NOVEL FUNCTIONAL ETHYLENE/PROPYLENE ELASTOMERS: SYNTHESIS AND CHARACTERIZATION

A Thesis in
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By
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Abstract

This thesis discusses novel chemical approaches to prepare functional ethylene/propylene elastomers. The chemistry involves the preparation of poly(ethylene-co-propylene) reactive intermediate in which the reactive groups are randomly distributed in EP-backbone or located only at the chain-end, depending on the employed metallocene catalyst, type of comonomer/chain transfer agent, and reaction conditions. Several reactive comonomers can act as chain transfer agents, including \( p \)-methylstyrene (\( p \)-MS), \( p \)-hydroxystyrene (\( p \)-OHSt), allyl alcohol, allyl amine, and butenyl amine. They are systematically investigated to find the suitable reaction conditions. In turn, the resulting EP copolymers containing such reactive moieties, located in the side chain or at the chain end, are versatile for a wide range of applications. The combination of this reactive approach and metallocene technology enables us to prepare many novel reactive ethylene/propylene (EPR) copolymers with terminal functional groups.

In chapter I and II, some historical aspects related to Ziegler-Natta catalysts and subsequent polyolefin developments are discussed, and then followed with a brief summary of the current approaches of polyolefin modifications. I will provide some background information, especially the prior research approaches and experimental results in functionalization of polyolefins. So far, the most effective functionalization chemistry involves the combination of metallocene catalysis and reactive comonomers (or reactive chain transfer agents), which was developed in our group. The
chemistry has also been extended to prepare block and graft copolymers having a polyethylene (PE) or polypropylene (PP) main chain.

This thesis focuses on ethylene/propylene copolymerization that not only produces useful materials for a wide range of applications but also provides a good understanding in the involved chemistry and reaction mechanism.

In chapter III, a chemical route to prepare new ethylene/propylene copolymers (EP) containing a terminal reactive group, such as -CH$_3$ and -OH is discussed. The chemistry involves metallocene-mediated ethylene/propylene copolymerization in the presence of a consecutive chain transfer agent—a mixture of hydrogen and styrene derivatives carrying a CH$_3$ ($p$-MS) or a silane-protected OH (St-OSi). The major challenge is to find suitable reaction conditions that can simultaneously carry out effective ethylene/propylene copolymerization and incorporation of the styrenic molecule (St-f) at the polymer chain end. In other words, the reaction conditions can alter the St-f incorporation mode from copolymerization to chain transfer. A systematic study was conducted to examine several metallocene catalyst systems and reaction conditions. Both [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ and rac-Et(Ind)$_2$ZrCl$_2$, under certain H$_2$ pressures, were found to be suitable catalyst systems to perform the combined task. The presence of ethylene along with propylene in the polymerization system provides one more advantage in understanding the chemistry involved and consequently, the detailed behaviors of the applied catalysts. Therefore, the copolymer composition can be derived from an ethylene/propylene mole ratio which is very important information that
affords a good understanding of the polymerization mechanism. A broad range of St-f terminated EP copolymers (EP-t-p-MS and EP-t-St-OH), with various compositions and molecular weights, have been prepared with polymer molecular weight inversely proportional to the molar ratio of [St-f]/[monomer].

It is also interesting to search for other olefinic species that can behave like styrenic molecules in selective copolymerization or chain transfer reactions by controlling the reaction conditions. Therefore, in chapter IV, we describe the copolymerization of ethylene and propylene in the presence of protected allylalcohol, allylamine and butenylamine. These monomers were reported to be difficult in the preparation of functional PE and PP polymers, with low catalyst activities and low polymer molecular weights. Our strategy is to first protect the functional monomers with bulky protecting groups from poisoning the catalyst. Then, the protected functional monomer is introduced in the copolymerization reaction. It is very possible that the incorporated functional monomer at the propagating chain-end may stop the polymerization due to steric or electronic reasons. However, subsequent chain-transfer to hydrogen or MAO could take place and regenerate the catalyst for a new polymerization cycle. Therefore, the resulting polymer should contain a terminal functional group. The protection methods have been chosen in such a way that they would not only lead to the steric shielding, but also to afford electronic neutralization of the functional groups. A systematic study of metalloocene-mediated ethylene/propylene /protected polar monomer polymerization in the absence and presence of H₂, with varying catalysts, polar monomer concentrations, and hydrogen pressures, has been conducted. With a combination of a metalloocene catalyst
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In chapter V, a new chemical route to prepare graft copolymers containing both an elastic main chain and elastic side chains is discussed, especially EP-g-PI graft copolymers having ethylene/propylene copolymer (EP) main chain and several polyisoprene (PI) side chains. Such a polymer may provide the much needed solution to address the weak rubber-rubber interface adhesion problem, currently facing the tire industry. The chemistry is centered on a reactive EP copolymer intermediate containing few reactive side groups that are very effective for subsequent grafting reactions. The reactive EP-copolymers are used as the main chains for preparing graft copolymers, which involve both ‘living’ anionic graft-from and graft-onto polymerization with isoprene monomers. The incorporated reactive sites randomly distributed along the EP chain provide the grafting points to join the PI side chains. In the EP copolymer containing $p$-MS reactive groups, the benzylic protons in $p$-MS units were transformed to benzylic anions before introducing isoprene for an anionic graft-from reaction to prepare EP-g-PI graft copolymer.

Another way to prepare such a graft copolymer was the coupling reaction between the chloro group in EP-$p$-CMS and living polyisoprene anions via graft-onto reaction. A third studied system was the graft-from and graft-onto anionic copolymerization between EP-co-DVB and isoprene. An effective fractionation method was developed to separate any traces of
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In chapter VI, a novel method to synthesis reactive rubber particles is described. Considered as a frontier engineering material, reactive rubber particles will find the way in almost all applications. The process involves two steps: metallocene-mediated E/P/DVB terpolymerization followed by emulsion or suspension thermal crosslinking. The particles contain reactive styrenic moieties on the surface which are very versatile in many applications. The first step of preparing these reactive rubber particles involves the synthesis of linear ethylene-propylene/divinylbenzene (EP-DVB) terpolymer via metallocene-mediated polymerization using selected catalysts. Then, in the second step, this soluble EP-DVB terpolymer is emulsified using soap-in-situ method to sub-micro size particles, followed by crosslinking via a thermal coupling reaction of pendent styrene moieties in the bulk of particle. A suspension process in which EP-DVB terpolymer is suspended in water containing PVOH then thermally crosslinked to form 1 to 10 µm size particles was also developed. Some remaining styrene moieties on the surface were then used for further functionalization reactions, including maleation and epoxidation or graft reactions (via graft-onto, graft-from, and graft-through mechanisms) which provide excellent
adhesion with brittle polymers. Several polymers have been studied, including Nylon, PP, PS, and SAN polymers. The combination of SEM and TEM results indicates the effectiveness of the grafting reaction and consequently the interfacial adhesion between the dispersed rubber particles and the continuous polymer domain.

Finally, in Chapter VII, the conclusions of this work, with the emphasis on some important topics that need further investigation for future work are summarized.
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Chapter I.
Introduction

1.1. Polyolefins: Historical Aspects and Development

Polyolefins are materials used today in all fields of life. These materials have been discovered within this century and are now produced all over the world\(^1\). Polyolefins— including polyethylene (PE), polypropylene (PP), poly(1-butene), poly(1-octene), poly(4-methyl-1-pentene), ethylene-propylene elastomer (EPR) and ethylene-propylene-diene rubber (EPDM) — are the most widely used commercial polymers, with over 53 billion pounds (24 million tons)\(^2\) US annual production (about 40% worldwide) in 1999, or close to 60% of the total polymer produced. By controlling crystallinity and molecular weight, polyolefins with a wide range of thermal and mechanical properties have been produced for a wide range of commercial applications\(^3\). The products are presented in various forms, such as films, sheets, fibers, even waxes, and viscous liquids. They are greatly influencing our day-to-day life, and range from common items like bread bags, garbage bags, milk jugs, bottles, containers, hoses, outdoor-indoor carpets, tires, bumpers, and trims, to bullet-proof jackets.

The simplest molecular structure of linear polyethylene (HDPE) with ultra-high molecular weight (such as the commercial spectrum fiber used in bullet-proof jackets) has near 100% crystallinity and melting temperature \(T_m\) of \(~140^\circ\text{C}\). Its mechanical strength is greater than any known existing materials\(^4\) (i.e., including steel, Kevlar, carbon fiber, etc.). On the other
hand, ethylene-propylene copolymers (EPR), containing about 40-45 mol% propylene, are completely amorphous elastomers with glass transition temperature \((T_g)\) as low as \(-65^\circ C\). The key success factors for polyolefins are the following ones: the raw materials (monomers) are easily accessible and reasonable based on oil or natural gas. The production costs are low due to very efficient catalyst technology and energy saving large volume reaction processes. The products easily processible and recyclable thus contributing to the principle of sustainable development\(^6\). Most polyolefins are routinely fabricated by all available methods – including extrusion, injection molding, compression molding, injection blow molding, and calendaring – into film, sheet, pipe and fiber products with various shapes and sizes. In addition, these materials are also known to be the most recyclable commercial polymers\(^7\). After loss of performance these polymers can be burned having combustion energies like oil. Therefore, they are also called solid white oil\(^8\).

All of these products can be tailored to reach excellent product quality in respect to processing and final product performance. Some of these products can be identified as polymer alloy\(^9\). Starting from simple raw materials like ethylene, propylene or other \(\alpha\)-olefins and using catalytic polymerization processes, a broad spectrum of valuable polymer products can be synthesized, as illustrated in Scheme 1.1\(^{10}\).

1.2. Ziegler-Natta vs. Metallocene Catalysts and Polymerization

  Ziegler – Natta catalysts are “mixture of a metal alkyl of group I to III and a transition metal of group IV to VIII”\(^{11}\). Both homogeneous and
heterogeneous catalysts have been extensively investigated and shown useful in \( \alpha \)-olefin polymerization. In the past, the heterogeneous systems offered better stereospecific addition for the preparation of isotactic structure. The soluble systems are generally used for polyethylene and EPR copolymers where tacticity is irrelevant. However, the new Metallocene-based homogeneous catalysts clearly demonstrate the stereospecific insertion largely dependent on the structure symmetry at the active site.

In traditional heterogeneous Ziegler-Natta catalysts, the base metal component, most often an aluminum alkyl, serves as an alkylating agent for the transition metal salt. The most common one, \( \text{TiCl}_3 \), is a crystal of alternating layers of \( \text{Ti}^{3+} \) and \( \text{Cl}^- \) ions. At the edges, and in cracks or defects, the alkylation takes place on titanium atoms with an unsaturated coordination sphere. The exact polymerization mechanism was controversial
for a long time. The most reasonable theory stated that the polymer growth takes place at a transition metal carbon bond. This theory stated that the polymerization mechanism proceeds by successive olefin coordination and insertion into the growing polymer chain and was later proven by deuterium labeling experiments. Scheme 1.2 illustrates the polymerization mechanism for isotactic polymers.

Scheme 1.2: Polymerization mechanism for isotactic polymers

The reaction cycle starts with the coordination of the π-electrons in α-olefin to the vacant d-orbital of the octahedral Ti metal (I) to form metal-olefin complex (II), before inserting into the Ti-C bond (III). The insertion regenerates the vacant d-orbital (IV) with a configuration opposite that of the original (I). In isotactic polymerization, with a very limited opening at the active site, only one prochiral face of the monomer (with less steric...
hindrance primary carbon) is able to approach the Ti-C bond. The steric repulsion between the active site (ligand) and the bulky substitute (R) in the monomer regulates α-olefin insertion into the Ti-C bond in a 1,2-fashion. In addition, the steric hindrance around the active site (IV) also prevents immediate α-olefin coordination/insertion. Instead, the following propagation only continues after the polymer chain in the active site (IV) migrates back to its original site (I) with the regeneration of the original configuration of the vacant d-orbital. In summary, the combination of stereoregular coordination/insertion and facial polymer chain migration in each reaction cycle results in the isospecific addition reaction of α-olefin and assures the formation of isotactic polymer.

The Metalloocene catalyst is a new class of homogeneous Ziegler-Natta catalyst with the unique characteristics of well-defined molecular structure and good solubility in hydrocarbon media. Not all metalloccenes can serve as catalysts for olefin polymerization, the transition metals most suitable for olefin polymerization are titanium, zirconium and hafnium, which are group IVB metal atoms. Metalloccenes are organometallic compounds with one or two cyclopentadienyl rings or their derivatives which are π-bonded to the central transition metal atoms. Metalloocene catalysts result from the reactions between Metalloccenes and co-catalysts. The co-catalysts can be divided into two categories: one is organoaluminum compounds such as alkylaluminums or alkylaluminoxanes and the other is anionic counterions, such as borates or fluorinated borates.

As early as the 1950’s, metalloocene/alkylaluminum systems were used for the polymerization of olefins\textsuperscript{15}. Due to the extremely low activity, the
research was limited to the mechanism study. There was no breakthrough in this area until 1977 when methylaluminoxane (MAO) was synthesized and used as cocatalyst by Kaminsky and Sinn\textsuperscript{16}. The combinations of titanocenes and zirconocenes, such as $\text{Cp}_2\text{Ti(CH}_3)_2$, $\text{Cp}_2\text{Zr(CH}_3)_2$ and $\text{Cp}_2\text{ZrCl}_2$ with MAO produced polyethylene with much higher activity than the commercially used Ziegler catalysts. The synthesis of \textit{ansa} titanocenes and zirconocenes by Brintzinger et. al.\textsuperscript{17} in 1982 was another key step in this area. In 1984, Ewen\textsuperscript{18} synthesized both isotactic and atactic PP using \textit{rac/meso} mixture of \textit{ansa} ethylene(bisindenyl)titanium dichloride ($\text{Et(Ind)}_2\text{TiCl}_2$) with MAO as cocatalyst, and correlated catalyst symmetry with polymer microstructure and reaction mechanism. In 1985, Kaminsky and Brintzinger\textsuperscript{19} reported highly isotactic PP by using chiral \textit{ansa} zirconocenes/MAO catalyst. Since then, worldwide industrial and academic research in Metallocene catalysis for olefin polymerization has taken off. It has been growing so fast that after 10 years this advanced technology has been brought to commercialization. Several excellent recent review papers have been published to cover the whole story\textsuperscript{20}.

The driving force for the rapid development of metallocene catalysts is attributed to their excellent characteristics, including: I) well-defined and controllable single catalytic site, II) excellent ability to incorporate high $\alpha$-olefins, III) production of polyolefins with well-defined molecular structures and properties, and IV) potential usefulness for polymerization of polar functional monomers and copolymerization with $\alpha$-olefins. Among all $\alpha$-olefin polymerization catalysts, metallocenes are the only catalysts that are able to control both molecular weight and microstructure (i.e. tacticity,
regioregularity and comonomer distribution) of polyolefins over a very wide compositional range.

Cocatalysts play a key role in the metallocene for olefin polymerization. Methylaluminoxane (MAO) is the most widely used cocatalyst, since it is able to activate the largest number of metallocenes and other soluble transition complexes. It is usually synthesized by controlled hydrolysis of trimethylaluminum (TMA). The techniques for the preparation of MAO have been reviewed by Reddy et al.\textsuperscript{21} It is believed that MAO consists of oligomers with many (MeAlO) units, the optimal molecular weight estimated by cryoscopic measurement in benzene lies between 1000 – 1500 g/mol. However, the exact structure and composition of MAO are not very clear so far. The latest studies suggested a three-dimensional cage structure with four-coordinate aluminum centers resembling a half opened dodecahedron \([\text{Al}_{16}\text{O}_{12}\text{(CH}_3\text{)}_{24}]^{22}\). This cage can seize an anion from the metallocene to form a stable \(\text{AlX}_4^-\) anion due to the delocalization of the electrons over the whole cage. The functions of MAO mainly include alkylation of halogenated metallocene complexes, serving as scavengers for moisture or other impurities, reactivation of inactive complexes formed by hydrogen transfer reaction between active species and MAO\textsuperscript{23}, and stabilization of active species.

Usually, a large excess amount of MAO (Al/M = 1000 – 50,000) is required to reach optimal activity. This is the main drawback of using MAO as cocatalyst, as preparation of MAO is expensive and the large excess of aluminum residual after polymerization has to be removed from the resulting polymers. Many attempts have been made to reduce the Al/M ratio,
including: modification of metallocenes by adjusting the substituents in Cp-rings to decrease the possibility of catalyst deactivation, and immobilization of metallocenes on inert substrates to stabilize the active species by minimizing deactivation via bimetallic mechanism\textsuperscript{24}. Polar solvent, such as \(\text{CH}_2\text{Cl}_2\), has also been reported to reduce the amount of MAO by a factor of 20 (compared with toluene as a solvent) without affecting the isotacticity of the polymer\textsuperscript{25}.

The other solution to this problem is the use of boron compounds, such as \(\text{B(C}_6\text{H}_5)_3\)\textsuperscript{26}, highly Lewis acidic \(\text{B(C}_6\text{F}_5)_3\), \(\text{NR}_3\text{H}^+ \text{B(C}_6\text{F}_5)_4^-\) and \(\text{PhC}_3^+ \text{B(C}_6\text{F}_5)_4^-\), as substituents for MAO in combination with metallocene dialkyls\textsuperscript{27}. About 1 to 1 ratio of boron compound to metallocene can form a reactive catalyst for olefin polymerization. However, this system is very sensitive to moisture and other impurities and the stability of the resulting metallocene complexes is much lower than that formed with MAO. Usually, alkylaluminum (such as triisobutylaluminum) is added to the system to scavenge the impurities and to stabilize the complex\textsuperscript{28}.

There is great evidence that the nature of the active species for olefin polymerization is cationic. In \(\text{L}_2\text{MX}_2/\text{MAO}\) system, active species is \(\text{L}_2\text{M(CH}_3\text{)}^+\), the cation is stabilized by \((\text{MAOX})^-\) anion\textsuperscript{29}. In \(\text{L}_2\text{MR}_2/\text{borate}\) system, the active species is \(\text{L}_2\text{M}^+\text{R[}\text{B(C}_6\text{F}_5)_4\text{]}\) or \(\text{L}_2\text{M}^+\text{R[}\text{B(C}_6\text{F}_5)_3\text{ R]}\). The anion is weakly coordinated with metallocene cation without negative effect to the coordination of the monomer.

One of the most useful features of metallocene catalysts is their strong ability to produce copolymers with narrow molecular weights and
composition distributions, which are very difficult to achieve by heterogeneous Ziegler-Natta catalysts. In all polymerization cases using metallocene catalysts, the molecular weight distribution of the produced polymers are close to 2, which strongly indicates a single catalytic site in metallocene polymerization. Metallocene catalysts always produce almost completely random copolymers which results in a much greater decrease in polymer crystallinity for a given amount of comonomer concentration and much lower amount of extractables than that of copolymers produced by Ziegler-Natta catalysts\textsuperscript{30}. In addition, high α-olefins and bulky cyclic monomers can readily be incorporated into polyolefins by metallocene catalysts\textsuperscript{31}. The active site of the catalysts could be tailored by using different ligands during catalysts preparation. Bridge between ligands provides catalysts with constrained geometry by pulling two ligands together, resulting in the decrease in Cp-M-Cp angle, and consequently forcing the active site to be much more opened. This geometry favors the incorporation of high α-olefins or other bulky monomers and also increases the copolymerization activity\textsuperscript{32}. In general, one atom bridge opens active sites more than multi-atom bridges. Under the same conditions, $C_5$-symmetric metallocenes are more effective in incorporating α-olefins into an ethylene copolymer than $C_2$-symmetric metallocenes or $C_{2V}$-symmetric ones (unbridged)\textsuperscript{33}. Dow’s Insite catalyst $[(C_5\text{Me}_4)\text{SiMe}_2\text{N(\text{t-Bu})}]\text{TiCl}_2/$MAO, which has highly constrained ligand geometry (active site more opened), can incorporate more than 30 mol % of high α-olefins without broadening molecular distribution and can even incorporate long chain branches with thousands of molecular weight\textsuperscript{34}. 
Another important feature of metallocene catalysts is their ability to produce polyolefins with controllable molecular microstructures and properties. Metallocenes can be divided into five categories in terms of symmetry and chirality. They are achiral $C_{2v}$-symmetric metallocenes, such as $\text{Cp}_2\text{MCl}_2$, $[\text{Me}_2\text{Si}(\text{Cp})_2]\text{MCl}_2$ and $\text{meso-Et(Ind)}_2\text{ZrCl}_2$; chiral $C_{2v}$-symmetric metallocenes, such as $\text{rac-Et(Ind)}_2\text{ZrCl}_2$, $C_s$-symmetric metallocenes like $[\text{Me}_2\text{C(Cp)}(\text{Flu})]\text{MCl}_2$; $C_1$-symmetric metallocenes like $[\text{Me}_2\text{C(Flu)(3-RCp)}]\text{ZrCl}_2$, and oscillating metallocenes that are unbridged but have a significant rotation barrier due to bulky substituted ligands.

Different types of metallocene catalysts produce polyolefins with different microstructures and consequently different properties. For example, $C_{2v}$-symmetric catalysts produce atactic PP; $C_2$-symmetric catalysts produce isotactic PP; $C_s$-symmetric catalysts produce syndiotactic PP; $C_1$-symmetric catalysts produce hemiisotactic PP, thermoplastic elastomeric PP (TPE-PP) containing both isotactic and atactic PP segments, or isotactic PP. Oscillating metallocene catalysts, such as $(2\text{-Ph-Ind})_2\text{ZrCl}_2/\text{MAO}$, produce TPE-PP. Furthermore, in each catalyst system, by adjusting the position and bulkiness of the substituents on the Cp-rings, one can further control the catalyst activity, stereoregularity and molecular weight of the polymer.

There is some evidence that the major termination reactions in most metallocene catalytic polymerization of $\alpha$-olefins are $\beta$-H elimination and/or $\beta$-H chain transfer with monomers. $\beta$-CH$_3$ elimination has also been observed in some catalysts for propylene polymerization. This is the reason why in most cases molecular weights of PP by metallocene catalysts are not high. $\beta$-H transfer reaction can be effectively suppressed by adjusting the substituents in the Cp-rings and very high molecular weight PP has been
achieved\textsuperscript{41c, 44}. On the other hand, these well-defined termination reactions could be utilized to produce PP with chain-end unsaturation, which is reactive for further modification\textsuperscript{45}.

Difficulty in controlling the morphology of the polyolefins produced by metallocene catalysts has hindered the industrial use of the catalysts. One solution to this problem is the heterogenization of metallocene catalysts by supporting them on inert substrates. Many methods have been reported to support metallocene catalysts on SiO\textsubscript{2}, Al2O3, MgCl\textsubscript{2}, Zeolites and polymers\textsuperscript{46}. Overall, supported metallocene catalysts have much better morphology control. Improved stereo- and regioregularity and molecular weight of polymers were also demonstrated by the appropriate choice of supporting methods and conditions. In addition, Al/M ratio could be reduced by supporting of metallocene catalysts. However, the activities of the supported metallocene catalysts are always inferior to that of related homogeneous catalysts.

It is worthy to note that metallocene catalysts have been reported to polymerize polar monomers. Collins et al\textsuperscript{47} reported the effective polymerization of methyl methacrylate (MMA) by using a two-component catalyst system comprised of Cp\textsubscript{2}ZrMe\textsubscript{2} and [Cp\textsubscript{2}ZrMe\textsubscript{2}(THF)]\textsuperscript{+}[BPh\textsubscript{4}]\textsuperscript{−}, which provides partially syndiotactic PMMA in a high yield with narrow molecular weight distribution. The further kinetic study showed that the mechanism involves the formation of a neutral enolate complex between catalyst and monomer\textsuperscript{48}. Soga et al\textsuperscript{49} reported the polymerization of MMA using Cp\textsuperscript{*}2ZrMe\textsubscript{2}/[Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] along with a large excess of ZnR\textsubscript{2}, isotactic PMMA with narrow molecular weight distribution (MWD) was
obtained. The polymerization of MMA by \( \text{Cp}_2\text{M(CH}_3\text{)}_2 \) (\( \text{M} = \text{Ti, Zr, Hf} \))/MAO or \( \text{B(C}_6\text{F}_5\text{)}_4 \) or \([\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5\text{)}_4]\) in the presence of \( \text{Zn(C}_2\text{H}_5\text{)}_2 \) has been reported by Deng et al\(^5\). Syndiotactic-rich PMMA with narrow MWD (except MAO case in which very broad MWD was observed) was produced. Zirconocene gave the highest yield; hafnocene gave a very low yield, while titanocene gave no polymer. \( \text{tert-Butylacrylate} \) was also polymerized by \( \text{rac-Et(Ind)}_2\text{ZrMe}_2 \) / \( \text{Ph}_3\text{CB(C}_6\text{F}_5\text{)}_4 \) / \([\text{bis(2,6-di-tert-butyl-4-methylphenoxy)}\) methyl]aluminum\(^5\). When \( \text{CH}_2\text{Cl}_2 \) was used as solvent, high yield, high molecular weight and narrow MWD were achieved. The exact mechanism for these polymerization reactions is not clear yet. Most recently, Hayakawa et al\(^5\) reported a successful living ring-opening polymerization of lactones using cationic zirconocene catalysts. However, copolymerization of polar monomers with olefins comonomers by metalloocene catalysts has not been reported so far, which could be another breakthrough of the metalloocene catalysis if successful.

1.3. Ethylene-Based Elastomers: (EPR and EPDM)

Ethylene-propylene copolymers (EPR) and ethylene-propylene-diene terpolymers (EPDM) are very important materials with diverse properties and practical applications. Their properties can cover the full range of polymeric materials, from soft elastomers to hard thermoplastics depending on the relative comonomer composition and their distribution. Random copolymers of ethylene and propylene with less than 6% ethylene units and isotactic propylene sequence are thermoplastic materials\(^5\). Compared to corresponding homopolymers, the random copolymers are softer and have a lower flexural modulus and higher impact strength.
In 1940, the first all-hydrocarbon elastomer containing limited olefinic functionality, butyl rubber, was announced. Because of its resistance to embrittlement by aging, cracking on exposure to ozone, its impermeability to gases, and high damping capacity, these elastomers found use in inner tubes, cable insulation and miscellaneous hose, grommet, and gasket applications, generally lumped together as mechanical goods. It was the chemist’s desire to prepare elastomers from other simple inexpensive olefins, varying the structure to meet property requirements and using limited functionality to accommodate vulcanization. But no such preparative scheme was found, and instead, attention was turned to modifications of known substantially saturated hydrocarbon polymers to affect elastomeric properties and vulcanizability or to prepare elastomers from other raw materials. Typical examples being Hypalon (chlorosulfonated, low density polyethylene) and polymers derived from epoxides and acrylates. However, K. Ziegler and coworkers pursued the matter of dimerization or oligomerization of olefins with metal alkyls until a breakthrough was made, and the catalyst system now known as Ziegler or Mulheim catalysts was discovered. This basic discovery, initially applied to the polymerization of ethylene, was expanded by Natta and his group and others to preparation of entirely new polymer structures. And, while attention was initially devoted to the preparation of miscellaneous stereoregular, crystalline homopolymers from simple olefins, it was virtually axiomatic that it would inevitably turn to the preparation of elastomeric copolymers. So, like the development of butyl rubber from polyisobutylene, ethylene/propylene elastomers (EPR) were followed by their olefin-containing terpolymers (EPDM), all of which are commercially prepared today.
Commercial ethylene-propylene rubber (EPR) is most often prepared by vanadium-aluminum alkyl halide Ziegler-Natta catalysts\textsuperscript{59}. Because of the absence of unsaturation needed for sulfur vulcanization, EPR has its limited usages, and the introduction of a controlled amount of ethylenic unsaturation into the polymer via copolymerization with a non-conjugated diene is the classic industrial functionalization\textsuperscript{60}. One of the most commercial polyolefin elastomers is EPDM terpolymer, i.e. poly (ethylene-ter-propylene-ter-1,4-hexadiene) and poly(ethylene-ter-propylene-ter-5-ethylidene-2-norbornene), with glass transition temperature (T\textsubscript{g}) usually below -45°C. One of the double bonds of the diene is incorporated into the main chain of the rubber while the other does not react and remains as a pendant group and serves for the subsequent vulcanization\textsuperscript{61}. To prevent the potential crystallization of ethylene consecutive units and maintain a low T\textsubscript{g}, the terpolymer with approximately equal amounts of ethylene and propylene (55/45 mole ratio) is preferred in many EP rubber products.

Block copolymers of ethylene and propylene are also commercially available and are classified as heterophase copolymers\textsuperscript{62}. The copolymers are a mixture of tapered or block copolymers with crystalline homopolymers and amorphous copolymers. EPR and EPDM could also be used in thermoplastic olefin elastomers (TPO) which combine both the processing advantage of thermoplastics and physical properties of chemically vulcanized elastomers. Soft and hard segments are both required to introduce suitable physical molecular tie points to produce a network like structure which behaves similarly to that of chemical crosslinks. Examples of these include graft copolymers of crystallizable side chains onto elastic backbone, e.g. EPDM-g-pivaloacetone; and dynamically vulcanized elastomer-
thermoplastic blends, e.g. EPDM – isotactic PP blend\textsuperscript{63} in the presence of EPDM curatives. Blending of rubbery EPR with stiff, relatively brittle PP yields heterophase materials with balanced toughness – stiffness properties.

Being elastomers, EPR and EPDM have the ability to rapidly recover their shape after the removal of the strain and they are characterized by the increase in their entropically derived equilibrium modulus with temperature\textsuperscript{64}. EPR (random copolymers) with 70-80 mol\% ethylene content can be used as viscosity modifying additives in motor oils\textsuperscript{65}.

1.4. Polymer Alloy and Automotive Applications

Polymer alloy is of great current interest in industrial applications, because the joining of polymers can allow one to combine properties of more than one material. The usage of thermoplastic polyolefins (TPOs) in interior and exterior automotive applications has increased rapidly over the past decade. TPOs are replacing traditional engineering thermoplastics and thermosets in automotive parts such as bumper fascia, claddings, air dams and instrument panels. The replacement is due mainly to the performance properties, formulation flexibility and low cost offered by TPOs. Amorphous EPDM and high molecular weight semicrystalline EPR have been widely used as impact modifier for TPOs. However, a high percentage of an impact modifier will decrease the rigidity and heat properties of blends. Polypropylene copolymer has been introduced to enhance the toughness and rigidity with the trade-off of increasing price\textsuperscript{66}.
The most important application of EPDM is in the manufacture of tires which are formed from numerous layers of elastomers, or rubbers (as shown in Figure 1.1), reinforced by carbon black filler\textsuperscript{67}. EPDM elastomer is widely used as the sidewall compound for tire because of the excellent combination of extendibility, good low temperature properties, aging characteristics and freedom from ozone induced cracking\textsuperscript{68}. Fillers are widely used in polymer blends and nanocomposites because they can improve the physical properties of the material; blends containing carbon black or clay have been shown to improve the thermal, physical, and gas permeability properties of polymers\textsuperscript{69}. Thus, the addition of carbon black to the rubbers in tires strengthens the individual components of the product.

![Figure 1.1. Tire Design\textsuperscript{64}](image)

However, tread separation can occur as a result of weak adhesion at the polymer interfaces\textsuperscript{70}, which recently causes a lot of problems associated with car accidents\textsuperscript{71}. When immiscible polymers joined together, they repel
each other due to unfavorable enthalpic interactions, making the adhesion between these materials poor. In general, adhesion occurs at polymer interfaces via the migration of polymer chains, diffusion across interfaces and entanglement of polymer chains on both sides. What the tire companies needed at least during the intervening years was a solution to the problem of incompatibility in the sense of covulcanization.
1.5. References


   (c) Albizzati, E.; Giannini, U.; Collina, G.; Noristi, L.; Resconi, L.,
       Publishers, Chapter 2, 11-111.

(c) Koide, Y.; Bott, S.G.; Barron, A.R., Organometallics, 15, 2213, 1995.


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67 www.tiredefects.com


70 www.tiredefects.com/rollover/Default.htm

Chapter II.
Functional Polyolefins and Applications

2.1. Introduction

Polyolefins, especially polyethylene, polypropylene and their copolymers, are used in a wide range of applications, since they incorporate an excellent combination of mechanical, chemical and electrical properties and processability as well as cost effectiveness. These polymers are greatly influencing our day-to-day life ranging from minor items like milk bottles, containers, hoses, carpets to major engineering applications such as tires, car parts and aircraft accessories. So, polyolefins are considered the most unexpensive high performance polymers. Their monomers are mainly produced from the catalytic cracking of hydrocarbons obtained during petroleum processing. Moreover, due to their excellent chemical and physical properties, and the ease of processability and recyclability, polyolefins are considered the most preferred choice among other commercial polymers.

Unfortunately, because of their inert nature which significantly limits their end uses, polyolefins have poor miscibility with other materials and are very difficult to afford adhesion, painting, or dyeing. Therefore, the functionalization of polyolefins is very important, however, because of their chemical inertness, it is very difficult to modify them chemically. Indeed, it has long been a scientific challenge in exploring the routs to the functionalization of polyolefins, specially polyethylene and polypropylene.
Various methods have been employed to alter the chemical and physical properties of polyolefins. Conventionally, there are two routes to the functionalization of polymers; including direct incorporation of functional monomers by copolymerization with α-olefins and post modification of existing polymers.

2.2. Methods of Functionalization of Polyolefins

2.2.1. Direct Copolymerization of Functional Monomers

It would be ideal to produce functionalized polyolefins by direct copolymerization of olefins with functional monomers. As early as in the 1950’s, Natta realized the importance of introducing functional group into polyolefins, he and his coworkers investigated the polymerization of metal based monomers\(^2\). They found that Si and Sn containing α-olefinic monomers, \((\text{CH}_3)_3\text{M-}(\text{CH}_2)_3\text{CH=CH}_2\), where M is Si or Sn, could be polymerized although yields were very low. The copolymers of α-olefins and Si-containing monomers were also synthesized. However, very limited further reactions were done from Si- and Sn- containing polyolefins\(^3\). Neither Si nor Sn groups are polar enough to greatly affect the polymer properties or versatile enough for further functionalization reactions.

Since halo-groups had been thought stable to Ziegler-Natta catalysts due to the existence of halogen in the catalysts, a considerable amount of research were aimed at the Ziegler-Natta copolymerization of ω-halo-α-olefins and α-olefins\(^4\). However, it was found that the halogen containing monomers could be polymerized only if the Lewis acidity of the catalyst was decreased by complexing with Lewis base like pyridine and the space
between halogen and double bond was large enough. Copolymers of propylene, 1-hexene with 8-bromo-1-octene have been synthesized\textsuperscript{4d}. The studies have shown that $\omega$-halo-$\alpha$-olefins and $\alpha$-olefins polymerization is favored by increasing the size of halogen atoms (-I > -Br > -Cl > -F), as well as increasing the number of spacers between the halogen and the double bond\textsuperscript{4e}. Unfortunately, the more desirable (reactive) halogens, such as -Br and -I, are not stable at the processing conditions of polyolefins, especially at high temperature. Only chloro-containing monomers may be practical. Most recently, Bruzaud et al\textsuperscript{5} reported co- and terpolymerization of $\omega$-halo-$\alpha$-olefins with $\alpha$-olefins in the presence of $rac$-Et(Ind)$_2$ZrCl$_2$/MAO catalyst. The results showed that 5-chloropent-1-ene could be neither homopolymerized nor copolymerized with $\alpha$-olefins. On the other hand, 11-chloroundec-1-ene with a larger spacer between chlorine and double bond was copolymerized with ethylene and terpolymerized with ethylene and propylene under certain conditions in a relatively low yield. However, it could not be homopolymerized. The resulting chloro-containing polyolefins were converted into other functional groups under some inconvenient transformation reaction conditions.

In most cases, monomers containing polar functional groups can not be polymerized by Ziegler-Natta catalysts, presumably due to the high reactivity of the metal-carbon bonds present in organometallic compound and to the fact that both catalyst components are Lewis acidic and consequently tend to interact with monomers containing atoms with lone pair of electrons, such as O and N, to form complexes which are too stable to be active for polymerization\textsuperscript{6}. This is called catalyst poisoning\textsuperscript{7}. 
Theoretically, there are two approaches, including catalyst modification and functional group protection, could be used to address this problem.

The modification of catalysts is usually done by the addition of a weak Lewis base as a third catalyst component. This Lewis base weakly complexes the catalyst to decrease its Lewis acidity. Unfortunately, this modification usually also decreases the catalyst activity and stereoregularity. One example for this approach was the copolymerization of olefins with halogen-containing monomers, as described above\(^4\).

The protection of functional groups is the most widely studied method in the direct copolymerization approach. One route was to use bulky alkyl groups on both hetero-atoms on the functional monomers and aluminum component of the catalysts to sterically hinder the interaction between them. Ginannini et al\(^8\) systematically studied the polymerization of \(\text{CH}_2=\text{CH-(CH}_2)_n\text{-NR}_2\) in the presence of \(\text{TiCl}_3\cdot\text{AA/AIR}_m\text{Cl}_3\cdot\text{m}\) catalyst systems. They found that, the influence of the nitrogen atom was minimal when \(\text{R}\) group was isopropyl or isobutyl group and \(\text{R'}\) was also a bulky branched alkyl group. On the other hand, nitrogen was found to completely deactivate the catalyst when \(\text{R}\) or \(\text{R'}\) was methyl, ethyl, or 1-butyl groups. It was shown that the presence of branched alkyl groups bonded to both nitrogen atoms of amine monomers and aluminum atoms of the organometallic compound minimized the formation of a complex between the two compounds. The minimum number of spacers between nitrogen atom and double bond was found to be 3 to prevent electronic and steric deactivation, even though bulky groups (\(\text{R}\)) were used. Bertolini et al\(^9\) used 2,2,6,6-tetramethyl piperidine containing norbornene monomer to produce a self-stabilized
polyolefin by direct copolymerization with ethylene in the presence of \( \text{Vac}_3/\text{AlEt}_2\text{Cl} \) catalyst system, the functional monomer did not inhibit (but retarded) polymerization due to the steric hindrance.

The second route to prevent catalyst poisoning was to protect functional groups by pre-complexing them with aluminum alkyl (electron-withdrawing) compounds before polymerization. By prior complexing with AlEt\(_2\text{Cl}\), 5-N,N-dimethylamino-1-pentene and 5-N,N-diethylamino-1-pentene were polymerized to amorphous high polymers by TiCl\(_3\).AA/AlEt\(_2\text{Cl}_2\) catalyst\(^8\). Datta, et al.\(^{10}\) conducted a terpolymerization of ethylene, propylene, and a third functional monomer in the presence of a Ziegler-Natta catalyst. The functional group was protected by masking with trialkyl aluminum. The resulting aluminum containing terpolymer precursor was then unmasked to give a functional EP copolymer. Wilen et al.\(^{11}\) reported copolymerization of propylene and 4-(\(\omega\)-alkenyl)-2,6-di-t-butylphenol using a highly active supported TiCl\(_4\)/MgCl\(_2\)/AlEt\(_3\) catalyst. The 4-(\(\omega\)-alkenyl)-2,6-di-t-butyl phenol was pretreated with a stoichiometric molar amount of trimethylaluminum prior to copolymerization. The results showed that the copolymerization yield as well as the phenol content of the resulting copolymer increased with an increase in the number of spacer atoms between double bond and phenol group. Purgett, et al.\(^{12}\) investigated the Ziegler-Natta polymerization of a series of \(\omega\)-alkenoate derivatives. Polymerization was possible only if functional groups were precomplexed with alkylaluminum compounds and the number of spacer atoms was greater than 3. Landoll, et al\(^{13}\) synthesized polypropylene ionomers by copolymerization of propylene and ethylchloroaluminum-10-undecennoate.
The functional monomer, ethyl chloroaluminum-10-undecennoate, was very similar to the pre-complexed monomers except that the electron-withdrawing aluminum was directly attached to the ester oxygen. Most recently, Aaltonen, et al.\textsuperscript{14} reported a series of studies in the direct copolymerization of ethylene, propylene with functional monomers by metallocene catalysts. Similar results were observed except higher activity comparing to heterogeneous Ziegler-Natta catalysts. Presumably, the functional groups were protected by large excess of MAO required for polymerization.

The third route used to minimize the interaction between functional groups and catalysts to reduce the electron-donating ability of heteroatoms in the functional groups by attaching silane substituents onto the functional groups. Ginannini et al.\textsuperscript{8} protected O and N with \(-\text{Si}(\text{CH}_3)_3\) group to sterically shield and decrease electron density of O and N atoms through the \(\text{d}\pi-\text{p}\pi\) bond between Si and O or N. Siloxanic and silazanic monomers could be polymerized only if a bulky hindered aluminum alkyl was used and the number of spacer was greater than three. After polymerization, the O-Si and N-Si bonds were hydrolyzed in acidic alcohol solutions to give -OH and -NHR containing polymers. More recently, Kesti, et al.\textsuperscript{15} reported the homopolymerization of \(\alpha\)-olefins containing silyl-protected alcohols and tertiary amines using cationic group 4B metalloecne catalysts.

So far, the direct copolymerization approach has achieved only limited success in the functionalization of polyolefins due to several reasons. First, the functional monomers, although protected, always retard the polymerization; the catalytic activity is too low to be practically useful.
Second, bulky groups make the monomer difficult to be incorporated into polyolefins, so the concentration of functional group is very limited. In addition, the functional groups with bulky substituents in polymers are usually too inert to be useful in many applications due to the same steric reason. Last, multiple reaction steps increase the production cost, a major concern in commercialization.

However, in Chapter IV of this thesis, permissible results will be discussed through the copolymerization of ethylene and propylene in the presence of some protected OH and NH$_2$ containing monomers using selective metallocene catalysts. The major objective is to incorporate only one functional group at the polymer chain end. Since only a minimal amount of functional group involved, the concerns in the protecting approach are significantly reduced. With the combination of metallocene catalyst, selected protection group of the polar monomer, and a controlled hydrogen pressure, it’s possible to direct the incorporation of the polar group, from copolymerization mode to chain transfer mode, to form OH or NH$_2$ terminated EP copolymers with a broad range of polymer molecular weight and E/P mole ratios.

### 2.2.2. Modification of Existing Polyolefins

Chemical modification of existing polyolefins (post process) could provide functional polyolefins that would be difficult or impossible to obtain by direct copolymerization. Unfortunately, due to their highly chemical inertness, regular polyolefins are extremely difficult to be chemically
modified. In many cases, this type of modification results in serious side reactions, such as degradation and crosslinking reactions.

Most of the commercial modification processes are based on post-polymerization process. Numerous papers and reports have been published and summarized by several recent review papers\textsuperscript{16} to address the mechanism of this modification process. Usually, the functionalization reaction of polyolefin involves activation of polymer chain by breaking some stable C-H bonds, as illustrated in Scheme 2.1, because there are no any other facial reaction sites in the saturated PE, PP and EPR polymers. This leads to the formation of free radicals along the polymer chain\textsuperscript{17}. The resulting polymeric radicals then undertake addition reactions in the presence of functional monomers, which is accompanied with many undesirable side reactions such as crosslinking, degradation and homopolymerization as shown in Scheme 2.1\textsuperscript{18}. Overall, this process only affords low degree of functionalization and is far away from the ideal one. The products are barely satisfactory for industrial need.

The ability to create radical sites along the polymer backbone is essential for a free radical modification process. Since the stability of the carbon radical decreases in the order tertiary $>$ secondary $>$ primary, the susceptibility of hydrogen abstraction follows the same trend. Accordingly, among the three most investigated polyolefins, PE, PP and EPR, PP is the easiest to be attacked by free radicals. PE is the most difficult one, where chain rigidity and crystallinity also hinder the reactions to some extent\textsuperscript{19}. 

In general, free radical modification processes require high temperatures. In addition to functionalization reaction, there are many potential side reactions, as illustrated in Scheme 2.1. For polymeric radicals on tertiary carbons, such as the PP case, \(\beta\)-scission reactions usually take place prior to the functionalization reaction. In fact, this chemistry has been
used to produce PP resins with controlled rheology (CR) during melt-extrusion\textsuperscript{16b}. However, $\beta$-scission reactions are always undesirable to produce low molecular weight polymers during functionalization reactions. Another undesirable side reaction is a coupling between polymeric radicals, which results in a cross-linked product. For PP, degradation is the most significant side reaction while cross-linking is the main problem for PE. Both degradation and cross-linking are significant for EPR rubber. In addition, homopolymerization, chain transfer to monomer, solvent, and disproportionation termination reactions are all possible, and in most cases these reactions dominate to form deeply colored materials. The same problems extend to all free radical modifications involving other free radical sources, such as radiation, plasmas, etc. Tremendous efforts have been made to minimize these undesirable side reactions. The effects of initiators, functional monomers and reaction conditions have been extensively investigated\textsuperscript{20}. To minimize side reactions with solvent, free radical processes are usually performed in bulk, however, overall results were always unsatisfactory.

Although many functional monomers have been used for the functionalization of polyolefins in post modification processes, the most investigated monomer is maleic anhydride (MA)\textsuperscript{21}. MA modified polyolefins are the most widely used commercial functionalized polyolefins. The double bond of maleic anhydride is very reactive to free radicals and due to steric hindrance, has very low tendency to homopolymerize. Therefore, homopolymerization during functionalization reactions is minimal\textsuperscript{22}. Most importantly, the anhydride group is very reactive to many reagents. All these advantages plus its cost effectiveness make MA modified
polyolefins very attractive and useful commercial products. Various reaction conditions including solution, suspension, and melt-extrusion have been used to produce MA modified polyolefins. Reactive extrusion is the most popular process in industrial production, although polymer degradation is still significant and a very low concentration of MA can be incorporated.

Halogenation is another important method to introduce functional groups onto polyolefin backbone. The halogenation reactions also involve free radical process. The most widely used commercial process is performed by bubbling halogen into an aqueous suspension of polyolefins in the presence of an initiator such as UV light or peroxide. Again, like other free radical processes, halogenation reactions are also accompanied by many undesirable side reactions.

Surface modification of polyolefins has attracted great interest, since it is considered as an easy, cost-effective and environmentally friendly method to introduce functional groups on polyolefins to improve surface properties (such as adhesion) without altering bulk properties. Surface modification can be accomplished in many ways including physical treatments and chemical modifications. Chemical modifications are the most effective and widely studied methods. Bergbreiter summarized the different approaches used in the surface modification of polyethylene and polypropylene in his review paper. Surface modification of polyolefins induced by cold plasma has attracted considerable attention. The formation of peroxide radicals, after treatment with various cold plasmas such as CO₂, O₂ and CF₄, etc., allow the subsequent grafting of acrylate monomers and
other functional groups on the PP surface\textsuperscript{27}. Radiation-induced modification has also been widely used\textsuperscript{28}.

Overall, post-modification of polyolefins always involves free radical mechanism and requires severe reaction conditions such as high temperature, radiation, plasmas, etc., which would be inevitably accompanied by many undesirable side reactions, namely degradation of the polymer backbone and cross-linking. In addition, it would be very difficult to control the concentration and homogeneity of the functional group in the polyolefins.

As a result, either direct or post-polymerization processes have their own limitations that greatly hinder their successful applications. It is also known that the preparation of chain end functionalized polymers has been largely limited to the living polymerization in which the chain end comes from the initiator bearing it\textsuperscript{29} or by control termination reaction of the living polymerization\textsuperscript{30}. These types of functionalization have the limitations that there are only very few transition metals coordination catalysts exhibiting living polymerization\textsuperscript{31}. Besides, the living polymerization is very expensive polymer preparation process, only producing one polymer chain per initiator.

\textbf{2.2.3. Functionalization of Polyolefins via Reactive Approach}

Since both direct copolymerization and post modification approaches have only achieved very limited success and have many drawbacks, there has been growing interest in exploring other routes to facilitate functionalization of polyolefins that can provide products possesses well-
controlled compositions, molecular weights and structures. Our group, led by Professor Chung, has developed a novel approach for the functionalization of polyolefins, which is called: “Reactive Polyolefin Approach”. In this method, functionalization of polyolefins can be achieved by the copolymerization reaction of α-olefin and a selected ‘reactive’ comonomer using metallocene catalysts.

The first step includes the synthesis of reactive polyolefins via copolymerization of α-olefins with reactive monomers in the presence of Ziegler-Natta or metallocene catalyst systems. The formed reactive copolymer serves as an intermediate for the preparation of functional polyolefins, which involve very effective and selective transformation reactions, as illustrated in Scheme 2.2. This approach provides precise control on the distribution, location (side chains or chain-end), and concentration of functional groups. The structure of the copolymer was designed in such a way that the “reactive” site is pendent away from the polyolefin backbone. Accordingly, reactive polyolefins with relatively well-defined composition and structure were achieved, and undesirable side reactions, such as degradation or cross-linking were completely avoided.

As will be discussed later, functional polymer formed has the advantages of exhibiting high molecular weight with relatively narrow distribution (Mw/Mn ≥2) and desirable physical properties (such as melt flow, melting temperature, glass transition temperature, crystallinity…etc.), typically as those of the unmodified materials. Moreover, the introduced functional groups serve as interesting active sites for many applications such
α-Olefin + “Reactive” Comonomer

Polyolefin Copolymer Containing Reactive Side Groups

Functionalization Reaction

Graft-From Reaction

Polyolefin Containing Functional Side Groups or Chain-ends

Graft Copolymer

Scheme 2.2

as adhesion improvement\textsuperscript{34}, subsequent polymerization or coupling reaction to form block and graft copolymers\textsuperscript{35}. There are two different approaches for the synthesis of graft copolymers. In one method, the functional groups on the polymer backbone act as the initiator for the polymerization of another monomer, the so called ‘graft-from’. The other method, ‘graft-onto’, involves the termination of a growing polymer chain end by the functional group on the polymer backbone or by the coupling between the polymer having the end functional group with the pendant functional group on the polymer backbone\textsuperscript{36}, (Scheme 2.3).
One of the most interesting applications of the reactive polyolefin approach is the ability to improve compatibility of the polymer blends. This can be accomplished by the addition of a suitable polyolefin graft copolymer to the blend which reduces the domain sizes and increase the interfacial interaction between domains\textsuperscript{37}.

In general, graft copolymers present unique properties obtained from either of there separate homopolymers which act as compatibilizers when employed in multiphase polymer system. By adding a suitable compatibilizer containing segments identical or similar to the blend components, the incompatible polymer blends alter their morphology, by decreasing the size of the dispersed domains and enhancing the interaction between the phases. This results in improved physical properties, such as tensile and impact strengths\textsuperscript{38}.
This functionalization approach is a relatively new one in which a reactive copolymer intermediate can be effectively synthesized and subsequently interconvert to functional polymer. By this technique, several new reactive comonomers can be effectively incorporated into the polyolefin in the side chains or at the chain end to produce new polyolefin products, including functional graft or block copolymers, respectively.

### 2.3. Reactive Comonomers

The design of a comonomer containing a reactive group is considered the key factor in the reactive functionalization approach and should fulfill the following requirements. The reactive comonomer should have good copolymerizability with α-olefins and should be soluble in hydrocarbon polymerization media. Besides, the reactive group must be stable to metallocene catalysts and must be facial in the subsequent interconversion reactions to form polar groups under mild reaction conditions\(^\text{\textsuperscript{18}}\). In addition, the reactive monomer should be commercially available or easy to synthesize and not too expensive.

Several new reactive comonomers have been effectively incorporated into polyolefins, where our group has conducted exclusive research in this particular interesting field. Three reactive comonomers - including boron monomers \[^{[39]}\], p-methylstyrene \[^{[40]}\] and divinylbenzene \[^{[41]}\] - have been incorporated into a broad compositional range of polyolefins with narrow molecular weight and composition distributions. The formed polyolefin copolymers, containing these reactive groups are very versatile in the subsequent transformation reactions, both in functionalization and graft
reactions [42]. In addition, the concentration of the functional groups is proportional to the concentration of the reactive sites.

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH} \\
\text{(CH}_2\text{)}_n \quad \text{B} \\
\text{CH}_3
\end{align*}
\]

Borane Monomer  p-Methystyrene  Divinylbenzene

2.3.1. Borane Monomers

Borane monomers were found to be convenient choice when copolymerized with \(\alpha\)-olefins to prepare borane-containing polyolefins. The good solubility of these monomers and their copolymers in hydrocarbon solvents in addition to the stability and the versatility of the borane groups make the advantage of these monomers. A broad range of borane-containing polyolefin copolymers with uniform structure has been prepared\(^{43}\). Subsequently, the incorporated borane groups can be effectively interconverted to various functional groups under mild reaction conditions and also easily transferred to polymeric radicals for graft-from reaction to prepare some polyolefin graft copolymers with controllable composition and molecular microstructures.
2.3.2. \textit{para}-Methylstyrene Monomer

Besides its commercial availability, \textit{p}-methylstyrene has the advantages of having easy incorporation into polyolefins and versatility of the formed copolymers\textsuperscript{44}. The benzylic protons are known to be facial in many chemical transformations, oxidation\textsuperscript{45}, halogenation\textsuperscript{46}, and metallocene\textsuperscript{47} forming desirable functional groups at the benzylic position under mild reaction conditions. Moreover, the benzylic protons can readily be lithiated to form stable anionic initiator for living anionic graft-from polymerization\textsuperscript{48}. Graft-from polymerization of methylmethacrylate (MMA) and acrylonitrile (AN) in non polar hydrocarbon solvents were successfully performed using this chemistry with negligible amount of ungrafted polyethylene homopolymer\textsuperscript{49}.

In chapter III of this thesis, we will discuss the copolymerization of ethylene and propylene in the presence of \textit{p}-methylstyrene (\textit{p}-MS). From our detailed study to this system, we are able to control the mode of the \textit{p}-MS incorporation; copolymer or chain-end depending on the reaction conditions (i.e. catalyst system and hydrogen pressure).

2.3.3. Diene Monomers

Another way to prepare a functionalized olefin-based polymer is to copolymerize or terpolymerize \textit{\alpha}-olefins with diene monomers. Many diene monomers, including symmetric aliphatic\textsuperscript{50}, asymmetric aliphatic\textsuperscript{51}, cyclic\textsuperscript{52}, and aromatic dienes\textsuperscript{53} have been extensively studied (scheme 2.4). Introducing of unsaturation to polyolefins has long been an area of
increasing interest in polyolefins field because of the potential chemical reactivity of the unsaturation. Dienes are believed to be very convenient monomers for the introduction of functional groups into the polymers if only one C=\( \text{C} \) double bond is participated in the copolymerization while the other remain intact. The C=\( \text{C} \) double bonds left in the resulting copolymers can be further converted into other functional groups\textsuperscript{54}. Unsaturated polyolefins are normally synthesized by copolymerization of \( \alpha \)-olefins with diene monomers in the presence of Ziegler-Natta catalysts, including conventional heterogeneous titanium catalysts, homogeneous vanadium catalysts and metallocene catalysts.

There have been many papers and patents reported in this area. Most of them dealt with terpolymerization reactions of ethylene, propylene and diene to synthesize EPDM terpolymer. The dienes used for commercial EPDM are primarily 5-ethyldiene-2-norbornene\textsuperscript{55}, or 1,4-hexadiene\textsuperscript{56}, and the catalysts are most vanadium based Ziegler-Natta catalysts. However, for both technical and economical reasons, the incorporation of these dienes in ethylene-propylene chains are very limited (less than 2 mol\%). The presence
of dienes dramatically decrease the catalyst activity, and side reactions also take place during the polymerization resulting in chain branching and crosslinking. When 1,5-hexadiene and 1,7-octadiene are used as comonomers, it is recognized that the cyclization of dienes predominantly occurs. Furthermore, it is found very difficult to copolymerize olefins with linear \( \alpha, \omega \)-dienes selectively without any side reactions such as cyclization and crosslinking\(^\text{57}\). However, 1,4-hexadiene was reported as a satisfactory termonomer for EPDM using metallocene catalysts. Although 1,4-hexadiene was found to reduce the polymerization activity, but high concentration of diene in the terpolymer could be achieved\(^\text{58}\). Almost no cyclization or crosslinking were observed during the terpolymerization, indicating that the di-substituted (internal) double bond in the 1,4-hexadiene is completely inert to metallocene catalysts.

Recent report\(^\text{59}\) showed that in EPDM synthesis, both linear non-conjugated diene, 5,7-dimethyl-octa-1,6-diene (5,7-DMO), and 5-ethylidene-2-norbornene (ENB) rapidly reduce the activity of vanadium based catalysts due to the rapid reduction of the active sites. The reduction was proposed to associate with the di- and tri-substituted double bond in the dienes. However, both double bonds in ENB were found very sensitive to acidity of catalyst components resulting in cationic side reactions that were believed to be responsible for the chain branching and crosslinking. This factor limited the utilization of ENB to a low concentration range. The non-conjugate asymmetric linear diene, on the other hand was found less sensitive to cationic reactions. The mono-substituted double bond selectively inserted into ethylene/propylene chain leaving multi-substituted double bond pendant away from the polymer backbone, which results in a well controlled
EPDM structure. The same authors\textsuperscript{60} also reported a comparison study of catalyst effect on EPDM synthesis in the presence of both dienes. They found that metallocene catalysts have many advantages over the conventional vanadium based catalysts in terms of catalyst activity, diene incorporation ability and polymer structure. The results indicated that the reactivity of the linear diene was close to that of cyclic diene. Both dienes have high selectivity in the presence of metallocene catalysts and the catalysts are relatively stable to the diene-induced reduction reactions. However, the metallocene catalysts still suffered activity depression by the presence of these diene monomers.

1,3-Butadiene, a conjugated diene, was also used as a comonomer or termonomer for the synthesis of unsaturated polyolefins in the presence of titanium based\textsuperscript{61}, vanadium based\textsuperscript{62}, and metallocene catalysts\textsuperscript{63}. In each case, the conjugated diene was found to reduce the polymerization activity as well as the polymer molecular weight. The insertion of butadiene into polymer chain was found to be mainly via trans-1,4-insertion\textsuperscript{64} which maintains double bonds in the polymer backbone. However, some cis-1,4-insertion, cyclization and small amount of 1,2-insertion, were also observed. The drawbacks in using this diene are associated with the formation of unsaturation and the generation of allylic tertiary carbon atoms within the resulting polymer backbone. Both structures are responsible for the poor thermal and UV-light resistance of the resulting polymers.

Divinylbenzene (DVB) and 4-(3-butenyl)styrene (4-BSt) were also reported as co- or termonomers for polymerization with $\alpha$-olefins. 4-BSt is a very distinctive diene monomer because of its two double bonds, $\alpha$-olefin
and styrene olefin, which can engage in polymerization reaction under very different catalyst systems. It was reported that the polymerization selectively takes place on the α-olefin unit and produce a copolymer with many pendant styrene units, however, the incorporation of 4-BSt was found to be very small\textsuperscript{65}. In the case of using divinylbenzene (DVB), most polymerization methods, including free radical, cationic, and anionic processes, result in polymers with crosslinking structures. Several reports\textsuperscript{66} discussed the copolymerization of α-olefins (ethylene and propylene) and DVB by Ziegler-Natta catalysts. The resulting polymers were very inhomogeneous, showing broad composition and molecular weight distribution. The DVB content in ethylene and propylene copolymers was below 0.3 mol% and the overall DVB conversion was only a few percent in each case. In addition, the catalyst activity was inversely proportional to the concentration of DVB in the monomer feed. The extent of side reactions was not reported, and may be very difficult to determine due to the very low concentration of DVB in the copolymer. Machida et al\textsuperscript{67} reported the copolymerization reaction of ethylene and DVB using metallocene catalyst. In general, the copolymers obtained have a long-chain branched molecular structure. In other words, some of the incorporated DVB units engaged in double enchainments with both olefinic groups.

Led by Professor Chung, our group has been investigating the metallocene catalysts that can prepare α-olefin/DVB copolymers with a linear, and well-defined molecular structure\textsuperscript{68}. In general, there are two extremes of metallocene catalysts\textsuperscript{69}; one extreme is the class of catalysts with non-bridged ligand geometry, such as Cp\textsubscript{2}ZrCl\textsubscript{2} with a small opening
active site that can incorporate a very low concentration of such dienes. The other extreme is the class of catalysts with constrained ligand geometry, such as [(C₅Me₄)SiMe₂N(⁴-Bu)]TiCl₂ with a large opening active site that can incorporate both double bonds of the diene monomer, which results in copolymers with branched and/or cross-linked structures. However, one can control the mode of diene incorporation into the polymer chain in such a way that only one double bond is incorporated, leaving the other double bond as pendant side chain. This can be done by the perfect choosing of the metallocene catalyst with narrowly defined opening at the active site. An extensive research in our group⁷⁰ has been performed in such area to produce functional polyolefins with linear structure and contain pending styrenic moieties. The reaction mechanism of the diene during the E/P copolymerization is illustrated in Scheme 2.5⁷¹.

![Scheme 2.5](image-url)

Overall, the valuable unsaturated polyolefins should have unsaturation exclusively in the side chain, pendant far away from the polymer backbone,
controllable composition and molecular weight distribution without crosslinking. In addition, the unsaturation should be versatile for the subsequent modification at moderate reaction conditions.

The pendant styrenic groups could be incorporated into metallocene graft-onto polymerization system. By this way, EPDVB could be transformed to EP-g-PP graft copolymer containing continuous polypropylene domains and discrete EP domains, which exhibits high impact strength\textsuperscript{72}.

In chapter V of this thesis, EPDVB terpolymer will be used in anionic graft-from and graft-onto polymerization. EPDVB terpolymer was lithiated to generate pendant benzylic anions which could initiate living anionic polymerization of isoprene monomer. These graft copolymers may be very useful in improving the adhesion between the different rubbers involved in tires, and consequently, prevent tread separation that can occur as a result of weak adhesion at the polymer interfaces.

In chapter VI, we will discuss another valuable application for EPDVB. It could be used in the synthesis of reactive rubber particles via crosslinking in an emulsion or suspension processes. These reactive rubber particles can find a wide range of applications.
2.4. References


(b) Aaltonen, P.; Fink, G.; Lofgren, B.; Seppala, J., *Macromolecules*, 29, 5255, **1996**.


37 T. C. Chung; D. Rhubright, *Macromolecules*; 27,1313, **1994**.

38 (a) Lohse, D.J.; Datta, S.; and Kresge, E.N. *Macromolecules*, 24 561, **1991**.


(b) Chung, T.C., *US Patent* 4,812,529 (**1989**).

(c) Ramakrishnan, S.; Berluche, E.; and Chung, T.C., *Macromolecules*, 23, 378, **1990**.


41 Chung, T.C. and Dong, J.Y., *US Patent* 6,096,849 (**2000**).


(b) Chung, T.C., *Olefin Polymerization; Emerging Frontiers* (Arjunan, P.; McGrath, J.E.; and Hanlon, eds) ACS Book, 749, 104, **1999**.


(b) Powers, K.W.; Wang, H.C.; Chung, T.C.; Jias, A.J. and Olkusz, J.A.,

(a) Onopchenko, A.; Schulz, J.G.D. and Seekircher, R.J., J. Org. Chem.,
37, 1414, 1972.


(b) Jones, R.G. and Matsubayashi, Y., Polymer, 33, 1069, 1992.
(c) Pini, D.; Settambolo, R.; Raffaelli, A. and Salvadori, P.,

(a) Nagasaki, Y. and Tsuruta, T., Makromol. Chem., Rapid Commun., 7,
437, 1986.
(b) Bonaccorsi, F.; Lezzi, A.; Prevedello, A.; Lanzini, L. and Roggero,


Chung, T.C. Metallocene-based reactive polyolefin copolymers

(b) Etherton, B.P.; McAlpin, J.J.; Kresge, E.N., U.S. Patent 5,504,171
(1996).


(a) Chung, T.C. and Dong, J.Y., *US Patent* 6,096,849 (**2000**).
(b) Machida, S.; Tani, N., *Jap. Patents* 05-194665 and 05-194666 (**1993**).

(b) Sivaram, S.; Marathe, S., *Macromolecules*, 27, 1083, **1994**.

(c) Ver Strate, G., *Encyclopedia of Polymer Science and Engineering*, J. Wiely, NY, 6, 522, **1985**.


62 (a) Bruzzone, M.; Carbonaro, A.; Corno, C., *Makrmol. Chem.*, 179, 2173, **1978**.

(b) Lin, S.; Wu, Q.; Sun, L., *Catalytic Olefin Polymerization*, Ed. Keii, T.; Soga, K., El-Sevier, Amsterdam, p245, **1989**.


(c) Bruzzone, M.; Carbonaro, A.; Corno, C., *Makrmol. Chem.*, 179, 2173, **1978**.

(d) Lin, S.; Wu, Q.; Sun, L., *Catalytic Olefin Polymerization*, Ed. Keii, T.; Soga, K., El-Sevier, Amsterdam, p245, **1989**.


(c) Chung, T. C.; Lu, H. L.; Ding, R. D. Macromolecules 1997, 30, 1272.


Chapter III.  
Synthesis of EPR Containing Pendent and Chain-end Styrenic Functional Groups

3.1. Introduction

Metallocene technology has opened up the unprecedented opportunity for preparing polyolefins with well-defined molecular structures and predictable physical properties. In the copolymerization reactions, the well-defined single catalytic site can be tailor designed for incorporating high α-olefins into copolymers with high comonomer incorporation, high catalyst activity, and narrow composition and molecular weight distributions. This well-controlled polymerization mechanism was also extended to chain transfer reaction for controlling the polymer chain end structure and polymer molecular weight, while still maintaining high catalyst activity. Some polyolefin homopolymers -- including polyethylene (PE), polypropylene (PP), and syndiotactic polystyrene (s-PS) -- with predetermined molecular weight and a selective terminal group (including polar groups) have been prepared by using several specially-designed chain transfer agents, such as silanes, boranes, allyl alcohol and styrene/hydrogen, in conjunction with selective metallocene catalysts.

Among the chain transfer agents, the styrene system is the most intriguing one, in which styrene usually serves as a comonomer in most metallocene catalyses. However, we recently have demonstrated the possibility of altering the styrene comonomer mode to chain transfer mode
in PE and PP cases\textsuperscript{7} using Cp\textsubscript{2}ZrCl\textsubscript{2} and \textit{rac}-Me\textsubscript{2}Si-[2-Me-4-ph(Ind)]\textsubscript{2}ZrCl\textsubscript{2} catalysts, respectively, under a sufficient amount of H\textsubscript{2}. It’s very interesting to expand this facile reaction process, involving simple reagents and a one-pot process, to prepare other important polyolefins, such as ethylene/propylene (EP) copolymers, containing a terminal reactive group. This environmentally-stable EP copolymer\textsuperscript{9} is not only used as an elastomer for tires and automotive parts, but also as a viscosifier in lube oils. An EP copolymer with a terminal functional group, such as OH, COOH, NH\textsubscript{2} with strong metal-coordination capability - as will be discussed here in this chapter and in chapter IV of this theses - would be a very desirable additive in motor oils that could provide both viscosity and detergent functions.

3.2. Experimental Details

3.2.1. Instrumentation and Materials

All \textsuperscript{1}H NMR spectra were recorded at room temperature on a Bruker AM-300 spectrometer with the DISNMR software. The NMR samples were prepared in d-chloroform that is a good solvent for all polymers. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution cast films on KBr windows. The molecular weight was determined by a Waters GPC that was operated at 35\textdegree C with a refractive index (RI) detector and a set of \(\mu\)-Styrage\textsubscript{6}, \(\mu\)-Styrage\textsubscript{5}, \(\mu\)-Styrage\textsubscript{4}, and \(\mu\)-Styrage\textsubscript{3} Å pore size in series. A flow rate of 0.7 ml/minute was used and the mobile phase was THF. The calibration curve was established by measuring polystyrene standards.
All O₂ and moisture sensitive manipulations were performed inside an argon filled Vacuum Atmosphere dry box equipped with a MO-40-1 dry-train. p-Methylstyrene (p-MS) was dried and distilled over calcium hydride under argon. High-purity grade ethylene and propylene gases were obtained from MG Industry and were used as received. Methylaluminoxane (MAO) (10 wt%), rac-Et(Ind)₂ZrCl₂ (Aldrich), Diphenylsilyl (cyclopentadienyl-9-fluorenyl)ZrCl₂ (Crompton), and (C₅Me₄)₂SiMe₂N(t-Bu)TiCl₂ (Boulder Scientific) were used as received. rac-Me₂Si-[2-Me-4-ph(Ind)]₂ZrCl₂ was prepared as described in the literature¹⁰. All solvents were deoxygenated by argon purge before refluxing with sodium/benzophenone for 48 hours and then distilling from their respective green or purple solution under argon.

3.2.2. Synthesis of 4-(t-butyldimethylsilyloxy) styrene and 4-(t-butyl-diphenyl silyloxy) styrene

Both reagents were synthesized in two steps, following the literature procedure¹¹. In the preparation of 4-(t-Butyldimethylsilyloxy)styrene, 70.4 g (1.02 mol) of imidazole was mixed with 52.4 g (0.42 mol) of 4-hydroxybenzaldehyde and 77.4 g (0.52 mol) of t-butyldimethylsilyl chloride/THF solution in a 500 ml flask equipped with a magnetic stirring bar. The mixture was stirred at ambient temperature for 4 hours before being poured into cold water. The organic layer was separated and extracted with ether, then dried with magnesium sulfate. After evaporating the solvent, 94 g of 4-(t-butyldimethylsilyloxy) benzaldehyde (90% yield), a deep yellow color liquid, was obtained. The second reaction step was performed under a nitrogen atmosphere. In a 500 ml flask equipped with a magnetic stirring bar, 123.6 g (0.38 mol) of methyltriphenylphosphonium bromide suspended
in THF was treated with 149.6 ml (0.19 mol) of \( n \)-butyllithium(2.5 M in hexane). After 1 hour, 80.0 g (0.34 mol) of 4-(t-butyldimethylsilyloxy) benzaldehyde was introduced dropwise into the red solution. The mixture was stirred overnight at room temperature and then poured into cold water. The organic layer was separated by ether extraction and dried with magnesium sulfate. Further purification was performed by distillation under vacuum (10 Torr) at elevated temperature (80°C). 65 g of 4-(t-butyldimethylsilyloxy) styrene was obtained with a yield of more than 90%. Its structure was confirmed by \(^1\)H NMR spectrum.

3.2.3. Polymerization of E/P/p-MS with and without \( H_2 \)

In a typical reaction (run II-B-9 in Table 3.2), a Parr 300 mL stainless autoclave equipped with a mechanical stirrer was charged with 50 mL of toluene and 4.5 mL of MAO (10 wt% in toluene). The reactor was then injected with 0.5 mL (0.076M) of \( p \)-MS and charged through mass flow controller with 107 psi of ethylene/propylene gas mixture (in ratio 1:1) at 55°C. About \( 2.5 \times 10^{-6} \) mol of \((C_{5}Me_{4})SiMe_2N(t-Bu)TiCl_2\) in toluene solution was then syringed into the rapidly stirring solution under the gas mix pressure to initiate the polymerization. Additional ethylene/propylene gas mixture was fed continuously into the reactor to maintain a constant pressure (107 psi) during the course of the polymerization. After 10 minutes of reaction at 55°C, the polymer solution was quenched with methanol/HCl, and the isolated polymer was purified by repeating a solution/dissolution process by THF and methanol three times before drying under vacuum at 50°C for 8 hours. About 8.4 g of E/P/p-MS terpolymer was obtained with a
catalytic activity of 20,140 kg/mol of Zr.h, and polymer molecular weight of Mn= 111,600 g/mole.

The same procedure was repeated in the presence of hydrogen gas. In a typical reaction (run II-B-11), 50 mL of toluene and 4.5 ml of MAO (10 wt.% in toluene) were mixed in the reactor before purging with hydrogen (15 psi). After injecting with 0.5 mL (0.076M) of \( p\)-MS and charging through mass flow controller with 107 psi of ethylene/propylene gas mixture (in ratio 1:1) at 55\(^\circ\)C, \(2.5 \times 10^{-6}\) mol of \((C_8Me_4)SiMe_2N(t-Bu)TiCl_2\) in toluene solution was then syringed in to initiate the polymerization. Additional ethylene/propylene (1/1 pressure ratio) was fed continuously into the reactor to maintain a constant pressure (122 psi) during the course of the polymerization. After 10 minutes of reaction at 55\(^\circ\)C, the reaction solution was quenched with methanol/HCl, and the isolated polymer was purified by repeating a solution/dissolution process by THF and methanol three times before drying under vacuum at 50\(^\circ\)C for 8 hours. About 9.2 g of EP-t-p-MS polymer was obtained with a catalyst activity of 22,080 kg/mol of Zr.h. and polymer molecular weight of Mn= 27,700 g/mole.

3.2.4. Synthesis of EP-t-St-OSi and EP-t-Si-OH Polymers

EP-t-St-OSi polymers were synthesized by using 4-(\(t\)-butyldiphenylsilyloxy)styrene as a chain transfer agent in E/P polymerization. In a typical reaction (run III-B-5 in Table 3.3), a Parr 450 mL stainless autoclave reactor equipped with a mechanical stirrer was charged with 50 mL of toluene and 4.5 ml of MAO (10 wt.% in toluene) before purging with hydrogen (15 psi). Then 0.2 ml (0.028 M) of 4-(\(t\)-butyldiphenylsilyloxy)styrene was injected
into the reactor and 107 psi of ethylene and propylene (2/1 pressure ratio) was charged, bringing the total pressure to 122 psi at 55°C. About $1.25 \times 10^{-6}$ mol of $(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{N}(\text{t-Bu})\text{TiCl}_2$ catalyst in toluene solution was then injected into the rapidly stirring solution to initiate the polymerization reaction. Additional ethylene/propylene (2/1 ratio) was fed continuously into the reactor to maintain a constant pressure (122 psi) during the course of the polymerization. After 10 minutes of reaction at 55°C, the reaction solution was quenched with methanol and filtered, washed extensively with methanol before drying under vacuum at 50°C for 8 hours. About 4 g of EP-t-St-OSi polymer was obtained with a catalyst activity of 12,460 kg of EP-t-St-OSi/mol of Zr.h.

EP-t-St-OH polymers were prepared in the same way as EP-t-St-OSi polymers, except that the polymer solution after polymerization was quenched with HCl aqueous solution. Alternatively, the isolated EP-t-St-OSi polymer (2 g) was suspended in 50 ml of THF before adding 5 ml of acetic acid and tetrabutylammonium fluoride (2 mol per t-butyldiphenylsilyl group). The mixture was stirred at 50°C for 4 hours and then poured into water. The polymer was then collected by filtration and extensively washed with water for several times. The polymer was dried under vacuum at 50°C for 8 hours. The polymer yield was quantitative.

3.3. Results and Discussions

The chemistry is centered on metalloocene catalysts that can simultaneously carry out ethylene/propylene copolymerization and styrene/hydrogen chain transfer reaction. In other words, the ideal
metallocene catalyst has an active site with an opening that allows effective incorporation of high α-olefins and styrenic monomers, but is also limited to incorporating only one styrenic unit at the polymer chain end in the presence of H₂, as illustrated in Equation 3.1.

\[ \text{CH}_2-\text{CH}_2 + \text{CH}_2=\text{CH} \xrightarrow{\text{Zr-H}} \text{H}_3\text{C}-(\text{CH}_2=\text{CH}_2)_x-(\text{CH}_2=\text{CH})_y \]

\[ \xrightarrow{2,1\text{-insertion}} \]

\[ \xrightarrow{\text{H}_2} \text{CH}_2=\text{CH}_2 \]

\[ \text{CH} = \text{CH}_2 \]

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Ideally, during the course of ethylene/propylene copolymerization, the propagating M\(^{\text{+}}\)-C site (II) will react with a styrenic molecule, such as \(p\)-methylstyrene (\(p\)-MS), via 2,1-insertion\(^{12}\) to form a \(p\)-MS capped propagating site (III). The combination of steric congestion at the active site (especially for propylene and \(p\)-MS insertions) and some acid-base interaction between the adjacent electron-rich phenyl group and metal cation may significantly reduce its reactivity toward monomers, which requires acid-base interaction between an acidic propagating site and basic vinyl monomers. Such a slow down in the propagation rate can significantly enhance the facile hydrogenation of a \(p\)-MS capped propagating site (III) to form chain end functionalized EP polymer (IV) and a new active site (I) for continuing the catalytic cycles. Obviously, the extent of the chain transfer reaction versus copolymerization at the \(p\)-MS capped propagating site (III) will be governed by the catalyst and reaction conditions -- especially the hydrogen pressure.

3.3.1. Catalyst Effects

The goal of the first study was to determine the suitable catalysts that can effectively incorporate \(p\)-MS units in high EP copolymer in ethylene/propylene/\(p\)-MS terpolymerization, before thinking about altering the \(p\)-MS incorporation mode from copolymerization to chain transfer reaction. Four commonly known bridged metallocene catalyst systems were investigated, including \(rac\)-Et(Ind)\(_2\)ZrCl\(_2\) (A), [(C\(_5\)Me\(_4\))SiMe\(_2\)N(t-Bu)]TiCl\(_2\) (B), \(rac\)-Me\(_2\)Si-[2-Me-4-ph(Ind)]\(_2\)ZrCl\(_2\) (C), and Ph\(_2\)Si-[(Cp)(Flu)]ZrCl\(_2\) (D), as illustrated below.
Table 3.1 compares the experimental results of ethylene/propylene copolymerization with and without \( p \)-MS. The combination of IR, \(^1\)H NMR and GPC was used to determine the polymer structure. The mole ratio of ethylene/propylene in the polymer was conveniently determined by an IR technique\(^{13}\) (following ASTM standard method), which compares the integrated intensity between the absorption at 1460 cm\(^{-1}\), corresponding to the C-H bonds, and the absorption at 1379 cm\(^{-1}\), corresponding to the CH\(_3\) group in the propylene unit. GPC determines the polymer molecular weight and polydispersity index (PDI), and \(^1\)H NMR spectrum is used to determine the \( p\)-MS content.

Figure 3.1 shows the \(^1\)H NMR spectra of a comparative set of ethylene/propylene/\( p\)-MS polymers (runs I-A-2, I-B-5, I-C-3, and I-D-3), prepared by \( rac\)-Et(Ind)\(_2\)ZrCl\(_2\) (A), [(C\(_5\)Me\(_4\))SiMe\(_2\)N(t-Bu)]TiCl\(_2\) (B), \( rac\)-Me\(_2\)Si-[2-Me-4-ph(Ind)]\(_2\)ZrCl\(_2\) (C), and Ph\(_2\)Si-[(Cp)(Flu)]ZrCl\(_2\) (D) catalysts, respectively, under similar reaction conditions. The concentration of the incorporated \( p\)-MS units was determined by the integrated intensity ratio of the chemical shift at 0.6 and 1.6 ppm, corresponding to ethylene and propylene units, and the chemical shifts between 7.0 and 7.2 ppm, corresponding to aromatic protons in the \( p\)-MS units, and the number of
Table 3.1 Summary of Ethylene/Propylene/p-MS Terpolymerization Using Various Catalyst Systems

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat.</th>
<th>E/P ratio</th>
<th>E/P pressure (psi)</th>
<th>p-MS (mol/L)</th>
<th>Time/Temp (min/°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mol%)</th>
<th>p-MS (mol%)</th>
<th>Mn (g/mole)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-A-1</td>
<td>A</td>
<td>1/1</td>
<td>70</td>
<td>0</td>
<td>5/60</td>
<td>26,540</td>
<td>48.6/51.4</td>
<td>0</td>
<td>37,000</td>
<td>2.0</td>
</tr>
<tr>
<td>I-A-2</td>
<td>A</td>
<td>1/1</td>
<td>70</td>
<td>0.152</td>
<td>5/60</td>
<td>20,830</td>
<td>58.6/41.0</td>
<td>0.4</td>
<td>30,000</td>
<td>2.1</td>
</tr>
<tr>
<td>I-A-3</td>
<td>A</td>
<td>1/1</td>
<td>70</td>
<td>0.46</td>
<td>5/60</td>
<td>14,500</td>
<td>69.3/29.5</td>
<td>1.2</td>
<td>27,000</td>
<td>2.2</td>
</tr>
<tr>
<td>I-A-4</td>
<td>A</td>
<td>1/1</td>
<td>70</td>
<td>0.76</td>
<td>5/60</td>
<td>11,420</td>
<td>77.6/20.9</td>
<td>1.5</td>
<td>26,000</td>
<td>2.1</td>
</tr>
<tr>
<td>I-A-5</td>
<td>A</td>
<td>1/1</td>
<td>70</td>
<td>1.52</td>
<td>5/60</td>
<td>10,030</td>
<td>79.3/18.4</td>
<td>2.3</td>
<td>22,000</td>
<td>2.1</td>
</tr>
<tr>
<td>I-A-6</td>
<td>A</td>
<td>2/1</td>
<td>70</td>
<td>0.008</td>
<td>5/60</td>
<td>20,740</td>
<td>71.9/28.0</td>
<td>0.1</td>
<td>36,000</td>
<td>2.4</td>
</tr>
<tr>
<td>I-A-7</td>
<td>A</td>
<td>2/1</td>
<td>70</td>
<td>0.152</td>
<td>5/60</td>
<td>17,210</td>
<td>78.5/21.0</td>
<td>0.5</td>
<td>30,000</td>
<td>2.2</td>
</tr>
<tr>
<td>I-A-8</td>
<td>A</td>
<td>2/1</td>
<td>70</td>
<td>0.46</td>
<td>5/60</td>
<td>14,240</td>
<td>83.0/16.1</td>
<td>0.9</td>
<td>24,000</td>
<td>2.1</td>
</tr>
<tr>
<td>I-B-1</td>
<td>B</td>
<td>1/1</td>
<td>107</td>
<td>0</td>
<td>10/55</td>
<td>23,500</td>
<td>35.0/65.0</td>
<td>0</td>
<td>125,000</td>
<td>1.9</td>
</tr>
<tr>
<td>I-B-2</td>
<td>B</td>
<td>1/1</td>
<td>107</td>
<td>0.008</td>
<td>10/55</td>
<td>20,090</td>
<td>37.3/62.5</td>
<td>0.2</td>
<td>102,000</td>
<td>2.1</td>
</tr>
<tr>
<td>I-B-3</td>
<td>B</td>
<td>1/1</td>
<td>107</td>
<td>0.015</td>
<td>10/55</td>
<td>22,130</td>
<td>38.5/61.2</td>
<td>0.3</td>
<td>114,400</td>
<td>1.9</td>
</tr>
<tr>
<td>I-B-4</td>
<td>B</td>
<td>1/1</td>
<td>107</td>
<td>0.076</td>
<td>10/55</td>
<td>20,140</td>
<td>38.2/60.9</td>
<td>0.9</td>
<td>111,600</td>
<td>1.9</td>
</tr>
<tr>
<td>I-B-5</td>
<td>B</td>
<td>1/1</td>
<td>107</td>
<td>0.152</td>
<td>10/55</td>
<td>15,000</td>
<td>41.2/57.0</td>
<td>1.8</td>
<td>100,100</td>
<td>2.0</td>
</tr>
<tr>
<td>I-B-6</td>
<td>B</td>
<td>2/1</td>
<td>107</td>
<td>0</td>
<td>10/55</td>
<td>24,050</td>
<td>51.6/48.4</td>
<td>0</td>
<td>104,500</td>
<td>1.8</td>
</tr>
<tr>
<td>I-B-7</td>
<td>B</td>
<td>2/1</td>
<td>107</td>
<td>0.152</td>
<td>10/55</td>
<td>16,320</td>
<td>52.0/46.9</td>
<td>1.1</td>
<td>94,300</td>
<td>1.7</td>
</tr>
<tr>
<td>I-C-1</td>
<td>C</td>
<td>1/1</td>
<td>107</td>
<td>0</td>
<td>30/60</td>
<td>14,400</td>
<td>52.4/47.6</td>
<td>0</td>
<td>20,000</td>
<td>1.9</td>
</tr>
<tr>
<td>I-C-2</td>
<td>C</td>
<td>1/1</td>
<td>107</td>
<td>0.076</td>
<td>30/60</td>
<td>13,960</td>
<td>60.2/39.5</td>
<td>0.4</td>
<td>20,800</td>
<td>1.9</td>
</tr>
<tr>
<td>I-C-3</td>
<td>C</td>
<td>1/1</td>
<td>107</td>
<td>0.152</td>
<td>30/60</td>
<td>12,030</td>
<td>59.8/39.7</td>
<td>0.5</td>
<td>17,200</td>
<td>1.9</td>
</tr>
<tr>
<td>I-D-1</td>
<td>D</td>
<td>1/1</td>
<td>107</td>
<td>0</td>
<td>5/50</td>
<td>13,390</td>
<td>64.9/35.1</td>
<td>0</td>
<td>240,000</td>
<td>2.1</td>
</tr>
<tr>
<td>I-D-2</td>
<td>D</td>
<td>1/1</td>
<td>107</td>
<td>0.008</td>
<td>5/50</td>
<td>7,920</td>
<td>71.7/28.3</td>
<td>0</td>
<td>186,000</td>
<td>2.2</td>
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<td>I-D-3</td>
<td>D</td>
<td>1/1</td>
<td>107</td>
<td>0.152</td>
<td>5/50</td>
<td>2,980</td>
<td>79.8/20.2</td>
<td>0</td>
<td>146,000</td>
<td>2.0</td>
</tr>
<tr>
<td>I-D-4</td>
<td>D</td>
<td>1/1</td>
<td>107</td>
<td>0.46</td>
<td>5/50</td>
<td>1,730</td>
<td>82.3/17.7</td>
<td>0</td>
<td>116,000</td>
<td>2.3</td>
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Figure 3.1. $^1$H NMR spectra of ethylene/propylene/p-MS polymers prepared by (a) rac-Et(Ind)$_2$ZrCl$_2$, (b) [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$, (c) rac-Me$_2$Si-[2-Me-4-ph(Ind)]$_2$ZrCl$_2$, and (d) Ph$_2$Si[(Cp)(Flu)]ZrCl$_2$ (D) catalysts, respectively.
protons both chemical shifts represent. Several chemical shifts between 2.3 and 2.7 ppm provide detail information about the incorporation modes of \( p \)-MS units (discussed later). The minor peaks at 4.7-4.9 ppm and 2.0 ppm, corresponding to vinylidene and methyl protons in \( \text{CH}_2=\text{C(CH}_3\text{)} \)- unit, and at 5.0 and 5.9 ppm, corresponding to vinyl protons in \( \text{CH}_2=\text{CH-CH}_2\text{-} \) unit, are resulted from spontaneous chain transfer reaction by \( \beta \)-hydride elimination at propylene-caped propagating chain end after 1,2- and 2,1- insertion of propylene\(^{14} \), respectively.

In general, the copolymerization efficiency of \( p \)-MS for these catalysts follows the order: \( B > A \sim C > D \), which is directly related to the spatial opening at the active site. The constrained geometry \([\text{C}_5\text{Me}_4(\text{SiMe}_2\text{NtBu})\text{TiCl}_2]\) catalyst (B) with an open active site shows the highest reactivity in incorporating \( p \)-MS units into ethylene/propylene/\( p \)-MS terpolymer (E/P/\( p \)-MS) with high molecular weight and only slightly reduced catalyst activity. These results imply a highly reactive \( p \)-MS capped EP propagating site (III) for all three monomers, which may pose a difficulty for the selective hydrogenation reaction shown in Equation 3.1, unless the \( p \)-MS capped propagating site (III) shows significantly high reactivity toward hydrogen. On the other hand, \( \text{rac}\)-Et(Ind)\(_2\)ZrCl\(_2\) catalyst (A) seems to have balanced properties, exhibiting adequate incorporation of \( p \)-MS units, and both the catalyst activity and polymer molecular weight reduce somewhat. These results clearly indicate some difficulty at the \( p \)-MS capped EP propagating site (III) in continuing the copolymerization, which provides a good opportunity for hydrogenation to take place and complete the catalytic cycle, as illustrated in Equation 3.1. However, there is a concern relative to
spontaneous chain transfer reaction by $\beta$-hydride elimination (shown in Figure 3.1, a) that may result in some imperfect chain ends.

Both $\text{rac-Me}_2\text{Si-}[2-\text{Me}-4-\text{ph(Ind)}]\text{ZrCl}_2$ (C) and $\text{Ph}_2\text{Si-}[(\text{Cp})(\text{Flu})] \text{ZrCl}_2$ (D) catalysts are not suitable in this ethylene/propylene/$p$-MS polymerization. Although catalyst (C) is excellent for propylene polymerization$^9$ to prepare $i$-PP with high molecular weight and high catalyst activity, it only produces low molecular weight EP copolymers with significant $\beta$-hydride elimination (shown in Figure 3.1, c) and reduction of catalyst activity even without $p$-MS. On the other hand, $\text{Ph}_2\text{Si-}[(\text{Cp})(\text{Flu})] \text{ZrCl}_2$ catalyst (D) is a very good initiator in producing EP copolymers$^{15}$ with high molecular weight and high catalyst activity, but it exhibits very poor incorporation of styrenic molecules. In fact, $p$-MS concentration $>0.15$ M almost stops the E/P copolymerization, and the trace polymer formed shows no $p$-MS content.

### 3.3.2. $p$-MS Effects

It’s very interesting to closely examine the effects of $p$-MS in ethylene/propylene/$p$-MS polymerization using $\text{rac-Et(Ind)}_2 \text{ZrCl}_2$ (A) and $[(\text{C}_3\text{Me}_4)\text{SiMe}_2\text{N(t-Bu)}]\text{TiCl}_2$ (B) catalyst systems. The correlations of $p$-MS concentration to the catalyst activity, ethylene/propylene incorporation ratio, polymer molecular weight, etc., may provide valuable information about the state of the $p$-MS capped propagating chain end, which may in turn offer us the reaction conditions that can alter $p$-MS copolymerization mode into consecutive chain transfer reaction with hydrogen, as illustrated in Equation 3.1.
Figures 3.2 and 3.3 compare the plots of E/P mole ratio, catalyst activity, and polymer molecular weight versus \( p\)-MS content in the resulting ethylene/propylene/\( p\)-MS (E/P/\( p\)-MS) terpolymers (runs I-A-1 to I-A-5 and I-B-1 to I-B-5 in Table 3.1), prepared by \( \text{rac-Et(Ind)}_2\text{ZrCl}_2 \) (A) and \([\text{C}_5\text{Me}_4\text{SiMe}_2\text{N(t-Bu)}]\text{TiCl}_2 \) (B), respectively. In \( \text{rac-Et(Ind)}_2\text{ZrCl}_2 \) cases, the E/P mole ratio in the terpolymer significantly increases with increasing \( p\)-MS concentration, while catalyst activity and polymer molecular weight are proportionally decreased.

The results clearly reflect the competitive nature of coordination at the metallocene active site. Once the propagating EP chain has the chance to react with \( p\)-MS via 2,1-insertion, the bulky phenyl group in the last unit of the growing chain (III) is adjacent to the central metal atom and slows down the propagation process. This \( p\)-MS capped propagating site (III) may face difficulties in reacting with propylene and \( p\)-MS due to steric hindrance, but only allows the insertion of ethylene, which continues the propagation process with a reduced rate.

In the presence of hydrogen (discussed later), this slow propagating site (III) shall significantly enhance the chance of hydrogenation to form chain end functionalized EP polymer (IV) and a new active site (I) for continuing the catalytic cycles. Considering the significant increase in ethylene content, it may be possible to have a weak intermolecular interaction between cationic active site and the delocalized \( \pi \)-electrons in \( p\)-MS monomer (similar to cage effect), which may crowd the active site and partially attribute to the serge of ethylene incorporation.
Figure 3.2. Plots of E/P mole ratio, catalyst activity, and polymer molecular weight vs. \( p \)-MS content in E/P/p-MS terpolymers (runs I-A-1 to I-A-5), prepared by \( rac \)-Et(Ind)\(_2\)ZrCl\(_2\)/MAO.
Figure 3.3. Plots of E/P mole ratio, catalyst activity, and polymer molecular weight vs. p-MS content in E/P/p-MS terpolymers (runs I-B-1 to I-B-5), prepared by [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂/MAO.
It is very interesting to note that the spontaneous chain transfer reaction by β-hydride elimination shown in rac-Et(Ind)2ZrCl2-mediated E/P polymerization is diminished with the presence of p-MS. Figure 3.4 compares the 1H NMR spectra of three E/P/p-MS terpolymers (runs I-A-6, I-A-7, and I-A-8) prepared by the same ethylene and propylene feeds but varying p-MS concentration, using rac-Et(Ind)2ZrCl2/MAO catalyst. All peak intensities at 2.0 and 4.7-4.9 ppm for CH2=C(CH3)- unit, and at 5.0 and 5.9 ppm for CH2=CH-CH2- unit, are systematically decrease with the increase of p-MS content, and there is only minor reduction in polymer molecular weight (shown in Table 3.1). The combined results indicate a new chain transfer reaction mechanism associated with p-MS incorporation, and the role of p-MS in not only comonomer but also chain transfer agent.

On the other hand, the [(C5Me4)SiMe2N(t-Bu)]TiCl2 catalyst system exhibits a much smaller p-MS effect -- the increase of p-MS feed linearly increases p-MS incorporation (runs IB-1 to I-B-5 in Table 3.1), but has only a mild effect on E/P mole ratio, catalyst activity, and polymer molecular weight, as shown in Figure 3.3. The p-MS capped propagating site (III) seems to have no significant problem in continuing the propagation process, except for a small preference in ethylene incorporation. This non-discriminatory active site is also shown in all comparative E/P and E/P/p-MS polymerization reactions (such as runs I-A-1 vs. I-B-1 and I-A-2 vs. I-B-5), with significantly low ethylene content in the polymers prepared by [(C5Me4)SiMe2N(t-Bu)]TiCl2 catalyst, comparing with all other catalysts that show some favoritism toward smaller size ethylene monomer. Despite the effect of p-MS incorporation, all polymers formed exhibit narrow molecular weight distribution (PDI~ 2), a strong characteristic of well-
Figure 3.4. $^1$H NMR spectra of three comparative E/P/p-MS terpolymers prepared by the same E/P feed ratio (2/1) but varying $p$-MS concentration (a) 0.008, (b) 0.152, and (c) 0.46 M, using rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst.
3.3.3. Hydrogen Effects

It’s very interesting to understand the effect of hydrogen in both rac-Et(Ind)₂ZrCl₂ (B) and [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ (A) systems during the E/P/p-MS polymerization. The major objective is to find the ideal hydrogen pressure that can completely alter p-MS incorporation mode from copolymerization to chain transfer reaction to form EP-t-p-MS polymer. In the presence of hydrogen, the active site (III) in the rac-Et(Ind)₂ZrCl₂ (B) catalyst system will engage in a facile hydrogenation, which leads to an EP copolymer with a terminal p-MS group. On the other hand, the same hydrogenation of the p-MS capped active site (III) in the [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ case may be much more difficult to complete, due to favorable copolymerization reactions. However, it would be ideal to use this catalyst system since it produces high molecular weight ethylene/propylene copolymers with narrow molecular weight and composition distribution, and can be operated in a wide temperature range with good catalyst activity.

Table 3.2 summarizes several comparative runs of ethylene/propylene copolymerization using rac-Et(Ind)₂ZrCl₂/MAO and [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ catalysts in the presence of p-MS and varying H₂ concentrations. Comparing runs II-A-1 to II-A-5, it is interesting to notice the effect of hydrogen pressure on catalyst activity and E/P mole ratio in the copolymer – a small amount of H₂ increases catalyst activity and decreases ethylene incorporation, but the effect becoming invariant after 7 psi H₂ pressure. On the other hand, there is almost no change in p-MS incorporation with or without H₂. The combined results indicate a facile
Table 3.2 Summary of Ethylene/Propylene/p-MS Terpolymerization Using Various Hydrogen Pressures

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat.</th>
<th>H</th>
<th>p-MS (mol/L)</th>
<th>E/P ratio</th>
<th>Time/Temp (min/°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mol%)</th>
<th>p-MS (mol%)</th>
<th>Mn (g/mole)</th>
<th>PDI</th>
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<td>II-A-1</td>
<td>A</td>
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<td>0.125</td>
<td>1/1</td>
<td>10/55</td>
<td>24,500</td>
<td>58.6/41.0</td>
<td>0.4</td>
<td>35,400</td>
<td>1.9</td>
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<td>10/55</td>
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<td>11,000</td>
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<td>10/55</td>
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<td>10/55</td>
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<td>54.5/45.0</td>
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<td>35.0/65.0</td>
<td>0</td>
<td>125,000</td>
<td>1.9</td>
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<td>1/1</td>
<td>10/55</td>
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<td>1/1</td>
<td>10/55</td>
<td>24,700</td>
<td>34.6/65.4</td>
<td>0</td>
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<td>10/55</td>
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<td>10/55</td>
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<td>10/55</td>
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<td>10/55</td>
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<td>0.125</td>
<td>1/1</td>
<td>10/55</td>
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<td>44.6/54.3</td>
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<td>1/1</td>
<td>10/55</td>
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<td>2/1</td>
<td>10/55</td>
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<td>18,000</td>
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<td>0.125</td>
<td>2/1</td>
<td>10/55</td>
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<td>53.8/45.6</td>
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<td>0.125</td>
<td>2/1</td>
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<td>17,100</td>
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<td>18,000</td>
<td>53.7/45.8</td>
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<td>15,900</td>
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</tbody>
</table>

1. Catalyst: rac-Et(Ind)2ZrCl2 (A), [(C5Me4)SiMe2N(t-Bu)]TiCl2 (B)  2. Total ethylene and propylene pressure = 107 psi
hydrogenation at the p-MS capped propagating site (III), which relieves the steric hindered metal center that slows down the propagation process due to the incapable insertion of propylene and p-MS.

As expected, the EP polymer molecular weight is reduced following the chain transfer to p-MS/H₂. Figure 3.5 shows the GPC curves of a comparative set (runs II-A-1 to II-A-5) of EP-t-p-MS polymers prepared by rac-Et(Ind)₂ZrCl₂/MAO catalyst under similar reaction conditions, except for varying hydrogen pressure. The polymer molecular weight shows an initial sharp decrease with a low H₂ pressure and becomes much less sensitive in high H₂ pressure range, which indicates a much higher hydrogenation rate at the p-MS capped propagating site than those at ethylene and propylene-capped propagating sites. A linear plot of polymer molecular weight (Mn) versus the mole ratio of 1/[p-MS] implies the chain transfer reaction to p-MS/H₂ as the dominant termination process. All results consistently point to the consecutive chain transfer reaction to p-MS/H₂, which alters p-MS incorporation from copolymerization to chain transfer mode.

End group analysis provides direct evidence of a terminal p-MS group in EP-t-p-MS polymer, which is only possible for the polymers with relatively low molecular weight due to the NMR sensitivity. Figure 3.6 compares ¹H NMR spectra of two E/P/p-MS polymers (runs II-A-1 and II-A-3) that were prepared by rac-Et(Ind)₂ZrCl₂/MAO catalyst without and with 15 psi H₂ pressures, respectively. The peaks located at 2.35 ppm (ϕ-CH₃), 2.43 ppm (-CH₂-CH(ϕ)-), and 2.58 ppm (-CH₂-ϕ) provide the information on p-MS incorporation modes, and several minor peaks at 2.0
Figure 3.5. GPC curves of a comparative set of EP-t-p-MS polymers (runs II-A-1 to II-A-5) prepared by rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst under similar reaction conditions, except for varying hydrogen pressure (a) 0, (b) 7, (c) 15, (d) 25, and (e) 35 psi.
Figure 3.6. $^1$H NMR spectra of two E/P/p-MS polymers (runs II-A-1 and II-A-3) prepared by rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst (a) without and (b) with H$_2$ pressure.
and 4.7-4.9 ppm for CH$_2$=C(CH$_3$)- unit and at 5.0 and 5.9 ppm for CH$_2$=CH-CH$_2$- unit show the activities of β-hydride elimination. As hydrogen pressure increases, the chemical shift at 2.43 ppm (multiplet), corresponding to -CH$_2$-CH(φ)- formed by copolymerization mode, was diminished to an undetectable level, with an increasing relative intensity of the chemical shift at 2.58 ppm (triplet), corresponding to -CH$_2$-CH$_2$-φ-CH$_3$ at the polymer chain end. In addition, the multiple aromatic proton peaks between 7.0 and 7.2 ppm merge into a single peak at 7.12 ppm, also indicating a terminal phenyl group. It’s important to note that the spontaneous chain transfer reaction, due to β-hydride elimination of the propylene-capped propagating site resulting in an imperfect chain end, is almost undetectable. Overall, most of the resulting EP polymer chains prepared from E/P/p-MS/H$_2$ polymerization using rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst contain a terminal p-MS group.

It’s a curious fact that the [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ (A) system has a much smaller p-MS effect (discussed before) and produces high molecular weight uniform E/P/p-MS terpolymers with narrow composition and molecular weight distributions. As shown in Table 3.2 (runs II-B-1 to II-B-4), this catalyst system exhibits low chain transfer activity, including β-hydride elimination and direct hydrogen chain transfer reaction. There is almost no change in EP molecular weight, E/P mole ratio, and catalyst activity with an increase of hydrogen pressure from 0 to 35 psi. Insensitivity of this catalyst to hydrogen in E/P copolymerization provides a favorable condition for using higher H$_2$ pressure in p-MS/H$_2$ chain transfer reaction.
Table 3.2 compares several systematic results with a fixed amount of 
\(p\)-MS and varying hydrogen pressure during \((C_5Me_4)SiMe_2N(t-Bu)TiCl_2/MAO\) mediated E/P/\(p\)-MS polymerization. Hydrogen seems to have no significant effect in catalyst activity and E/P mole ratio, but changes the polymer molecular weight and reduces \(p\)-MS incorporation, especially in high \(p\)-MS cases.

Figure 3.7 shows the GPC curves of a representative set of the resulting E/P/\(p\)-MS polymers (runs II-B-21 to IIIB-25) using 0.152 M \(p\)-MS concentration. Figure 3.8 shows the plot of polymer molecular weight (Mn) versus the \(H_2\) pressure for all comparative sets. Generally, the same trend in each comparative run was observed with a relatively sharp decrease in polymer molecular weight with low \(H_2\) pressure (~7 psi), and only minor variation in the higher \(H_2\) pressure range. Similar trends were observed in Figure 3.5, which forms EP-t-\(p\)-MS polymers by rac-Et(Ind)_2ZrCl_2/MAO catalyst. Apparently, a facile hydrogenation reaction takes place at the \(p\)-MS capped active site (III) mediated by the \((C_5Me_4)SiMe_2N(t-Bu)TiCl_2/MAO\) system -- a great departure from the corresponding ethylene and propylene-capped active sites with very low hydrogenation activities, which may be associated with the reduction of cationic nature at the \(p\)-MS capped propagating site due to \(\pi\)-electron donation from phenyl group. Such a facile hydrogenation reaction alters \(p\)-MS incorporation mode from copolymerization to chain transfer reaction and allows the preparation of EP-t-\(p\)-MS polymers with a broad range of polymer molecular weight. It is interesting to note that the use of E/P=2/1 feed ratio (runs II-B-26 to II-B-30) prepares EP-t-\(p\)-MS polymers with about 1/1 E/P mole ratio that is similar to those of commercial EP elastomers.
Figure 3.7. GPC curves of E/P/p-MS polymers prepared by [(C₅Me₄) SiMe₂N(t-Bu)]TiCl₂/MAO under similar reaction conditions, except for varying hydrogen pressure (a) 0, (b) 7, (c) 15, (d) 25, and (e) 35 psi.
Figure 3.8. Plot of polymer molecular weight (Mn) of E/P/p-MS polymers prepared by [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$/MAO catalyst using (a) 0, (b) 0.008, (c) 0.015, (d) 0.076, (e) 0.152 M p-MS concentration and varying H$_2$ pressure.
Figure 3.9 compares $^1$H NMR spectra of two E/P/p-MS polymers (runs II-B-21 and II-B-23) prepared by (C$_5$Me$_4$)SiMe$_2$N(t-Bu)TiCl$_2$/MAO catalyst under the same reaction conditions except hydrogen pressures of 0 and 15 psi. In Figure 3.9(a), the multiple peaks at $\sim$7.0 ppm, corresponding to the aromatic protons of -CH$_2$-CH(\phi)-CH$_2$- in side chains, almost completely merge into a single peak corresponding to the aromatic protons of CH$_2$-\phi-CH$_3$ at the polymer chain end, shown in Figure 3.9(b). In the inset of magnified region, the other broad peak at 2.4 ppm (-CH$_2$-CH(\phi)-CH$_2$-) also diminishes to undetectable levels. On the other hand, the peaks at 2.3 ppm (singlet) and 2.57 ppm (triplet), corresponding to -\phi-CH$_3$ and CH$_2$-\phi-CH$_3$, respectively, are clearly visible. Overall, the results clearly show an unexpectedly strong effect of hydrogen on the p-MS-capped propagating site, which stops p-MS copolymerization and changes to chain transfer reaction.

3.3.4. Chain End Functionalization EP-t-St-OH

It is very interesting to prepare EP copolymers containing a terminal functional (polar) group, such as an OH group, that exhibits good chemical and physical reactivity with other materials for polymer blends and alloys. The terminal p-MS group in EP-t-p-MS can be metallated by s-BuLi/TMEDA reagent\textsuperscript{16} to form a stable polymeric anion that then transforms to OH-terminated PE (PE-t-OH) and COOH-terminated PE (PE-t-COOH), by reacting with ethylene oxide and CO$_2$, respectively. However, it is much more desirable to directly synthesize chain end functionalized EP polymers during the \textit{in situ} polymerization (one-pot process).
Figure 3.9. $^1$H NMR spectra of two E/P/p-MS polymers (runs II-B-21 and II-B-23) prepared by $[(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2/MAO$ catalyst (a) without and (b) with $H_2$ pressure.
Table 3.3 Summary of Ethylene/Propylene/St-OSi Polymerization under Various Hydrogen Pressures

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat.</th>
<th>H₂ Pressure (psi)</th>
<th>St-OSi (mol/L)</th>
<th>E/P ratio</th>
<th>Time/Temp (min/°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mole%)</th>
<th>St-OSi (mole%)</th>
<th>Mn (g/mole)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-B-1</td>
<td>B</td>
<td>0</td>
<td>0.028</td>
<td>1/1</td>
<td>10/55</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III-B-2</td>
<td>B</td>
<td>0</td>
<td>0.028</td>
<td>2/1</td>
<td>10/55</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III-B-3</td>
<td>B</td>
<td>0</td>
<td>0.028</td>
<td>2/1</td>
<td>10/55</td>
<td>10,680</td>
<td>45.50/54.43</td>
<td>0.07</td>
<td>111,800</td>
<td>1.8</td>
</tr>
<tr>
<td>III-B-4</td>
<td>B</td>
<td>7</td>
<td>0.028</td>
<td>2/1</td>
<td>10/55</td>
<td>11,240</td>
<td>45.28/54.65</td>
<td>0.07</td>
<td>50,600</td>
<td>2.0</td>
</tr>
<tr>
<td>III-B-5</td>
<td>B</td>
<td>15</td>
<td>0.028</td>
<td>2/1</td>
<td>10/55</td>
<td>12,460</td>
<td>47.45/52.47</td>
<td>0.08</td>
<td>41,700</td>
<td>2.0</td>
</tr>
<tr>
<td>III-B-6</td>
<td>B</td>
<td>25</td>
<td>0.028</td>
<td>2/1</td>
<td>10/55</td>
<td>12,530</td>
<td>48.53/51.41</td>
<td>0.06</td>
<td>39,000</td>
<td>1.8</td>
</tr>
<tr>
<td>III-B-7</td>
<td>B</td>
<td>0</td>
<td>0.084</td>
<td>2/1</td>
<td>10/55</td>
<td>6,320</td>
<td>49.55/50.30</td>
<td>0.15</td>
<td>97,000</td>
<td>1.9</td>
</tr>
<tr>
<td>III-B-8</td>
<td>B</td>
<td>7</td>
<td>0.084</td>
<td>2/1</td>
<td>10/55</td>
<td>6,990</td>
<td>51.65/48.21</td>
<td>0.14</td>
<td>37,000</td>
<td>1.8</td>
</tr>
<tr>
<td>III-B-9</td>
<td>B</td>
<td>15</td>
<td>0.084</td>
<td>2/1</td>
<td>10/55</td>
<td>7,500</td>
<td>53.73/46.16</td>
<td>0.11</td>
<td>36,400</td>
<td>1.8</td>
</tr>
<tr>
<td>III-B-10</td>
<td>B</td>
<td>25</td>
<td>0.084</td>
<td>2/1</td>
<td>10/55</td>
<td>7,350</td>
<td>52.71/47.19</td>
<td>0.10</td>
<td>33,000</td>
<td>1.9</td>
</tr>
</tbody>
</table>

a) Catalyst: [(C₅Me₄)SiMe₃N(t-Bu)]TiCl₂ (B).
b) St-OSi is 4-(t-butyldimethylsilyloxy)styrene in III-B-1 and III-B-2 and 4-(t-butyldiphenylsilyloxy)styrene for other runs.
c) Total ethylene and propylene pressure = 107 psi.
In other words, the styrenic chain transfer agent will carry a protected functional group that does not poison the catalyst and is easily deprotected after polymerization. Table 3.3 compares the experimental results involving two silane protected St-OH (St-OSi) chain transfer agents containing $t$-butyldimethylsilane and $t$-butyldiphenylsilane groups, respectively, during $(C_5\text{Me}_4)\text{SiMe}_2\text{N(t-Bu)}\text{TiCl}_2/\text{MAO}$ catalyzed polymerization of E/P/St-OSi. A small amount of $t$-butyldimethylsilane protected St-OSi effectively stops the polymerization, indicating catalyst poisoned by a $\text{–O-Si}(t-C_4\text{H}_9)(\text{CH}_3)_2$ group that may not be sufficiently bulky to prevent oxygen from this opened active site. However, the bulky $t$-butyldiphenylsilane protecting group shows satisfactory results with good catalyst activity and alternating St-O-Si incorporation mode from copolymerization to chain transfer reaction in the presence of hydrogen.

![Figure 3.10. $^1$H NMR spectra of (a) EP-t-St-OSi polymer (Mn= 22.0 x 103; Mw/Mn= 2.0) and (b) the corresponding EP-t-St-OH polymer.](image-url)
Figure 3.10 shows the $^1$H NMR spectra (with inset of magnified region) of a EP-t-St-OSi polymer ($M_n = 22.0 \times 10^3$; $M_w/M_n = 2.0$) and the corresponding EP-t-St-OH polymer. In addition to three major peaks between 0.9 and 1.6 ppm for the $\text{CH}_3$, $\text{CH}_2$, and $\text{CH}$ groups in the EP backbone and a minor peak at 2.5 ppm for $-\text{CH}_2\phi-\text{O-Si}$ group, Figure 3.10(a) shows two sets of aromatic proton peaks at 6.7 and 6.9 ppm for $-\text{CH}_2\phi-\text{O-Si}$ group and at 7.4 and 7.7 ppm for $\text{Si-(\phi)}_2$ group, with integrated peak intensity ratio of 2:2:5:5. In Figure 3.10(b), the chemical shifts at 7.4 and 7.7 ppm are completely disappeared, and the integrated peak intensity ratio at 2.5, 6.7, and 6.9 ppm is about 1:1:1, indicating the occurrence of a very effective deprotection reaction during the sample work-up step by using HCl solution.

3.4. Conclusion

The systematic study of metallocene-mediated ethylene/propylene/$p$-MS polymerization in the presence of H$_2$, with varying catalysts, $p$-MS concentrations, and hydrogen pressures, provides the detailed reaction mechanism. With a combination of metallocene catalyst and a controlled hydrogen pressure, it’s possible to direct the incorporation of $p$-MS molecules, from copolymerization to chain transfer mode, to form $p$-MS terminated EP copolymers (EP-$t$-$p$-MS) with a broad range of polymer molecular weight and E/P mole ratios. This chemistry (one-pot process) can be extended to prepare chain end functionalized EP copolymers, such as EP-t-St-OH. However, the functional styrenic chain transfer agent has to be well protected by a bulky group to prevent catalyst poison, especially by using a $[\{(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{N(t-Bu)}\}\text{TiCl}_2$ catalyst system with an opened active site.
3.5. References


   
   
   

   
   

   
   
   
   

(c) Koo, K.; Fu, P.-F.; Marks, T. J. Macromolecules 1999, 32, 981.

6 (a) Xu, G.; Chung, T. C. J. Am. Chem. Soc. 1999, 121, 6763.
(b) Xu, G.; Chung, T. C. Macromolecules 1999, 32, 8689.
(c) Chung, T. C.; Xu, G.; Lu, Yingying; Hu, Youliang, Macromolecules 2001, 34, 8040.

(b) Hagihara, H.; Tsuchihara, K.; Sugiyama, J.; Tazuhiko, T.; Shiono, T. Macromolecules 2004, 37, 5145

(b) Dong, J. Y.; Chung, T. C. Macromolecules 2002, 35, 1622.


11 Xu, Y.; Painter, P. C.; Coleman, M. M. Polymer 1993, 34, 3010.


13 ASTM standard method; Designation D-3900-95.


Chapter IV
Synthesis of EPR Containing Pendent and Chain-end Allyl or Butenyl Functional Monomer Units

4.1. Introduction

Following the results in chapter III, it is interesting to search for other olefinic species that can behave like styrenic molecules in selective copolymerization or chain transfer reaction by controlling the reaction conditions. Ironically, these reagents have to be able to slow down the polymerization process after being incorporated at the propagating chain end. In addition, the subsequent facial chain transfer reaction has to take place to complete the polymerization cycle. Therefore, this incorporated reagent is located right at the chain end after each polymerization cycle. Obviously, specific reaction conditions, including metallocene catalyst, internal or external chain transfer agent, reaction temperature, etc., have to work in concert to achieve the ideal polymerization/chain transfer situation. As discussed in chapter III, in E/P copolymerization the E/P incorporation ratio provides valuable information on finding suitable reaction conditions. In this chapter, we will focus on E/P copolymerization with allyl and butenyl functional monomers that were reported to be difficult monomers in the preparation of functional PE and PP polymers, with low catalyst activities and low polymer molecular weights.

As discussed in Chapter II, the direct copolymerization of functional monomers containing O, N, and halogen heteroatoms by early transition
metals (Z-N and metallocene catalysts) is very difficult. The constraint in this approach is the poisoning of catalyst components by polar groups\textsuperscript{1}. Although Ziegler-Natta catalysts containing group 4 transition metals are known for their highly oxophilic nature\textsuperscript{2}, zirconocene/methylaluminoxane (MAO) catalysts were successful in copolymerizing ethylene with 10-undecen-1-ol\textsuperscript{3} or other polar monomers\textsuperscript{4} having long CH\textsubscript{2} spacers between polar and vinyl groups. However, the catalyst activity decays with the concentration of 10-undecen-1-ol\textsuperscript{5}. Shell has claimed the copolymerization of \textit{N}-phenyl-10-undecenamine with 1-hexene (9-13 wt \% comonomer incorporation) with TiCl\textsubscript{3} in the presence of excess Et\textsubscript{2}AlCl\textsuperscript{6}.

Tertiary amine-functionalized olefins with sufficient steric hindrance around the nitrogen atom and long CH\textsubscript{2} spacer are not difficult to polymerize and copolymerize by using group IV catalysts\textsuperscript{7}. Smaller monomers (such as dimethyl and diethylamines) can be polymerized if 1 equivalent of a proper alkylaluminum protecting group is used\textsuperscript{8}. However, in a review Boffa\textsuperscript{9} stated that if the amine functionality is too close to the double bond (short spacer), the additional steric bulk provided by the aluminum species may actually inhibit monomer coordination and polymerization. A similar trend was observed by Giannini in a systematical Z-N polymerization study by using diisopropylamines having 1, 2, 3, 5, or 9 methylene spacers between the double bond and the amine\textsuperscript{10}. Both studies suggest that a minimum of three carbons between the functional groups is generally necessary to achieve well-controlled polymerization behavior.

In general, there are three thoughts to circumvent the catalyst deactivation problem, including (a) using less oxophilic late transition metal
catalysts, (b) synthesizing polar monomers with long CH$_2$ spacers between polar and vinyl groups, and (c) protecting the polar functional groups. Although late transition metal catalysts are less oxophilic and much more tolerant to polar functional groups containing O and N atoms than early transition metal systems, they often produce highly branched polymers and cannot control polymer tacticity and crystallinity that are crucial to polyolefin properties. The branching structure was attributed to the chain-walking mechanism with facial chain transfer reaction, involving β-hydride elimination and a reinsertion process$^{11}$. On the other hand, the functional monomer with a large number of CH$_2$ spacers between polar and vinyl groups are not commercially available and need to be synthesized. In addition, catalyst activity decay is still a major concern. The protection of functional monomers is the most widely studied, as discussed in chapter II. The ideal protection agent would not only have the capability to minimize catalyst deactivation, but also would provide convenient and effective protection and deprotection reactions. Additionally, the protected functional monomer should be very soluble in the polymerization solvents (i.e. hexane, toluene, or monomers).

Intuitively, both allyl and butenyl functional monomers with only 1 and 2 CH$_2$ spacers, respectively, are expected to be very poor comonomers in Ziegler-Natta and metallocene polymerizations. In fact, several attempts have been reported in trying to copolymerize α-olefins with protected allyl alcohol and allyl amine. Most of the results were very discouraging with poor catalyst activity and poor incorporation of the functional monomer; catalyst poisoning was attributed as the major problem.
Based on our knowledge in styrenic molecules, discussed in chapter III, these stubborn allyl and butenyl functional monomers may indeed offer an excellent opportunity to prepare chain end functionalized polyolefins. Our strategy is to first protect the functional monomers with bulky protecting groups from poisoning the catalyst. Then, the protected functional monomer will involve the copolymerization reaction. It is very possible that the incorporated functional monomer at the propagating chain-end may stop the polymerization due to steric or electronic reasons, as shown in styrenic molecule cases. However, in the presence of hydrogen, the subsequent chain-transfer to hydrogen could take place and regenerate the catalyst continuing the polymerization cycle. The resulting polymer should contain a terminal functional group.

4.2. Experimental Details

4.2.1. Instrumentation and Materials

All O\textsubscript{2} and moisture sensitive manipulations were performed inside an argon-filled atmosphere dry box equipped with a MO-40-1 dry-train. All solvents were deoxygenated through argon purge before refluxing with sodium/benzophenone for 48 hours, then distilling them from their respective green or purple solution under argon. Lithium bis(trimethylsilyl)amide, chloromethyl methylether, silver iodide, allylbromide, allylmagnesium bromide (1M in ether), allylalcohol, allylamine, tert-butyldiphenylchloro-silane, trimethylaluminum (TMA) (30% in toluene), \text{Al}_2\text{(SO}_4)_3\cdot14\text{H}_2\text{O} and \textit{rac}-\textit{Et}(\text{Ind})\text{2ZrCl}_2 from Aldrich were used as received. Diphenylsilyl (cyclopentadienyl-9-fluorenyl)\text{ZrCl}_2 (Crompton), and (\text{C}_5\text{Me}_4)\text{SiMe}_2\text{N(t-Bu)}\text{TiCl}_2 (Boulder Scientific) were used
as received. \textit{rac}-Me$_2$Si-[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$ was prepared as described in the literature\textsuperscript{12}. Methylaluminoxane (MAO) was synthesized according to the literature\textsuperscript{13}. High-purity grade ethylene and propylene gases were obtained from MG Industry and were used as received.

All \textsuperscript{1}H NMR spectra were recorded at room temperature on a Bruker AM-300 spectrometer with the DISNMR software. The NMR samples were prepared in d-chloroform which is a good solvent for all polymers. In the copolymers of the oxygen-containing comonomers, the comonomer contents were calculated from \textsuperscript{1}H NMR spectra with the signals of the protons attached to methylene carbon next to oxygen\textsuperscript{14}, while the comonomer contents in the copolymers of the nitrogen-containing comonomers were calculated from \textsuperscript{1}H NMR spectra with the signals of the protons attached to the nitrogen in its ammonium salt after treating with HCl\textsuperscript{15}. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution cast films on KBr windows. The molecular weights were determined by a Waters GPC that was operated at 35 °C with a refractive index (RI) detector and a set of \textmu-Styragel columns of 10\textsuperscript{6}, 10\textsuperscript{5}, 10\textsuperscript{4}, and 10\textsuperscript{3} Å pore sizes in series. A flow rate of 0.7 mL/minute was used and the mobile phase was THF. The calibration curve was established by measuring polystyrene standards.

\textbf{4.2.2. Synthesis of Methylaluminoxane (MAO)}

Under a nitrogen atmosphere, 250 mL of 30 wt\% Al(CH$_3$)$_3$ (75 g, 1.04 mol) was added dropwise over a 2 h period through an addition funnel to a cooled (0 °C) suspension of Al$_2$(SO$_4$)$_3$.14H$_2$O (53.44 g, 1.31 mol of H$_2$O) in
toluene (140 mL) placed in a three-neck round bottomed flask equipped with a stirrer bar. The mixture was stirred at 0 °C for overnight and was then warmed to room temperature. Stirring was continued at room temperature for 24 h. The mixture was warmed to 60 °C for another 24 h, cooled, and filtered under vacuum. The solvent and excess TMA were evaporated and the resulting powder was dried under vacuum at 40 °C overnight. The isolated yield was 65% and its purity was confirmed by $^1$H NMR.

4.2.3. Synthesis and Protection of Functional Monomers

4.2.3.1. But-3-enyl bis(trimethylsilyl)amine

But-3-enyl bis(trimethylsilyl)amine, i.e. BuN(SiMe$_3$)$_2$, was synthesized in two preparative steps as shown in Scheme (4.1). Into a 500 mL flask equipped with a magnetic stirr bar, 50 g (0.299 mol) of lithium bis(trimethylsilyl)amide was slowly dissolved in 100 mL of THF into mixture of 25 mL (0.329 mol) of chloromethyl methyl ether and 50 mL of THF at 0 °C under a nitrogen atmosphere. After the addition was complete, the solution was allowed to warm to room temperature and stir overnight. The precipitated powder was filtered off and the excess chloromethyl methylether was evaporated using a rotary vapor pump. N,N-bis(trimethylsilyl)methoxy-methylamine (80% yield) was isolated by distillation and its purity was confirmed by $^1$H NMR.

In the second step, 43.4 g (0.211 mol) of N,N-bis(trimethylsilyl) methoxymethylamine placed in 100 mL dry ether in a 500 mL flask equipped with stirr bar, was treated with with 264 mL (0.264 mol) of allylmagnesium bromide (1M in ether) over a period of 1 h at 0 °C. The
solution was warmed up to room temperature and stirred overnight before adding 100 mL of aqueous NaOH solution (30%). The organic layer was separated and dried with magnesium sulfate, and the residual was then distilled over CaH₂ to give analytically pure (¹H NMR) but-3-enyl bis(trimethylsilyl)amine in 70% yield.

![Scheme 4.1](image)

4.2.3.2. Allylaminebis(dimethylaluminum)⁷

25 mL (0.334 mol) of dry allylamine was diluted with 70 mL of dry toluene in a 1 L flask equipped with a magnetic stirr bar. Then, 80.3 mL (0.334 mol) trimethylaluminum (30 wt% in toluene) was diluted with 70 mL dry toluene and added dropwise through an addition funnel to the above solution over a period of 1 h at -78 °C under argon atmosphere. The flask was warmed up to room temperature and stirred for 3 days. The solvent was
removed under vacuum to give a quantitative yield of allylaminebis-(dimethylaluminum) as yellow oil (Scheme 4.2).

![Scheme 4.2]

4.2.3.3. Allylbis(trimethylsilyl)amine\textsuperscript{17}

In the dry box, 40 g (0.239 mol) of lithium bis(trimethylsilyl)amide was combined with 11.6 g (0.049 mol) of silver iodide in a 500 mL flask equipped with a condenser and stirr bar. Outside the dry box, it was dissolved in 80 mL dry THF and the mixture was allowed to stir at room temperature for 1 h. To the resulting homogeneous solution, 25 mL of allylbromide was added dropwise in 1 h. The mixture was refluxed in THF overnight, then filtered and concentrated. The resulting crude oil was distilled to afford 90% yield of an analytically pure product as colorless oil (Scheme 4.3). Its structure was confirmed by $^1\text{H}$ NMR spectrum.

![Scheme 4.3]
4.2.3.4. Allyloxydimethylaluminum\textsuperscript{18}

In a 1 L flask equipped with a stirr bar was placed 28.37 mL (0.416 mol) of dry allyl alcohol and diluted with 70 mL of dry hexane. Then, 100 mL (0.416 mol) trimethylaluminum (30wt% in toluene) was diluted with 100 mL dry hexane and added dropwise through an addition funnel to the above solution in a period of 1 h at -78 °C under argon atmosphere. The flask was warmed up to room temperature and stirred overnight. The solvent was removed under vacuum to give a quantitative yield of two isomers in 1:1 ratio; allyloxydimethylaluminum and diallyloxydimethyl-aluminum as colorless oil as shown in Scheme (4.4). Its structure was confirmed by \textsuperscript{1}H NMR spectrum.

\begin{center}
\includegraphics[width=\textwidth]{scheme4.4}
\end{center}

Scheme 4.4

4.2.3.5. Allyloxy-tert-butyldiphenylsilane\textsuperscript{19}

In a 500 mL flask equipped with a magnetic stirr bar, 21.1 g (0.306 mol) of imidazole was dissolved in 150 mL of dry THF and mixed with 14 mL (0.205 mol) of allylalcohol and 45 g (0.164 mol) of \textit{t}-butyldiphenylsilyl chloride. The mixture was stirred at ambient temperature overnight before being poured into cold water. The organic layer was separated and extracted with ether, then dried with magnesium sulfate.
Further purification was performed by distillation under vacuum (10 Torr) at elevated temperature (80 °C). 44.5 g (92% yield), of allyloxy-tert-butyldiphenylsilane a light yellow color oil, was obtained. Its structure was confirmed by $^1$H NMR spectrum (Scheme 4.5).

![Scheme 4.5](image)

4.2.4. Copolymerization of Ethylene and Propylene in the Presence of Protected Functional Monomers (With and Without $H_2$)

In a typical reaction (run IN1 in Table 4.10), a Parr 300 mL stainless autoclave equipped with a mechanical stirrer was charged with 50 mL of toluene and 0.5 g of MAO. The reactor was then injected with 0.5 mL (0.076M) of BuN(SiMe$_3$)$_2$ and charged through a mass flow controller with 107 psi of ethylene/propylene gas mixture (in ratio 1:1) at 55 °C. About 2.5 × 10$^{-6}$ mol of rac-Et(Ind)$_2$ZrCl$_2$ in toluene solution was then syringed into the rapidly stirring solution under the gas mix pressure to initiate the polymerization. Additional ethylene/propylene gas mixture was fed continuously into the reactor to maintain constant pressure (107 psi) during the course of the polymerization. After 10 minutes of reaction at 55 °C, the polymer solution was quenched with methanol/HCl, and the isolated polymer was purified by repeating a solution/dissolution process by THF.
and methanol three times before drying under vacuum at 50 °C for 8 hours. About 12.1 g of E/P/ BuN(SiMe₃)₂ terpolymer was obtained with a catalytic activity of 31,460 kg/mol of Zr.h and polymer molecular weight of Mn= 34,700 g/mol.

The same procedure was repeated in the presence of hydrogen gas. In a typical reaction (run IN2), 50 mL of toluene and 0.5 g of MAO were mixed in the reactor before purging with hydrogen (7 psi). After injecting with 0.5 mL (0.076M) of BuN(SiMe₃)₂ and charging through a mass flow controller with 107 psi of ethylene/propylene gas mixture (in ratio 1:1) at 55 °C, 2.5 × 10⁻⁶ mol of rac-Et(Ind)₂ZrCl₂ in toluene solution was then syringed in to initiate the polymerization. Additional ethylene/propylene (1/1 pressure ratio) was fed continuously into the reactor to maintain a constant pressure during the course of the polymerization. After 10 minutes of reaction at 55 °C, the reaction solution was quenched with methanol/HCl, and the isolated polymer was purified by repeating a solution/dissolution process by THF and methanol three times before drying under vacuum at 50 °C for 8 hours. About 13.9 g of EP-t-BuN(SiMe₃)₂ polymer was obtained with a catalyst activity of 33,430 kg/mol of Zr.h and polymer molecular weight of Mn= 22,200 g/mole.

4.2.5. Deprotection of the Protecting Group

E/P/BuNH₂ polymers were prepared in the same way as E/P/BuN(SiMe₃)₂ polymers, except that the polymer solution after polymerization was quenched with HCl aqueous solution. Alternately, the isolated E/P/BuN(SiMe₃)₂ polymer (2 g) was suspended in 50 mL of THF
before adding 5 mL of acetic acid and tetrabutylammonium fluoride (2 mol per trimethylsilyl group). The mixture was stirred at 50 °C for 4 hours and then poured into water. The polymer was then collected by filtration and extensively washed with water several times. The polymer was dried under vacuum at 50 °C for 8 hours.

4.2.6. Coupling Reaction of EP-t-NH₂ and PPMA and EPMA

In the case of coupling with maleic anhydride grafted PP (PP-g-MA), a mixture 1 g of EP-t-NH₂ and 2 g of PP-g-MA was dissolved in 50 mL of xylene in a 250 mL flask equipped with a stirr bar and a condenser and refluxed overnight under argon atmosphere. The product was cooled to room temperature and precipitated with methanol. Then, 0.5 g of the dry product was tested for solubility by dissolving in hot toluene. After stirring in hot toluene (130 °C) for 30 min., the solution was cooled down to room temperature and centrifuged to separate the liquid part from the product. Then, methanol was added to the liquid part to check if there was any unreacted EPR. The insoluble part was washed with methanol and dried under vacuum at 50 °C for 8 h before analyzed by 1H NMR.

In the case of coupling with EP-g-MA, a mixture of 1 g of EP-t-NH₂ and 1 g of EP-g-MA was dissolved in 50 mL of xylene in a 250 mL flask equipped with a stirr bar and a condenser and refluxed overnight under argon atmosphere. The product was cooled to room temperature and precipitated with methanol. Then, the product was checked for solubility at room temperature.
4.3. Results and Discussions

In this chapter, we will focus on the copolymerization of ethylene and propylene in the presence of protected allylalcohol, allylamine and butenylamine. The functional groups of these polar monomers are well-protected to overcome the catalyst decay problem. The protection methods used here have been chosen in such a way that they would not only lead to the steric shielding, but also to afford electronic neutralization of the functional groups. As discussed in Chapter II, the most common protecting reagents for functional monomers containing alcohol and amine are trialkylsilyle and trialkylaluminum groups. The protection of the functional monomers, allylamine, allylalcohol, and butenylamine, have been successfully performed as shown in the experimental section of this chapter.

To understand the effect of a functional group to the polymerization, it is also very important to study the copolymerization of ethylene and propylene in the presence of saturated alcohols and amines. These control reactions can provide valuable information about the origins of lower productivities and/or molecular weight reductions. During the reaction, propylalcohol and propylamine were also protected by the same procedure used in allyl functional monomers.

4.3.1. Protection of Functional Monomers

All the protected functional monomers were analyzed by $^1$H NMR. Figures (4.1 to 4.5) show the $^1$H NMR spectra of AllylN{Al(CH$_3$)$_2$)$_2$, AllylOAl(CH$_3$)$_2$, AllylOSi(Ph)$_2$Bu, AllylN[Si(CH$_3$)$_3$], BuN[Si(CH$_3$)$_3$],
respectively, and the corresponding saturated species. The chemical equations and peak assignments (with the integrated peak intensities) are also included to examine the product purities.

Figures 4.1. $^{1}$H NMR of AllylN{Al(CH$_3$)$_2$)$_2$}
Figures 4.2. $^1$H NMR of AllylOAl(CH$_3$)$_2$ (top) and PropylOAl(CH$_3$)$_2$ (bottom)
**Figures 4.3.** $^1$H NMR of AllylOSi(ph)$_2$t-Bu (top) and PropylOSi(ph)$_2$t-Bu (bottom)
Figures 4.4. $^1$H NMR of Allyl[N(Si(CH$_3$)$_3$)$_2$] (top) and PropylN[Si(CH$_3$)$_3$)$_2$ (bottom)
Figures 4.5. $^1$H NMR of CH$_3$O CH$_2$N[Si(CH$_3$)$_3$]$_2$ (top) and BuN[Si(CH$_3$)$_3$]$_2$ (bottom)
In general, the silane protection products in Figures 4.3, 4.4, and 4.5, including both unsaturated and saturated species, are very pure with the expected chemical shifts and peak intensities. They show almost no detectable impurity. Both silation methods, using trialkylsilylelchloride and lithium bis(trimethylsilyl)amide reagents, for protecting OH and NH₂ groups, respectively, are highly effective. On the other hand, the aluminum protection methods shown in Figure 4.1 and 4.2 exhibit much more complicated reaction mixtures. The common synthesis route of directly reacting Al(CH₃)₃ with both OH and NH₂, used in many previous papers, seem to be inadequate to protect functional groups in monomers. In the reaction between Al(CH₃)₃ and allyamine (Figure 4.1) for 3 days at ambient temperature, the N-H broad peak at ~ 2 ppm is still clearly visible. Based on its peak intensity, the major product is the half-protected N(-H)(-Al(CH₃)₂) species, which may cause catalyst deactivation during the polymerization. In Figure 4.2, the reaction between allylalcohol and Al(CH₃)₃ produces both monomeric and dimeric species, which are difficult to separate. The dimeric species, with very minimum steric and electronic protection, may not be able to prevent oxygen from the acidic catalytic site during the polymerization.

4.3.2. Copolymerization of Ethylene and Propylene in the Presence of Allyl-OSi(Ph)₂t-Bu

Three commonly known bridged metallocene catalyst systems for E/P copolymerization were investigated, including rac-Et(Ind)₂ZrCl₂ (i), Ph₂Si-[(Cp)(Flu)]ZrCl₂ (c) from Crompton Chemical Co., and [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ (d) from Dow Chemical Co., as illustrated below.
Table 4.1 compares the experimental conditions and results of terpolymerization of ethylene/propylene/allyl-OSi(Ph)$_2$t-Bu using these three catalyst systems. The study was performed by running the reaction under the same E/P=1/1 mole ratio, total pressure of 107 psi, reaction temperature of 55 °C, and reaction time of 10 minutes, but varying functional monomer concentration for each run. The combination of FT-IR, $^1$H NMR and GPC was used to determine the polymer structure. The mole ratio of ethylene/propylene in the polymer was conveniently determined by an FT-IR technique$^{20}$ (following ASTM standard method), which compares the integrated intensity between the absorption at 1460 cm$^{-1}$, corresponding to the C-H bonds, and the absorption at 1379 cm$^{-1}$, corresponding to the CH$_3$ group in the propylene unit. GPC determines the polymer molecular weight and polydispersity index (PDI), and $^1$H NMR spectrum was used to determine the allyl monomer content.

4.3.3. Effect of Catalyst

It is clear from Table 4.1 that the effect of allyl-OSi(Ph)$_2$t-Bu to the catalyst activity is very different among the catalysts, which may be relative
to their ligand geometry and consequently, the opening at the active site. Both (i) and (c) catalysts show some activities in the presence of allyl-OSi(Ph)$_2$t-Bu, with the initial big drop at very low concentration, then becoming relatively flat after further increasing the functional monomer concentration. On the other hand, catalyst (d) is completely poisoned by the functional group. The t-butyldiphenylsilane protecting group may not be sufficient to prevent the Ti-O interaction in this highly opened active site.

The presence of both ethylene and propylene in this system provides an advantage of understanding the polymerization mechanism. Comparing E/P ratio of terpolymer in all catalyst (i) and (c) runs (Table 4.1), the mole % of ethylene increases from 47% to about 80-90% in the absence and presence of allylOSi(Ph)$_2$t-Bu, respectively. This jump in ethylene content in the terpolymer indicates the presence of strong discrimination at the active site among the three monomers in their incorporation which is in the favor of ethylene. This may be explained by the presence of some interaction between polar groups and an active site which hinders the incorporation based on the monomer size. It is known that functional monomers interact with Ziegler-Natta catalysts via intra- and intermolecular modes$^{21}$. Therefore, this terpolymerization can be illustrated as shown in Scheme 4.1 & 4.2.

In general, during the course of ethylene/propylene copolymerization, the propagating $M^+\mathrm{C}$ site (II) will react with a allyl-OSi(Ph)$_2$t-Bu functional monomer to form an allyl-capped propagating site (III). The combination of steric congestion at the active site (especially for propylene and allyl insertions) and some acid-base interaction between the adjacent electron-rich
Scheme 4.1

Scheme 4.2
Table 4.1 Ethylene/Propylene/Allyl-OSi(Ph)\textsubscript{2}t-Bu Polymerization Using Various Catalyst Systems

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<th>E/P pressure (psi)</th>
<th>Time/Temp (min/°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mol%)</th>
<th>AllylOSi (mol%)</th>
<th>Mn (g/mole)</th>
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polar group and metal cation may significantly reduce its reactivity toward monomers, which requires acid-base interaction between an acidic propagating site and basic vinyl monomers. In addition, this leads to higher ethylene incorporation than propylene.

Two possible interactions are illustrated in Scheme 4.2: an intermolecular coordination of the surrounding polar groups (in polymers or monomers) and an intramolecular coordination of the polar group from the last inserted monomer unit. Both processes compete with olefin insertion. In an attempt to decouple these two effects, copolymerizations of ethylene and propylene in the presence of the saturated monomer analogue, propyl-OSi(Ph)$_2$t-Bu, were investigated using the same catalysts and reaction conditions. The experimental results are summarized in Table 4.2, which show an overall dramatic reduction of functional group effect. In rac-Et[Ind]ZrCl$_2$ catalyst system, propyl-OSi(Ph)$_2$t-Bu shows little or no effect on catalyst activity, E/P ratio, and molecular weight of the resulting polymer. In the case of Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ catalyst (c), all three parameters only change slightly. It is interesting to observe some catalyst activity in the catalyst (d) that is completely deactivated by a small amount of ally-OSi(Ph)$_2$t-Bu (Table 4.1). Overall, the effect of propyl-OSi(Ph)$_2$t-Bu on catalyst (d) is also relatively small.

It can be concluded that the effect of the OSi(Ph)$_2$t-Bu group to the catalyst mostly arises from intra-molecular interaction between the incorporated functional groups in the polymer, especially the last functional monomer unit, and metal cation at the propagating chain end, as illustrated in Scheme 4.2. This intra-molecular interaction dramatically reduces catalyst
activity and increases ethylene content (Table 4.1). As will be discussed later, it also alters polymer chain releasing modes (chain transfer reactions) to ally-OSi(Ph)$_2$-t-Bu, without significantly changing polymer molecular weight. The degree of this intra-molecular interaction is very dependent on the catalyst, which may be directly relative to the spatial opening of the active site. [((C$_5$Me$_4$)SiMe$_2$N(t-Bu))TiCl$_2$ catalyst (d) with much opened active site is mostly vulnerable toward coordinating with polar group.

It’s very important to realize that the intra-molecular interaction between the last functional monomer unit and metal cation happens in both catalysts (i) and (c) systems during the polymerization. As will be discussed later, this interaction provides possible conditions for the preparation of chain end functionalized polymers.

Figures 4.6 and 4.7 show $^1$H NMR spectra of E/P/allyl-OSi(Ph)$_2$-t-Bu terpolymers prepared by catalysts rac-Et[Ind]ZrCl$_2$ and Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$, respectively (Table 4.1). In addition to the three major peaks between 0.8 and 2.0 ppm for the CH$_3$, CH$_2$, and CH groups in the EP backbone, there are two sets of aromatic proton peaks at 7.4 and 7.7 ppm for the protecting Si-(Ph)$_2$ group. In addition, a new peak appears at 3.5 ppm which is due to CH$_2$-O. The peak intensities for this ether peak and aromatic peaks increase with the increase of allyl-OSi concentration in the feed. Several minor peaks at 4.7-4.9 ppm, corresponding to vinylidene protons in CH$_2$-C(CH$_3$)- unit, and at 5.0 and 5.9 ppm, corresponding to internal olefinic protons in CH$_3$-CH=CH- unit, are also detectable, which result from spontaneous chain transfer reaction by β-hydride elimination at propylene-cape propagating chain end after 1,2- and 2,1-insertion of propylene$^{22}$,
Table 4.2 Ethylene/Propylene Copolymerization in the Presence of Propyl-OSi(Ph)₂t-Bu
Using Various Catalyst Systems

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Figure 4.6. $^1$H NMR spectra of four comparative E/P/allyl-OSi(Ph)$_2$t-Bu terpolymers prepared by the same E/P feed ratio (1/1) but varying the amount of allyl-OSi(Ph)$_2$t-Bu (a) 0.25, (b) 0.5, (c) 1.0 and (d) 2.0 mL, using rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst.
Figure 4.7. $^1$H NMR spectra of four comparative E/P/allyl-OSi(Ph)$_2$-Bu terpolymers prepared by the same E/P feed ratio (1/1) but varying the amount of allyl-OSi(Ph)$_2$-Bu (a) 0.25, (b) 0.5, (c) 1.0 and (d) 2.0 mL, using Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ / MAO catalyst.
respectively. The extent of β-hydride elimination is significantly higher in rac-Et(Ind)₂ZrCl₂ case, which also reflects in the lower polymer molecular weight (Table 4.1). Note that this spontaneous chain transfer reaction by β-hydride elimination shown in rac-Et(Ind)₂ZrCl₂-mediated E/P polymerization is diminished with the increase of allyl-OSi monomer and goes to an undetectable level in case of Ph₂Si-[(Cp)(Flu)]ZrCl₂. The allyl-OSi group seems to gradually take over the chain transfer reaction, and such a reaction will result in allyl-OSi group terminated PP polymer.

4.3.4. Effect of Hydrogen on E/P/allyl-OSi(Ph)₂-t-Bu Polymerization

In the absence of hydrogen, the results clearly reflect the competitive nature of coordination at the metallocene active site. Once the propagating EP chain has the chance to react with allyloxy-tertbutyldiphenylsilane monomer, the intra-molecular interaction between the polar groups and the central metal atom as well as the bulkiness of the protecting group will slow down the propagation process. This allyl-O-capped propagating site (III) may face difficulties in reacting with propylene and allyl monomer due to steric hindrance, but only allows the insertion of ethylene, which continues the propagation process with a reduced rate.

In the presence of hydrogen, this slow propagating site (III) is expected to enhance the chance of hydrogenation to form chain end functionalized EP polymer (V) and generate a new active site (I) for continuing the polymerization cycle (Scheme 4.1). Table 4.3 summarizes several comparative runs of ethylene/propylene copolymerization using rac-Et(Ind)₂ZrCl₂ (i) and Ph₂Si-[(Cp)(Flu)]ZrCl₂ (c) catalysts in the presence of
allyl-OSi(Ph)\textsubscript{2}t-Bu and varying H\textsubscript{2} concentrations. Hydrogen seems to have no significant effect in catalyst activity, E/P mole ratio, and allyl-OSi content, but changes the polymer molecular weight. Figures 4.8 and 4.9 show the GPC curves of two comparative sets of E/P/allylOSi(Ph)\textsubscript{2}t-Bu polymers prepared by rac-Et(Ind)\textsubscript{2}ZrCl\textsubscript{2} and Ph\textsubscript{2}Si-[(Cp)(Flu)]ZrCl\textsubscript{2} catalysts, respectively, under similar reaction conditions, except for varying hydrogen pressure. Figure 4.10 shows the plot of polymer molecular weight (Mn) versus H\textsubscript{2} pressure for these two E/P/allyl-OSi(Ph)\textsubscript{2}t-Bu polymer sets.

The direct hydrogen chain transfer reaction to the propagating polymer chain may happen in all polymerization reactions with hydrogen, which may be accompanied with hydrogenation reaction at the allylOSi-capped active site (III) in Scheme 4.1. In other words, hydrogen fails to selectively direct the incorporation of allylOSi(Ph)\textsubscript{2}t-Bu to every polymer chain end. This situation is very different from that of styrenic monomer cases, discussed in Chapter III, in which 2,1-insertion of styrenic monomer stops the polymerization, then the subsequent hydrogenation reaction regenerates the active site and forms the polymer containing a terminal styrenic molecule. AllylOSi(Ph)\textsubscript{2}t-Bu has low polymerization reactivity, and its 1,2-insertion adduct only slows down the polymerization reaction.

4.3.5. Effect of Protecting Group: AllylOSi(Ph)\textsubscript{2}t-Bu vs. AllylOAl(CH\textsubscript{3})\textsubscript{2}

It is interesting to study the alternative protecting group for allyl alcohol and to compare its effectiveness with -Si(Ph)\textsubscript{2}t-Bu group. As discussed earlier in the experimental part, trimethylaluminum was also used for protecting allyl alcohol. Aluminum compound offers some process
Table 4.3 Ethylene/Propylene/Allyl-OSi(Ph)₂t-Bu Polymerization Using rac-Et(Ind)₂ZrCl₂ and Ph₂Si-[(Cp)(Flu)]ZrCl₂ Catalysts at Various Hydrogen Pressures

<table>
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<th>Run</th>
<th>Cat.</th>
<th>E/P ratio</th>
<th>H₂ total (psi)</th>
<th>AllylOSi (mL)</th>
<th>Time/Temp (min/°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mol%)</th>
<th>AllylOSi (mol%)</th>
<th>Mn (g/mole)</th>
<th>PDI</th>
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<td>i</td>
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<td>0</td>
<td>107</td>
<td>0</td>
<td>10/55</td>
<td>32,860</td>
<td>47.0/35.0</td>
<td>0</td>
<td>37,500</td>
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<tr>
<td>iO1</td>
<td>i</td>
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<td>0</td>
<td>107</td>
<td>0.25</td>
<td>10/55</td>
<td>10,200</td>
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<td>114</td>
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<td>10/55</td>
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<td>0</td>
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Figure 4.8. GPC curves of a comparative set of EP-t-OSi polymers (runs iO1 to iO5) prepared by rac-Et(Ind)₂ZrCl₂/MAO catalyst under similar reaction conditions, except for varying hydrogen pressure: (b) 0, (c) 7, (d) 15, (e) 25, and (f) 35 psi; run (a) is EP only for comparison.
Effect of H₂ using Ph₂Si-[(Cp)(Flu)]ZrCl₂ with (AllylOSi)

Figure 4.9. GPC curves of a comparative set of EP-t-OSi polymers (runs iO1 to iO5) prepared by Ph₂Si-[(Cp)(Flu)]ZrCl₂/MAO catalyst under similar reaction conditions, except for varying hydrogen pressure: (a) 0, (b) 7, (c) 15, (d) 25, and (e) 35 psi
The results indicate that the effect of both protection methods is similar with only a slight difference on catalyst activity. The catalyst activity in the presence of allyl-OSi(Ph)$_2$-t-Bu is slightly higher than that in case of allyl-OAl(CH$_3$)$_2$. This may be attributed to the steric difference associated
with each type of protecting group where Si(Ph)$_2$-Bu group is much bulkier than Al(CH$_3$)$_2$ group. The difference is noticeable when a small amount of polar monomer is used but almost disappears at higher concentrations of polar groups around the active site. This may be explained as: by increasing the concentration of polar groups around the active site, the intra- and intermolecular interaction increase until reaching a saturation point after which the activity reaches steady state.

4.3.6. Copolymerization of Ethylene and Propylene in the Presence of AllylN(SiMe$_3$)$_2$

It is important to extend this functionalization process to synthesize amine containing ethylene-propylene rubber. The protected amine group contains two substitutions, which may have better protection and perform better than the corresponding alcohol group containing only one substitution. Polymerizations of ethylene/propylene and protected allyl amine was conducted in the presence and absence of hydrogen. Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ (c), and [((C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ (d) catalysts have been chosen for this study because of their ability to produce high molecular weight polymers with minimum undesirable chain transfer reactions, such as β-hydride elimination.

As discussed earlier in this chapter, polymer structure has been determined by the combination of FT-IR, $^1$H NMR and GPC. The mole ratio of ethylene/propylene in the polymer was conveniently determined by an FT-IR technique$^{24}$ (following ASTM standard method), which compares the integrated intensity between the absorption at 1460 cm$^{-1}$, corresponding to
Table 4.4. Comparative Study of the Effect of the Protecting Group. AllylOSi(Ph)$_2$t-Bu vs. AllylOAl(CH$_3$)$_2$

in Ethylene/Propylene Polymerization Using rac-Et(Ind)$_2$ZrCl$_2$ Catalyst

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<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mol%)</th>
<th>AllylO- (mol%)</th>
<th>Mn (g/mole)</th>
<th>PDI</th>
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<td>10/55</td>
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Figure 4.11. GPC of E/P/allylOAl(CH$_3$)$_2$ (top) and E/P/allylOSi(Ph)$_2$t-Bu (bottom) prepared by rac-Et(Ind)$_2$ZrCl$_2$ with varying the allyl monomer concentrations.
the C-H bonds, and the absorption at 1379 cm$^{-1}$, corresponding to the CH$_3$ group in the propylene unit. GPC determines the polymer molecular weight and polydispersity index (PDI).

Table 4.5 summarizes the results of terpolymerization of ethylene/propylene/allylbis(trimethylsilyl)amine prepared by using Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ (c) and [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ (d) catalysts. The study was performed by running the reaction at different concentrations of the functional monomer for each catalyst system. It is clear that there are dramatic reductions in the catalyst activity and polymer molecular weight in case of catalyst (d); but only a mild effect on E/P mole ratio. On the other hand, the Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ catalyst system exhibits a much smaller allylN(SiMe$_3$)$_2$ effect; the increase of allylN(SiMe$_3$)$_2$ in the feed has only a mild effect on catalyst activity, polymer molecular weight, and E/P mole ratio. The presence of allylN(SiMe$_3$)$_2$ seems to have no significant problem in Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$-mediated E/P polymerization, except for a small preference in ethylene incorporation. As discussed before, ligand geometry around each catalyst plays a very important role in the catalyst performance. The completely opened active site in catalyst (d) is much easier for interacting with polar monomer than in the case of the crowded catalyst (c). Overall, the incorporation of allylN(SiMe$_3$)$_2$ in all runs are very small, almost below the NMR detection level.

It is interesting to note the difference between protected allyl amine and allyl alcohol (discussed before). Comparing both results, we can find that protected amine monomer provides better protection than the corresponding protected alcohol. This may be attributed to the fact that the
polar group (N) in allylN(SiMe$_3$)$_2$ has two substitutions while the oxygen atom in allylOSi(Ph)$_2$t-Bu has only one substitution. This double substitution on the nitrogen atom affords better protection efficiency of amines than alcohols. However, the significant steric congestion of allylN(SiMe$_3$)$_2$ may also reduce its reactivity during the polymerization. All polymers formed exhibit narrow molecular weight distribution (PDI~2), a strong characteristic of well-defined metallocene polymerization.

As discussed before, the presence of a polar monomer in the system is associated with two possible interactions (Scheme 4.2): an intermolecular coordination of the surrounding polar groups and an intramolecular coordination of the incorporated polar group in the polymer chain, especially the last inserted allylN(SiMe$_3$)$_2$ unit.

Because these two interactions compete with olefin insertion, it was peculiar to copolymerize ethylene and propylene in the presence of the saturated monomer analogue, propylN(SiMe$_3$)$_2$ using the same catalysts and reaction conditions (Table 4.6). The results indicate that, in the case of Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ catalyst (c), propylN(SiMe$_3$)$_2$ has little effect on activity, mole % of E, and molecular weight in ethylene/propylene copolymerization. On the other hand, in the case of [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ (d) catalyst, propylN(SiMe$_3$)$_2$ has a significantly decreasing effect on activity and molecular weight and shows little effect on the E/P ratio.

It can be concluded from these results that, in the case of Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ catalyst (c), the well-protected allyl amine has little interaction (both inter- and intra-) with the metal center.
Table 4.5 Ethylene/Propylene/Allylbis(trimethylsilyl)amine Polymerization Using [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ (d) and Ph₂Si-[(Cp)(Flu)]ZrCl₂ (c) Catalyst Systems

<table>
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<th>Cat.</th>
<th>E/P ratio</th>
<th>E/P pressure (psi)</th>
<th>AllylNSi (mL)</th>
<th>Time/Temp (min/o°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E (mol%)</th>
<th>P (mol%)</th>
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Table 4.6 Ethylene/Propylene Copolymerization in the Presence of PropylN(SiMe$_3$)$_2$ Using Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ (c) and [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ (d) Catalyst Systems

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<th>P (mol%)</th>
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The overall reactivity of allylN(SiMe$_3$)$_2$ is extremely low in this catalyst (c) system. In contrast, [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ catalyst (d) with an opened active site engages inter-molecular interaction between the polar group and metal cation.

4.3.7. Effect of Hydrogen on Ethylene/Propylene/AllylN(SiMe$_3$)$_2$ Polymerization.

Table 4.7 compares several systematic results with a fixed amount of allylN(SiMe$_3$)$_2$ and varying hydrogen pressure during [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$/MAO and Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$/MAO mediated E/P/allylN(SiMe$_3$)$_2$ polymerization. Figure 4.12 shows GPC curves of the resulting E/P/AllylN(SiMe$_3$)$_2$ polymers prepared by [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ catalyst; (top) varying the allyl monomer concentrations and (bottom) with varying H$_2$ pressure.

In the case of using [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ (d) catalyst, hydrogen seems to slightly increase catalyst activity and reduce E/P mole ratio toward normal level in simple E/P copolymerization, and systematically reducing the polymer molecular weight to a saturated level with high hydrogen pressure. Overall, it implies that some consecutive chain transfer reaction to AllylN(SiMe$_3$)$_2$ then H$_2$ may happen to form EP polymer with a terminal AllylN(SiMe$_3$)$_2$ group. However, with the relatively small effects it can not rule out some significant direct chain transfer reaction to hydrogen to form unfunctionalized EP polymer. However, in the case of Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$/MAO mediated E/P/allylN(SiMe$_3$)$_2$ polymerization, hydrogen has no effect to the polymer molecular weight, but reducing
Figure 4.12. GPC of E/P/ AllylN(SiMe$_3$)$_2$ prepared by [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ catalyst; (top) with varying the allyl monomer concentrations and (bottom) with varying H$_2$ pressure.
catalyst activity and increasing ethylene incorporation. The introduction of hydrogen seems to do more harm than good in the attempt to form chain-end functional polymer.

4.3.8. End group analysis of E/P/AllylN(SiMe$_3$)$_2$ Polymerization.

End group analysis$^{25}$ based on NMR alone is very difficult to determine allylN(SiMe$_3$)$_2$ incorporation mode in the E/P copolymer. Although it’s possible to determine the allylN(SiMe$_3$)$_2$ content in low molecular weight polymer, it is almost impossible to distinguish its incorporation modes between pedant side chains (copolymerization mode) and chain end (chain transfer mode).

An alternative method was applied to evaluate the mode of allylN(SiMe$_3$)$_2$ incorporation, which involves coupling reaction between E/P/AllylNH$_2$ polymer (after deprotection) and two reagents, i.e. maleated EP (EPMA) and PP (PPMA) polymers. As shown in Scheme 4.3, E/P/allylNH$_2$ polymer samples (dn2, dn6, cn1 and cn4 in Table 4.5) were introduced in coupling reactions with EPMA and PPMA. As expected, the chain end NH$_2$-terminated EP will form soluble EP-g-EP and PP-g-EP graft copolymers, soluble at ambient temperature in EP-g-EP case and at an elevated temperature for PP-g-EP case. On the other hand, the side chain NH$_2$-functionalized EP (containing multiple functional groups) will cause insoluble cross-linked products in both cases. If some unfunctionalized EP polymer does present itself in the product, this polymer will be always soluble at ambient temperature, which can be easily separated after maleation reaction with PPMA reagent.
All E/P/allylNH₂ polymer samples (dn2, dn6, cn1 and cn4 in Table 4.5) coupled with EPMA were completely soluble in toluene at room temperature, and the samples coupled with PPMA were completely soluble in hot toluene. It was surprising to learn that after cooling down the toluene solution of samples coupled with PPMA, the most part of the product was precipitated from polymer solution. Only traces (almost no polymer) remain in the solution part when checked with adding methanol. Figure 4.13 shows the ¹H NMR spectra of the coupling products, confirming PP-g-EP and EP-g-EP polymers. On the other hand, the corresponding samples dn8 and dn10 (Table 4.7) prepared in the presence of hydrogen and sample dPrN1 (Table 4.6) prepared in the presence of saturated propyN(SiMe₃)₂ show a major portion of pure (unfunctionalized) EP polymer that are soluble at ambient temperature after reacting with PPMA under similar reaction conditions.

Overall, the solubility study indicates that most of the resulting E/P/allylNH₂ polymers (Table 4.5), with high molecular weight and normal E/P ratio (similar to that of simple E/P copolymerization), prepared by both catalysts (c) and (d) are capped with an NH₂ terminal group. The presence of
enchainment incorporation is so small to the level that cannot be detected by either NMR or solubility tests.

It’s very interesting to note that allyN(SiMe$_3$)$_2$ can serve as a chain transfer agent to form NH$_2$-terminated EP polymers without hydrogen. In fact, hydrogen gives negative effect to the product (discussed before). Due to the two bulky silane protecting groups causing steric congestion around olefinic group during the polymerization, it is very difficult to incorporate this monomer into the E/P polymer. However, once it is incorporated, the resulting propagating chain end cannot further react with all monomers, including ethylene, propylene, and allyN(SiMe$_3$)$_2$. The only reaction option is to complete chain transfer reaction, possibly with Al-CH$_3$ (MAO) existing in the solution. This mechanism is different from that of p-MS/H$_2$ chain transfer reaction, discussed in Chapter III, in which p-MS capped EP polymer becomes very selective in reacting with ethylene. The current mechanism also helps to explain the flat E/P ratio with various allyN(SiMe$_3$)$_2$ concentration. One major drawback in this reaction scheme is its low reactivity of allyN(SiMe$_3$)$_2$. In other words, it’s very difficult to control the resulting polymer molecular weight.

**4.3.9. Effect of Protecting Group: AllylN(SiMe$_3$)$_2$ vs. AllylN[Al(CH$_3$)$_2$]$_2$**

An alternative method for protecting the nitrogen atom was developed by treating allyl amine with trimethylaluminum, as described in the experimental part. Ethylene/propylene copolymerization has been conducted with Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$/MAO catalyst system in the presence of
Table 4.7 Ethylene/Propylene/AllylN(SiMe\(_3\))\(_2\) Polymerization Using [(C\(_5\)Me\(_4\))SiMe\(_2\)N(t-Bu)]TiCl\(_2\) (d) and Ph\(_2\)Si-[(Cp)(Flu)]ZrCl\(_2\) (c) Catalysts at Various Hydrogen Pressure

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<th>Cat. Actv. (Kg/mol.hr.)</th>
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<th>P (mol%)</th>
<th>Mn (g/mole)</th>
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Figure 4.13. $^1$H NMR spectra of coupling product with PPMA and EPMA. (a) PP, (b) PP-g-EP and (c) EP-g-EP.
AllylN[Al(CH₃)₂]₂ using similar reaction conditions that were applied in case of AllylN(SiMe₃)₂. Table 4.8 compares two sets of terpolymers prepared by two different protection groups. Overall, trimethylaluminum group shows weak protection. Both catalyst activity and molecular weight decrease and E/P ratio increases with increasing AllylN[Al(CH₃)₂]₂ concentration in the feed. This may be again attributed to the existence of some mono-substituted allyl amine that can not be separated from the main di-substituted one. Consequently, both intra- and intermolecular interactions with the metal cation lead to lowering catalyst activity and increasing polymer E/P ratio. In addition, these interactions pose difficulty at active site (III) to propagate and facilitate termination leading to a decrease in the polymer molecular weight.

As mentioned before, end group analysis can provide direct evidence of the mode of incorporation of the polar monomer, which is only possible for polymers with relatively low molecular weight due to NMR sensitivity. It was easy to calculate mole % of allyl alcohol incorporated in the EP polymer from the spectra of ¹H NMR (chemical shift of the methylene protons of the -CH₂O-). On the other hand, it was very hard for the -CH₂N-protons in a high molecular weight EP-allylamine polymer sample to show a measurable chemical shift. For this reason, low molecular weight polymer samples have been prepared and effectively characterized as shown in Table 4.8 (samples: cnal9 and cnal10). E/P/AllylN[Al(CH₃)₂]₂ polymerizations were run at only 35 psi E/P monomer mixture pressure for run (cnal9) and 35 psi E/P plus 25 psi H₂ for run (cnal10).
Figure 4.14 shows \(^1\)H NMR spectra of E/P/AllylN[Al(CH\(_3\)]\(_2\)]\(_2\) prepared by Ph\(_2\)Si-[(Cp)(Flu)]ZrCl\(_2\)/MAO catalyst system (cnal10). The measurement was done for a neat EP-t-NH\(_2\) (a) and for an HCl treated sample (b). Comparing the NMR results of both samples, we notice that the chemical shift in the range 2.6-2.9 ppm in the HCl treated sample is clear and distinguishable. In addition, another new chemical shift appears in the range 8.3-8.4 ppm due to the three protons of NH\(_3\)Cl\(^-\) group\(^{27}\).

Again, it is clear from the results of these two runs that there is no need for hydrogen to introduce the NH\(_2\) at the chain end, however AllylN[Al(CH\(_3\)]\(_2\)]\(_2\) behaves as a chain transfer agent by itself.

### 4.3.10. Copolymerization of Ethylene and Propylene in the Presence of BuN[Si(CH\(_3\)]\(_2\)]\(_2\)

Since the steric congestion in allylN[Si(CH\(_3\)]\(_2\)]\(_2\) results in low reactivity, it is curious to increase the spacer between polar group and vinyl group with the objective to increase functional monomer incorporation. Therefore, BuN[Si(CH\(_3\)]\(_3\)]\(_2\) monomer having two methylene spacer was synthesized and investigated in E/P/BuN[Si(CH\(_3\)]\(_3\)]\(_2\) polymerization. BuN[Si(CH\(_3\)]\(_3\)]\(_2\) monomer was synthesized with the procedures described in the experimental part. The first study was to determine the suitable catalysts that can effectively incorporate BuN[Si(CH\(_3\)]\(_3\)]\(_2\) monomer in E/P copolymerization, before thinking about altering the BuN[Si(CH\(_3\)]\(_3\)]\(_2\) incorporation mode from copolymerization to chain transfer reaction. The same three commonly known bridged metallocene catalyst systems were investigated, including rac-Et(Ind)\(_2\)ZrCl\(_2\) (i), Ph\(_2\)Si-[(Cp)(Flu)]ZrCl\(_2\) (c),
Table 4.8. Comparative Study of the Effect of the Protecting Group. AllylN(SiMe$_3$)$_2$ vs. AllylN[Al(CH$_3$)$_2$]$_2$ in Ethylene/Propylene Polymerization Using Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$/MAO Catalyst

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<tr>
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(a) cnal9: H$_2$=0 psi and total mix pressure = 35 psi
(b) cnal10: H$_2$=25 psi and total mix pressure = 60 psi
Figure 4.14. $^1$H NMR spectra of E/P/AllylN[Al(CH$_3$)$_2$]$_2$ prepared by Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$/MAO catalyst system: (a) cnal10, (b) cnal10 after treating with HCl
and [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ (d) as illustrated earlier in this chapter. The terpolymerization of E/P/BuN[Si(CH₃)₃]₂ was performed by running the reaction at different concentrations of the functional monomer for each catalyst system. Table 4.9 summarizes the experimental results.

Overall, BuN[Si(CH₃)₃]₂ shows significantly different from allyN[Si(CH₃)₃]₂ in all catalyst systems, with much higher BuN[Si(CH₃)₃]₂ incorporation. Both rac-Et[Ind]ZrCl₂ and Ph₂Si-[(Cp)(Flu)]ZrCl₂, exhibit excellent stability to N[Si(CH₃)₃]₂ group and good response to BuN[Si(CH₃)₃]₂ functional monomer, with increasing ethylene incorporation and reducing polymer molecular weight. The incorporation of BuN[Si(CH₃)₃]₂ units also increase ethylene content and reduce polymer molecular weight, especially in rac-Et[Ind]ZrCl₂ and Ph₂Si-[(Cp)(Flu)]ZrCl₂ cases. Such a combination increases the likelihood of altering BuN[Si(CH₃)₃]₂ copolymerization mode into consecutive chain transfer reaction with hydrogen, as illustrated in Scheme 4.1, to form chain end functionalized polymer with control polymer molecular weight.

In rac-Et(Ind)₂ZrCl₂ (i) cases, the E/P mole ratio in the terpolymer show a gradual increase with increasing BuN[Si(CH₃)₃]₂ concentration, while polymer molecular weight proportionally decreased without altering the catalyst activity. In addition, the increase of BuN[Si(CH₃)₃]₂ concentration linearly increase BuN[Si(CH₃)₃]₂ incorporation. The BuN[Si(CH₃)₃]₂ capped propagating site (III) seem to have no significant problem in continuing the propagation process, except for a small preference in ethylene incorporation.
The effect of BuN[Si(CH₃)₃]₂ in Ph₂Si-[(Cp)(Flu)]ZrCl₂ (c) cases significantly change E/P incorporation ratio and slightly reduce the catalyst activity. BuN[Si(CH₃)₃]₂ capped propagating site (III) may face difficulties in reacting with propylene and BuN[Si(CH₃)₃]₂ due to steric hindrance, but only allows the insertion of ethylene, which continues the propagation process with a reduced rate.

On the other hand, [(C₅Me₄)SiMe₂N(t-Bu)]TiCl₂ (d) catalyst has an opened active site that is easily accessible by the three monomers, as well as coordination with the functional group. As expected, BuN[Si(CH₃)₃]₂ may increase incorporation level, but the interaction between the active site and N[Si(CH₃)₃]₂ may reduce catalyst activity. Similar to allyN(SiMe₃)₂, two bulky silane protecting groups at BuN[Si(CH₃)₃]₂-capped chain end may cause steric congestion around the active site for further polymerization.

Figures 4.15 and 4.16 show the ¹H NMR spectra of E/P/ BuN[Si(CH₃)₃]₂ terpolymers prepared by catalysts rac-Et[Ind]ZrCl₂ and Ph₂Si-[(Cp)(Flu)]ZrCl₂, respectively (Table 4.9). In addition to the three major peaks between 0.9 and 1.6 ppm for the CH₃, CH₂, and CH groups in the EP backbone, there are two new peaks appearing at (2.8-3.0) and 0.2 ppm due to CH₂-N and [Si(CH₃)₂]₂, respectively. The intensities of these last two peaks increase with the increase of BuN[Si(CH₃)₃]₂ concentration in the feed. In Figure 4.15, the minor peaks at 4.7-4.9 ppm and 2.0 ppm, corresponding to vinylidene and methyl protons in CH₂=C(CH₃)- unit, and at 5.0 and 5.9 ppm, corresponding to vinyl protons in CH₂=CH-CH₂- unit, result from spontaneous chain transfer reaction in rac-Et[Ind]ZrCl₂ system by β-hydride elimination at propylene-caped propagating chain end after
Table 4.9. Ethylene/Propylene/BuN[Si(CH$_3$)$_3$]$_2$ Polymerization Using Various Catalyst Systems

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<th>BuN[Si(CH$_3$)$_3$]$_2$ (mL)</th>
<th>Time/Temp (min/°C)</th>
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<td>Cat. Actv. (Kg/mol.hr.)</td>
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<tr>
<td>CN15</td>
<td>c</td>
<td>1/1</td>
<td>107</td>
<td>2</td>
<td>10/55</td>
<td>25,390</td>
<td>85.92/13.17</td>
</tr>
<tr>
<td>EP-</td>
<td>d</td>
<td>1/1</td>
<td>107</td>
<td>0</td>
<td>10/55</td>
<td>23,500</td>
<td>35.05/64.95</td>
</tr>
<tr>
<td>DN5</td>
<td>d</td>
<td>1/1</td>
<td>107</td>
<td>0.25</td>
<td>10/55</td>
<td>9,580</td>
<td>47.23/52.46</td>
</tr>
<tr>
<td>DN1</td>
<td>d</td>
<td>1/1</td>
<td>107</td>
<td>0.5</td>
<td>10/55</td>
<td>7,080</td>
<td>48.74/50.75</td>
</tr>
<tr>
<td>DN3</td>
<td>d</td>
<td>1/1</td>
<td>107</td>
<td>1</td>
<td>10/55</td>
<td>3,480</td>
<td>44.70/54.42</td>
</tr>
<tr>
<td>DN4</td>
<td>d</td>
<td>1/1</td>
<td>107</td>
<td>2</td>
<td>10/55</td>
<td>2,280</td>
<td>52.16/45.74</td>
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</table>
Figure 4.15. $^1$H NMR spectra of E/P/BuN[Si(CH$_3$)$_3$]$_2$ terpolymers prepared by rac-Et(Ind)$_2$ZrCl$_2$ catalyst with different amounts of BuN[Si(CH$_3$)$_3$]$_2$, (a) 0.5 mL, (b) 1.0 mL, and (c) 2.0 mL.

Figure 4.16. $^1$H NMR spectra of E/P/BuN[Si(CH$_3$)$_3$]$_2$ terpolymers prepared by Ph$_2$Si-[(Cp)(Flu)]ZrCl$_2$ catalyst with different amounts of BuN[Si(CH$_3$)$_3$]$_2$, (a) 0.25 mL, (b) 0.5 mL, (c) 1.0 mL and (d) 2.0 mL.
Figure 4.17. $^1$H NMR spectra of E/P/BuNH$_3^+$Cl$^-$ prepared by [(C$_5$Me$_4$) SiMe$_2$N(t-Bu)]TiCl$_2$/MAO catalyst system.

1,2- and 2,1-insertion of propylene$^{28}$, respectively. It is also very interesting to note that this spontaneous chain transfer reaction by β-hydride elimination shown in rac-Et(Ind)$_2$ZrCl$_2$ mediated E/P polymerization is diminished with the increase of BuN[Si(CH$_3$)$_3$]$_2$ monomer. On the other hand, there is no undetectable β-hydride elimination in Ph$_2$Si-[((Cp)(Flu)]ZrCl$_2$ system, which always produces high molecular weight polymers. The combination of increasing BuN[Si(CH$_3$)$_3$]$_2$ incorporation and reducing polymer molecular weight indicates the tendency of incorporating BuN[Si(CH$_3$)$_3$]$_2$ monomer at the polymer chain end.

As an example, Figures 4.17 shows the $^1$HNMR spectra of E/P/BuN[Si(CH$_3$)$_3$]$_2$ terpolymer prepared by [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]- TiCl$_2$/MAO and treated with HCl. Figures 4.18, 4.19 and 4.20 show the GPC curves of
E/P/BuN[Si(CH₃)₃]₂ terpolymers prepared by the three mentioned catalysts with varying the amount of BuN[Si(CH₃)₃]₂. Note that in rac-Et[Ind]ZrCl₂ and Ph₂Si-[(Cp)(Flu)]ZrCl₂ cases, the increase in BuN[Si(CH₃)₃]₂ concentration reduces the molecular weight of high molecular weight portion with a minor effect on the low molecular weight analog. As a result shown in Table 4.9, the produced polymers have narrower polydispersity index with higher BuN[Si(CH₃)₃]₂ concentrations. The copolymerization mode of incorporating BuN[Si(CH₃)₃]₂ units in high molecular weight polymer may gradually engage in chain transfer mode as BuN[Si(CH₃)₃]₂ concentration increases.

4.3.11. Effect of Hydrogen on E/P/BuN[Si(CH₃)₃]₂ Polymerization

It is interesting to understand the effect of hydrogen during the E/P/BuN[Si(CH₃)₃]₂ polymerization. The major objective is to find the ideal hydrogen pressure that can completely alter BuN[Si(CH₃)₃]₂ incorporation mode from copolymerization to chain transfer reaction to form EP-t-NH₂ polymer. Table 4.10 summarizes several comparative runs of ethylene/propylene copolymerization using these three catalysts in the presence of a fixed amount of BuN[Si(CH₃)₃]₂ and varying H₂ concentrations.

Comparing runs IN1 to IN5 prepared by rac-Et(Ind)₂ZrCl₂ (i) catalyst, the catalyst activity maintains very high, and the EP polymer molecular weight is reduced following the chain transfer to BuN[Si(CH₃)₃]₂/H₂ as expected. In addition, mole % NH₂ does not change, which implies a decrease of the number of NH₂ units per polymer chain. The number of NH₂ units per polymer chain is 7 in
the case of IN1 ($H_2 = 0$ psi) while it becomes 1.7 in the case of IN5 ($H_2 = 35$ psi). Hydrogen seems to have a mild effect on both activity and E/P ratio in the case of this catalyst (i).

Figure 4.18. GPC of E/P/BuN[Si(CH$_3$)$_3$]$_2$ prepared by $rac$-Et(Ind)$_2$ZrCl$_2$ with varying the butenyl monomer concentration.
**Figure 4.19.** GPC of E/P/BuN[Si(CH$_3$)$_3$]$_2$ prepared by Ph$_2$Si-[Cp(Flu)]ZrCl$_2$ with varying the butenyl monomer concentration.

**Figure 4.20.** GPC of E/P/BuN[Si(CH$_3$)$_3$]$_2$ prepared by [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)]TiCl$_2$ with varying the butenyl monomer concentration.
Table 4.10 Ethylene/Propylene/ BuN[Si(CH$_3$)$_3$]$_2$ Polymerization Using Different Catalyst Systems; Effect of Hydrogen

<table>
<thead>
<tr>
<th>Run</th>
<th>Cat.</th>
<th>E/P ratio</th>
<th>H$_2$ (psi)</th>
<th>total (psi)</th>
<th>BuN[Si(CH$_3$)$_3$]$_2$ (mL)</th>
<th>Time/Temp (min/°C)</th>
<th>Cat. Actv. (Kg/mol.hr.)</th>
<th>E/P (mol%)</th>
<th>BuN[Si(CH$_3$)$_3$]$_2$ (mol%)</th>
<th>Mn (g/mole)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP-i</td>
<td>i</td>
<td>1/1</td>
<td>0</td>
<td>107</td>
<td>0</td>
<td>10/55</td>
<td>32,860</td>
<td>47.0/35.0</td>
<td>0</td>
<td>37,500</td>
<td>2.0</td>
</tr>
<tr>
<td>IN1</td>
<td>i</td>
<td>1/1</td>
<td>0</td>
<td>107</td>
<td>0.5</td>
<td>10/55</td>
<td>31,460</td>
<td>53.84/45.68</td>
<td>0.49</td>
<td>34,700</td>
<td>1.7</td>
</tr>
<tr>
<td>IN2</td>
<td>i</td>
<td>1/1</td>
<td>7</td>
<td>114</td>
<td>0.5</td>
<td>10/55</td>
<td>33,430</td>
<td>51.69/47.84</td>
<td>0.48</td>
<td>22,200</td>
<td>1.7</td>
</tr>
<tr>
<td>IN3</td>
<td>i</td>
<td>1/1</td>
<td>15</td>
<td>122</td>
<td>0.5</td>
<td>10/55</td>
<td>34,390</td>
<td>54.16/45.39</td>
<td>0.48</td>
<td>21,600</td>
<td>1.6</td>
</tr>
<tr>
<td>IN4</td>
<td>i</td>
<td>1/1</td>
<td>25</td>
<td>132</td>
<td>0.5</td>
<td>10/55</td>
<td>34,080</td>
<td>52.85/46.73</td>
<td>0.45</td>
<td>15,600</td>
<td>1.6</td>
</tr>
<tr>
<td>IN5</td>
<td>i</td>
<td>1/1</td>
<td>35</td>
<td>142</td>
<td>0.5</td>
<td>10/55</td>
<td>40,780</td>
<td>53.62/46.06</td>
<td>0.40</td>
<td>13,200</td>
<td>1.6</td>
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<td>107</td>
<td>0</td>
<td>10/55</td>
<td>40,420</td>
<td>47.2/52.8</td>
<td>0</td>
<td>228,400</td>
<td>1.7</td>
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<tr>
<td>CN8</td>
<td>c</td>
<td>1/1</td>
<td>0</td>
<td>107</td>
<td>0.5</td>
<td>10/55</td>
<td>29,230</td>
<td>66.81/32.94</td>
<td>0.37</td>
<td>100,200</td>
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</tr>
<tr>
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<td>c</td>
<td>1/1</td>
<td>7</td>
<td>114</td>
<td>0.5</td>
<td>10/55</td>
<td>14,260</td>
<td>75.33/24.49</td>
<td>0.35</td>
<td>74,700</td>
<td>1.6</td>
</tr>
<tr>
<td>CN10</td>
<td>c</td>
<td>1/1</td>
<td>15</td>
<td>122</td>
<td>0.5</td>
<td>10/55</td>
<td>13,340</td>
<td>78.04/21.81</td>
<td>0.33</td>
<td>66,900</td>
<td>1.7</td>
</tr>
<tr>
<td>CN11</td>
<td>c</td>
<td>1/1</td>
<td>25</td>
<td>132</td>
<td>0.5</td>
<td>10/55</td>
<td>8,740</td>
<td>76.36/23.48</td>
<td>0.33</td>
<td>54,900</td>
<td>1.7</td>
</tr>
<tr>
<td>CN12</td>
<td>c</td>
<td>1/1</td>
<td>35</td>
<td>142</td>
<td>0.5</td>
<td>10/55</td>
<td>8,110</td>
<td>77.94/21.89</td>
<td>0.36</td>
<td>52,700</td>
<td>1.7</td>
</tr>
<tr>
<td>EP-d</td>
<td>d</td>
<td>1/1</td>
<td>0</td>
<td>107</td>
<td>0</td>
<td>10/55</td>
<td>23,500</td>
<td>35.05/64.95</td>
<td>0</td>
<td>125,000</td>
<td>1.9</td>
</tr>
<tr>
<td>DN1</td>
<td>d</td>
<td>1/1</td>
<td>0</td>
<td>107</td>
<td>0.5</td>
<td>10/55</td>
<td>7,080</td>
<td>48.74/50.75</td>
<td>0.50</td>
<td>49,600</td>
<td>1.5</td>
</tr>
<tr>
<td>DN2</td>
<td>d</td>
<td>1/1</td>
<td>35</td>
<td>114</td>
<td>0.5</td>
<td>10/55</td>
<td>6,600</td>
<td>49.62/49.95</td>
<td>0.46</td>
<td>13,900</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Similar results were observed in the \[((\text{C}_5\text{Me}_4)\text{SiMe}_2\text{N}(\text{t-Bu}))\text{TiCl}_2\]\n
catalyst (d) case, which produces polymers with about 10 \(\text{NH}_2\) units per polymer chain for run DN1 (0 psi \(\text{H}_2\)) which becomes only 2 \(\text{NH}_2\) units per polymer chain for run DN2 at 35 psi \(\text{H}_2\).

On the other hand, the \(\text{Ph}_2\text{Si-[(Cp)(Flu)]ZrCl}_2\]\ncatalyst (c) shows a negative response to hydrogen. Similar to the \(\text{allyN}[\text{Si(\text{CH}_3)_3}]_2\) case (Table 4.7), hydrogen reduces catalyst reactivity and increases E/P ratio in the copolymer. Hydrogen reduces polymer molecular weight and \(\text{NH}_2\) content from 14 \(\text{NH}_2\) units per polymer chain in run CN8 (0 psi \(\text{H}_2\)) to about 6 \(\text{NH}_2\) units per polymer chain at 35 psi \(\text{H}_2\) pressure.

### 4.3.12. End group analysis of E/P/BuN[Si(\text{CH}_3)_3]_2 Polymerization.

As discussed before in section 4.3.7, end group analysis has been performed by investigating the coupling products of these samples with EPMA and PPMA. In this method, E/P/BuN[Si(\text{CH}_3)_3]_2 polymer samples (IN5, CN12 and DN2 in Table 4.10) were introduced in coupling reactions with EPMA and PPMA as shown in the experimental part and Scheme 4.3.

Both IN5 and DN2 samples coupled with EPMA were completely soluble in toluene at room temperature, and when coupled with PPMA were completely soluble in hot toluene. In addition, after cooling down the toluene solutions of these two samples coupled with PPMA and separating the precipitated polymer from solution, traces (almost no polymer) remain in the solution part when checked with adding methanol. On the other hand, sample CN12 produces crosslinked coupling product with both EPMA and
PPMA. These results are completely in consistence with the data obtained by $^1$H NMR analysis and GPC. Samples prepared in the absence of H$_2$ have been introduced into the same coupling reactions for comparison, and all show crosslinked materials.

Overall, catalysts (i) and (d) are suitable for producing EP-t-NH$_2$ polymers in the presence of a certain amount of hydrogen. With a controlled hydrogen pressure, it’s possible to direct the incorporation of BuN[Si(CH$_3$)$_3$]$_2$, from copolymerization to chain transfer mode, to form BuN[Si(CH$_3$)$_3$]$_2$ terminated EP copolymers (EP-t-NH$_2$) with a broad range of polymer molecular weight and E/P mole ratios.

4.4. Conclusion

In this chapter, we describe the copolymerization of ethylene and propylene in the presence of protected allylalcohol, allylamine and butenylamine. The functional groups of these polar monomers were protected to overcome the catalyst decay problem. The protection methods used here have been chosen in such a way that they would not only lead to the steric shielding, but also afford electronic neutralization of the functional groups. The systematic study of metallocene-mediated ethylene/propylene /protected polar monomer polymerization in absence and presence of H$_2$, with varying catalysts, polar monomer concentrations, and hydrogen pressures, provides the detailed reaction mechanism. With a combination of metallocene catalyst and a controlled hydrogen pressure, it’s possible to direct the incorporation of simple polar monomers, from copolymerization
to chain transfer mode, to form NH$_2$ and OH terminated EP copolymers with a broad range of polymer molecular weights and E/P mole ratios.

4.5. References


   (b) Schneider, M. J.; Schafer, R.; Mulhaupt, R.; *Polymer* **1997**, *38*, 2455.


15 Spectral Database For Organic Compounds SDBS, http://www.aist.go.jp/RIODB/SDBS/cgi


Xu, Y.; Painter, P. C.; Coleman, M. M. Polymer 1993, 34, 3010.

ASTM standard method; Designation D-3900-95.


ASTM standard method; Designation D-3900-95.


http://www.aist.go.jp/RIODB/SDBS/cgi


Chapter V
Preparation of EP/Polyisoprene Graft Copolymers
(EP-g-PI) via Anionic Polymerization.

5.1. Introduction

In Chapters (III) and (IV), we have shown a new class of functionalized EP copolymers, containing reactive groups at the chain end or/and in the side chains. Various functional EP copolymers with a broad range of compositions and well-defined molecular structures are available in our laboratory. It is very interesting to further explore the application of these functional EP copolymers, especially relative to the improvement of interfacial adhesion problem between rubber-rubber (i.e. EP/polyisoprene) interfaces in tires, which causes many accidents and lives due to tire failure.

One major advantage of the p-methylstyrene (p-MS) containing copolymers is their versatility [1] of the benzylic protons in the p-methylstyrene unit that can be converted to various functional groups. When lithiated with sec-BuLi/TMEDA, the benzylic anion in the p-MS unit can effectively initiate living anionic polymerization of isoprene monomer to form EP/polyisoprene graft and block copolymers with a living manner. Alternately, EP-g-PI graft copolymers can also be synthesized by direct coupling of living polyisoprene anions and p-chloromethylstyrene (p-ClMS) containing EP copolymer, using a grafting-onto scheme.
In the case of the divinylbenzene (DVB) containing EP copolymers (synthesis will be discussed in Chapter VI), the pending styrene units can serve as monomers, initiators and chain transfer agents, in a subsequent graft reaction with other olefinic monomers, including graft-from, graft-onto and graft through processes [2].

In this chapter, we focus on connecting two rubbers together to prepare EP/polyisoprene (EP-g-PI) graft copolymers via anionic graft polymerization by taking the advantage of reactive groups, including p-MS, p-ClMS, and DVB units, located along the EP backbone.

5.2. Experimental Details
5.2.1. Instrumentations and Materials

All instruments were the same as described in previous chapters. Isoprene monomer (Aldrich) was dried and distilled over calcium hydride under argon. N,N,N’,N’-tetramethyl-ethylenediamine (TMEDA), sec-BuLi (1.4 M in hexane), n-BuLi (1.6 M in hexane) (Aldrich), were used as received. All solvents were purified by refluxing with sodium/benzophenone under argon for 48 hours before distillation. All oxygen and moisture – sensitive manipulations were performed inside an argon–filled dry box.

5.2.2. Synthesis of EP-g-PI based using p-MS unit

The first reaction step is a lithiation reaction of EP-co-p-MS copolymer. In an argon-filled dry box, 1.5 g of EP-co-p-MS was dissolved
in 100 mL dry cyclohexane in a 250 mL air-free flask with a magnetic stirrer bar. Then, 0.5 mL (0.63 mol) of sec-BuLi (1.4M solution in hexane) and 0.1 mL (0.63 mol) of TMEDA were added and the flask was brought out of the dry box and heated to 60 °C for 8 hours under argon. The reaction was then cooled to room temperature before adding the dry isoprene monomer. The anionic polymerization was performed by distilling the dry isoprene monomer (10 mL) into the flask -using vacuum line and let it to polymerize at room temperature for overnight. After terminating the reaction with methanol, the produced polymer was fractionated to separate any isoprene homopolymer, and then dried with vacuum for 8 h before analysis.

5.2.3. Fractionation

Since s-BuLi was used in a little excess to assure effective initiation, so some isoprene homopolymer may be generated along with the anionic grafting polymerization. Thus, removal of these contaminates before characterization was necessary, so that the copolymer composition would be reliable. The fractionation method was based on the solubility difference of the graft copolymer and the contaminating homopolymer. So, isoprene homopolymer was isolated from EP-g-PI by sequential extraction with selective solvents: THF and MEK in 1:2 v/v ratio. Details of the fractionation procedure are schematically shown in Scheme 5.1. This method of separation was found to be effective. The isolated amount of homopolymer was less than 10% and the major separated product was EP-g-PI graft copolymer. This was confirmed by \(^1\)HNMR analysis for both fractionation products and for a pure sample of polyisoprene prepared for comparison.
Scheme 5.1: Block diagram of graft copolymer fractionation process

5.2.4. Synthesis of EP-g-PI copolymers using p-ClMS units

Isoprene monomer (35 mL) in 200 mL anhydrous cyclohexane was anionically polymerized with 0.5 mL of 1.6 M n-BuLi/hexane and 0.1 mL (TMEDA) at room temperature for overnight. The resulting yellow solution
was then used to titrate a THF solution of p-chloromethylstyrene containing 3.0 g EP copolymer up to the first change in color[3-4]. The coupling reaction was left to react for overnight before termination and precipitation with methanol. The precipitated polymer was subjected to the same fractionation method mentioned before where the separation components were analyzed by $^1$H-NMR.

5.2.5. Synthesis of EP-g-PI using DVB units

Anionic graft-from polymerization: (Using TMEDA)

In an argon filled dry box, 2.0 g of EP-co-DVB copolymer was dissolved in 100 mL of anhydrous cyclohexane in a 250 mL air-free flask with a magnetic stirrer bar. Then, the prescribed amounts of n-BuLi/TMEDA (1/1 mole ratio) were added to the reactor. The resulting mixture was stirred at ambient temperature for 3 hours before adding the isoprene monomer. An anionic graft-from reaction was then carried out at ambient temperature for 4 hours before adding 10 mL of methanol to terminate the reaction. The produced polymer was isolated, subjected to fractionation and then dried with vacuum for 8h before analysis.

Anionic graft-from polymerization: (Without TMEDA)

In an argon filled dry box, 2.0 g of EP-co-DVB copolymer was dissolved in 100 mL of anhydrous cyclohexane in a 250 mL air-free flask with a magnetic stirrer bar. Then, the prescribed amount of n-BuLi was placed into the reactor. Then, the reactor was sealed, carried out of the dry box and was heated to 60 °C for 1 h. The reaction was then cooled to room
temperature before adding the dry isoprene monomer. The anionic polymerization was performed by distilling the dry isoprene monomer (10 mL) into the flask -using vacuum line and let it to polymerize at room temperature for 4 hours. After terminating the reaction with methanol, the produced polymer was fractionated to separate any isoprene homopolymer, and then dried with vacuum for 8h before analysis.

Anionic graft-onto polymerization:

Isoprene monomer (30 mL) in 200 mL anhydrous cyclohexane was anionically polymerized with 0.4 mL of 1.6 M n-BuLi/hexane at room temperature for 4h. The calculated amount of the isoprene living polymer was added to a solution of 2.0 g of EP-co-DVB in 100 mL of anhydrous cyclohexane. An anionic graft-onto reaction was then carried out at ambient temperature for 8 hours before adding 10 mL of methanol to terminate the reaction. The produced polymer was isolated, subjected to fractionation and then dried with vacuum for 8 h before analysis.

5.3. Results and Discussion

5.3.1. Anionic graft-from polymerization via p-MS reactive group

The lithiation reaction was performed by mixing s-butyllithium/TMEDA (N,N,N’,N’- tetramethylethylenediamine) complex [5] with EP-co-p-MS solution in cyclohexane at 60°C for a few hours. It was reported that this metallation is selective towards the p-methyl group using s-BuLi/TMEDA, (see Scheme 5.2) [1]. Then, the living anionic polymerization took place at room temperature for overnight similar to the well-known solution
anionic polymerization [6]. The reaction mixture was usually subjected to the separation of the graft copolymer from the polyisoprene homopolymer. The method of separation is based on the different solubility behaviors, where polyisoprene homopolymer is completely soluble in methylethylketone (MEK) while EP-co-p-MS is not, making it easy to remove PI homopolymer. Further separation step was performed to make sure the complete removal of any PI homopolymer.

*M: Isoprene or any other anionic polymerizable monomer such as: styrene, p-MS, butadiene, MMA, AN, …etc

Scheme 5.2
Figure 5.1 shows the $^1$H-NMR spectra of EP-co-p-MS (top), and EP-g-PI (bottom) derived from it (containing 45 mole % IP content). By comparing both spectra, we can notice that, two additional chemical shifts arise at (4.5-5.03) ppm corresponding to two external olefinic protons (\(=\text{CH}_2\)) in the 1,2 and 3,4 structures, and at 5.68 ppm corresponding to internal protons (\(-\text{CH}=-\)) in the 1,2 structure. A new chemical shift arises at 2.0 ppm which is due to \((-\text{CH}_3\)) in the isoprene structure. The relative integrated peak areas at 0.8 to 1.8 ppm, (4.5-5.03) ppm and 5.68 ppm and the number of protons each peak represents quantitatively give the total PI graft content and mole ratio of 1,2- and 3,4-microstructures.

It should be taken into account that the incorporation mode of isoprene in the graft depends on the polarity of the polymerization medium [7]. So, the predominant 1,2 and 3,4 additions of isoprene over the 1,4 mode must have been due to the existence of the polar chelating agent TMEDA (from lithiation reaction) at the \(\text{Li}^+\) active site. Overall, the mole % of isoprene content in the graft copolymer estimated by $^1$H-NMR calculations was in good agreement with that estimated by the weight increase in the graft copolymer.
Figure 5.1. $^1$H-NMR of: EP-co-pMS (Top), EP-g-PI (Bottom)
Figure 5.2 compares the GPC curves of the starting EP-co-p-MS (Mn = 22,000 & Mw/Mn = 2.2) and the EP-g-PI copolymer (Mn = 70,000 & Mw/Mn = 1.04).

![Figure 5.2. GPC curves of EP68 and EP-g-PI](image)

Similar results were observed in other graft-from reactions using high molecular weight EP-co-p-MS copolymers. Figure 5.3 compares the $^1$H-NMR spectrum of three separation fractions derived from high molecular weight EP-g-p-MS copolymer (EP107). In addition to a very small fraction of the unreacted EP-co-p-MS copolymer, the major portion is EP-g-PI graft copolymer containing 46 mole % of PI. GPC shows a slight increase of polymer molecular weight, which may be attributed to a high graft density (number of graft side chains per 1000 carbon of the EP-backbone) [8]. However, it is also known that the same hydrodynamic volume increase would not be observed in the graft copolymer [9].
Figure 5.3. $^1$H-NMR of: EP107 (Top), EP107-g-IP (Middle) and washed out PIP homopolymer (Bottom)
5.3.2. Anionic graft-onto polymerization via p-ClMS reactive group.

In this case, macro-anions of isoprene are grafted onto a substrate of EP containing p-chloromethylstyrene units (EP-co-p-CLMS). The addition of TMEDA in this reaction is very important in suppressing side reactions such as metal – halogen exchange and cross – linking and to improve the overall grafting efficiency [10]. During this method [4], isoprene was first polymerized using n-BuLi/TMEDA in dry cyclohexane. Then, the resulting yellow solution was used to titrate a THF solution of p-chloromethylstyrene containing EP copolymer up to the first change in color. See Scheme (5.3)

Scheme 5.3: Coupling reaction between p-chloromethylstyrene and polyisoprenyl living anions

It was reported that this anionic graft-onto process is very sensitive to the polarity of reaction medium [11]. Reduction of solvent polarity has a negative effect to the coupling efficiency (< 40 % in hydrocarbon solvents), while it can reach > 95 % in mixed benzene/THF solvent (1:2 v/v). Two EP-
co-p-CLMS samples, containing 0.65 and 0.1 mole % of p-CLMS units, were used in this graft-onto reaction. Most of reaction products are graft copolymers with 69 and 56 mole % of PI contents, respectively. Figure 5.4 shows the $^1$H-NMR spectra (from top to bottom), the separated ungrafted EP-p-ClMS, the grafted sample, the washed out PI-homopolymer, and a standard PI homopolymer for comparison. In the figure of the washed out part, we can notice that the chemical shift at 0.9 ppm due to (CH$_3$) in the EP-backbone existing in the pure ungrafted EP-p-ClMS and in the grafted sample, was completely disappear, indicating pure PI homopolymer.

The coupling graft-onto approach provides good control over the total graft molecular weight. Graft length can be controlled by the size of the polyisoprene macroanions, and graft density is basically determined by the mole % of p-ClMS units in EP-p-ClMS starting copolymer.

5.3.3. Anionic graft-from and graft-onto polymerization using EP-co-DVB copolymer

In anionic graft-from polymerization, as illustrated in Scheme 5.4, an EP-co-DVB terpolymer (E: 67.3 mole %; P: 32.3 mole %; DVB: 0.4 mole %) was lithiated with n-BuLi to form EP containing pending benzylic anions that could be used as macro-initiator for initiating living anionic polymerization of isoprene. By controlling n-BuLi and monomer feed, we can pre-determine the molecular structure (graft density and graft length) of the resulting EP-g-PI graft copolymer. Since this graft-from process involves a living anionic polymerization, it is reasonable to assume that each benzylic anion produces one polymer side chain with similar molecular weight.
Figure 5.4. $^1$H-NMR of (from top to bottom): the separated ungrafted EP-co-p-ClMS, the grafted sample, the washed out PI homopolymer and a standard PI homopolymer.
Scheme 5.4: Anionic graft-from and graft-onto reactions by using EP-co-DVB copolymer to prepare EP-g-PI graft copolymer

Due to the sensitivity of solvent polarity to the PI microstructures, with polar solvent resulting in undesirable high Tg 1,2- and 3,4-structures, the graft-from reaction was carried out in hydrocarbon solvents, such as cyclhexane, at elevated temperatures (> 60 °C). The resulting graft copolymer was found to have largely 1,4-polyisoprene structure.
It is also possible to apply this EP-g-DVB copolymer in a graft-onto reaction scheme. In other words, isoprene monomer was first polymerized in cyclohexane using n-BuLi to form 1,4-polyisoprene with certain molecular weight, then EP-co-DVB solution in cyclohexane was added to the anionic polymerization solution. Scheme 5.4 illustrates both graft-from and graft-onto mechanisms.

Figure 5.5 shows the $^1$H-NMR spectra of the graft samples: Fig.5.5 (top) is the graft-from copolymer initiated by n-BuLi/TMEDA, Fig.5.5 (middle) is the graft-from copolymer initiated by n-BuLi at 60 °C, and Fig.5.5 (bottom) represents an example of the graft-onto method. In all figures, we can notice the complete disappearance of all vinyl peaks while new peaks appear corresponding to isoprene units. In Fig 5.5(a), two new chemical shifts arise at (4.5-5.03) ppm and at 5.68 ppm corresponding to 1,2 and 3,4 isoprene structure. On the other hand, in Fig.5.5 (b&c), each shows two new chemical shifts - one major at 5.1 ppm and one minor at 4.8 ppm - corresponding to 1,4 isoprene structure. Polyisoprene content was about 55, 61 and 75 mole % in samples A, B and C, respectively.
Figure 5.5. $^1$H-NMR of EP-g-IP based on DVB (from top to bottom):

a) graft-from (n-BuLi/TMEDA)

b) graft-from (n-BuLi/60°C)

c) graft-onto method
Figure 5.6 compares GPC curves of a starting EP-co-DVB and a resulting EP-g-PI graft copolymer. The significant increase of graft polymer molecular weight also indicates the effectiveness of this grafting process.

Figure 5.6. GPC curves EP-co-DVB and EP-g-PI copolymer

In addition to EP-g-PI graft copolymers, it can be expected that a wide range of graft and block copolymers, with well-defined molecular weight and narrow molecular weight distribution, can also be derived from this grafting reaction technique, by the combination of EP-co-DVB copolymers and anionic polymerization reactions.
5.4. Conclusion

Our experimental results clearly demonstrate that it is possible to apply the metallocene-mediated EP reactive copolymers, containing p-MS, p-ClMS, and DVB units, to prepare EP-g-PI graft copolymers with well-controlled molecular structure (graft density and graft length) and desirable 1,4-polyisoprene microstructure. The p-methylstyrene (p-MS) side groups can be effectively lithiated to form stable benzylic anions, which then initiate living anionic graft-from polymerization of isoprene monomer to form EP-g-PI copolymers. It is convenient to use chlorinated p-MS (p-ClMS) groups in EP copolymer as the reactive sites for coupling reaction with polymeric polyisoprene anion to form EP-g-PI graft copolymers. Such a graft-onto method offers pre-determined main chain and side chain structures. The most desirable method is the one started with EP-co-DVB copolymer that contains several reactive styrene groups. These pending styrene groups are shown to be very suitable in both anionic graft-from and graft-onto polymerization of isoprene to prepare EP-g-PI graft copolymers containing both low Tg EP main chain and 1,4-polyisoprene side chains under mild reaction conditions.

5.5. References


(7) (a) Halasa, A. F.; Schulz, D. N.; Tate, D. P.; Mochel, V. D. Adv. Organomet. Chem. 1980, 16, 55;


Chapter VI
Synthesis of Cross-Linked Rubber Particles Containing Surface Reactive Groups

6.1. Introduction

Generally, the mechanical properties of brittle polymers are enhanced by the introduction of a dispersed rubbery phase\(^1\). The number of polymers that have been treated by this “toughening” procedure has grown to include every basic polymer product\(^2\). Many papers were published each year concerning rubber toughening of plastics. Although many approaches have been used to toughen brittle polymers, the most common one is still based on physical mixing of elastic polymer (10-40%) with plastic material. Due to the lack of control morphology and poor rubber dispersion, the resulting polymer blends usually exhibit very limited improvement of toughness but some deterioration in stiffness\(^3\). In addition, the insufficient interfacial adhesion between the rubber domains and the plastic matrix is a major concern, which can cause catastrophic failure during the usage.

Acrylonitrile-butadiene-styrene (ABS) terpolymer and high impact polystyrene (HIPS) are of the most successful and commonly-used rubber-toughen engineering plastics because of their good combination of high impact strength and rigidity, as well as maintaining optical and electrical properties of their plastic components. Both polymers involve chemically grafting of poly(styrene-co-acrylonitrile) and polystyrene, respectively, to 1,4-polybutadiene elastomer (~ 25%) to secure rubber-plastic interfaces. In
addition, the dispersed elastomer domains are cross-linked to form stable elastic rubber particles.

Despite the commercial success of ABS and HIPS, most of their usages are limited to indoor applications, due to their unsaturated 1,4-polybutadiene component that exhibits poor heat and ozone resistances and weatherability\(^4\). As will be discussed in this chapter, one of our research objectives is to replace the unsaturated 1,4-polybutadiene component to a completely saturated ethylene/propylene rubber (EPR) (in the form of cross-linked particles) in ABS polymer. In other words, we will discuss a new acrylonitrile-EPR-styrene (AEPS) polymer that is the saturated analogue of acrylonitrile-butadiene-styrene (ABS) engineering plastic. As a result, this new material potentially could extend the usage of ABS to the outdoor applications, which is very desirable in today plastic world.

In this chapter, we will focus on the synthesis of the key component of “reactive” rubber particles, which are cross-linked and contain some reactive groups on the particle surfaces. The facile chemistry allows us to design surface “reactive” groups with various functionalities that afford good interfacial adhesion (chemical bonding) with a broad range of plastics at the interfaces, as illustrated below.
The preparation of this “reactive” EP rubber particle involves two steps, including ethylene/propylene/divinylbenzene terpolymerization by metallocene catalyst, which results in E/P/DVB terpolymer containing some pending styrene units. The second step is to transform this E/P/DVB terpolymer into stable rubber particles with a desirable particle size, via emulsion or suspension processes before cross-linking reaction of E/P/DVB terpolymer. The cross-linking reaction involves either thermal cyclization or radical addition of internal pendent styrene units. On the other hand, the external pendent styrene units are remained on the surfaces, which are very versatile for both \textit{in situ} and post grafting or functionalization processes.

6.2. Experimental Details

6.2.1. Instrumentations and Materials

All $^1\text{H}$ NMR spectra were recorded on a Bruker AM 300 instrument in chloroform-$d$ at room temperature. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution cast films on KBr windows. The molecular weight was determined by a Waters GPC that was operated at 35°C with a refractive index (RI) detector and a set of $\mu$-Styragel columns of $10^6$, $10^5$, $10^4$, and $10^3$ Å pore size in series. A flow rate of 0.7 ml/minute was used and the mobile phase was THF. The combination of IR, $^1\text{H}$ NMR and GPC was used to determine the E/P/DVB terpolymer structure.

All O$_2$ and moisture sensitive manipulations were performed inside argon filled Vacuum Atmosphere dry box. Toluene was deoxygenated by argon purge before refluxing with sodium/benzophenone for 48 hours and
then distilling from its respective purple solution under argon. Polyvinylalcohol (PVOH), palmitic acid, potassium hydroxide, ammonium persulfate, nylon11, m-chloroperbenzoic acid, maleic anhydride, rac-Et(Ind)₂ZrCl₂ from Aldrich and were used as received. Divinylbenzene (Aldrich) was dried and distilled over calcium hydride under argon. Acrylonitrile and styrene were distilled out from the inhibitor before use. Methylaluminoxane (MAO) was synthesized according to the literature⁸. High-purity grade ethylene and propylene gases were obtained from MG Industry and were used as received.

Particle size distribution and volume-average diameters of the latex particles were determined by light-scattering analyzer. Bulk morphology in the polymer films was examined by scanning electron microscope (SEM), using a Topcon International Scientific Instruments ISI-SX-40 with secondary electron imaging. SEM samples were prepared from films cryofractured in liquid N₂. Samples were mounted on an aluminum stub and gold coated to form a conductive coating. Transmission Electron Microscopy (TEM) was performed at 120 kv using model JEOL JEM 1200 EXII equipped with a video camera, a Gatan Bioscan 792 camera and a high resolution Tietz F224 camera and a PGT Prism light element detector. Samples were prepared by dipping the grid in a dilute polymer solution in chloroform followed by evaporating the solvent which affords a very thin film for TEM analysis.
6.2.2. Synthesis of E/P/DVB Terpolymer

In a typical reaction, a Parr 300 mL stainless autoclave equipped with a mechanical stirrer was charged with 50 mL of toluene and 0.5g of MAO. The reactor was then injected with required amount of DVB and charged through mass flow controller with 70 psi of ethylene/propylene gas mixture (1/1 ratio) at 50 °C. About $2.5 \times 10^{-6}$ mol of $rac\text{-}\text{Et(Ind)}_2\text{ZrCl}_2$ in toluene solution was then syringed into the rapidly stirring solution to initiate the polymerization. Additional ethylene/propylene gas mixture was fed continuously into the reactor to maintain a constant pressure (70 psi) during the course of the polymerization. After 10 minutes of reaction at 50 °C, the polymer solution was quenched with methanol/HCl, and the isolated polymer was purified by repeating a solution/dissolution process by THF and methanol three times before drying under vacuum for 8 hours. The produced polymer has $M_n\sim35,000$ g/mol, $PDI\sim2.0$, and mole % composition: E~64%, P~34% and DVB~2%.

6.2.3. Synthesis of EP Rubber Particles by Suspension

In a 500 mL three-neck flask equipped with a mechanical stir and a condenser was placed 0.5 g of PVOH in 100 mL deionized H$_2$O. The E/P/DVB terpolymer (5.0 g, $M_n = 35,000$) was dissolved in 50 mL pentane and slowly added to the above vigorously stirred solution. After stirring for 30 min, the reactor was warmed to 45 °C while applying a little vacuum to remove the organic solvent (~30 mL). The strongly stirred suspension was heated to 85 °C and stirred for 12 hours under argon atmosphere. The heating bath was removed and the flask was cooled to room temperature.
while stirring. The product was precipitated with methanol and washed with water to remove PVOH before drying under vacuum for 8 hours.

### 6.2.4. Synthesis of EP Rubber Particles by Emulsion.

E/P/DVB terpolymer (5.0 g, Mn = 35,000) and 5 % (wt) of palmitic acid were dissolved in 50 mL hexane and slowly added to a vigorously stirred solution of KOH in 100 mL deionized H₂O such that the final emulsion has pH slightly alkaline. After strong stirring for 30 min., the emulsion was homogenized by sonification for another 30 min. Then, the solvent (hexane) was removed by distillation and the flask was purged with N₂ for 30 min before rising the temperature to 60 °C and adding 1.0 wt% of ammonium persulfate as a free radical initiator. In case of the in situ grafting, styrene monomer or styrene/acrylonitrile monomer mixture were added after 2 hrs and the reaction was run for additional 12 hrs. The product was coagulated by HCl/methanol, re-dissolved in chloroform and precipitated with methanol to remove the surfactant before drying under vacuum for 8 hours.

### 6.2.5. Functionalization of Rubber Particles.

#### 6.2.5.1. Maleation:

In 250 mL flask equipped with a stirrer and a condenser, 2.0 g of EP rubber particle was dispersed in 100 mL of xylene, along with 5.0 g of maleic anhydride and 0.1 g of free radical inhibitor. Under a N₂ atmosphere, the solution was heated to 140 °C for 5 hrs. The maleated particles were
isolated by precipitation in methanol. Repeated washings with methanol were performed before drying the product under vacuum.

6.2.5.2. Epoxidation:

EP rubber particles (1.0 g) was dispersed in 80 mL toluene in a flask with 1.8 g of m-chloroperbenzoic acid. The reaction was performed at 70 °C for 4 hrs under stirring and a N₂ atmosphere, then the product was obtained by precipitating with methanol, washed and vacuum dried.

6.2.6. Coupling Reaction of the Maleated Rubber Particles

6.2.6.1. With Nylon11:

In 250 mL flask equipped with a stir and a condenser, 1.0 g of maleated rubber particle was dispersed in 30 mL of 1,3-dichlorobenzene. Nylon11 (4.0 g) was dissolved in 50 mL m-cresol and was added to the above flask. The coupling reaction was performed under argon overnight at 170 °C. The product was precipitated and washed with methanol before drying under vacuum.

6.2.6.2. With PP-t-NH₂:

Coupling with PP-t-NH₂ was performed in xylene at 150 °C. The amino terminated PP was prepared by our group. In 250 mL flask equipped with a stir and a condenser, 4.0 g of PP-t-NH₂ was dissolved in 30 mL of hot xylene. Then, 1.0 g of maleated rubber particle dispersed in 20 mL xylene was added to the above stirred solution under argon atmosphere. The
reaction was performed at 150 °C for overnight. The coupling product was coagulated and washed with methanol before vacuum drying.

6.3. Results and Discussion
6.3.1. Ethylene/Propylene/Divinylbenzene Terpolymer

New metallocene technology\textsuperscript{13} provides well-defined catalysts and polymerization mechanisms. With a specific metallocene catalyst, our group led by Professor Chung has successfully synthesized linear E/P/DVB terpolymers that are completely soluble in common organic solvents and contain a controlled amount of pendent styrene units. In other words, the catalyst incorporates DVB into E/P copolymer through single enchainment, and the styrenic moieties already enchained in the resulting terpolymer do not further react, as illustrated in Scheme 6.1. One major advantage of this E/P/DVB terpolymer is the existence of several pendent styrenic moieties along the backbone that are very reactive in many chemical reactions, including functionalization and grafting.

Scheme 6.1
6.3.2. EP Reactive Rubber Particle via Suspension Process

EP Rubber particles of the size 1 to 10 µm can be synthesized by suspension process while that of sub-micron size (0.05 - 1.0 µm) is known to be produced by emulsion\textsuperscript{14} as will be discussed later. In suspension process, E/P/DVB terpolymer is first dissolved in a low boiling point solvent; in our case we used pentane that can be easily removed later. The polymer was slowly added to deionized water containing a stabilizer (PVOH). Because of the ease of PVOH removal after the reaction, the process is simple and the produced material is pure. In addition, the product is free from initiator residues; no need for free radical initiator to perform the crosslinking reaction. Thermal crosslinking (styrene-styrene cyclization) was successfully performed. The produced particles were dispersed in THF along with polystyrene homopolymer for film casting. SEM shows completely dispersed particles in the PS matrix as shown in Figure 6.1.

6.3.3. EP Reactive Rubber Particle via Emulsion Process

The polymer was emulsified and crosslinked as described in the experimental part. The emulsion technique used here, which is the most effective one, is referred to as \textit{soap-in-situ} method\textsuperscript{15}. The fatty acid component of the soap is dissolved in the polymer solution, and the alkali component is dissolved in water, before combining together to afford stable emulsion. The method derives its effectiveness from the fact that soap forms spontaneously wherever a new polymer particle-water interface is created, until of course, ether the fatty acid or the alkali becomes exhausted. This process, namely, ionization of the fatty acid molecules at the polymer
particle interface, ensures the formation of soap at just those locations where it is required and where it can be most effective (Scheme 6.2).

**Figure 6.1.** SEM of suspension rubber particles blended with PS

**Scheme 6.2**
The first study was to examine the degree of crosslinking and EP rubber particle size. Table 6.1 summarizes some experimental results. In emulsion, it is easier to sample out some samples at different time intervals during the course of the reaction than in suspension; stirring can not be stopped in case of suspension process. Figure 6.2a shows the change in particle size by light scattering with the reaction time and Figure 6.2b shows the $^1$H NMR of the double bond pattern. The double bonds consumed during the crosslinking and consequently, the particle diameter.

**Table 6.1. The Change in Particle Size with Reaction Time**

<table>
<thead>
<tr>
<th>Run #</th>
<th>Time (hrs)</th>
<th>$^1$H NMR (ratio)</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>vinyl</td>
<td>aliphatic</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>317.27</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1</td>
<td>872.05</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>1</td>
<td>904.54</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>1</td>
<td>1187.6</td>
</tr>
<tr>
<td>5</td>
<td>12.0</td>
<td>1</td>
<td>1195.5</td>
</tr>
</tbody>
</table>

It is clear that, as the reaction running, more double bonds are consumed during the cross-linking reaction and the particle shrinks more. Therefore, the particle size diameter reduced with the reaction time.

6.3.4. Versatility of the Reactive EP Rubber Particles

During the cross-linking reaction of forming stable EP rubber particles, the internal pendent styrene units react each other by either thermal cyclization or radical addition reaction. However, most of external pendent styrene units on the surfaces are much more difficult to find each other and are remained on the surfaces, which are very valuable in the subsequent functionalization reactions. Scheme 6.3 illustrates some of the possible transformation reactions, including maleation, epoxidation and grafting reactions with styrene and styrene/acrylonitrile. The products from these
reactions were characterized by $^1$H-NMR spectra, which indicate complete disappearance of the styrenic double bonds and the appearance of new peaks corresponding to the protons of the functional group.

![Scheme 6.3](image)

$P = \text{PS, PP, PMMA, SAN,...etc}$

$\text{EPDVB} = \text{crosslinked E/P rubber particle}$

**Scheme 6.3**

Figure 6.3 shows the $^1$H NMR spectra of (a) E/P/DVB terpolymer, (b) cross-linked EP rubber particles via emulsion process, and (c) epoxidized EP rubber particles (c). By comparing (a) and (b) spectra, it is clear that the ratio of the vinyl to aliphatic intensity reduces due to the consumption of styrene units during the cross-linking reaction. The styrenic residues were completely disappeared on epoxidizing with $m$-chloroperbenzoic acid
(Figure 6.3 c) and two new peaks in a ratio of 1:2 appear at 3.7 and 3.0-3.4 ppm that can be attributed to CH and CH$_2$ of the epoxy ring, respectively$^{11}$.

**Figure 6.3.** $^1$H NMR (a) E/P/DVB terpolymer, (b) cross-linked EP particles containing styrene residues, and (c) epoxidized EP rubber particles.

Figure 6.4 and 6.5 shows $^1$H NMR spectra of EPR-graft-polystyrene and EPR-graft-poly(styrene-co-acrylonitrile) (AEPS), respectively. The $^1$H NMR spectrum of a commercial ABS polymer is also shown in Figure 6.5 (a) for comparison. As discussed, polystyrene and poly(styrene-co-acrylonitrile) are known to be commercially toughened with polybutadiene (PB) which has limited outdoor stability. The replacement of PB rubber content with EP rubber particles is very desirable; such materials could potentially open up outdoor applications for both graft copolymers.
Figure 6.4. $^1$H NMR of the EPR particle-graft-polystyrene

Figure 6.5. $^1$H NMR spectra of (a) a commercial ABS$^{16}$ and (b) our corresponding AEPS polymers.
6.3.5. Morphological Studies

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) were used to characterize the morphology of graft copolymers and their polymer blends\textsuperscript{17}. SEM shows the liquid N\textsubscript{2}-fracture surface, representing the undistorted polymer bulk. On the other hand, TEM graph provides a 3-D view of the EP rubber particles in plastic matrix. The following macrographs show some representative examples.

6.3.5.1. Scanning Electron Microscopy (SEM) Results

Four graft polymer systems, including EPR-g-nylon11, EPR-g-PP, EPR-g-styrene, and EPR-g-poly(styrene-co-acrylonitrile) (AEPS), were examined by SEM, and their micrographs are shown in Figures 6.6, 6.7, 6.8 and 6.9, respectively. All samples were prepared by fracturing the polymer films under liquid nitrogen conditions, and SEM micrographs were taken on the fractured surfaces. For comparison, each graft copolymer sample is side-by-side compared with the corresponding simple polymer blend (physical mixing of main and side chain polymers). In each case, a lot of convex particles and concave holes exist on the fracture surfaces of the simple polymer blends. The existence of these particles or holes is a clear indication of poor interface adhesion that results in clean separation or pullout of the rubber particles from the continuous polymer matrix during fracturing the blend sample. On the other hand, the grafted copolymers show no convex particles or concave holes on their fracture surfaces. The uniform fracture surface implies the cohesive failure in the continuous plastic matrix, not at the rubber particle-plastic matrix interfaces.
Figure 6.6. SEM Micrographs of EPR-g-nylon11 (bottom), EPR-blend-nylon11 (top).
Figure 6.7. SEM Micrographs of EPR-g-PP (bottom), EPR-blend-PP (top).
Figure 6.8. SEM Micrographs of EPR-g-styrene (bottom), EPR-blend-styrene (top).
Figure 6.9. SEM Micrographs of AEPS (bottom), EPR-blend-SAN (top).
Figure 6.10. TEM Micrographs of an AEPS Sample (with two different magnifications).
6.3.5.2. Transmission Electron Microscopy (TEM) Results

Transmission electron microscope (TEM) was also used to examine polymer morphology. Sample preparation was done as explained in the experimental part, where several polymer solutions with different concentrations were prepared for grid dipping. After evaporating the solvent, the suitable semi-transparent thin film with proper thickness on the grid was selected by optical microscopy before taking TEM micrograph. Figure 6.10 shows two TEM micrographs (with different magnifications) of an AEPS samples. It is clear that the EP rubber particles are well-dispersed in the SAN matrix, strongly indicating the graft structure\(^{18}\).

6.4. Conclusion

A novel method for synthesizing reactive rubber particles has been developed. The process involves two steps: metallocene-mediated E/P/DVB terpolymerization followed by emulsion or suspension thermal crosslinking. The particles contain several reactive styrene moieties on the surface, which are very versatile for many applications. The first step requires some specific metallocene catalysts to prepare linear ethylene/propylene/divinylbenzene (EP-DVB) terpolymer. In the second step, this soluble EP-DVB terpolymer is emulsified using soap-in-situ method to form sub-micro size particles, followed by crosslinking via thermal coupling reaction of pendent styrene moieties in the bulk of particle. Suspension process in which EP-DVB terpolymer is suspended in water containing PVOH and thermally crosslinked to form 1 to 10 µm size particles was also developed.
Some remaining styrene moieties on the surface were then used for further functionalization reactions including maleation and epoxidation or graft reaction (via graft-onto, graft-from, and graft-through mechanisms) to provide the important interface adhesion with the brittle plastic polymers. Several plastics were studied, including Nylon, PP, PS, and SAN polymers. The combination of SEM and TEM results indicates the effectiveness of grafting reaction and consequently the interfacial adhesion between the dispersed EP rubber particles and the continuous polymer domain.

6.5. References

(1) Jansen, B.J.P.; Rastogi, S.; Meijer, H.E.H.; Lemstra, P.J., 


(3) Liu, Y.; Zhang, X.; Geo, J.; Huang, F.; Tan, B.; Wei, G.; Qiao, J., 
*Polymer*, 2004, 45, 275.


Chapter VII.
Conclusion and Future Work

7.1. Summary of the Present Study

In this thesis, we have demonstrated the syntheses and some potential applications of functional ethylene/propylene elastomers by two approaches. With these approaches, metallocene catalysts provide us effective synthetic methods that not only produce reactive copolymers with narrow molecular weight and composition distribution, but also enable us to control the concentration and location of the reactive unit incorporation. So, with the advantage of metallocene technology as well as the advanced functionalization approaches invented in our group, we have successfully synthesized several reactive ethylene/propylene copolymers that contain reactive chain ends.

In addition, the presence of ethylene along with propylene in our polymerization system provides one more advantage in understanding the chemistry involved and consequently, the detailed behaviors of the applied catalysts. Therefore, we can get the copolymer composition from ethylene/propylene mole ratio which is very important information that affords a good understanding of the polymerization mechanism.

The first synthetic method is by the reactive copolymerization approach that offers a facial and clean method to prepare ethylene/propylene copolymers terminated with styrenic moiety and have well-defined
molecular structure. With a combination of metallocene catalyst and a controlled hydrogen pressure, it’s possible to direct the incorporation of p-MS molecules, from copolymerization to chain transfer mode, to form p-MS terminated EP copolymers (EP-t-p-MS) with a broad range of polymer molecular weight and E/P mole ratios. So, by introducing hydrogen during the course of E/P/p-MS polymerization, most of the incorporated p-MS units are located at the chain ends, which is highly desirable for block copolymerization. In addition, this chemistry (one-pot process) can be extended to prepare chain end functionalized EP copolymers, such as EP-t-St-OH. However, the functional styrenic chain transfer agent has to be well protected by a bulky group to prevent catalyst poison, especially by using a \([(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2\) catalyst system with an opened active site.

The second approach is based on the direct copolymerization of ethylene and propylene in the presence of protected allylalcohol, allylamine or butenylamine. The functional groups of these polar monomers were protected to overcome the catalyst decay problem. The protection methods have been chosen in such a way that they would not only lead to the steric shielding, but also to afford electronic neutralization of the functional groups. The systematic study of metallocene-mediated ethylene/propylene /protected polar monomer polymerization in absence and presence of H_2, with varying catalysts, polar monomer concentrations, and hydrogen pressures, provides the detailed reaction mechanism. With a combination of metallocene catalyst and a controlled hydrogen pressure, it’s possible to direct the incorporation of simple polar monomers, from copolymerization to chain transfer mode, to form NH_2 and OH terminated EP copolymers with a broad range of polymer molecular weights and E/P mole ratios.
Many functional comonomers were successfully induced in such E/P copolymerization (including \( p \)-MS, \( p \)-CMS, \( p \)-OHSt, \( p \)-NH\(_2\)St, allylalcohol, allylamine, butenylamine, DVB and 4-BSt) without disrupting the polymer structure. For the application part of such terpolymers, two reaction steps was involved: a) synthesis of EP copolymer contains reactive group during metallocene-mediated ethylene/propylene copolymerization, and b) the pendent reactive groups located along the prepared EP backbone serve effectively as active sites for subsequent crosslinking or graft copolymerization.

The versatility of these reactive groups was further demonstrated by anionic copolymerization between these reactive groups and isoprene monomer. The homogeneous anionic reaction condition prevented the isolation of the lithiated polymer, which led to the generation of some isoprene homopolymer. However, an effective fractionation method was developed and the \(^1\)HNMR analysis as well as GPC showed the effectiveness of the separation and allowed us to obtain pure grafted copolymers. The \( p \)-methylstyrene side groups could be effectively lithiated to form stable benzylic anions, which then initiate living anionic polymerization of isoprene monomer forming EP-g-IP. It was also interesting to use the function group of the EP-co-\( p \)-CMS as a coupling centre in a graft-onto anionic manner to connect two polymers together. In addition, a third method which was found to be versatile is the case in which the functionalized EP serves as monomer in a simple anionic reaction. So, divinylbenzene was an example showing good reactivity in both graft-from and graft-onto anionic polymerizations.
Another potential application of such reactive ethylene/propylene copolymers was in the field of synthesizing reactive rubber particles. A novel method for synthesizing reactive rubber particles has been developed where the process involves two steps: metallocene-mediated ethylene/propylene/divinylbenzene (EP-DVB) terpolymerization followed by emulsion or suspension thermal crosslinking to form reactive rubber particles. The particles contain reactive styrenic bonds which is very versatile in many applications. The first step of preparing these reactive rubber particles involves the synthesis of linear EP-DVB terpolymer via metallocene-mediated polymerization using selected catalysts. Then, in the second step, this soluble EP-DVB terpolymer is emulsified using soap-in-situ method to sub-micro size particles, followed by crosslinking via thermal coupling reaction of pendent styrene moieties in the bulk of particle. Suspension process in which EP-DVB terpolymer is suspended in water containing PVOH and thermally crosslinked to form 1 to 10 µm size particles was also developed.

Some remaining styrene moieties on the surface were then used for further functionalization reactions including maleation and epoxidation or graft reaction (via graft-onto, graft-from, and graft-through mechanisms) to provide the adhesion with the brittle polymers. Several polymers have been studied, including nylon, PP, PS, and SAN polymers. The combination of SEM and TEM results indicates the effectiveness of grafting reaction and consequently the interfacial adhesion between the dispersed rubber particles and the continuous polymer domain.
7.2. Future Work

Despite the successful results obtained through this thesis, there are still many topics that need to be investigated to thoroughly conclude this research. In a few publications, attempts to synthesis poly(propylene-co-allyl-X); where X is NH$_2$ or OH groups, were limited to very low molecular weights and activities. It is very important and will be interesting to extend our simple (one-pot) chemistry to synthesis isotactic PP terminated with such reactive terminals.

It will be also very interesting to extend the reactive approach for the preparation of long chain branching polypropylene, polyethylene and ethylene-propylene copolymers. Long chain branched EP may be achieved by studying the metalloocene-mediated polymerization of E/P in the presence of such reactive intermediate (EP-co-DVB). In this case, the styrenic double bond will serve as a chain transfer process and can produce long chains of EP grafted on another long chain of EP. This system may also be further applied to other $\alpha$-olefins (including ethylene, propylene …etc) to prepare long chain branching of such $\alpha$-olefin on the EP backbone.

Long chain branched PP may also be prepared by introducing reactive rubber particles during PP polymerization using metalloocene catalysts and hydrogen. In this case the styrenic residues, in the presence of hydrogen, will serve as chain transfer during the course of propylene polymerization.

This novel material, reactive rubber particles, is an area of a wide range of both academic and commercial applications. The thesis has
presented the detailed synthesis but some applications. However, this area needs more research and digging deeper to cover more of other possible applications. For example, these reactive rubber particles with those styrene moieties on the surface may serve as cross-linker for a lot of applications. They can also be used instead of styrene monomer in curing unsaturated polyesters. Another suggested example is that ethylene oxide can be polymerized (graft-from) in the presence of the epoxidized rubber particles. The produced polyethylene oxide (hydrophilic) planted on the surface of the crosslinked rubber particles (hydrophobic) can serve for drug delivery.

In general, the presence of styrenic groups on the rubber particle surfaces provides the versatility of this material. This styrene double bond can be introduced in a tremendous number of reactions that will consequently lead to a huge number of potential applications. This is due to the fact that the styrenic double bond can be transformed to a wide range of other functional groups with simple organic reactions. In addition, styrene is known to be polymerized with the all known methods of polymerizations including free radical, anionic, cationic and coordination polymerizations.
VITA

Usama was born on December 18, 1965 in Suez, Egypt. After graduating from Suez Military high school, he attended Cairo University, where he obtained the BS degree in Chemistry in 1988 with honors. He has been employed as a research assistant at the Egyptian Petroleum Research Institute (EPRI) in 1988 where he continued graduate study with connection to Cairo University, and obtained MS degree in Polymer Science in 1997. Then, he was promoted to an assistant researcher at EPRI (1997-2001). In 2001, he was awarded a scholarship from the Egyptian Government to pursue a graduate study in the United States. In the fall of 2001, he enrolled in the Polymer Science Program of the Material Science and Engineering Department, the Pennsylvania State University and was received a MS degree in 2004. He is a member of the American Chemical Society, Division of the Polymer Chemistry and the Division of Polymer Materials.