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RESEARCH ARTICLE

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Design and synthesis of structurally well-defined functional polypropylenes via transition metal-mediated olefin polymerization chemistry

Abstract Functionalization of polyolefins is an industrially important yet scientifically challenging research subject. This paper summarizes our recent effort to access structurally well-defined functional polypropylenes via transition metal-mediated olefin polymerization. In one approach, polypropylenes containing side chain functional groups of controlled concentrations were obtained by Ziegler-Natta-catalyzed copolymerization of propylene in combination with either living anionic or controlled radical polymerization of polar monomers. The copolymerization of propylene with 1,4-divinylbenzene using an isospecific $MgCl_2$-supported $TiCl_4$ catalyst yielded polypropylenes containing pendant styrene moieties. Both metalation reaction with n-butyllithium and hydrochlorination reaction with dry hydrogen chloride selectively and quantitatively occurred at the pendant reactive sites, generating polymeric benzyllithium and 1-chloroethylbenzene species. These species initiated living anionic polymerization of styrene (S) and atom transfer radical polymerization (in the presence of CuCl and pentamethyldiethylenetriamine) of methyl methacrylate (MMA), respectively, resulting in functional polypropylene graft copolymers (PP-*g*-PS and PP-*g*-PMMA) with controllable graft lengths. In another approach, chain end-functionalized polypropylenes containing a terminal OH-group with controlled molecular weights were directly prepared by propylene polymerization with a metallocene catalyst through a selective aluminum chain transfer reaction. Both approaches proved to be desirable polyolefin functionalization routes in terms of efficiency and polymer structure controllability.

Keywords polypropylene-functionalization, Ziegler-Natta catalyst, metallocene catalyst, copolymerization, chain transfer reaction

1 Introduction

Ever since the commercialization of polyethylene (PE) and polypropylene (PP) in the 1950s, the functionalization of polyolefins has been a very interesting research subject attracting attentions from both academic and industrial communities [1–5]. The so-called polyolefin functionalization is explained as introducing polar functional groups into polyolefins. With the precondition of maintaining the desired properties of polyolefins, polyolefin functionalization confers reactivity to polyolefins, improving adhesion and compatibility between polyolefins and other materials, such as pigments, paints, glass fibers, metals, carbon black, and most polymers. The application of polyolefins after functionalization can be extended to such areas that involve catalyst supporting, medicament, photoelectron material, biomaterial, photo material, and environmental protection, which have never been previously accessed by polyolefins [6].

As for the chemistries to achieve polyolefin functionalization, the most traditional one is the chemical modification of preformed polyolefins (the post-polymerization approach, the product is named functionalized polyolefins) [7–10]. However, due to the inert nature of polyolefins, this approach has to resort to a high-energy source (such as molecular radical, irradiation and plasma) to break the stable C–H bonds in polyolefins to form polymeric radicals. The polymeric radicals will then react with polar chemical reagents present in the modification system via either addition or coupling reaction to combine functional groups with polyolefins [9–12]. In general, because there is no obvious reaction site in polyolefins, the functionalization efficiency using the post-polymerization approach is quite low. The obtained functionalized polyolefins usually possess complex molecular structures coupled with nonuniform distributions of functional groups (functional groups are

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mainly contained by low molecular weight polymers) [12].

In the history of polymer chemistry, the past half-century has witnessed a rapid development of transition metal-mediated olefin coordination polymerization. To date, both the transition metal catalysts and the knowledge of their olefin polymerization mechanism have proliferated. The development of chemistry stimulates the evolvement of polymer. In particular, the newly developed single site catalysts (including metallocene and post metallocene catalysts), with a great combination of high activity and possibility of tailoring polymer properties such as molecular weight and molecular weight distribution, comonomer incorporation and distribution, and stereoregularity by simply tuning catalyst structure, have proven themselves attractive and promising catalysts for olefin polymerization in the new century. There exists abundant evidence showing the molecular design of functional polyolefins is executable with the assistance of transition metal-mediated olefin coordination polymerization chemistry.

In this paper, we summarize recent progress in our laboratory in the functionalization of polyolefins using transition metal-mediated olefin polymerization chemistry, which was aimed at functional polyolefins with well-defined structures. In one research [13], Ziegler-Natta-catalyzed propylene polymerization was targeted at polypropylenes containing pendant styrene groups, which were then combined with either living anionic or controlled radical polymerization of polar monomers to reach side chain-functionalized PP with controlled functional group concentration while retaining the desired PP thermal properties such as high melting point and high crystallinity. In another research [14], selective chain transfer by aluminum cocatalyst was found to dominate the chain termination process in propylene polymerization with a highly isospecific metallocene/methylaluminoxane (MAO) catalyst system, resulting in aluminum-terminated isotactic polypropylenes that can be further utilized to prepare terminally functionalized polyolefins as well as polyolefin-based block copolymers containing polar polymer segments.

2 Experimental

Materials and instruments

All O_2- and moisture-sensitive manipulations were carried out inside an argon-filled Vacuum Atmosphere drybox equipped with a dry train. Pure 1,4-divinylbenzene was isolated from a commercially available divinylbenzene mixture (Aldrich Chemical Co.). Styrene (St, 99%), and methyl methacrylate (MMA, 99%) were vacuum-distilled and stored under argon. Anisole (99%) was deoxygenated by argon purge before refluxing for 24 h and then distilled over CaH_2. CP-grade heptane was deoxygenated by argon purge before refluxing for 48 h and then distilled over sodium. $AlEt_3$ (1.8 M in toluene), dimethoxydiphenylsilane (DDS), CuCl (98%), and pentamethyldiethylenetriamine (PMDETA, 99%) were from Aldrich and used without further purification. Polymerization grade propylene was supplied by Yansan Petrochemical Co. of China. The $MgCl_2$/diisobutyl phthalate (DIBP)/$TiCl_4$ catalyst was kindly donated by Xiangyang Chemical Co. of China with a Ti content of 2.5 weight%. MAO (10 wt.% in toluene) was purchased from Albermarle and used without further purification. The catalyst, *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2 ZrCl_2$, was synthesized according to a published procedure [15].

All ^1H-NMR spectra were recorded on a Bruker AM-300 instrument in 1,1,2,2-tetrachloroethane-d_2 at 115 ^oC. The melting and glass transition temperatures as well as the crystallinities of the polymers were measured by a differential scanning calorimeter (DSC) using a Perkin-Elmer DSC-7 instrument controller operating from 30 ^oC to 180 ^oC with a heating rate of 20 ^oC/min. The data were collected on the second heating cycle. The intrinsic viscosity [η] of the polymers was measured in decahydronaphthalene at 135±0.1 ^oC. Gel permeation chromatography (GPC) measurement was performed using a Waters Alliance GPC 2000V instrument operated at 150 ^oC with 1,2,4-trichlorobenzene as the eluent to determine polymer molecular weight and molecular weight distribution.

Copolymerization of propylene and 1,4-divinylbenzene by the $MgCl_2$-supported Ziegler-Natta catalyst

In a typical reaction (run no. 3 in Table 1), 50 ml of heptane was added into a 250 ml three-neck glass reactor equipped with a magnetic stirrer. The reactor was then saturated with atmospheric pressure of propylene at 50 ^oC. 1 g of 1,4-divinylbenzene, 3.88 ml of $AlEt_3$ (1.8 M in toluene), and 4.13 ml of DDS (0.7 mmol) were subsequently injected with syringe with an Al/Si molar ratio of 10/1. The polymerization was started by adding 0.1 g of $MgCl_2$/DIBP/$TiCl_4$ catalyst into the reactor. After 30 min of reaction, 10 ml of acidic methanol was added to terminate the reaction. The product was collected by filtration and repeatedly washed with methanol, THF and water and dried at room temperature under high vacuum for 24 h to obtain 5.36 g of white polymer powder.

Lithiation reaction of poly(propylene-co-1,4-divinylbenzen e)

In an argon filled drybox, 3 g of poly(propylene-*co*-1,4-divinylbenzene) copolymer containing 0.44 mol% of divinylbenzene units was suspended in 50 ml of anhydrous cyclohexane in a 100 ml flask equipped with a magnetic stirrer. Then 1 ml of 1.6 M *n*-BuLi in hexane and 1 ml (6.5 mmol) of TMEDA were added to the flask. The flask was then brought out of the drybox and heated up to 40 ^oC. The lithiation reaction was allowed to proceed for 4 h before the reaction mixture was filtered and repeatedly washed with cycohexane. A yellow polymer powder was obtained after drying under vacuum at 60 °C for 4 h (lithiated poly (propylene-*co*-1, 4-divinylbenzene)).

Silylation reaction of lithiated poly(propylene-co-1,4-divinvbenzene)

Lithiated poly(propylene-co-1,4-divinylbenzene) (1.0 g) was suspended in 30 ml of dry cyclohexane, to which 2 ml of Me_3SiCl was added using a syringe. The reaction mixture was stirred at 40 °C for 2 h. After filtration and repeatedly washing with THF, methanol, and water, the solid polymer was collected and dried under vacuum at 60 °C for 8 h. The ^1H NMR spectrum shows a strong peak at 0.05 ppm corresponding to the methyl proton adjacent to Si.

Hydrochlorination of poly(propylene-co-1,4-divinylbenzene)

In a 250 ml round-bottomed flask equipped with a magnetic stirrer, 2.0 g of poly(propylene-co-1,4-divinylbenzene) polymer containing 0.44 mol% of 1,4-divinylbenzene units was suspended in 100 ml of 1,1,2,2-tetrachloroethane at 80 °C. Dry hydrogen chloride (HCl) that was generated by adding hydrogen chloride acid (36%) dropwise into concentrated sulfuric acid was bubbled into the suspension. After 6 h, the suspension was poured into 200 ml ethanol, filtered, and washed with ethanol several times. The final product was dried at room temperature under high vacuum for 24 h to obtain white polymer powder.

Grafting of styrene from poly(propylene-co-1,4-divinylbenzene)

In one experiment (Fig. 4a), 0.26 g of the above-obtained lithiated poly(propylene-co-1,4-divinylbenzene) copolymer was suspended in 50 ml of anhydrous cyclohexane, to which 4 ml of styrene was added at room temperature using a syringe. After 0.5 hour's stirring at room temperature, 10 ml of methanol was added to terminate the graft reaction. The precipitated polymer was filtered and dried under vacuum to give 0.32 g of *i*-PP-*g*-PS, which accounts for about 18.0 wt.% of polystyrene in the graft copolymer. Soxhlet extraction experiment performed on the *i*-PP-*g*-PS graft copolymer using THF resulted in no soluble polymer, indicating there was no homo-polystyrene polymer formed during the graft-from reaction.

In another experiment (Fig. 4b), with the same amounts of monomer and initiator, the graft reaction was prolonged to 1 h and generated 0.46 g of *i*-PP-*g*-PS containing 46.0 wt.% of polystyrene segments.

Grafting of MMA from hydrochlorinated poly(propylene-co-1,4-divinylbenzene)

In one experiment (Fig. 4c), a dry round-bottomed flask was charged with anisole (10 ml), CuCl (0.043 g, 0.3 mmol), PMDETA (0.051 g, 0.3 mmol), MMA (3 g, 30 mmol), and the above-obtained hydrochlorinated poly(propylene-co-1, 4-divinylbenzene) (0.15 g). The flask was sealed and filled with purified argon. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 95 °C for 40 minutes. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum to give 0.19 g of PP-*g*-PMMA graft copolymer containing 22.4 wt% of PMMA segments. Soxhlet extraction experiment performed on the graft copolymer using acetone resulted in no soluble polymer, indicating there was no homo-PMMA polymer formed during the graft-from reaction.

In another experiment (Fig. 4d), with the same amounts of solvent, monomer, catalyst, ligand, and initiator, the graft reaction was prolonged to 1.5 h and generated 0.24 g of *i*-PP-*g*-PMMA containing 37.3 wt.% of polystyrene segments.

Propylene polymerization with an oxidative workup process

In a typical reaction (run no. 3 in Table 2), a 300 mL three-necked round bottom flask was charged with 134 mL of toluene, 16 ml of MAO and 1 bar of propylene at 30 °C. About 0.75×10^{-6} mol (5.0×10^{-6} M) of *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph(Ind)]_2ZrCl_2$ catalyst was then added to initiate the polymerization. During the course of reaction, additional propylene was continuously fed into the flask to maintain a constant pressure (1 bar). After 30 min of reaction at 30 °C, the polymerization was terminated by stopping the monomer gas flow. The dry oxygen was bubbled into the polymer solution through a syringe needle for 2 h at the ambient temperature. Then 29 ml of aqueous hydrogen peroxide solution (30 wt.%) and 10 g of sodium hydroxide (in 20 ml of aqueous solution) were added and the reaction mixture was heated to 50 °C. After stirring for 4 h, the reaction mixture was poured into excess acidic ethanol (10%) and filtered. The product was purified by repeatedly washing with water, acidic ethanol and water, and dried under vacuum at 60 °C for 8 h.

3 Results and discussion

Design and synthesis of side chain-functionalized polypropylenes via reactive polypropylene intermediate

For the functionalization of polyolefins, there have been tremendous interests in recent years in the design and synthesis of polyolefins containing reactive groups [16]. This is because the direct copolymerization of an α–olefin with a functional vinyl monomer by Ziegler-Natta or metallocene catalysts, the most straightforward way of preparing functional polyolefins, usually suffers from significantly reduced catalyst activity and polymer molecular weight due to the deactivation of catalyst by heteroatom (O, N, etc.) –containing functional groups [17]. As an alternative approach, by designing and synthesizing a polyolefin containing reactive groups that are free of catalyst-deactivating heteroatoms but very facile in functional transformation reactions, the functionalization of polyolefins via the reactive polyolefin "intermediate" is able to effectively avoid catalyst deactivation and produces functional polyolefins with well-defined molecular structures. A variety of reactive polyolefins, including polyolefins containing alkylborane groups [18], polyolefins containing *p*-methylstyrene units [19], and various unsaturated polyolefins [20] have been synthesized by Ziegler-Natta or metallocene catalysts via the copolymerization of *α*–olefin monomer with the corresponding reactive group-containing comonomers and applied as "intermediates" to prepare functional polyolefins possessing versatile functionalities. We recently reported the copolymerization of ethylene [21] and terpolymerization of ethylene and propylene, ethylene and 1-octene [22] with 1,4-divinylbenzene by a metallocene catalyst, resulting in polyethylene and ethylene-*co*-propylene and ethylene-*co*-1-octene copolymers containing pendant styrene groups. Owing to the versatile interconversion reactions involving styrene, a polyolefin containing many pendant styrene groups was shown to be an effective "intermediate" to access a broad range of functional polyolefins. However, as we tried to incorporate 1,4-divinylbenzene units into isotactic polypropylene (*i*-PP), another important type of polyolefins, to prepare *i*-PP containing pendant styrene groups, we failed with metallocene catalysts. The copolymerization reactions between propylene and 1,4-divinylbenzene were unfruitful by typical isospecific metallocene catalysts including *rac*-$Et(Ind)_2ZrCl_2$/MAO, *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO, *rac*-$Me_2Si(2\text{-}Me\text{-}Ind)_2$ $ZrCl_2$/ MAO, and *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind)_2ZrCl_2$/MAO. This phenomenon was repeated in the cases of propylene copolymerization with other styrenic monomers including styrene [23, 25] and *p*-methylstyrene [24, 25] and was reasoned by the defined yet contradictive regio-specificities of metallocene catalyst to the insertions of propylene (via a 1,2- manner) and styrene (via a 2,1- manner) that caused serious steric jamming around the active center to fatally retard the consecutive monomer propagation during the polymerization..

Despite the unsuccessful copolymerization of propylene and 1,4-divinylbenzene by metallocene catalysts, the goal of introducing some styrene groups into *i*-PP still deserves to be pursued. Our approach to gain this goal was to resort to heterogeneous Ziegler-Natta catalysts for the copolymerization of propylene and 1,4-divinylbenzene with the idea that Ziegler-Natta-catalyzed polymerization could only proceed via a 1,2-insertion mode in both the propylene and styrene incorporations [25] so that the copolymerization would not abort due to the steric congestion of the active sites (Scheme 1). On the other hand, because the two styrene moieties in a divinylbenzene molecule are both polymerizable in a Ziegler-Natta-catalyzed copolymerization reaction, it is also very important and interesting to explore if the heterogeneous isospecific Ziegler-Natta catalysts are able to control the incorporation of 1,4-divinylbenzene in a selective way of reacting with only one of the two vinyl groups.

The Ziegler-Natta-catalyzed copolymerization reactions between propylene and 1,4-divinylbenzene were performed in heptane solution under an atmospheric pressure of propylene using a $MgCl_2$-supported $TiCl_4$ catalyst containing an internal electron donor (diisobutyl phthalate, DIBP)combined with $AlEt_3$ activator and dimethoxydiphenylsilane (DDS) external donor. The copolymerization was examined by varying the concentrations of 1,4-divinylbenzene in the copolymerization feed as well as other polymerization conditions. Table 1 summarizes the results of the copolymerization reactions.

Table 1 A summary of copolymerization reactions between propylene and 1,4-divinylbenzene catalyzed by a $MgCl_2$-supported $TiCl_4$ catalyst

Run no.	Polymerization conditions [a]		Yield	Activity [b]	1,4-DVB in polymer	$M\eta$ [c]	T_m	χ_c
	1,4-DVB (mol/L)	T (ºC)	(g)		(mol %)	(×10^5g/mol)	(°C)	(%)
1	0	50	8.26	236	0	1.21	159.2	47.5
2	0.058	50	7.14	204	0.29	1.89	156.7	39.4
3	0.154	50	5.36	153	0.53	1.47	154.6	38.8
4	0.308	50	4.30	123	0.56	1.30	153.9	34.7
5	0.615	50	3.99	114	0.65	0.86	152.6	31.1
6	0.154	30	6.30	180	0.44	2.25	157.1	38.3
7	0.154	70	1.82	52	0.49	1.22	153.1	38.4

[a] Other conditions: atmospheric pressure of propylene, 50 ml heptane, $MgCl_2$ /DIBP/$TiCl_4$ catalyst, [Ti] = 0.07 mmol, $AlEt_3$ cocatalyst, DDS external donor, [Al]/[Ti] =100, [DDS]/[Ti]= 10/1 , polymerization time=30 min. [b] Catalyst activity: kilograms of polymer per mole of Ti per hour. [c] The viscosity-averaged molecular weight was calculated according to the equation of $[\eta]=1.10\times10^{-4}M_\eta^{0.8}$ [26].

As expected, in spite of the slightly decreased catalyst activities at higher concentrations of 1,4-divinylbenzene in the copolymerization feed, which was due to the lower reactivity of 1,4-divinylbenzene relative to propylene, the copolymerization reactions catalyzed by the isospecific Ziegler-Natta catalyst generally proceeded at fairly satisfactory rates, suggesting that there was no steric jamming of active site occurring during the propagation of polymer chains. The catalyst still maintained a high activity value (114 kg polymer/molTi.h) when a relatively high concentration of 1,4-divinylbenzene was added in the copolymerization (run no. 5 in Table 1).

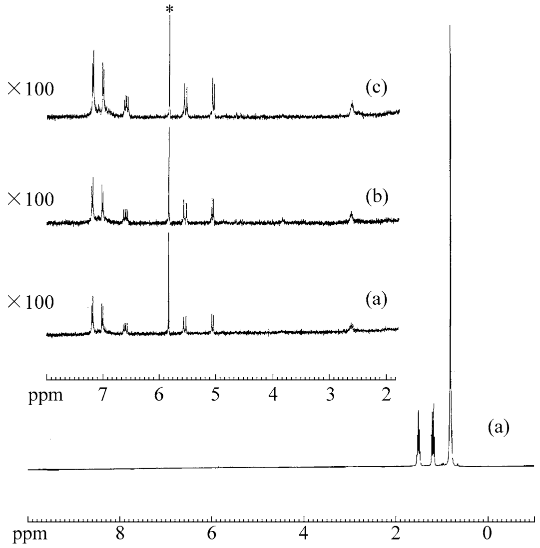


Fig. 1 ^{1}H NMR spectra of three poly(propylene-*co*-1,4-divinylbenzene) copolymers containing (**a**) 0.29 mol%, (**b**) 0.44 mol% and (**c**) 0.65 mol% of 1,4-divinylbenzene units. (Solvent: 1,1,2,2-tetrachloroethane-d_2; T: °C)

All the obtained copolymers are completely soluble in common organic solvents, such as xylene, 1,1,2,2-tetrachloroethane and 1,2.4-trichlorobenzene at elevated temperatures, which allows the detailed structural analyses by using nuclear magnetic resonance (NMR). Figure 1 shows ^{1}H NMR spectra of three propylene-1,4-divinylbenzene copolymers containing 0.29, 0.44 and 0.65 mol% of 1,4-divinylbenzene units. In addition to the major peaks at 0.95, 1.35 and 1.65 ppm corresponding to the CH_3, CH_2, and CH groups in the propylene units, several chemical shifts are observed at 2.6 ppm ($CH_2C\mathbf{H}(Ph)CH_2$), 5.2 and 5.7 ppm (doublet, $CH{=}C\mathbf{H}_2$), and 6.7 ppm (doublet of doublet, $C\mathbf{H}{=}CH_2$) and aromatic proton peaks at 7.1 and 7.4 ppm ($C_6\mathbf{H}_4$). It is very interesting to compare the integrated intensities of these 6 minor peaks as they contain important information about the incorporation modes of 1,4-divinylbenzene. All the obtained copolymers show near 1:1:1:1:2:2 ratios between the peaks at 2.6, 5.2, 5.7, 6.7, 7.1, and 7.4 ppm, suggesting (I) the selective enchainment of 1,4-divinylbenzene via only one of its two double bonds and (II) the in-chain instead of chain-end placement of the incorporated 1,4-divinylbenzene units. Considering the generally low incorporations of 1,4-divinylbenzene in the obtained copolymers, we attribute the selective mono-enchainment of 1,4-divinylbenzene in the copolymers to the combined advantages of the presence of abundant free 1,4-divinylbene comonomer in the copolymerization systems and the use of Ziegler-Natta catalysts for the copolymerization that show poor capability of incorporating bulky monomers. After all, the steric hindrance at the residual double bond of the incorporated 1,4-divinylbenzene units would be further enhanced by the adjacent polymer chain and thus effectively prevented them from further participating in the polymerization reaction.

To further confirm the linear structure of the obtained poly(propylene-*co*-1,4-divinylbenzene) copolymers, we subjected one sample to gel permeation chromatography (GPC) analysis. In Fig. 2 is shown the GPC curve of a poly(propylene-*co*-1,4-divinylbenzene) copolymer containing 0.53 mol% of incorporated 1,4-divinylbenzene units. Giving a molecular weight (M_n) and molecular weight distribution of 36,170 *g*/mol and 7.22, respectively, the GPC curve exhibits a smooth, unimodal signal and shows no sign of the existence of crosslinked polymers.

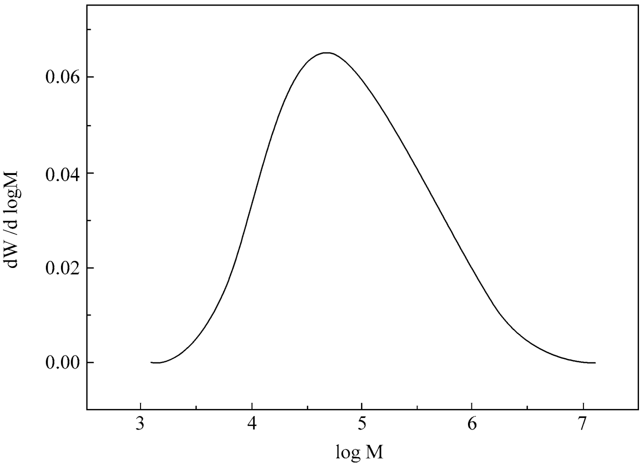
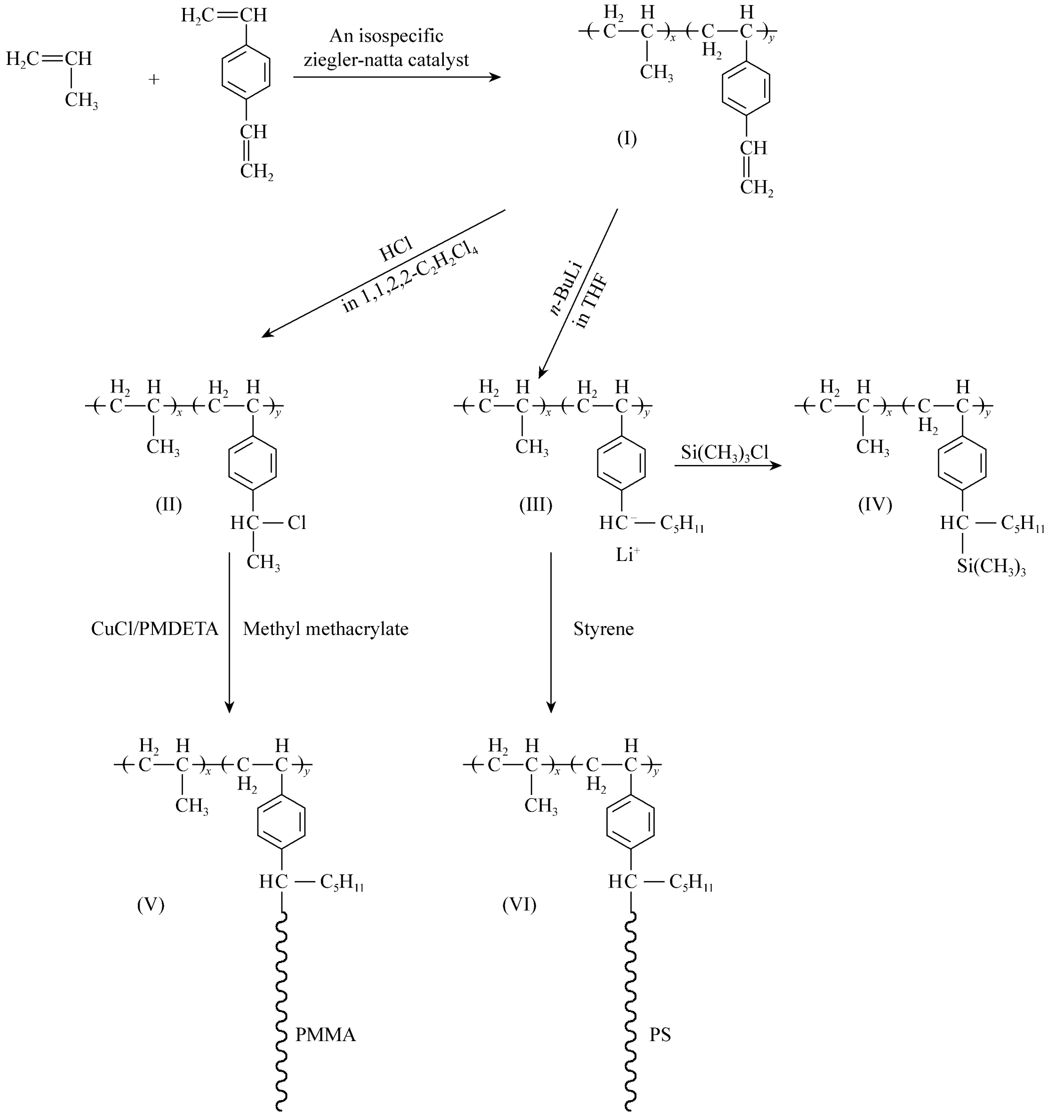


Fig. 2 GPC trace of a poly(propylene-*co*-1,4-divinylbenzene) copolymer containing 0.53 mol% of 1,4-divinylbenzene units (run no. 3 in Table 1).

The 1,4-divinylbenzene contents as well as styrene group concentrations of the copolymers were calculated based on the comparison of the integration of anyone of the peaks at 5.2, 5.7, or 6.7 ppm with that of the sum of peaks at 0.95, 1.35 and 1.65 ppm together with the consideration of the number of protons each chemical shift represents. Despite the rapid increase of the concentrations of 1,4-divinylbenzene in the copolymerization feeds, its incorporations in the copolymers increase very slowly due to the large reactivity difference between propylene and the bulky styrenic monomer. As such adjusting the polymerization conditions did not significantly affect the comonomer incorporations. The maximum incorporation of 1,4-divinylbenzene in the copolymer under our current conditions is lower than 1 mol%.

In general, the copolymerization results of propylene and 1,4-divinylbenzene involving catalyst activities and comonomer incorporations using the $MgCl_2$-supported $TiCl_4$ catalyst are consistent with those obtained by Soga and Yanagihara [27], Gao and Lin [28] and Lu and Chung [24] in the cases of propylene copolymerization with other styrenic monomers including styrene and *p*-methylstyrene by heterogeneous Ziegler-Natta catalysts. Despite the satisfactory catalyst activities, the incorporations of the bulky styrenic comonomers are usually very difficult to be able to reach high values, which is due to the generally poor copolymerization capability of heterogeneous Ziegler-Natta catalysts. However, the low comonomer incorporations in the *i*-PP copolymers are propitious to preserve the original desired properties of *i*-PP. As shown in Table 1, both the molecular weights and melting temperatures of the poly(propylene-co-1,4-divinylbenzene)copolymers obtained show only slightly decrease as compared with those of the propylene homopolymer.



Scheme 1 Synthesis and functionalization of polypropylene containing pendant styrene groups

The limited incorporations of 1,4-divinylbenzene by the Ziegler-Natta catalyst resulted in low concentrations of reactive groups in the *i*-PP polymers, which posed a great challenge for the subsequent functionalization reactions. However, thanks to the high reactivity of styrene groups in the interconversion reactions into the initiating groups for living anionic [22] and atom transfer radical (ATRP) [29] polymerizations, the *i*-PP containing few pendant styrene groups was still able to serve as reactive "intermediate" to access functional *i*-PP with controlled amounts of functional groups by synthesizing *i*-PP graft copolymers. Both the metalation reaction by *n*-butyllithium and the hydrochlorination reaction by anhydrous HCl of the poly(propylene-*co*-1,4-divinylbenzene) copolymers could reach quantitative level under mild reaction conditions, which conveniently provided polymeric benzyl lithium and polymeric benzyl chloride initiating sites for the anionic and ATRP graft-from polymerizations of polar monomers (Scheme 1). As an example, in Fig. 3 are shown the ^{1}H NMR spectra of the metalated and subsequently silylated (Fig. 3a) and hydrochlorinated (Fig. 3b) products of poly(propylene-co-1,4-divinylbenzene) copolymer containing 0.44 mol% of 1,4-divinylbenzene units (run no. 6 in Table 1, pendant styrene group concentration is also 0.44 mol%). The starting poly(propylene-co-1,4-divinylbenzene) copolymer has a viscosity-averaged molecular weight of

225 kg/mol, a melting point of 157.1 °C and a crystallinity of 38.3%. While the hydrochlorination reaction was performed by bubbling HCl gas into a suspension of the polymer in 1,1,2,2-tetrachloroethane at 80 °C, the metalation reaction was carried out in cyclohexane at 40 °C using *n*-butyllithium as the metalating reagent followed by a silylation reaction with trimethylsilyl chloride to quantitate the efficiency of the metalation reaction (Scheme 1). As shown in Fig. 3a and 3b, all the peaks corresponding to the styrenic vinyl groups at 5.2, 5.7 and 6.7 ppm completely disappear after metalation and hydrochlorination. The new peaks at 0.05 ppm in Fig. 3a and at 5.1 ppm in Fig. 3b correspond to the $–Si(CH_3)_3$ and $–(C_6H_4)CHCl–$ groups, respectively. Interestingly, while the aromatic protons still show two separated peaks in the spectrum of the hydrochlorinated product as they do for the starting poly (propylene-co-1,4-divinylbenzene) copolymer, due to the presence of chlorine at the benzylic position, they exhibit one single peak in the spectrum of the metalated and subsequently silylated product because of the similar chemical environments around them. The experimental results indicate clean reactions and almost quantitative conversions in each of the metallation, silylation and hydrochlorination reactions.

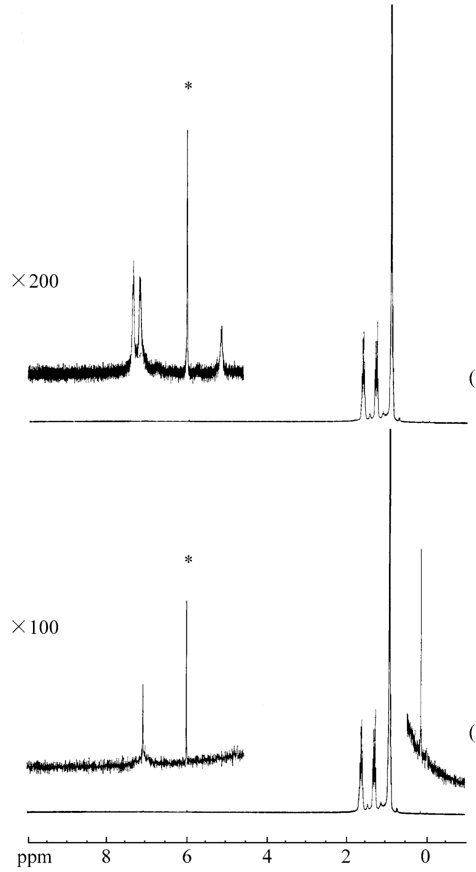


Fig. 3 ^1H NMR spectra of a poly(propylene-*co*-1,4-divinylbenzene) copolymer containing 0.44 mol% of 1,4-divinylbenzene units after (**a**) metalation with *n*-BuLi and subsequent silylation with trimethylsilyl chloride and (**b**) hydrochlorination with HCl. (Solvent: 1,1,2,2-tetrachloroethane-d_2; *T*: 110 °C)

The controllable introduction of polar functional groups into *i*-PP through the styrene group-containing "intermediate" was embodied in the preparation of *i*-PP-*g*-PS (polystyrene) and *i*-PP-*g*-PMMA (poly(methyl methacrylate)) graft copolymers. The above-obtained metalated and hydrochlorinated poly(propylene-co-1, 4divinylbenzene) copolymers were used to initiate the graft-from polymerization of styrene and methyl methacrylate (MMA) with living anionic and ATRP (in the presence of CuCl and pentamethyldiethylenetriamine) mechanisms, respectively. By controlling the monomer conversions during the graft polymerization reactions, functional *i*-PP polymers containing defined yet adjustable amounts of styrene and MMA units were achieved. Fig. 4 shows ^1H NMR spectra of two anionically-prepared *i*-PP-*g*-PS graft copolymers containing 18.0 wt.% (Fig. 4a) and 46.0 wt.% (Fig. 4b) of styrene units and two radically-prepared *i*-PP-*g*-PMMA graft copolymers containing 22.4 wt.% (Fig. 4c) and 37.3 wt.% (Fig. 4d) of MMA units, respectively. All the four graft copolymers were derived from the poly(propylene-*co*-1,4-divinylbenzene)

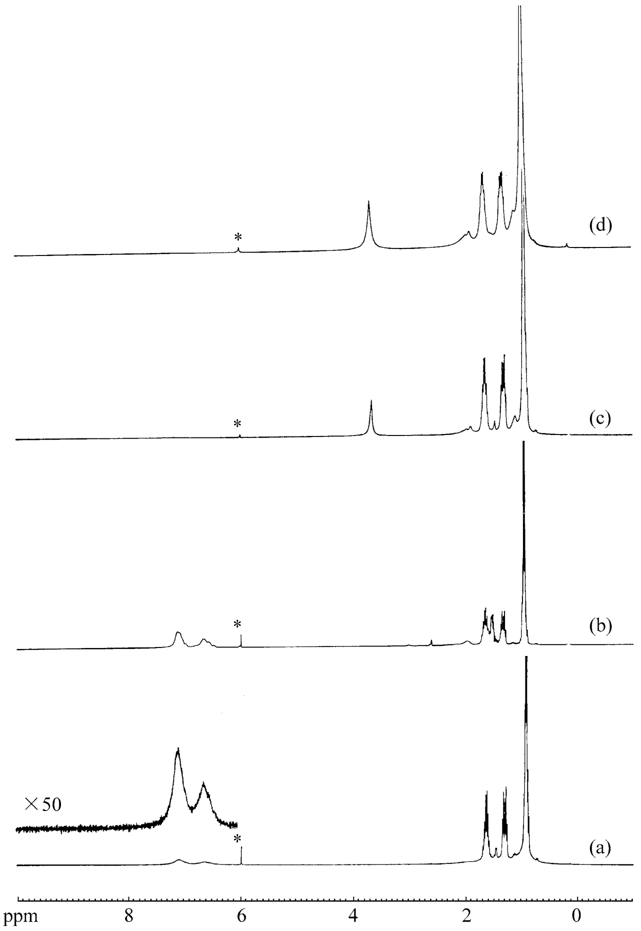


Fig. 4 ^1H NMR spectra comparison between two anionically-prepared *i*-PP-*g*-PS graft copolymers containing (**a**) 18.0 wt.% and (**b**) 46.0 wt.% of styrene units and two radically-prepared *i*-PP-*g*-PMMA graft copolymers containing (**c**) 22.4 wt.% and (**d**) 37.3 wt.% of MMA units. (Solvent: 1,1,2,2-tetrachloroethane-d_2; *T*: 110 °C)

copolymer containing 0.44 mol% of pendant styrene groups and were obtained by simply varying the monomer conversions during the respective graft polymerization reactions. In addition to the peaks at 0.95, 1.35 and 1.65 ppm corresponding to the three types of protons in *i*-PP backbone, the two *i*-PP-*g*-PS graft copolymers show aromatic proton peaks at 6.4–7.3 ppm in their spectra corresponding to consecutively arrayed styrene units which are indicative of PS graft segments. On the other hand, the two *i*-PP-*g*-PMMA graft copolymers exhibit the characteristic resonance of $-COOCH_3$ in MMA unit at 3.68 ppm, the integration of which indicates the polymeric form of MMA units.

Despite the high second polymer contents, the *i*-PP-based graft copolymers still possess high melting temperatures, which must be attributed to their well-preserved PP main chain structure due to the relatively low 1,4-divinylbenzene incorporation in the starting poly(propylene-co-1, 4-divinylbenzene)copolymer resulting in low graft densities. Fig. 5 compares DSC curves of the *i*-PP-*g*-PMMA graft copolymer containing 37.3 wt.% of MMA units and *i*-PP-*g*-PS containing 46.0 wt.% of styrene units with that of the starting poly(propylene-co-1,4-divinyl-benzene) copolymer having 0.44 mol% of 1,4-divinylbenzene incorporation. In addition to the glass transitions of the PMMA and PS grafts observed at 101.9 °C and 99.1 °C, the *i*-PP-*g*-PMMA and *i*-PP-*g*-PS graft copolymers exhibit their melting points at 158.4 °C and 156.9 °C, respectively, which are comparable with that of the starting poly(propylene-*co*-1,4-divinylbenzene) copolymer.

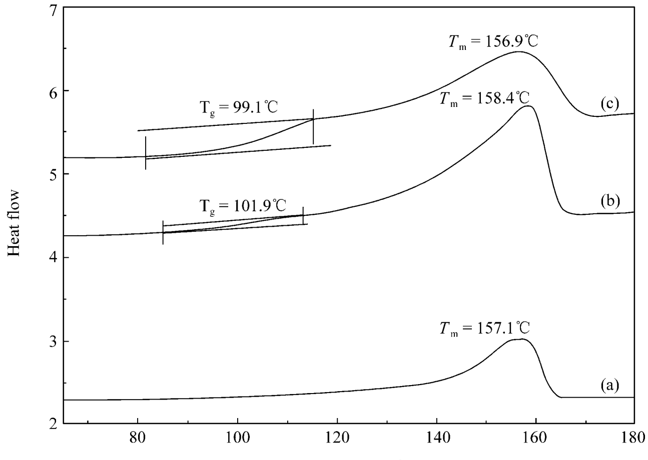


Fig.5 A comparison of DSC curves between (**a**) the poly(propylene- *co*-1, 4-divinylbenzene) copolymer containing 0.44 mol% of 1,4-divinylben zene units, (**b**) the *i*-PP-*g*-PMMA graft copolymer containing 37.3 wt.% of MMA units, and (**c**) the *i*-PP-*g*-PS graft copolymer containing 46.0 wt.% of styrene units

In summary, the experimental results clearly show the successful preparation of *i*-PP containing pendant styrene groups by the Ziegler-Natta-catalyzed copolymerization of propylene and 1,4-divinylbenzene. The formed poly(propylene-co-1,4-divinylbenzene) copolymers are completely soluble in common organic solvents at elevated temperatures and exhibit high molecular weights and melting temperatures and crystallinities. Despite the limited incorporations of 1,4-divinylbenzene units by the Ziegler-Natta catalyst, the *i*-PP polymers containing few pendant styrene groups are effective "intermediates" for the functionalization of *i*-PP due to the quantitative interconversion reactions of styrene groups to living anionic and ATRP initiating sites. *i*-PP polymers containing controllable amounts of styrene or MMA units were achieved by living anionic and ATRP graft-from polymerizations, respectively.

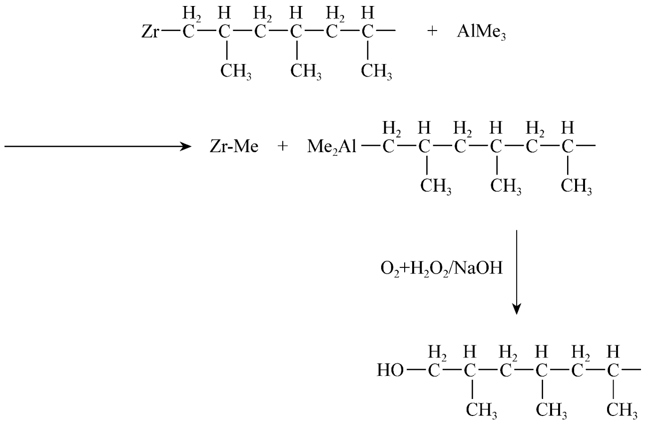
Design and synthesis of terminally functionalized polypropylenes via controlled and selective chain transfer reaction in metallocene-catalyzed propylene polymerization

Polyolefins containing a terminal reactive/functional group represent one important type of functional polyolefins in that they can not only confer some new properties to polyolefins, but are also useful for the construction of complex polyolefin architectures including block and graft copolymers. For the synthesis of such polyolefins, it is generally believed that a catalytic chain transfer process utilizing a chain transfer agent possessing the targeted reactive/functional group during olefin polymerization is more advantageous than a living polymerization process in terms of efficiency and feasibility. Zn- [30], silane- [31], borane- [32], and several styrenic molecules [33] -terminated polyolefins have been successfully prepared by employing externally added chain transfer agents including alkyl zinc, silane compounds, borane compounds, and styrene and substituted styrenes in Ziegler-Natta or metallocene-catalyzed olefin polymerization. On the other hand, the inherent chain transfer reaction to alkyl aluminum in olefin coordination polymerization using alkyl aluminum or alkyl aluminoxane as cocatalyst is also very valuable because the resultant aluminum-terminated polyolefins can be further utilized to prepare terminally functionalized polyolefins as well as polyolefin-based block copolymers containing polar polymer segments. The challenge in this art is how to direct the chain transfer reactions in olefin polymerization to a selective mode of transferring to aluminum while refraining the furthest other chain transfer reactions including β–H transfer in order to accomplish high synthetic yield. This is generally difficult to achieve in polymerizations using heterogeneous Ziegler-Natta catalysts because there still lacks adequate understanding of the nature of the active sites which prevents pertinent influence from being exerted on the catalyst as well as the polymerization to control the chain transfer reaction. In fact, to obtain aluminum-terminated polypropylene in high yields with a $MgCl_2$-supported $TiCl_4$ catalyst, Kang et al. [34] adopted a hydroalumination reaction after propylene polymerization to transform the terminal vinylidene groups formed by β–H transfer reaction to aluminum groups.

The recent development of homogeneous metallocene catalysts for olefin polymerization has opened many opportunities for the synthesis of new polyolefins with unprecedented molecular structures. Metallocene catalyst has the features of a single active site, which results in narrowly distributed molecular weight and composition of the obtained polyolefins, and well-defined yet easily adjustable structure. With myriads of catalysts having diversified structures available, the past intensive research on the polymerization of olefins using metallocene catalysts has accumulated a great deal of knowledge of the relations between catalyst structure and polymerization mechanism including insertion and termination. Consequently, it becomes possible to control the chain transfer mode in metallocene-catalyzed olefin polymerization by manipulating the catalyst structure as well as polymerization conditions. Lately, by choosing a non-bridged zirconocene catalyst possessing sterically bulky ligands ($(Me_5Cp)_2ZrCl_2$) and controlling the polymerization temperatures relatively low, Han et al. [35] successfully refrained β-H transfer reaction in ethylene polymerization and directed the chain transfer mode to a selective transfer reaction to aluminum cocatalyst, which resulted in aluminum-terminated polyethylene. Kang et al. [34] ever took advantage of the predominant β-H transfer reaction in propylene polymerization catalyzed by Cp_2ZrCl_2-and $Et(H_4\text{-Ind})_2ZrCl_2$-methylaluminoxane (MAO) systems to prepare vinylidene-terminated atactic and isotactic polypropylenes which, upon being treated with (iso-$C_4H_9)_2AlH$ via a hydroalumination reaction, resulted in aluminum-terminated polypropylenes. However, as far as aluminum-terminated isotactic polypropylene is concerned, there has been no report regarding a controlled chain transfer reaction predominantly to aluminum cocatalyst for a direct synthesis, presumably because there exists a much more complicated chain transfer mode in metallocene-mediated propylene polymerization than in ethylene polymerization. Moreover, the energy barrier for a unimolecular β-H transfer is reported to be substantially lower in propylene polymerization than in ethylene polymerization [36], which also adds difficulties for the control of chain transfer mode to a majority aluminum transfer reaction.

In this paper, we discuss a direct process of preparing aluminum-terminated isotactic polypropylene (*i*-PP) via a controlled chain transfer reaction predominantly to aluminum cocatalyst in propylene polymerization catalyzed by a MAO-activated *ansa*-metallocene catalyst. The chemistry is largely benefited by the unique structure and catalytic properties of the highly active, highly isospecific *rac*-dimethylsilanediylbis(2-methyl-4-naphthyl) indenyl-zirconium dichloride (*rac*-$Me_2Si[2\text{-Me-4-Naph-Ind}]_2ZrCl_2$) catalyst which, with a rigid ligand framework composed of two bridged indenyl moieties each substituted by a methyl group at their 2- positions and a sterically bulky naphthyl group at their 4- positions, enables the effective suppression of β-H transfer during the polymerization of propylene both to the metal and to the coordinated monomer. As β-H transfer reaction is suppressed, the other two major chain transfer reactions in metallocene-catalyzed propylene polymerization, namely, β-methyl transfer and transalkylation to the trimethyl aluminum ($AlMe_3$) present in MAO (Al transfer) will become relatively prominent. Logically, β-methyl transfer is of much higher activation energy than Al transfer. Therefore, by controlling the reaction conditions for polymerization, particularly the polymerization temperatures, we may be able to direct the chain transfer mode in *rac*-$Me_2Si[2\text{-Me-4-Naph-Ind}]_2ZrCl_2$ /MAO-catal-yzed propylene polymerization to a predominant Al transfer reaction to obtain directly in the polymerization reaction Al-terminated *i*-PP.

Propylene polymerization was conducted with *rac*-$Me_2Si[2\text{-Me-4-Naph-Ind}]_2ZrCl_2$ catalyst and MAO cocatalyst containing 13.0 mol% of $AlMe_3$ [37]. Normally, at the end of polymerization, the reaction would then undergo quenching with acidic alcohol to terminate the polymerization. However, for a fast yet unambiguous understanding and possible quantification of the occurring frequency of the aluminum transfer reaction, the polymerization reactions were exempted from termination by acidic quenching but subjected to an oxidative workup using dry O_2 and H_2O_2/NaOH to transform the formed alkylaluminum-terminated polymer chains to hydroxyl-capped ones. With this oxidative workup process, all possible chain ends that might result from β-hydride transfer, β-methyl transfer (unsaturated groups), and chain transfer to the aluminum cocatalyst (Scheme 2) would exhibit their distinctive characteristic resonances in a ^1H NMR spectrum.



Scheme 2 Chain transfer to aluminum in propylene polymerization

Propylene polymerization was first run under the conditions of Al/Zr ratio of 3000 and polymerization temperature of 60 °C (run no. 1 in Table 2). This reaction afforded, with a catalyst activity of 18.14×10^6 g PP/mol Zr.h.bar, polypropylene polymer having a number-average molecular weight (M_n) of 8150 g/mol, a molecular weight distribution (PDI) of 2.1 and a melting temperature (T_m) of 147.7 °C. In Fig. 6a is shown its ^1H NMR spectrum measured at 110 °C in *ortho*-dichlorobenzene-d_4. In addition to the three major peaks at 0.95~1.65 ppm corresponding to $\mathbf{CH}_3$, $\mathbf{CH}_2$ and **CH** protons in propylene repeating units, several minor peaks are observed at 3.0~6.0 ppm when the spectrum is adequately enlarged. These peaks are the fingerprints of polymer chain ends due to different chain transfer mechanisms. At the first glance, it has been clear that hydroxyl methyl ($–CH(CH_3)–CH_2–OH$), the chain end group formed by chain transfer to aluminum followed by hydroxylation with O_2 and H_2O_2/NaOH in the oxidative workup process, represents the uppermost chain end structure of the obtained polypropylene, as the peak at 3.3~3.5 ppm corresponding to $–C\mathbf{H}_2–OH$ protons exhibits an overwhelmingly strong intensity compared with the others. The peaks at 4.5~6.0 ppm assignable to protons on unsaturated groups formed by *β*-hydride and *β*-methyl transfer reactions all show very weak intensities. However, it is still necessary to corroborate that the hydroxyl methyl groups come exclusively from the aluminum-carbon bonds at the aluminum transfer-generated polymer chain ends. For such a purpose, we run a comparative polymerization under identical reaction conditions but terminating it by direct quenching with acidic alcohol to avoid the use of O_2 and H_2O_2/NaOH. ^{1}H NMR spectrum of thus-obtained polymer (Fig. 6b) was compared with that of its hydroxylated counterpart. Except for no signals observed at 3.3~3.5 ppm, the former spectrum is almost identical to the latter one. Both of them show the characteristic peaks of three types of unsaturated groups at 4.65~4.75 ppm (terminal vinylidene, $–C(CH_3)=C\mathbf{H}_2$), 4.9~5.0 (terminal allyl, $–CH=C\mathbf{H}_2$) and 5.7~5.8 ppm (terminal allyl, $–C\mathbf{H}=CH_2$), and 4.81~4.82 ppm (internal vinylidene, $–CH_2C(=C\mathbf{H}_2)CH_2–$) [38]. The integrated intensity ratios between each of these peaks and the main chain proton peaks at 0.95~1.65 ppm are of good consistency for these two spectra, indicating that, during the oxidative workup process in the presence of O_2 and H_2O_2/NaOH, no side reactions occurred with the unsaturated groups. These results strongly support the deduction that the hydroxyl methyl end groups are solely formed from the terminal aluminum-carbon bonds. On the basis of these experimental results, with the assumption of a nearly quantitative conversion of aluminum–carbon bonds to hydroxyl methyl groups, we may be able to roughly quantify the occurring frequency of the predominant aluminum transfer reaction in the overall chain termination reactions including *β*-hydride transfer, *β*-methyl transfer and chain transfer to the aluminum cocatalyst, provided that we identify and quantify all the corresponding chain end structures. In fact, as mentioned above, terminal vinylidene and allyl represent the only two detected chain ends resulting from chain termination via *β*-hydride and *β*-methyl transfer reactions, respectively. The formation of internal vinylidene, although also occurring through *β*-hydride transfer, does not necessarily lead to chain transfer, and so internal vinylidene is not taken into account as a result of *β*-hydride transfer-initiated chain termination reaction. For these three chain end structures including hydroxyl methyl, terminal vinylidene and allyl, their respective amounts are calculated from comparison of the relative intensities of the characteristic peaks (3.3~3.5 ppm for hydroxyl methyl, 4.65~4.75 ppm for vinylidene, and 4.9~5.0 ppm for allyl) with that of the main chain proton peaks at 0.95~1.65 ppm together with a consideration of the number of protons each peak represents. Values of 0.43 mol%, 0.031 mol% and 0.022 mol% are obtained for hydroxyl methyl, vinylidene and allyl groups, respectively. Comparing the amount of each chain end group with the total chain end amount gives the occurring frequency of the corresponding chain transfer reaction in the overall chain termination reactions. Values of 88%, 7% and 5% are obtained for chain transfer to aluminum, *β*-hydride and *β*-methyl transfer reactions, respectively, implying that a great majority of chain termination reactions occurred in the polymerization via chain transfer to the aluminum cocatalyst.

β-Methyl transfer is known to be a unimolecular process [39, 40]. *β*-Hydride transfer is also experimentally revealed to occur in *rac*-Me_2Si[2-Me-4-Naph-Ind]$_2$ $ZrCl_2$/ MAO-catalyzed propylene polymerization without monomer involvement [38]. Thus, further enhancement of the selectivity of the bimolecular aluminum transfer reaction might be expected by reducing the polymerization temperature. Propylene polymerization reactions were then conducted at some lower temperatures, i.e. 40 °C, 30 °C, 10 °C and 0 °C. The results are summarized in Table 2. In Fig. 7 are compared ^{1}H NMR spectra of the resultant polymers.

As expected, lowering the polymerization temperature effectively promotes the selectivity of aluminum transfer reaction. As shown in Table 2 and illustrated in Fig. 7, the relative frequencies of chain terminations via both *β*-hydride and *β*-methyl transfer reactions gradually decrease with the decrease of polymerization temperature. Propylene polymerization at 10 °C yields, with a still high catalyst activity, a completely saturated polymer free of any terminal and internal vinylidene and allyl groups, implying the effective avoidance of *β*-hydride and *β*-methyl transfer reactions during the polymerization. ^{1}H NMR spectrum of the polymer (Fig. 7c) reveals a strong hydroxylmethyl signal at 3.3~3.5 ppm, suggesting a still intense aluminum transfer reaction. These results indicate that chain transfer to aluminum has become dominant in the overall chain termination process under these conditions. Under these circumstances, further decreasing the polymerization temperature is of little significance. As a matter of fact, due to a significant suppression of aluminum transfer reaction, propylene polymerization at 0°C yields a polymer exhibiting a much weaker hydroxylmethyl signal in ^{1}H NMR spectrum as compared with that polymerized at 10 °C. The catalyst activity is also greatly reduced.

The domination of chain termination by chain transfer to aluminum results in an aluminum concentration dependence of polymer molecular weights. Table 2 includes the results of propylene polymerization at 10°C with varied Al/Zr ratios from 500 through 10000. ^{1}H NMR spectra prove the absence of chain terminations via *β*-hydride and *β*-methyl

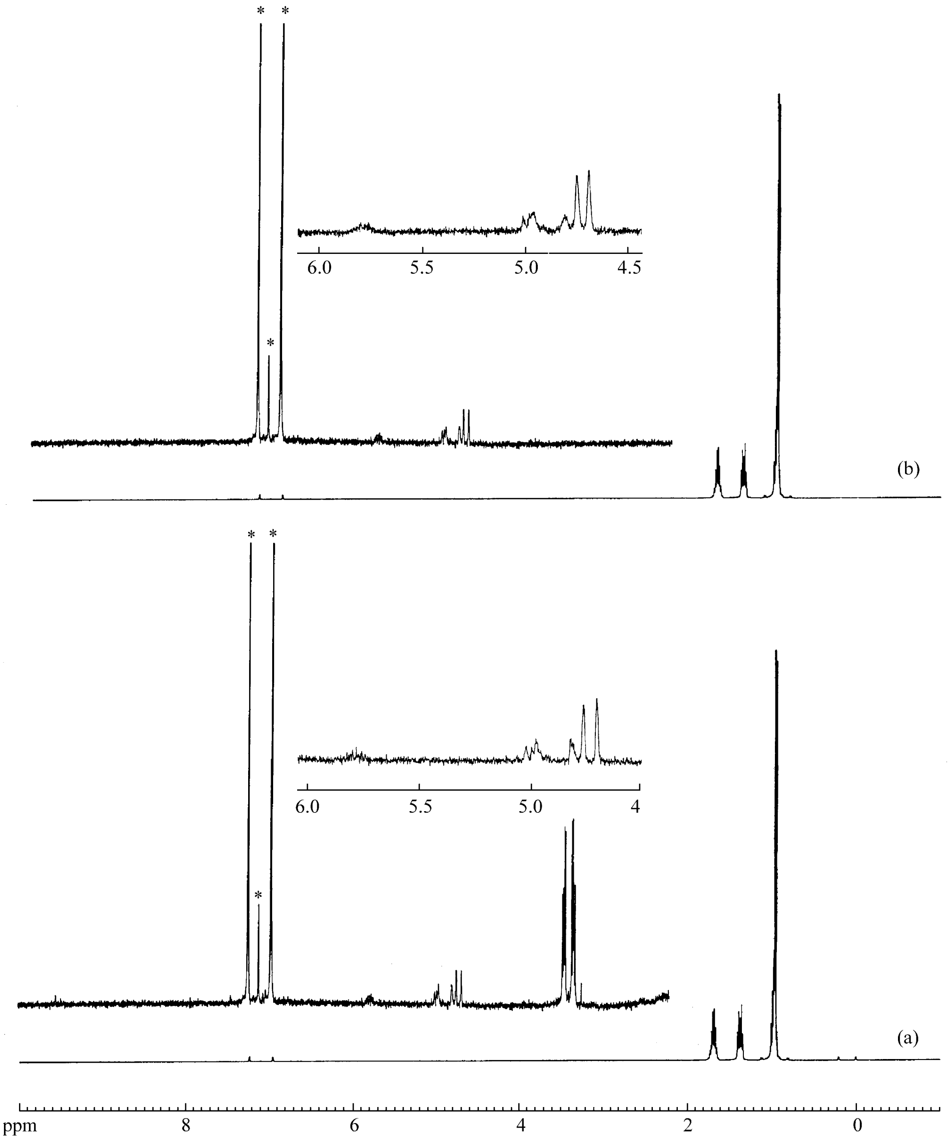


Fig. 6 ^{1}H NMR spectra of polypropylenes obtained (**a**) with an oxidative workup process and (**b**) without an oxidative workup process (polymerization conditions: temperature=60°C, Al/Zr=3000) (*solvent: *o*-dichlorobenzene-d_4, temperature:110°C).

transfer reactions in these polymerization reactions, as no polymer is revealed with evident vinylidene and allyl terminal groups. Only a very weak resonance representing the internal vinylidene group is detected at 4.81~4.82 ppm when a very low Al/Zr ratio (500) was adopted in the polymerization. The polymer number-average molecular weights (M_n) estimated from GPC examination exhibit a linearly decreasing trend with the increase of aluminum concentrations in the polymerization reactions (runs 9, 8, 4, 7 and 6).

Besides GPC estimation, M_n values of the polymers can also be calculated from ^{1}H NMR by the comparison of mol% of chain-end units to total propylene units. The results are listed in Table 2 (column 10). In general, the calculated M_n values are in fairly good accordance with those estimated by GPC (column 7), especially for polymers with relatively lower molecular weight, indicating a high accuracy of the chain end quantification. However it is also noted that the calculated M_n values are somewhat higher than their GPC-estimated counterparts when the polymers possess relatively higher molecular weight. Fig. 8 shows the plot of M_n calculated from ^{1}H NMR vs M_n estimated by GPC. This inconsistency may be caused by the reduced quantification accuracy of the chain ends at high polymer molecular weight. In addition, it is also possible that the oxidation of the alkylaluminum terminal may be a little away from completion when the polymer has high molecular weight, which will also cause an overhestimation of $M_{n.}$

In summary, this research clearly demonstrates that a predominant aluminum transfer reaction is achievable in metallocene-catalyzed isospecific polymerization of propylene by employing the highly hindered *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$ in combination with MAO. Aluminum-terminated *i*-PP with high end group selectivity as well as high melting points and controlled molecular weights are accessible with high yields.

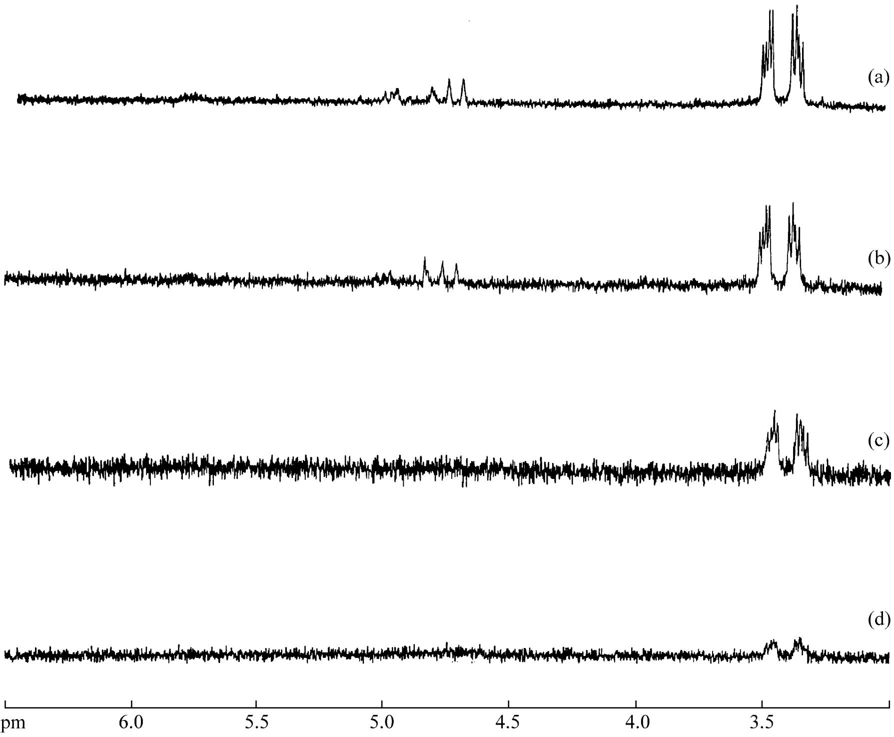


Fig. 7 Intercepted ^1H NMR spectra of polypropylenes prepared at (**a**) 40°C, (**b**) 30°C, (**c**) 10°C and (**d**) 0°C with a constant Al/Zr ratio of 3000 (solvent: *o*-dichlorobenzene-d_4, temperature:110°C).

Table 2 A summary of conditions[a] and results of propylene polymerization with *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind]_2ZrCl_2$/MAO catalyst undergoing an oxidative workup process

Run no.	Polym. temp. (℃)	[MAO] (mol • L^{-1})	[Al] / [Zr]	Yield (g)	A[b]	M_n[c]	PDI[d]	T_m (°C)	M_n[g]	Chain-end unit to total propylene units (mol%)[f]			Estimated frequency of each chain transfer reaction (%)		
										-C(CH_3) =CH_2	-CH =CH_2	-CH_2 -OH	*β*-H transfer	*β*-Me transfer	Al transfer
1	60	0.15	3000	6.79	18.1	0.81	2.10	147.7	0.87	0.031	0.022	0.425	≈7	≈5	≈88
2	40	0.15	3000	8.48	22.6	1.32	2.30	154.4	1.31	0.016	0.012	0.292	≈5	≈4	≈91
3	30	0.15	3000	7.69	20.5	1.55	2.58	157.5	1.61	0.008	0.007	0.246	≈3	≈3	≈94
4	10	0.15	3000	6.41	17.1	6.65	2.54	161.2	7.64	n.d[e]	n.d	0.055	≈0	≈0	≈100
5	0	0.15	3000	1.40	3.73	12.42	2.89	161.9	15.0	n.d	n.d	0.028	≈0	≈0	≈100
6	10	0.50	10000	11.7	31.2	2.46	2.10	158.2	3.50	n.d.	n.d.	0.120	≈0	≈0	≈100
7	10	0.25	5000	11.2	29.4	4.30	2.23	160.2	5.45	n.d.	n.d.	0.077	≈0	≈0	≈100
8	10	0.10	1500	7.42	19.8	8.61	2.94	160.5	11.05	n.d.	n.d.	0.038	≈0	≈0	≈100
9	10	0.025	500	5.81	15.5	17.90	2.49	160.7	23.33	n.d.	n.d.	0.018	≈0	≈0	≈100

[a] Other conditions: propylene = 1.0 ×105 Pa (1 bar), [Zr] = 5.0 ×10^{-6} M, time = 30 min, toluene as the solvent, solvent+MAO solution = 150 mL. [b] Activity: ×10^6 g of PP/mol Zr h bar. [c] *Mn*, ×10^4 g/mol, calculated from GPC measurement. [d] PDI, polydispersity index. [e] Not detectable. [f] mol% of functional groups to propene molecules incorporated in the main chain.[g] Mn, ×104 g/mol,calculated from ^1H NMR by the comparison of mol% of chain-end units to total propylene units.

4 Conclusions

In this paper, we summarize our recent effort to access structurally well-defined functional polypropylenes via transition metal-mediated olefin polymerization. In one approach, polypropylenes containing side chain functional groups of controlled concentrations were obtained by Ziegler-Natta-catalyzed copolymerization of propylene in combination with either living anionic or controlled radical polymerization of polar monomers. The copolymerization of propylene with 1,4-divinylbenzene using an isospecific

$MgCl_2$-supported $TiCl_4$ catalyst yielded polypropylenes containing pendant styrene moieties. Both metalation reaction with n-butyllithium and hydrochlorination reaction with dry hydrogen chloride selectively and quantitatively occurred at the pendant reactive sites, generating polymeric benzyllithium and 1-chloroethylbenzene species. These species initiated living anionic polymerization of styrene (S) and atom transfer radical polymerization (in the presence of CuCl and pentamethyldiethylenetriamine) of methyl methacrylate (MMA), respectively, resulting in functional polypropylene graft copolymers (PP-*g*-PS and PP-*g*-PMMA) with controllable graft lengths. In another approach, chain end-functionalized polypropylenes containing a terminal OH-group with controlled molecular weights were directly prepared by propylene polymerization with a metallocene catalyst through a selective aluminum chain transfer reaction. Both approaches proved to be desirable polyolefin functionalization routes in terms of efficiency and polymer structure controllability.

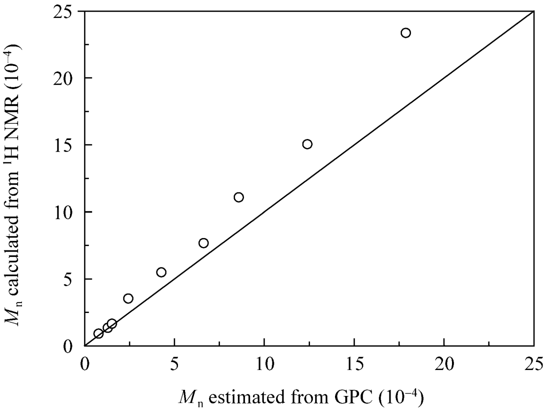


Fig. 8 Plot of M_n calculated from ^{1}H NMR vs M_n estimated by GPC.

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