catalyst, these single site type catalysts are highly active and can produce polymers with narrow molecular weight distribution and narrow chemical composition distribution.[1] In addition to metallocene catalysts, another milestone in the area of olefins polymerization catalysis was the discovery of the homogeneous single site α-diimine based late transition metal catalysts (Ni and Pd) in 1995.[2] Different from metallocenes, these catalysts can produce polyethylene with branch structure without the use of α-olefins comonomers.[2-9] Simple control over the catalyst structure and polymerization conditions (ethylene pressure and reaction temperature) allows one to readily produce a wide range of polyethylene grades from highly branched, completely amorphous materials to linear, semicrystalline, high-density materials.[2-4]

A great interest in these single site olefin polymerization catalysts has been driven by their ability to produce polyolefinic materials with new or improved performance parameters. In this context, there have been many studies focusing on utilizing these catalysts for the production of new polyolefinic materials or tailoring the characteristics of a specific polymer by employing different polymer blending methods. One method, which is widely used to enhance polymer processibility, involves the production of new polyolefins with broad molecular distribution by physical blending of two or more polymers with different molecular weights.[10,11] Another method involves the use of a series of multi-stage reactors with each operated at different polymerization conditions and thus producing polymers with different properties.[10,12]

The third method for the production of polymer blends, known as reactor blending, involves combining two or more types of catalysts to produce polymers with different and controlled properties in a single reactor.[10] In this method, each catalyst polymerizes ethylene independently generating different polyethylenes during the polymerization reaction, and thus forming a reactor blend.[10] The simplicity of this method allows the polymer properties to be tailored by simple adjustment of the catalyst ratio and polymerization conditions. Recently, a few studies have shown that ethylene polymerization with the combination of metallocene and nickel or iron diimine catalysts produces reactor blends of branched and linear polyethylene.[13-15] The combination of these catalysts showed high activity and gave materials with new properties.

In this work, we report the results of ethylene polymerization using a combination of [1,4-bis(2,6-diisoprpylphenyl) acenaphthene diimine nickel(II) dibromide] (1)/MMAO, known as active catalyst for the production of branched polyethylene, and [rac-ethylenebis(indenyl) zirconium dichloride] (2)/MMAO, which is known as active catalyst for the production of linear polyethylene (Scheme 6.1). The study investigates the effect of molar catalyst fraction of 1 and 2 and polymerization conditions on the catalyst activity and polymer properties. Our investigation explored the performance of the combined catalysts at low as well as high ethylene pressure.



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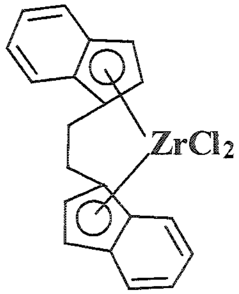

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Scheme 6.1 Chemical structures of the catalysts used in this work.

6.3 Experimental Part

6.3.1 Materials

All manipulation involving air and/or moisture sensitive compounds were performed in a dry nitrogen glove box or under ultra pure nitrogen protection. The α-diimine ligand and the catalyst precursor, [1,4-bis(2,6-diisoprpylphenyl) acenaphthene diimine nickel(II) dibromide](1), were synthesized following the procedures reported in the literatures.[2,3] The zirconocene catalyst precursor, [rac-ethylenebis(indenyl) zirconium dichloride] (2), was purchased from Boulder Scientific Company and used as received. The cocatalyst, modified methylaluminoxane (MMAO: with 65.9 mol% methane and 31.7 mol% isobutane) was purchased from Akzo-Nobel Corporation as 7.25 wt% aluminum in toluene. Polymerization-grade ethylene (99.9% purity) was purchased from Matheson Gas and further purified by passing it through CuO, ascarite, and molecular sieves. Anhydrous toluene from Aldrich was refluxed over sodium with benzophenone as indicator and distilled under ultra pure nitrogen atmosphere prior to use.

6.3.2 Polymerization Runs

(a) Ethylene Polymerization at 6 psig Ethylene Pressure

The polymerization was carried out in a 500 mL glass reactor equipped with a magnetic stirrer under 6 psig ethylene pressure. Toluene and MMAO were introduced into the reactor under nitrogen protection. The reactor was evacuated, pressurized with ethylene, and then placed into an oil bath set at the operating temperature. After equilibrium for 10 minutes, a prescribed amount of toluene solution of **1** or **2** was injected to start polymerization. For polymerization with binary catalyst **1**/**2**/MMAO, the prescribed amount of each catalyst (**1** and **2**) solution in toluene was injected simultaneously to initiate the concurrent polymerization. The reaction temperature and ethylene pressure was kept constant throughout the polymerization process. Magnetic stirring was applied. After 0.5 hr, the reaction was vented and quenched by injecting 20 ml methanol. The polymer produced was collected, washed with an acidified methanol, and then vacuum dried at 50 °C for 16 hours.

(b) Ethylene Polymerization at Higher Ethylene Pressure (100 psig)

The polymerization runs were carried out in a 1-liter Autoclave stainless steel reactor operated in a semi-batch mode. The reactor was carefully cleaned with acetone, vacuumed at 150 °C for 3 hours, and then purged four times with ultra pure nitrogen. Purified toluene was transferred to the reactor under nitrogen pressure through a transfer needle. The required amount of co-catalyst, MMAO, solution was injected to the reactor under nitrogen atmosphere using gas-tight syringes. The mixture was kept under stirring while the reactor was heated up to establish the desired polymerization temperature. Once the desired temperature is established, the prescribed amount of each catalyst (1 and 2) solution in toluene was injected simultaneously to initiate the concurrent polymerization. To start polymerization, the reactor is pressurized by ethylene to the desired pressure. The reactor was kept at constant pressure by continuous feeding of gaseous ethylene to the reactor. The reactor temperature was maintained within ±1 °C of desired temperature by water/ethylene glycol cooling circulation. The reaction was stopped by rapid depressurization of the reactor followed by quenching with methanol. The polymer produced was washed with acidic methanol to remove MMAO residue, then filtered and dried under vacuum at 60 °C for 16 hours.

6.3.3 Polymer Characterizations

Polymer molecular weight (MW) and molecular weight distribution (MWD) were measured at 140 °C in 1,2,4-trichlorobenzene using Waters Alliance GPCV 2000 with DRI detector coupled with an on-line capillary viscometer. A calibration curve was established using monodisperse polystyrene standards. The DSC analysis was carried out using Thermal Analysis 2910 instrument from TA Inc. in the standard DSC run mode. A 30 ml/min of ultra pure nitrogen gas was fed continuously to purge the calorimeter. Sample cooling was done using a refrigeration cooling unit attached to the DSC cell. The instrument was initially calibrated for melting point of an indium standard at a heating rate of 10 °C/min. The polymer sample, about 5 mg, was first equilibrated at 0 °C, then heated to 180 °C at a rate of 10 °C/min to remove thermal history. The sample was then cooled down to 0 °C at a rate of 10 °C/min. A second heating cycle was used for collecting DSC thermogram data at a ramping rate of 10 °C/min.

6.4 Results and Discussion

6.4.1 Effect of Catalyst 2 Molar Fraction (X_2) on Overall Catalyst Activity

We carried out ethylene polymerization at different levels of catalyst fractions, reaction temperatures, and ethylene pressures. Table 6.1 gives the results of ethylene polymerization reactions. The activities of the individual catalysts, **1** or **2**, varied depending on the polymerization conditions. At all the polymerization temperatures and pressures, the catalyst system **1**/MMAO showed lower activity than **2**/MMAO. With catalyst **1**/MMAO at 6 psig, the catalyst activity increased with the increase of the polymerization temperature from 5 to 30 °C but decreased at 50 °C due to catalyst deactivation. Contrarily, the activity of **2**/MMAO increased with temperature reaching a maximum value at 50 °C. It is also worth noting that increasing reaction temperature increased the difference in the catalyst activities obtained from systems **1**/MMAO and **2**/MMAO. The effect of ethylene pressure on catalyst activity for both catalyst systems is also clear as revealed from the data in Table 6.1. Increasing ethylene pressure from 6 to 100 psig increased the activity of both catalysts because the catalyst active sites were exposed to higher ethylene concentration at higher ethylene pressure.

Figure 6.1 shows the effects of polymerization temperature, ethylene pressure and molar fraction of catalyst **2** on the overall catalyst activity. The effect of catalyst **2** molar fraction X_2 on the overall catalyst activity can also be seen clearly from Figure 6.1. At 5 °C, there was very little influence of catalyst **2** molar fraction on the overall catalyst activity. The catalyst activity changed from 1.7 to 1.85 (x 10^3 kg PE/mol hr) when catalyst **2** molar fraction was increased from 0.01 to 0.5. However, variation of the catalyst **2** molar fraction at 30 and 50 °C yielded a significant effect on the catalyst activity. The overall catalyst activity increased linearly with catalyst **2** molar fraction. A linear dependency was also seen for polymerization carried out at 60 °C and 100 psig. This linear correlation between catalyst activity and X_2 suggested that interactions between catalyst **1** and **2** species were minimal, and the catalysts performed independently from each other.

Table 6.1 Ethylene Polymerization with Binary Catalytic System **1**/**2**/MMAO[a]

Run	Catalyst (X_2)[b]	T (°C)	P (psig)	Activity[c] (x 10^{-3})	M_w (Kg/mol)[d]	PDI[d]	T_m (°C)[e]	ΔH (J/g)[e]	X_c (%)[f]
1	0	5	6	1.95	588	2.8	107.6	66	23
2	0.01	5	6	1.71	495	2.5	107.4	67	23
3	0.1	5	6	2.10	388	2.1	106,112	53	18
4	0.5	5	6	1.85	478	2.3	97, 112	101	35
5	1	5	6	2.30	517	2.3	133	168	58
6	0	30	6	2.50	286	2.3	-	-	-
7	0.01	30	6	2.95	310	2.7	129	4	1.4
8	0.1	30	6	3.87	343	2.9	131	26	9
9	0.5	30	6	4.23	328	3.1	134	157	54
10	1	30	6	6.21	387	2.3	135	172	58
11	0	50	6	1.65	188	2.3	-	-	-
12	0.01	50	6	2.10	196	2.8	127	3.4	1.2
13	0.1	50	6	4.35	215	3.4	129	114	39
14	0.5	50	6	6.23	174	3.5	131	146	50
15	1	50	6	10.50	168	2.2	134	172	59
16	0	60	100	7.25	145	2.4	50	32.5	11.0
17	0.01	60	100	7.87	125	2.2	49,127	13,21	5 , 7
18	0.1	60	100	7.92	95	2.3	53,128	18,15	6 , 5
19	0.5	60	100	10.50	84	2.7	132	174	60
20	1	60	100	14.23	67	2.1	135	189	65

[a] Other reaction conditions: solvent, toluene; total volume, 250 ml for Run 1-15 and 450 ml for Runs 16-20; Reaction time, 30 min for Runs 1-15, 15 min for Runs 16-20; Al/(Ni+Zr) = 1500 (molar).
[b] X_2 = moles of **2** / (moles of **1** + moles of **2**).
[c] in kg of PE / mol (Ni + Zr) * hr
[d] Determined from GPCV measurement at 140 °C in 1,2,4-trichlorobenzene.
[e] Determined from DSC measurement.
[f] Crystallinity based on ΔH_m = 290 J/g for a perfect PE crystal.

6.4.2 Effect of Catalyst 2 Molar Fraction (X_2) on Polymer Properties

The effects of X_2, polymerization temperature, and ethylene pressure on the microstructure of the polymers produced were investigated by means of gel permeation chromatography (GPC) for molecular weight analysis and differential scanning calorimetry (DSC) for thermal analysis. We reported the DSC thermal analysis in terms of melting temperature (T_m), heat of fusion (ΔH_m), and degree of crystallinity (X_c). The melting behavior of polyethylene is mainly related to short chain branching. Increasing short chain branching density decreases lamellar thickness of the crystal structure and thus lowers melting temperature of the polymer. The short chain branching also affects the degree of crystallinity which is proportional to the fractional amount of crystalline phase in polymer sample. Figure 6.2 shows the effect of changing X_2 on the melting behavior of polymers produced with 1/2/MMAO system at 5 °C and 6 psig.

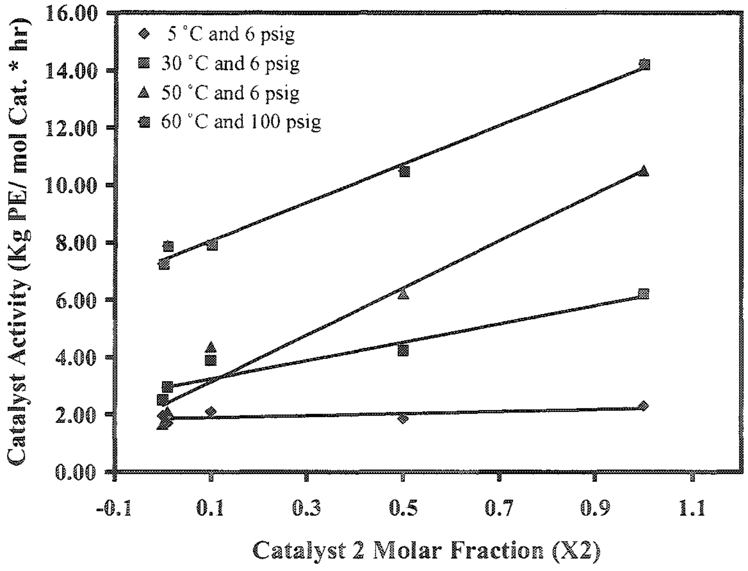

Figure 6.1 Effect of temperature, pressure and X_2 on catalyst activity.

It is known that catalyst 1/MMAO will homopolymerize ethylene to produce branched polyethylene, and the degree of branching increases with polymerization temperature.[2-4] As shown in Table 6.1, at 5 °C, catalyst 1/MMAO produced branched polyethylene with T_m = 107.6 °C and X_C = 23% (run 1) and catalyst **2**/MMAO produced linear polyethylene with T_m = 133 °C and X_C = 58% (run 5). As revealed from Table 6.1, it is also clear that the melting behavior of the polymer sample produced at 5 °C was affected by changing catalyst **2** molar fraction. For example, increasing catalyst 2 molar ratio from X_2 = 0.1 (run 3) to X_2 = 0.5 (run 4), the polymer crystallinity was increased from X_C = 18 % to X_C = 35%. This increase in the crystallinity was due to the increase of the linear polymer amount as we increased X_2. The DSC thermograms in Figure 6.2 show that at X_2 = 0.1 and X_2 = 0.5, both low and high melting peaks were shifted to lower temperatures compared to the melting peaks of the polymers produced with the individual catalysts. This observation probably suggests that there is a sort of competition and interference during the crystallization of both branched and linear polyethylene.

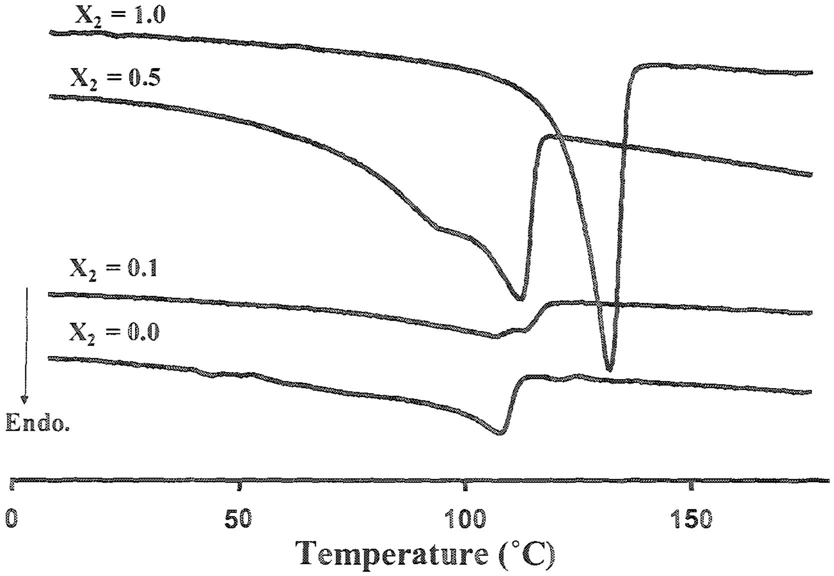

Figure 6.2 DSC thermograms for polymers produced with **1**/**2**/MMAO system

at 5 °C and 6 psig: effect of X_2 on polymer melting behavior.

In contrast, at 30 and 50 °C, the polymers produced with the catalyst **1**/MMAO system were totally amorphous due to high branching and therefore a different melting behavior was observed. At such conditions, the polymers produced with the binary catalyst system were mixtures of amorphous PE from catalyst **1**/MMAO and semicrystalline PE from catalyst **2**/MMAO. Therefore, there might be little interference and competition between both polymers during the crystallization process. Figure 6.3 shows the melting behavior of the polymer samples produced at 50 °C and different values of X_2. The DSC thermogram shows only single peaks of the crystalline polymers produced by catalyst **2**.

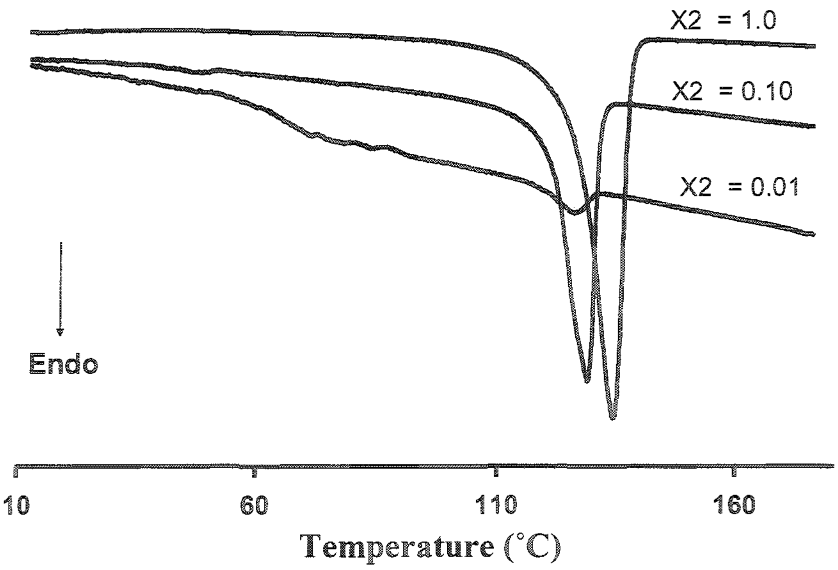

Figure 6.3 DSC thermograms for polymers produced with **1**/**2**/MMAO system at 50 °C and 6 psig: effect of X_2 on polymer melting behavior.

As shown in Table 6.1, it is also clear that increasing X_2 had a strong effect on the polymer crystallinity. For example, for the polymerization runs held at 50 °C, increasing catalyst 2 molar ratio from $X_2 = 0.01$ to $X_2 = 0.5$, the polymer crystallinity was increased from $X_C = 1.2$ % to $X_C = 50$.

It is known that ethylene pressure has a remarkable effect on the microstructure of polyethylene produced with catalyst **1**/MMAO.[4-9] In an attempt to understand the effect of ethylene pressure on the characteristics of the polymer produced with **1**/**2**/MMAO, ethylene polymerization runs were carried out at 60 °C and 100 psig. At such conditions, **1**/MMAO produced branched polyethylene with $T_m = 50$ °C and $X_C = 11.0\%$ (run 16) and catalyst **2**/MMAO produced linear polyethylene with $T_m = 135$ °C and $X_C = 65\%$ (run 20).

As revealed from the DSC data (Figure 6.4), the melting curves of the polymers produced with **1**/**2**/MMAO exhibited two distinct peaks with melting temperatures closely corresponding to those of the polymers produced with the individual catalysts; **1**/MMAO and **2**/MMAO. This observation suggested that the interference between both polymers was minimal during the crystallization process due to the big difference in the melting temperatures of the polymers produced with the individual catalysts. It also suggested that running **1**/**2**/MMAO at high ethylene pressure each individual catalyst behaved independently towards ethylene polymerization.

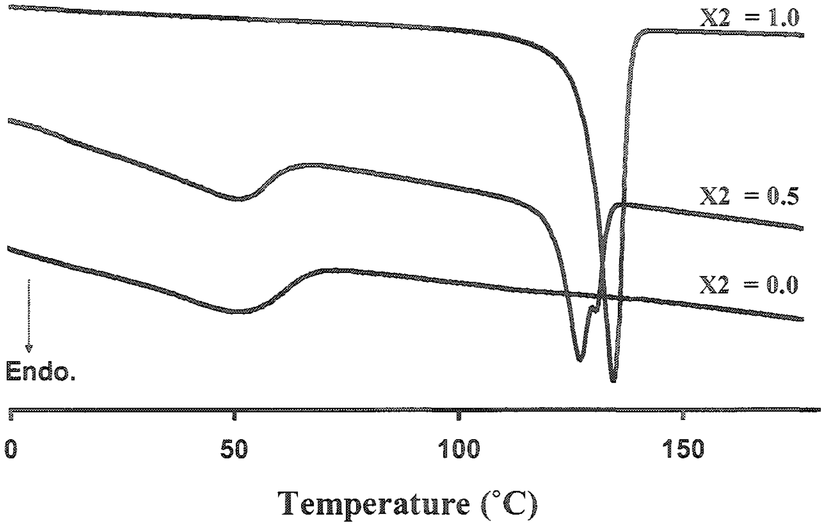

Figure 6.4 DSC thermograms for polymers produced with **1**/**2**/MMAO system at 60 °C and 100 psig: effect of X_2 on polymer melting behavior.

At 5 °C, the polyethylene samples produced with the catalyst systems **1**/MMAO and **2**/MMAO exhibited comparable weight average molecular weight of 588 kg/mol and 517 kg/mol, respectively. The polyethylene samples produced at various catalyst **2** molar fractions (X_2 = 0.01, 0.1 and 0.5) showed a slight reduction in M_w with a monomodal molecular weight distribution and narrow polydispersity.

When polymerization temperature was increased to 30 °C or 50 °C, the weight average molecular weights were reduced for the catalyst systems of **1**/MMAO and **2**/MMAO. This reduction in M_w for both catalysts was attributed to the enhancement of the chain transfer rate as we increased the polymerization temperature. As shown in Table 6.1, at 30 °C or 50 °C, the polyethylene samples produced with X_2 = 0.1 and 0.5, showed monomodal molecular weight distribution with slight broadness. For example, the polyethylene produced at 50 °C and $X_2 = 0.5$, showed polydispersity of 3.5, in comparison to polydispersities of 2.3 and 2.2 for the polymers produced with the individual catalysts, **1**/MMAO and **2**/MMAO, respectively.

At higher temperature and ethylene pressure (60 °C, 100 psig), the polyethylene produced showed far lower molecular weight than those produced at 6 psig and various polymerization temperatures and catalyst fractions. Similarly, the polymer produced showed monomodal molecular weight distribution and narrow polydispersities.

6.5 Conclusion

We demonstrated the synthesis of different reactor blends of linear and branched ethylene homopolymers by combining catalysts **1** and **2** at various polymerization conditions. At 5 °C and 6 psig, there was little influence of the catalyst **2** molar fraction on the overall catalyst activity. At higher temperatures of 30 and 50 °C, a linear correlation between the overall catalyst activity and X_2 indicated that the interactions between catalyst **1** and **2** species were minimal, and the two catalysts performed independently. At 60 °C and 100 psig, a similar linear correlation was observed. For the polyethylene produced at 5 °C and $X_2 = 0.5$, the DSC thermograms showed bimodal peaks with melting points shifted to lower temperatures compared to those of the polymers produced with the individual catalysts, suggesting that there was a sort of competition and interference during the crystallization of both branched and linear polyethylenes. At 30 and 50 °C, the polymer produced with the binary catalyst system was a mixture of amorphous PE from catalyst **1** and semicrystalline PE from catalyst **2**. This resulted in less interference and competition between both polymers during the crystallization process, thus leading to DSC curves with single melting peaks coming from catalyst **2** polymer. At 60 °C and 100 psig, the DSC thermograms of the polymers produced with **1**/**2**/MMAO exhibited two distinct peaks with melting temperatures closely corresponding to the melting temperatures of the polymers produced with the individual catalysts; **1**/MMAO and **2**/MMAO. The GPCV analysis for all the produced polyethylene samples showed monomodal molecular weight distributions with low polydispersities.

6.6 Reference

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Chapter 7

Research Contribution and Recommendation for Future Work

7.1 Significant Research Contributions of Thesis Work

This thesis work has made a number of significant contributions to the polyethylene research area. These contributions are summarized as follows:

Reported in Chapter 3 we carried out ethylene polymerization using three homogeneous nickel α-diimine catalysts ((ArN=C(An)-C(An)=NAr)$NiBr_2$ (**1**), (ArN=C(CH_3)-C(CH_3)=NAr)$NiBr_2$ (**2**) and (ArN=C(H)-C(H)=NAr)$NiBr_2$ (**3**); where An = acenaphthene and Ar = 2,6-(i-Pr)$_2C_6H_3$) activated with MMAO in a slurry semi-batch reactor. This work offered one of the first systematic comparative studies concerning the effects of changing α-diimine backbone structure and polymerization conditions (ethylene pressure and temperature) on catalyst activity and polymer properties such as molecular weight and distribution, and thermal characteristics of the final polymer. Different from previous studies and for the first time with these catalysts, this work explored a wide range of polymerization conditions to understand the broadest effect on the final polymer properties. One of the most important conclusions of this work reported for the first time was that the effect of the bulkiness of α-diimine backbone structure on the final polymer properties does not follow a simple and general trend but rather more specific to the individual catalyst structure. This conclusion was verified at different polymerization conditions. It was also demonstrated that changing the α-diimine backbone structure has a drastic effect on the chain walking rate and as a result affects the polymer melting behavior allowing for the synthesis of a wide range of polyethylene properties covering a wide range of grades from highly branched LLDPE, with catalyst **1** and **2**, to linear HDPE with catalyst **3**.

Reported in Chapter 4 was the synthesis of polyethylene using both homogeneous and MMAO-treated silica supported nickel-diimine catalyst (1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide) in a slurry semi-batch reactor. This work represented one of the few reports disclosed in the literature about supporting this newly developed homogeneous Ni-diimine catalyst system. This work described a systematic investigation of the effects of catalyst supporting and polymerization conditions (ethylene pressure and reaction temperature) on catalyst activity and polymer properties. It was demonstrated from experimental results that the supported catalyst system produces polyethylene with different microstructure as compared with those produced with the homogeneous catalyst. The supported catalyst system exhibited lower chain walking rates than the homogeneous catalyst, producing polymers with less branching content and, thus higher melting point. One of the important findings of this work was the melting characteristics of the polymer produced with the supported catalyst. Depending on polymerization conditions, two active site populations were observed during polymerization using supported catalyst; one population remained fixed on the surface of the support, and the other was extracted from the support exhibiting the same polymerization behavior, as the homogeneous catalyst.

Reported in Chapter 5 was the use of the first homogeneous binary tandem catalytic system for the synthesis of ethylene-1-hexene copolymers from ethylene stock as the sole monomer. This binary catalytic system employed the tandem action between an ethylene trimerization catalyst and a copolymerization metallocene catalyst. This work was the first thorough and systematic investigation of the performance of this tandem catalytic system at high temperatures and ethylene pressures. It was shown that by simple manipulation of the catalyst molar ratio and polymerization condition, a series of branched polyethylene samples with a broad range of melting temperatures, crystallinities, and 1-hexene percentages can be efficiently produced. It was shown that increasing ethylene pressure increases the reactivities of both catalysts of the tandem system at comparable rates, resulting in a minimal effect on the polymer melting behavior. In addition, it was concluded that effect of temperature increase on the copolymer melting behavior is not only attributed to the deactivation of the trimerization catalyst, but also to the increase in the ethylene propagation rate of the polymerization catalyst.

Reported in Chapter 6 we carried out the synthesis of a series of reactor blends of linear and branched polyethylene materials using a combination of [1,4-bis(2,6-diisoprpylphenyl) acenaphthene diimine nickel(II) dibromide](**1**)/MMAO, known as active catalyst for the production of branched polyethylene, and [rac-ethylenebis(indenyl) zirconium dichloride](**2**)/MMAO, which is active for the production of linear polyethylene. This work demonstrated that the combination of catalysts **1** and **2** produces different grades of polyethylene, depending on the polymerization conditions and catalyst molar fractions. This work also established a preliminary knowledge about the characteristics of the produced polyethylene grades in terms of their thermal properties and molecular weight data. This work also investigated the interactions between both catalysts and provided the preliminary data for the overall catalyst activity dependence on various values of catalyst fractions at different reaction conditions.

7.2 Recommendation for Future Research

In this thesis, polymers with different microstructures were synthesized and characterized in order to develop a better understanding of the influences of polymerization conditions and catalyst systems on polymer properties. However, there remains more research work to be conducted to further develop these products and their processes for future commercial applications. The followings are some recommendations for future research work:

7.2.1 Nickel-Diimine Catalyst Systems for the Synthesis of LLDPE

Different structures of nickel-diimine catalysts were used to synthesize a wide range of polyethylene products. The major advantage provided by these nickel catalysts is their ability to produce branched polyethylenes without the need for any comonomer. One of the major anticipated applications for these catalysts is the production of a range of LLDPE grades which have similar properties as those grades produced commercially using either the conventional Ziegler-Natta or metallocene catalysts. However, as a drawback, nickel diimine catalysts produce polyethylene with uncontrolled randomly distributed SCB with predominantly methyl branches, making it unsuitable to replace the conventional high α-olefin LLDPE. The branching structure and distribution of polyethylene produced with nickel diimine catalysts attributes to a catalytic mechanism known as "chain walking" which is mainly controlled by the catalyst structure. To alleviate this problem, possible research areas could be addressed: 1) conduct a detailed study on the relationship between the catalyst structure and the branching density, structure and distributions; and 2) accordingly design the proper catalyst system for better control on chain walking mechanism and the synthesis of polyethylene with branching structure similar to LLDPE.

7.2.2 Development of Heterogeneous Tandem Catalytic Systems for The Production of LLDPE directly from Ethylene in a continuous Polymerization Process

Tandem catalytic systems offer a promising synthetic route to the production of linear low density polyethylene (LLDPE). The advantage and efficiency of these catalytic systems for the synthesis of LLDPE has been investigated in Chapter 5 of this thesis and in the literatures. However, all of the work conducted so far on tandem catalytic systems has been based on homogeneous catalysts in a semi-batch processes. Most industrial production of LLDPE is currently performed using a continuous gas phase or slurry processes which will most likely continue in the future due to the many advantages of these processes. These processes are designed to handle heterogeneous catalyst systems. In order to satisfy the need of these commercial processes, development of supported tandem catalyst systems for continuous polymerization processes are highly recommended. The development of a successful supported tandem catalytic system will enable the commercial production of various grades of LLDPE from ethylene as the sole monomer. This will no doubt be a major breakthrough in the polyethylene industry.