Synthesis of isotactic polypropylene containing a terminal reactive group via metallocene-mediated polymerization/chain transfer reaction in the presence of protected allylamine

Usama F. Kandil*, Nahed M. Amer, Nevien O. Shaker, Ossama M. Abo-Elenien
Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, (EGYPT)
E-mail: alfa_olefins@yahoo.com
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ABSTRACT

This article discusses a direct (one-pot) polymerization process to prepare isotactic polypropylene (i-PP) having a terminal functional group (NH$_2$ group). The chemistry involves metallocene-mediated propylene polymerization using rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/methylaluminoxane complex in the presence of a bulky protected Allylamine followed by hydrogenation. The major challenge is to find suitable reaction conditions that can simultaneously carry out effective propylene polymerization and incorporation of the protected Allylamine molecule at the polymer chain end; in other words, altering the protected Allylamine incorporation mode from copolymerization to chain transfer. Apparently, the propylene propagating chain end engages in a facile consecutive chain transfer reaction, reacting with the protected Allylamine and then hydrogen, with high catalyst reactivity under the proper protected Allylamine and hydrogen concentrations. The silane and aluminum groups, used for protection, were hydrolyzed in acidic aqueous solution during the sample workup step to obtain the desirable i-PP polymers with a terminal NH$_2$ group (i.e., PP-t-Allyl-NH$_2$). The terminal functional group was confirmed by end group analysis and chain extension reaction. The polymer molecular weight was inversely proportional to the molar ratio of [Allylamine]/[propylene] with a chain transfer constant ($k_{tr}/k_p$) of 1/32. Despite the high molecular weight, the terminal functional group in PP engages a coupling reaction with polycaprolactone (PCL) and carboxy-terminated polystyrene (PS-t-COOH) in solution and melt to form PP-b-PCL and PP-b-PS diblock copolymers that are very effective compatibilizers in PP/PCL and PP/PS polymer blends.

KEYWORDS

Isotactic polypropylene; Polyolefin; Functionalization; Diblock copolymers; Compatibilizers.

INTRODUCTION

Metallocene technology has opened up the unprecedented opportunity for preparing polyolefins with well-defined molecular structures and predictable physical properties$^{[1-3]}$. Since the discovery of HPDE and PP about a half century ago, the functionalization of polyolefin has been a scientifically challenging and industrially important area$^{[4]}$. A polyolefin with a terminal functional group$^{[5]}$ is a very attractive material that pos-
sesses an unperturbed polymer chain structure and desirable physical properties (such as melting temperature, crystallinity, glass transition temperature, melt flow, etc.) that are almost the same as those of the pure polymer. Nevertheless, the terminal reactive group at the polymer chain end has good mobility and can provide a reactive site for many applications, such as adhesion to the substrates, formation of graft and block copolymers, and reactive blending to improve the compatibility of two dissimilar polymer blends. Therefore, the ultimate objective for the functionalization of polyolefin is to improve the poor interactive properties of polyolefins and to broaden polyolefin applications to high value products, especially in polymer blends and nanocomposite.

In chemistry, the preparation of chain end functionalized polymers has been largely limited to living polymerization with the use of an initiator bearing a functional group or a control termination (functionalization) reaction of the living polymer chain end. Unfortunately, there are only a few transition metal coordination catalysts that exhibit living polymerization behavior, and most of them are limited to the preparation of polyethylene and poly(1-hexene) cases. Furthermore, living polymerization only produces one polymer chain per initiator, which presents a relatively low rate of catalyst activity in the typical polyolefin preparation.

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. Recently, a new chemical route has been reported to prepare polyolefin (including PE, PP, EP, s-PS, etc.) with a terminal reactive group and obtain high catalyst activity. The chemistry is based on a chain transfer reaction involving a reactive chain transfer agent, including dialkylborane (H-BR₂) and p-methylstyrene/hydrogen (p-MS/H₂), during metallocene-mediated olefin polymerization. All polymers formed contain a terminal borane or p-MS group and have a relatively narrow molecular weight distribution (\(M_w/M_n \sim 2\)). The polymer molecular weight (from a few thousand to a hundred thousand) was basically controlled by the mole ratio of [chain transfer agent] /[olefin]. Both the terminal borane and p-MS groups are very versatile, and can serve as the reactive sites for subsequent functionalization reactions or conversion to living initiators for chain extension reactions. This metallocene-mediated α-olefin polymerization/chain transfer scheme is applicable to all polyolefin homo- and copolymers.

It is very desirable to extend this chemical route to directly prepare polyolefin with a desirable terminal functional group, such as NH₂. In other words, the ideal reaction is a one-pot process, and no chain end functionalization would be needed after the polymerization/chain transfer reaction. Primary amine is very interesting terminal group with good chemical reactivity in many applications. As will be discussed later, it can be engaged in coupling reactions with many polar polymers (such as polyesters and polyamides) in the reactive (solution and melt) polymer blending. The in situ forming diblock copolymers (located right at the interfaces) provide good compatibility between two otherwise incompatible polymer blends with uniform and microphase-separated morphology.

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, it has been recently demonstrated the possibility of altering the styrene comonomer mode to chain transfer mode in PE and PP cases using \(\text{Cp}_2\text{ZrCl}_2\) and \(\text{rac-Me}_2\text{Si-[2-Me-4-ph(Ind)]}_2\text{ZrCl}_2\) catalysts, respectively, under a sufficient amount of H₂. Therefore, it is very 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 con-
certain to achieve the ideal polymerization/chain transfer situation. In this paper, we will focus on PP copolymerization with allyl functional monomer that was reported to be a difficult monomer in the preparation of functional PE and PP polymers, with low catalyst activities and low polymer molecular weights.

As known, 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[17]. Although Ziegler-Natta catalysts containing group 4 transition metals are known for their highly oxophilic nature[18], zirconocene/methylaluminoxane (MAO) catalysts were successful in copolymerizing ethylene with 10-undecen-1-ol[19] or other polar monomers[20] having long CH₂ spacers between polar and vinyl groups. However, the catalyst activity decays with the concentration of 10-undecen-1-ol[21]. Shell has claimed the copolymerization of N-phenyl-10-undecenamine with 1-hexene (9-13 wt % comonomer incorporation) with TiCl₃ in the presence of excess Et₂AlCl[22].

Tertiary amine-functionalized olefins with sufficient steric hindrance around the nitrogen atom and long CH₂ spacer are not difficult to polymerize and copolymerize by using group IV catalysts[23]. Smaller monomers (such as dimethyl and diethylamines) can be polymerized if 1 equivalent of a proper alkylaluminum protecting group is used[24]. However, in a review Boffa[25] 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[26]. 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 CH₂ 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[27]. On the other hand, the functional monomer with a large number of CH₂ 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. The ideal protecting agent will not only have the capability to minimize catalyst deactivation, but also will 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)[28].

Intuitively, both allyl and butenyl functional monomers with only 1 and 2 CH₂ 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, these stubborn allyl and butenyl functional monomers may indeed offer an excellent opportunity to prepare chain end functionalized polypropylene. 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.
EXPERIMENTAL DETAIL

Instrumentation and materials

All $^1$H NMR spectra were recorded on a Bruker AM 300 instrument in 1,1,2,2-tetrachloroethane-$d_2$ at 110°C. The melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller. The DSC curves were recorded during the second heating cycle from 20 to 200°C with a heating rate of 20°C/min. Molecular weights ($M_n$) and molecular weight distributions ($M_w/M_n$) of the polymers were measured using a PL GPC-220 with a DRI detector at 140°C using trichlorobenzene as the solvent. Bulk morphology in the polymer films was examined by scanning electron microscopy (SEM), using a Topcon International Scientific Instruments ISI-SX-40 with secondary electron imaging. SEM samples were prepared from films cryofractured in liquid $N_2$. Samples were mounted on an aluminum stub and gold coated to form a conductive coating.

All the manipulations were carried out inside an argon filled vacuum atmospheres drybox equipped with a dry train. CP grade toluene, tetrahydrofuran (THF), and ether were deoxygenated by argon purge before refluxing for 48h over sodium/benzophenone, 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), allylamine, tert-butylidiphenyl-chlorosilane, trimethylaluminum (TMA) (30% in toluene), Al$_2$(SO$_4$)$_3$.14H$_2$O, rac-Et(Ind)$_2$ZrCl$_2$, butylated hydroxytoluol (BHT), and polycaprolactone (PCL) were purchased from Aldrich and used as received. rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$ catalyst was prepared by the published procedures$^{[29]}$. Methylaluminoxane (MAO) was synthesized according to the literature$^{[30]}$. High-purity grade propylene gas was obtained from MG Industry and was used as received.

Synthesis of methylaluminoxane (MAO)$^{[30]}$

Under a nitrogen atmosphere, 250 mL of 30 wt% Al(CH$_3$)$_3$ (75 g, 1.04 mol) was added dropwise over a 2h 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 (140mL) 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 24h. The mixture was warmed to 60°C for another 24h, 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.

Synthesis and protection of functional monomers

but-3-enyl bis(trimethylsilyl)amine$^{[31]}$

But-3-enyl bis(trimethylsilyl)amine, i.e. BuN(SiMe$_3$)$_2$, was synthesized in two preparative steps as shown in Scheme 1. Into a 500 mL flask equipped with a magnetic stirrer 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 stirred overnight. The precipitated powder was filtered off and the excess chloromethyl methylether was evaporated using a rotary vapor pump. N,N-bis(trimethylsilyl)methoxymethylamine (80% yield) was isolated by distillation and its purity was confirmed by $^1$H NMR.

**Scheme 1**
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 stirrer bar, was treated with 264 mL (0.264 mol) of allylmagnesium bromide (1 M 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.

Allylaminebis(dimethylaluminum)²⁹

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 stirrer 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 2).

Allylbis(trimethylsilyl)amine

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 stirrer 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 3). Its structure was confirmed by ¹H NMR spectrum.

Synthesis of PP-t- Allyl-N(SiMe₃)₂ polymer

PP-t-Allyl-N(SiMe₃)₂ polymers were synthesized by using allylbis- (trimethylsilyl)amine as a chain transfer agent in propylene polymerization. In a typical reaction (run I-A-6 in TABLE 1), 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 (25 psi). Then 0.5 mL (0.049 M) of allylbis(trimethylsilyl)amine was injected into the reactor and 100 psi (3.24 M) of propylene was charged, bringing the total pressure to 125 psi at ambient temperature (30°C). About 1.25 X 10⁻⁶ mol of rac-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂ catalyst in toluene solution was then syringed into the rapidly stirring solution under propylene pressure to initiate the polymerization reaction. Additional propylene was fed continuously into the reactor to maintain a constant pressure (125 psi) during the course of the polymerization. After 15 min of reaction at 30°C, the reaction solution was quenched with methanol and filtered, washed extensively with THF to remove any allylbis(trimethylsilyl)amine homopolymer, and then dried under vacuum at 50°C for 8 h. About 20.4 g of PP-t-Allyl(N(SiMe₃)₂) polymer was obtained with a catalyst activity of 65280 kg of PP-t-Allyl(N(SiMe₃)₂)/mol of Zr₇h.

PP-t-AllylNH₂ polymers were prepared from PP-t-Allyl(N(SiMe₃)₂) polymers by treating them with hydrogen chloride, which can be accomplished during the sample workup step. Alternatively, the isolated PP-t-Allyl(N(SiMe₃)₂) (2 g) was suspended in 50 mL of THF at 50°C before adding dropwise 2 N methanolic hydrogen chloride solution. The mixture was stirred for 4 h at 50°C, and then poured into 1 N methanolic NaOH...
solution. The polymer was collected by filtration and washed with 1 M aqueous ammonia and water under a nitrogen atmosphere. The polymer was dried overnight at 50°C under vacuum. The polymer yield was quantitative.

**Synthesis of PP-b-PCL diblock copolymer**

The coupling reactions between chain end functionalized PP and ε-polycaprolactone (PCL) were carried out in both solution and melt. In a typical solution process, 3 g of PCL ($M_n = 50 \times 10^3$, $M_w/M_n = 2.0$) was first dissolved in toluene (200 mL) in a 500 mL flask equipped with a stirrer and a condenser installed on a sidearm (trap) containing $P_2O_5$ drying agent. About 2 g of PP-t-Allyl-NH$_2$ ($M_n = 45 \times 10^3$, $M_w/M_n = 2.0$) inhibited with BHT (∼1%) was then added into the stirring solution and refluxed under $N_2$ for 12 h. The refluxing toluene was contacted with $P_2O_5$ to maintain anhydrous conditions. The hot polymer solution was slowly poured into cold acetone, and the precipitated polymer was isolated by filtration. The insoluble polymer was then subjected to a vigorous Soxhlet extraction by boiling acetone to remove any unreacted PCL homopolymer. The purification continued until the composition of the insoluble portion became constant. After drying, 3.15 g of PP-b-PCL diblock copolymer was obtained.

**RESULTS AND DISCUSSION**

The basic idea in the direct preparation of the chain functionalized PP was to use the protected allylamine and buteneylamine that act as chain transfer agents that could engage in metalloene-mediated propylene polymerization/chain transfer reaction under some reaction conditions. The functional group (NH$_2$) of this polar monomer is well-protected to overcome the catalyst decay problem. The protection method used here has been chosen in such a way that it would not only lead to the steric shielding, but also to afford electronic neutralization of the functional group. As studied before\cite{28}, the most common protecting reagents for functional monomers containing primary amine are trialkylsilyl and trialkylaluminum groups. The protection of the functional monomers, allylamine and buteneylamine, have been successfully performed as shown in the experimental section. The silane groups not only provide effective protection for NH$_2$ functional group during the metallocene catalysis but also can be completely deprotected by methanolic HCl during the sample workup procedure.

**Protection of functional monomers**

All the protected functional monomers were analyzed by $^1$H NMR. Figures 1, 2 and 3 show the $^1$H NMR spectra of AllylIN[Al(CH$_3$)$_2$]$_2$, AllylIN[Si(CH$_3$)$_3$]$_2$, and BuN[Si(CH$_3$)$_3$]$_2$, respectively. The chemical equations and peak assignments (with the integrated peak intensities) are also included to examine the products purities.
In general, the silane protection products in Figures 2 and 3 are very pure with the expected chemical shifts and peak intensities; they show almost no detectable impurities. Silation method, using lithium bis(trimethylsilyl)-amide reagent for protecting NH$_2$ group was highly effective. On the other hand, the aluminum protection method showed in Figure 1 exhibit much more complicated reaction mixture. The common synthesis route of directly reacting Al(CH$_3$)$_3$ with -NH$_2$ group, used in many previous papers, seems to be inadequate to protect functional groups in monomers. In the reaction between Al(CH$_3$)$_3$ and allyamine (Figure 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(CH$_3$)$_2$) species, which may cause catalyst deactivation during the polymerization. Two commonly known bridged metallocene catalyst systems were investigated, including rac-Et(Ind)$_2$ZrCl$_2$ (A) and rac-Me$_2$Si[2-Me-4-Ph-(Ind)]$_2$ZrCl$_2$ (B) as illustrated in Chart 1.

The overall reaction especially benefits from the very small quantity of the chain transfer agent needed in the preparation of high polymers. Therefore, the additional protection-deprotection step causes almost no change in the polymerization conditions. The highly isospecific rac-Me$_2$Si[2-Me-4-Ph-(Ind)]$_2$ZrCl$_2$/MAO complex$^{[33]}$ used in the commercial production of i-PP would be very suitable in this reaction scheme. This catalyst system produces i-PP with high molecular weight and high melting temperature, and the bulky ligands around its specific opening active site may further prevent the catalyst from interacting with the protected functional group. This catalyst has also shown a selective chain transfer reaction$^{[15]}$ to styrene or p-MS during the propylene polymerization in the presence of hydrogen.

Equation 1 illustrates the general reaction scheme. During the course of propylene 1,2-insertion, the propagating M-C site (II) eventually reacts with an allylN[Si(CH$_3$)$_3$]$_2$ unit (k$_{12}$) (via 1,2-insertion) to form an allylN[Si(CH$_3$)$_3$] capped propagating site (III) with the nitrogen atom interacting with metal cation. The new propagating site (III) is incapable of continuing the insertion of allylN[Si(CH$_3$)$_3$]$_2$ (k$_{22}$) or propylene (k$_{21}$) due to the steric jamming.

![Chart 1](chart1.png)

**Equation 1**
However, it can react with hydrogen to complete the chain transfer reaction. This consecutive reaction with allylN[Si(CH$_3$)$_3$]$_2$ and hydrogen results in a PP-t-allylN[Si(CH$_3$)$_3$]$_2$ polymer chain (IV), and regenerates Zr-H species (I) that reinitiates the polymerization of propylene and continues the polymerization cycles. After the polymerization is complete, the desirable NH$_2$ terminal group in PP-t-allylNH$_2$ (V) can be easily recovered during the sample workup step using HCl alcoholic solution. Theoretically, the PP-t-allylNH$_2$ molecular weight should be linearly proportion to the molar ratio of [propylene]/[allylN[Si(CH$_3$)$_3$]$_2$].

TABLES 1 summarizes the experimental results of propylene polymerization in the presence of AllylN[Si(CH$_3$)$_3$]$_2$/H$_2$ as the chain transfer agent using rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyst system. The combination of FT-IR, $^1$H NMR and GPC was used to determine the polymer structure. GPC determines the polymer molecular weight and polydispersity index (PDI), and $^1$H NMR spectrum was used to determine the allyl monomer content. In all control reactions, a small amount of any allyl or butenyl amine derivatives effectively stops the polymerization of propylene. The introduction of hydrogen gradually restores the catalyst activity. As shown in the comparative reaction sets (including runs A1-A3, runs A4-A6, runs A7-A9, and runs A10-A12 in TABLE 1), hydrogen concentration does not affect the polymer molecular weight and molecular weight distribution but has a profound effect on the catalyst activity.

### TABLE 1: Summary of PP-t-Allyl-NH$_2$ polymers prepared by the combination of rac-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyst and allyl-NSi$_2$/H$_2$ chain transfer agent

<table>
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<th>Run</th>
<th>Propylene (psi)</th>
<th>AllylN[Si(CH$_3$)$_3$]$_2$ (mol/L)</th>
<th>H2 (psi)</th>
<th>Yield (g)</th>
<th>Cat. Actv.b (Kg/mol.hr.)</th>
<th>Allyl-NH$_2$ in PP (mol %)</th>
<th>Mn (X10-3)</th>
<th>PDI (Mw/Mn)</th>
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*aReaction conditions (Unless otherwise specified): 50 mL toluene, [Zr] = 1.25 X 10^-6 mol, [MAO]/[Zr] = 3000, temperature = 30°C, and time = 15 min. *bCatalyst activity = kg of PP/mol of catalyst.h.

The kinetic constants during the polymerization can be obtained from Figure 4 which shows a plot of the PP-t-Allylamine molecular weight ($M_p$) vs the molar ratio of [propylene]/[Allylamine] using AllylN[Si(CH$_3$)$_3$]$_2$/H$_2$ as a chain transfer agent. In general, the polymer molecular weight and molar ratio of [propylene]/[Allylamine] are linearly proportional which clearly indicates that the chain transfer reaction to Allylamine (with rate constant $k_{tr}$) is the dominant termination process, and that it competes with the propagating reaction (with rate constant $k_p$). The degree of polymerization ($X_n$) follows a simple comparative equation $X_n = k_p [olefin]/k_{tr} [Allylamine]$ with a chain transfer constant $k_{tr}/k_p \sim 1/32$. 

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It is intriguing that the $k_{tr}/k_p$ values are significantly lower than those seen in styrene and $p$-MS cases under similar reaction conditions. The bulky protected functional groups may reduce the frequency of chain transfer reaction.

**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 allylamine with trimethylaluminum, as described in the experimental part. Propylene polymerization has been conducted with $rac$-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyst system in the presence of AllylN[Al(CH$_3$)$_2$]$_2$ using similar reaction conditions that were applied in case of AllylN(SiMe$_3$)$_2$. Overall, trimethylaluminum group shows weak protection where both catalyst activity and molecular weight decreases with increasing AllylN[Al(CH$_3$)$_2$]$_2$ concentration in the feed. This is attributed to the existence of some mono-substituted allylamine 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. In addition, these interactions pose difficulty at active site (III) to propagate and facilitate termination leading to a decrease in the polymer molecular weight. Figure 5 shows $^1$H NMR spectra of PP-t-Allyl-NH$_2$ prepared by the combination of $rac$-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyst system (run I-A-12). The measurement was done for a neat PP-t-Allyl-NSi$_2$ (a) and for an HCL treated sample (b). Comparing the $^1$H 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. The split pattern of the resonance indicated that two protons of the methylene were not equivalent. 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.

**Figure 5 : $^1$H NMR spectra of PP-t-Allyl-NH$_2$ prepared by the combination of $rac$-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$/MAO catalyst and a) Allyl-NSi$_2$/H$_2$ chain transfer agent and b) after treating with HCl.**

**Coupling reaction: Synthesis of PP-b-PCL and PP-b-PS copolymers**

The existence of a terminal functional group in PP was further examined by a chain extension reaction using the terminal functional group as the reaction site. Specifically, the coupling reaction in solution between the terminal NH$_2$ in PP and the terminal COOH group in polycaprolactone and polystyrene has been investigated. The in situ formed diblock copolymers can be used as compatibilizers in PP/polyester and PP/polystyrene blends. Coupling reactions between PP-t-Allyl-NH$_2$ ($M_n = 45 \times 10^3$, $M_w/M_n = 2.0$) and polycaprolactone
(PCL: $M_n = 50 \times 10^3$ g/mol, $M_w/M_n = 2.0$) containing a terminal COOH group and with polystyrene containing a terminal COOH group (PS-\text{-}COOH, $M_n = 45 \times 10^3$ g/mol, $M_w/M_n = 1.2$); prepared by living anionic polymerization with CO$_2$ termination$^{30}$; have been carried out in refluxing toluene solution. The resulting PP-\text{-}b-PCL diblock copolymer (with an amide linkage) was subjected to a vigorous Soxhlet extraction by boiling acetone to remove any unreacted PCL homopolymer and the purification was continued until the composition of the insoluble portion became constant. Similarly, the resulting PP-\text{-}b-PS diblock copolymer was subjected to Soxhlet extraction by boiling THF to gain no detectable soluble PS homopolymer. In each case, the insoluble fraction (soluble in 1,1,2,2-tetrachloroethane at elevated temperature) is PP-\text{-}b-PCL and PP-\text{-}b-PS diblock copolymers which are evidenced by $^1$H NMR spectra. Figure 6 compares the $^1$H NMR spectra of the starting PP-\text{-}t-Allyl-NH$_2$ 6(a) and the resulting PP-\text{-}b-PCL 6(b) and PP-\text{-}b-PS 6(c) diblock copolymers.

In addition to the chemical shift at 1.9, 1.6, and 1.1 ppm, corresponding to methine, methylene, and methyl groups in polypropylene (Figure 6(b)), the new chemical shifts at 4.1 and 2.3 ppm correspond to methylene groups (CH$_2$-O) and (CH$_2$-C=O) in the PCL block, respectively. The quantitative analysis of the copolymer composition is calculated by the ratio of two integrated intensities between $\delta=4.1$ and $\delta=1.8-1.1$ ppm and the number of protons that both chemical shifts represent. These chemical shifts indicate about 25 mol % of PCL in the PP-\text{-}b-PCL diblock copolymer. Figure 6(c) shows the $^1$H NMR spectra of the formed PP-\text{-}b-PS diblock copolymer containing about 30 mol % of PS. The two broad peaks with chemical shifts at 6.6 and 7.1 ppm are attributed to the phenyl protons of the atactic polystyrene segments. The consistency of the copolymer composition between theoretical and experimental values clearly points to the effective coupling (amidation) reaction and the existence of a NH$_2$ group at each PP chain end.

**DSC curves of the PP-\text{-}b-PCL diblock copolymer**

Figure 7 compares the DSC curves of the PP-\text{-}b-PCL diblock copolymer containing 25% of PCL and two corresponding PP and PCL homopolymers. All samples were heat-treated by heating the samples to 200°C before cooling quiescently, and DSC curves were
recorded in the second heating cycle. Two distinctive crystalline structures formed in the diblock copolymer and exhibited melting temperatures (157 and 54°C) that were similar to those seen in the corresponding PP and PCL homopolymers. The resulting PP-b-PCL diblock copolymer (containing 25 mol% of PCL) was used as a compatibilizer in PP/PCL polymer blends. Two polymer blends – a PP/PCL (75/25 weight ratio), homopolymer blend, and a blend comprised of a 70/20/10 weight ratio of PP, PCL, and PP-b-PCL, respectively - were prepared by homogeneous mixing in a dichlorobenzene solution at 180°C before precipitating in hexane at ambient temperature. Films were then press-molded at 180°C.

**Conclusions**

Isotactic polypropylene with a terminal amino group has been prepared via metalloocene-mediated propylene polymerization, using rac-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyst complex in the presence of a silane protected allylamine. All of the experimental results support the formation of chain end functionalized PP polymers during direct (one-pot) metalloocene-mediated propylene polymerization/chain transfer reaction. The propylene propagating chain end engages in a facile consecutive chain transfer reaction, reacting with Allyl-NSi₂ and then hydrogen, with high catalytic activity under the proper reaction conditions. With the proper

**Morphological studies (SEM)**

Scanning electron microscopy (SEM) was used to characterize and compare the morphology of the PP/PCL homopolymer blend (Figure 8a) and with the PP-b-PCL as a compatibilizer within their polymer blend (Figure 8b). SEM shows the liquid N₂-fracture surface, representing the undistorted polymer bulk, where the samples were prepared by fracturing the polymer films under liquid nitrogen conditions, and SEM micrographs were taken on the fractured surfaces. For comparison, the simple blend sample; without compatibilizer; was side-by-side compared with the corresponding polymer blend (containing PP-b-PCL compatibilizer).
choice of reaction conditions, chain transfer agents, and catalyst system, it is very convenient and efficient (with high catalyst activity) to prepare i-PP with a terminal NH$_2$ group. The polymer molecular weight is proportional to the molar ratio of [propylene]/[Allyl-NSi$_2$]. The silane protecting group can be hydrolyzed in acidic solution during the sample work-up step to obtain the desirable i-PP polymers with a terminal NH$_2$ group. In turn, the PP polymer with a reactive functional (NH$_2$) group is a useful material that can be used to prepare diblock copolymers by coupling reactions (chain extension reaction), with polycaprolactone (PCL) and with PS in solution, to form PP-b-PCL and PP-b-PS diblock copolymers that are effective compatibilizers in PP/PCL and PP/PS polymer blends.

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