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A Novel Consecutive Chain Transfer Reaction to *p*-Methylstyrene and Hydrogen during Metallocene-Mediated Olefin Polymerization

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Abstract: This paper describes the first example of consecutive chain transfer reaction, first to *p*-methylstyrene (or styrene) and then to hydrogen, during metallocene-catalyzed propylene polymerization by *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO complex. The PP molecular weight is inversely proportional to the molar ratio of [*p*-methylstyrene]/[propylene] and [styrene]/[propylene] with the chain transfer constants of $k_{tr}/k_p = 1/6.36$ and $1/7.5$, respectively. Although hydrogen does not influence the polymer molecular weight, it greatly affects the catalyst activity. Each PP chain formed contains a terminal *p*-methylstyrene (or styrene) unit. The terminal *p*-MS unit can be metalated to form a stable polymeric anion for living anionic polymerization to prepare new PP diblock copolymers, such as PP-*b*-PS, which are very difficult to prepare by other methods. The overall process resembles a transformation reaction from metallocene to living anionic polymerization.

Introduction

The in situ chain transfer reaction during polymerization presents a very convenient route for introducing a reactive terminal group to the polymer chain end. It also offers an opportunity for the preparation of diblock copolymers by using the reactive terminal group as the linkage between two distinctive polymer blocks. This approach is particularly interesting in polyolefins¹ since the lack of functionality and poor compatibility with any other materials has imposed limitations on the application of polyolefins in many areas, such as in polymer blends and composites. The diblock copolymer is known to be the most effective compatibilizer² for improving the interfacial interaction between polymer and other materials.

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So far, there are only a few reports describing the introduction of a reactive terminal group to polyolefin through a chain transfer reaction with chain transfer agents. Marks³ first showed that some organosilanes having Si-H groups are effective chain transfer agents in metallocene-mediated polymerizations that result in silane-terminated polyolefins. In our laboratory, we observed that organoboranes having B-H groups are very effective chain transfer agents for forming borane-terminated polyolefins.⁴ The terminal borane group transforms to a stable free radical initiator for chain extension that results in polyolefin diblock copolymers. Hessen⁵ studied thiophene as a chain transfer agent in ethylene polymerization using a neutral lanthanum catalyst system. In general, the polymerization was sluggish with very low catalyst activity. Kim⁶ also observed various modes of chain transfer reactions in the copolymeriza-

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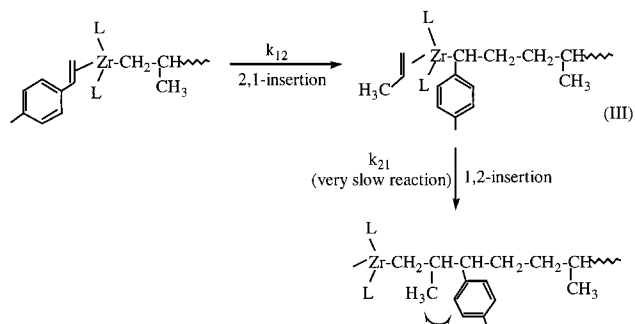
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tion of ethylene and allylbenzene using the zirconocene/MAO catalyst system. When highly substituted catalysts were used, chain transfer to aluminum was preferred rather than β -hydride elimination. The suppression of β -hydride elimination was attributed to the unfavorable β -agostic interaction at the propagating active site having an allylbenzene end unit.

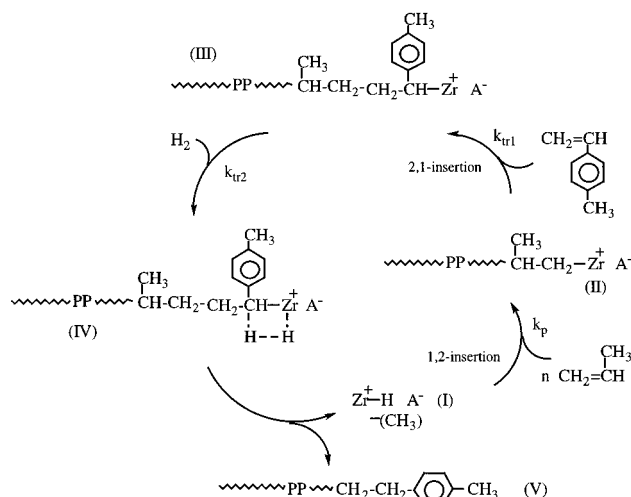
Results and Discussion

In this paper, we report a novel chain transfer reaction involving a combination of a styrenic molecule, including *p*-methylstyrene (*p*-MS) and styrene (S), and hydrogen during metallocene-catalyzed propylene polymerization. The research stemmed from several intriguing observations⁷ during the copolymerization of propylene and *p*-MS using the *rac*-SiMe₂[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO complex. The reaction was completely stalled in the very beginning of the copolymerization process. The catalyst's deactivation was speculated to be due to a steric jamming during the consecutive insertion of 2,1-inserted *p*-MS and 1,2-inserted propylene (k_{21} reaction), as illustrated in eq 1.



The combination of unfavorable 1,2-insertion of propylene (k_{21}) and lack of *p*-MS homopolymerization (k_{22} reaction) at the propagating site (III) drastically reduces catalyst activity. This hypothesis was supported by the effect⁷ of a small amount of ethylene dramatically improving the catalyst activity. The sluggish propagating chain end (III) (which poses a difficulty in both the k_{21} and k_{22} reactions) allows the insertion of ethylene, which renews the propagation process.

If the above hypothesis of catalyst deactivation proves correct, we might be able to take advantage of the dormant propagating site (III) to react with hydrogen, which not only recovers the catalytic site but also produces PP polymer with a terminal *p*-MS group. Equation 2 illustrates a general reaction scheme.



During the polymerization of propylene (with the 1,2-insertion method) the propagation Zr–C site (II) can also react with *p*-MS (with the 2,1-insertion method) to form a dormant propagating site (III) at the terminal *p*-MS unit. Although the catalytic Zr–C site in compound (III) becomes inactive to both propylene and *p*-MS, the dormant Zr–C site (III) can react with hydrogen to form *p*-MS terminated polypropylene (PP-*t-p*-MS) (V) and regenerate a Zr–H species (I) that is capable of reinitiating the polymerization of propylene and of continuing the polymerization cycles. In other words, the ideal chain transfer reaction will not significantly affect the rate of polymerization, but it reduces the molecular weight of the resulting polymer. The molecular weight of PP-*t-p*-MS will be linearly proportional to the molar ratio of [propylene]/[*p*-MS], and basically independent of the [propylene]/[hydrogen] ratio.

PP-*t*-S and PP-*t-p*-MS Polymers. This consecutive chain transfer reaction will be applicable to many α -olefin and styrenic molecules if several conditions are met to avoid undesirable side reactions, namely the copolymerization of α -olefin with styrenic molecules and several direct chain transfer reactions from the propagating olefinic chain end (II) to hydrogen, monomer, and β -hydride elimination. To this end, the *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyst is an excellent candidate⁸ that produces highly regio and styrenic regular PP polymers with high molecular weight, and which exhibits no copolymerization activity with styrenic monomers and low undesirable chain transfer activity. The regioselective 1,2-insertion⁹ of propylene is known to be the key factor to reduce the chain transfer reactions. As shown in two control reactions (3 and 4 in Table 1), this bridged catalyst system is quite insensitive to hydrogen, even in large dosages. Tables 1 and 2 summarize two systematic studies of propylene polymerization by using a *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyst in the presence of *p*-methylstyrene/hydrogen and styrene/hydrogen chain transfer agents, respectively. The reactions resulted in *p*-MS terminated PP (PP-*t-p*-MS) and styrene-terminated PP (PP-*t*-S), respectively. In general, both systems showed very similar results. The in situ chain transfer reaction to *p*-MS/hydrogen in *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyzed polymerization of propylene is evidenced by its comparison with two control reactions that were carried out under similar reaction conditions: without chain transfer agent (control 1) and with *p*-MS only (control 2). A small amount of *p*-MS effectively stops the polymerization of propylene. The introduction of hydrogen restores the catalyst activity, as shown in run A-1, which exhibits about 85% of the catalytic activity of control 1 (without chain transfer agents). Hydrogen is clearly needed to complete the chain transfer cycle during the polymerization. Comparing runs from A-1 to E-1 by altering *p*-MS concentration, we note that the higher the concentration of the *p*-MS, the lower the molecular weight of the resulting polymer. Polymer with very low molecular weight (just a few thousand) has been obtained, and the molecular weight distribution is generally narrow, which is consistent with single site polymerization processes. The catalyst activity was also proportionally depressed with the concentration of *p*-MS, which reflects the

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Table 1. Comparison of the Experimental Results in the *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO Catalyzed Polymerization^a of Propylene with *p*-MS/Hydrogen Chain Transfer Agents

run	<i>p</i> -MS (M)	H ₂ (psi)	cat. activity ^b	<i>p</i> -MS in PP (mol %)	<i>p</i> -MS conversion (%)	<i>M</i> _n (×10 ³)	PDI (<i>M</i> _w / <i>M</i> _n)	<i>T</i> _m (°C)
control 1	0	0	86 208	0		77.6	2.9	159.6
control 2	0.0305	0	0					
control 3	0	6	88 576	0		74.5	2.6	160.1
control 4	0	12	95 616	0		66.0	2.4	159.1
A-1	0.0305	28	73 760	0.15	50.51	56.1	1.9	159.3
A-2	0.0305	20	68 430	0.15	48.53	54.8	1.9	159.2
A-3	0.0305	16	52 536	0.14	38.78	53.6	1.9	159.7
A-4	0.0305	12	38 528	0.15	28.19	55.4	1.9	159.2
A-5	0.0305	6	25 728	0.15	18.83	54.8	2.0	159.2
A-6	0.0305	2	12 160	0.14	8.30	55.5	1.9	159.6
B-1	0.076	35	33 664	0.41	26.86	25.8	2.3	158.2
B-2	0.076	20	28 192	0.43	23.65	20.5	2.4	158.9
B-3	0.076	12	5 408	0.41	4.33	25.9	2.3	157.9
B-4	0.076	6	2 912	0.40	2.33	27.6	2.1	158.1
C-1	0.153	35	14 112	0.63	8.67	9.7	1.9	154.1
C-2	0.153	20	12 192	0.61	7.26	11.7	2.0	154.3
C-3	0.153	12	1 120	0.66	0.72	10.0	2.3	155.0
D-1	0.305	35	6 720	1.43	4.69	4.6	1.7 ^c	152.9
D-2	0.305	20	4 704	1.47	3.28	4.4	1.8 ^c	153.4
E-1	0.458	35	2 912	2.16	2.05	1.8	1.4 ^c	145.6
E-2	0.458	20	1 728	2.24	1.22	1.8	1.4 ^c	143.2

^a Reaction conditions: 50 mL of toluene, propylene (100 psi), [Zr] = 1.25 × 10⁻⁶ mol/L, [MAO]/[Zr] = 3000, temperature = 30 °C, time = 15 min. ^b Catalyst activity = kg of PP/mol of catalyst·h. ^c Product distribution narrowed may be due to loss of GPC sensitivity for low molecular weight oligomers.

Table 2. Comparison of the Experimental Results in the *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO Catalyzed Polymerization^a of Propylene

example	styrene (M)	H ₂ (psi)	cat. activity ^b	styrene in PP (mol %)	styrene conversion (%)	<i>M</i> _n (×10 ⁻³)	PDI (<i>M</i> _w / <i>M</i> _n)	<i>T</i> _m (°C)
control 1	0	0	86 208	0		77600	2.9	159.6
control 2	0.0865	0	~0		0			
A'-1	0.0346	20	74 176	0.11	35.1	53.4	2.0	159.0
B'-1	0.0865	20	28 512	0.33	16.9	26.1	1.7	157.2
C'-1	0.173	20	12 224	0.77	8.1	9.8	1.6	153.3
D'-1	0.346	20	6 720	1.45	4.1	4.6	1.5 ^c	153.1
E'-1	0.519	20	3 328	2.11	2.0	1.8	1.5 ^c	143.2
A'-2	0.0346	6	27 392	0.12	14.14	55.2	2.1	159.2
A'-3	0.0346	2	15 648	0.12	8.08	54.8	2.2	159.3
B'-2	0.0865	12	15 008	0.33	8.78	25.9	1.7	158.4
B'-3	0.0865	6	9 216	0.34	5.39	25.3	1.7	158.1
D'-2	0.346	35	11 392	1.41	6.97	4.6	1.5 ^c	152.1
D'-3	0.346	12	2 848	1.42	1.74	4.7	1.6 ^c	152.7

^a Reaction conditions: 50 mL of toluene, propylene (100 psi), [Zr] = 1.25 × 10⁻⁶ mol/L, [MAO]/[Zr] = 3000, temperature = 30 °C, time = 15 min. ^b Catalyst activity = kg of PP/mol of catalyst·h. ^c Product distribution narrowed may be due to loss of GPC sensitivity for low molecular weight oligomers.

competitive coordination at metallocene active sites between monomer and chain transfer agents.

It is very interesting to quantify the hydrogen concentration needed in the chain transfer reaction. Three comparative reaction sets (including runs from A-1 to A-6, runs from B-1 to B-4, and runs from C-1 to C-3) were conducted under the same reaction conditions except for varying the hydrogen pressure. In contrast with the results from the *p*-MS chain transfer agent, the change of hydrogen concentration does not affect the polymer molecular weight and molecular weight distribution, but has a profound effect on the catalyst activity. Therefore, hydrogen does not engage in the initial chain transfer reaction, but rather assists in the completion of the reaction cycle (as shown in eq 2). A sufficient quantity of hydrogen, proportional to the *p*-MS concentration, is needed to maintain high catalyst activity and *p*-MS conversion.

Similar effects of styrene and hydrogen were observed in the *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂/MAO catalyzed polymerization of propylene. As summarized in Table 2, all four comparative reaction sets show that hydrogen is necessary to complete the chain transfer reaction to styrene during the propylene

polymerization. Hydrogen concentration does not affect the molecular weight and molecular weight distribution of the resulting PP-*t*-S polymers. However, a sufficient quantity of hydrogen, increasing along with [styrene], is needed to maintain high catalyst activity. Figure 1 shows the GPC curves of PP-*t*-*p*-MS polymers (control 1, B-1, C-1, D-1, and E-1 in Table 1) prepared by *rac*-Me₂Si[2-Me-4-Ph(Ind)]₂ZrCl₂ mediated propylene polymerization in the presence of *p*-MS/hydrogen. The polymer's molecular weight clearly decreased with the increase in *p*-MS concentration. It is interesting to note that the polymer's molecular weight distribution stayed relatively narrow (*M*_w/*M*_n = ~2), indicating a single site polymerization with a clean chain transfer (termination) reaction. Similar GPC curves of PP-*t*-S polymers were also observed, with progressive reduction of polymer molecular weight and narrow molecular weight distribution while the styrene concentration was increased. Figure 2 shows the plot of the polymer molecular weight (*M*_n) versus the mole ratios of [propylene]/[*p*-MS] and [propylene]/[styrene]. There is a linear proportionality between the polymer molecular weight and molar ratio of [propylene]/[*p*-MS] or [propylene]/[styrene]. It is clear that the chain transfer

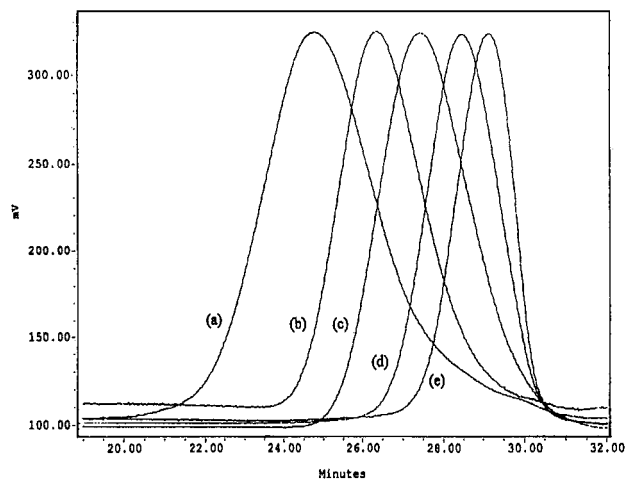


Figure 1. GPC curves of (a) PP (control 1) and several PP-*t*-*p*-MS polymers, (b) B-1, (c) C-1, (d) D-1, and (e) E-1 (in Table 1).

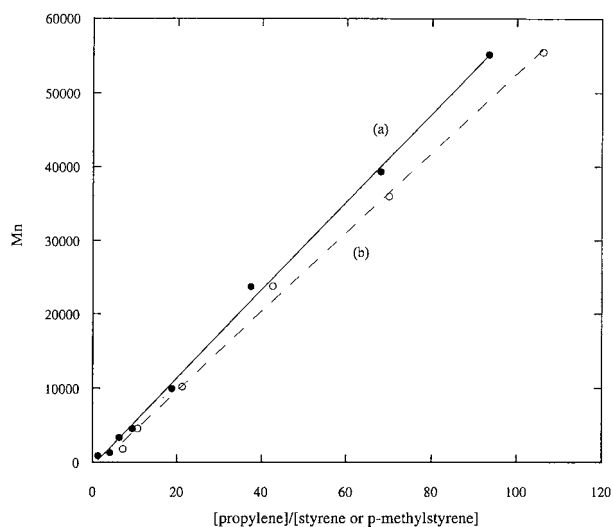


Figure 2. The plots of number average molecular weights (M_n) of (a) PP-*t*-S and (b) PP-*t*-*p*-MS polymers versus the mole ratios of [propylene]/[styrene] and [propylene]/[*p*-MS], respectively.

reaction to styrenic molecule (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 $X_n = k_p[\text{olefin}]/k_{tr}[\text{styrenic molecule}]$ with the chain transfer constant $k_{tr}/k_p \sim 1/6.36$ and $1/7.5$ for *p*-methylstyrene and styrene, respectively. The fact of the cationic nature of the catalyst site is reflected in its higher reactivity to *p*-methylstyrene than styrene during the chain transfer reactions.

End Group Analysis. End group structures at both polymer chain ends provide direct evidence of the chain transfer reaction. This analysis was greatly benefited by the low molecular weight polymers. Figure 3 shows its ^{13}C NMR spectrum of PP-*t*-*p*-MS sample ($M_n = 4600$ g/mol; $M_w/M_n = 1.7$), with an inset of the expanded aliphatic region. In addition to three major peaks ($\delta = 21.6, 28.5,$ and 46.2 ppm) corresponding to the CH_3 (mmmm), CH , and CH_2 groups in the PP backbone, the spectrum exhibits all of the carbon chemical shifts associated with both chain ends. Two types of polymer structures at the beginning of polymer chain are due to the initiation reaction of Zr^+-H (**I**) with 1,2- (top) and 2,1- (bottom) insertions¹⁰ of propylene. Although both

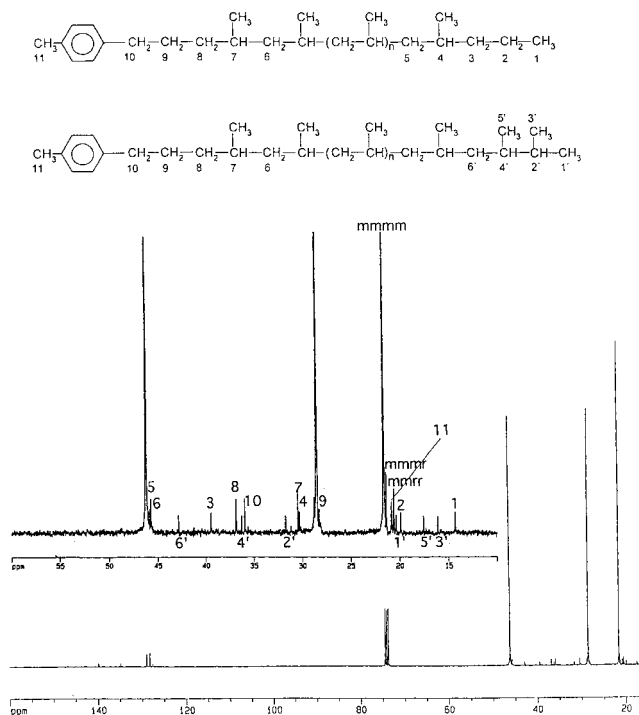


Figure 3. ^{13}C NMR spectra of PP-*t*-*p*-MS sample ($M_n = 4600$ g/mol; $M_w/M_n = 1.7$)

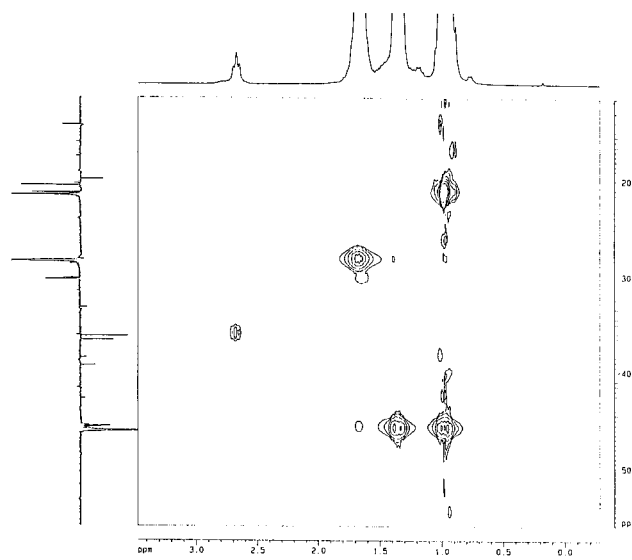
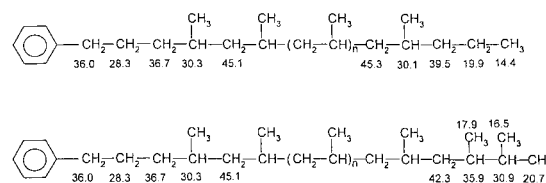


Figure 4. 2-D ^1H and ^{13}C (DEPT-135) NMR spectrum of the PP-*t*-S polymer (sample E-1).

insertion modes are allowed in the initiation step, it is generally accepted that isotactic polypropylene polymerization with zirconocene catalysts takes place by a regioselective 1,2-insertion⁸ of the propylene monomer at the Zr^+-C (**II**) active center. The peak intensity ratio indicates both polymer chain ends ($-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_3$ and $-\text{CH}_3$) with about a 1/1 mole ratio, and the PP-*t*-*p*-MS molecular weight estimated from the chain end and GPC curve is in good agreement. It is important

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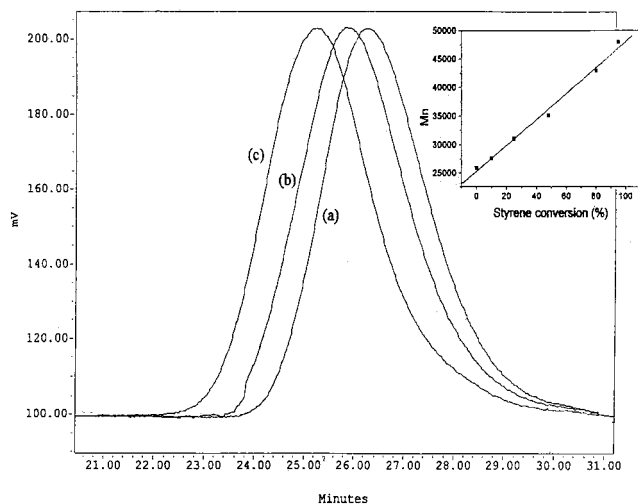
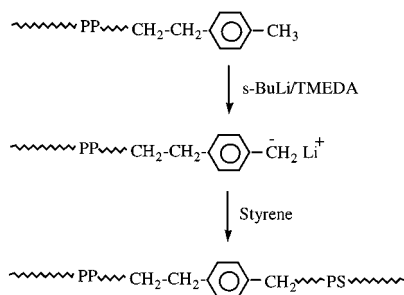


Figure 5. The GPC curve comparison between (a) PP-*t-p*-MS ($M_n = 25.8 \times 10^3$ g/mol; $M_w/M_n = 2.3$) and two PP-*b*-PS diblock copolymers with (b) $M_n = 34.1 \times 10^3$ and $M_w/M_n = 2.4$ and with (c) $M_n = 48 \times 10^3$ g/mol and $M_w/M_n = 2.5$ (solvent, trichlorobenzene; temperature, 135 °C) (Inset: molecular weight of PP-*b*-PS vs styrene monomer conversion).

to note that there is no detectable vinyl group associated with the conventional chain transfer process (via β -H elimination), nor any chemical shifts for $-\text{CH}-\text{C}_6\text{H}_4-\text{CH}_3$ associated with the copolymerization reaction.

Figure 4 shows the aliphatic region of the 2-D ^1H and ^{13}C (DEPT-135) NMR spectrum of a PP-*t*-S polymer (sample E-1 in Table 1; $M_n = 1800$ g/mol; $M_w/M_n = 1.5$). In addition to three major proton chemical shifts ($\delta = 0.95$, 1.35, and 1.65 ppm) corresponding to CH_3 , CH_2 , and CH groups in the PP backbone and minor peaks (between 7.2 and 7.4 ppm) corresponding to $\phi\text{-H}$ (not shown in this spectra), there is only a triplet proton chemical shift (at 2.67 ppm) corresponding to the end group $\text{CH}_2\text{-}\phi$. Furthermore, all the observed C chemical shifts associated with the aliphatic groups of both chain ends are in good agreement with the calculated ones (shown in Figure 4).

PP-*b*-PS Diblock Copolymers. The existence of a terminal *p*-MS unit in PP is further supported by a chain extension reaction. The terminal *p*-MS group was selectively metalated by *s*-BuLi/TMEDA reagent¹¹ and transformed to a stable polymeric anion for living anionic polymerization¹² of styrene as illustrated in eq 3. The resulting PP-*b*-PS diblock copolymer



was subjected to Soxhlet extraction by boiling THF to gain no detectable soluble PS homopolymer. The insoluble fraction (soluble in 1,1,2,2-tetrachloroethane at elevated temperatures) is PP-*b*-PS diblock copolymer. Figure 5 compares the GPC curves of the starting PP-*t-p*-MS polymer ($M_n = 25.9 \times 10^3$; $M_w/M_n = 2.3$) with two PP-*b*-PS diblock copolymers ($M_n = 34.1 \times 10^3$ and 47.5×10^3 , respectively) sampled after 1 and

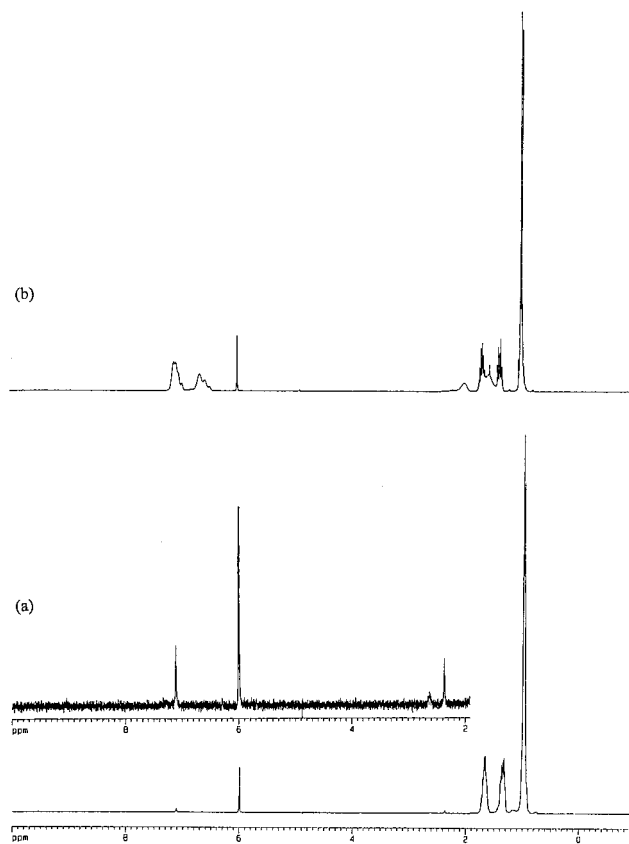


Figure 6. ^1H NMR spectra of (a) PP-*t-p*-MS ($M_n = 25.8 \times 10^3$ g/mol; $M_w/M_n = 2.3$) and (b) PP-*b*-PS diblock copolymer ($M_n = 48 \times 10^3$ g/mol; $M_w/M_n = 2.5$) (solvent, $\text{C}_2\text{D}_2\text{Cl}_4$; temperature, 110 °C).

5 h reaction time. The inset plots the polymer molecular weight vs monomer conversion during the chain extension process. The polymer linearly increased its molecular weight with the consumption of styrene monomers, an indication of the living anionic polymerization process. Despite the heterogeneous reaction condition, most of the styrene monomers were incorporated into diblock copolymer within 5 h. This combination of a monochromatic increase of the copolymer molecular weight (with only a slight broadening in the molecular weight distribution) and no detectable PP homopolymer clearly points to the existence of a *p*-MS group at each PP chain end. Figure 6 shows the ^1H spectra of PP-*t-p*-MS polymer ($M_n = 25.9 \times 10^3$; $M_w/M_n = 2.3$) and the corresponding PP-*b*-PS diblock copolymer ($M_n = 48 \times 10^3$; $M_w/M_n = 2.5$). New resonances at chemical shifts between 6.4 and 7.3 ppm in Figure 6b correspond to aromatic protons of the PS block. An about 1/1 mole ratio of [propylene]/[styrene] in the PP-*b*-PS copolymer is consistent with the polymer molecular weight estimated by GPC measurement.

Conclusion

In summary, this research clearly demonstrates a new in situ chain transfer reaction, first to the styrenic molecule (*p*-methylstyrene or styrene) and then to hydrogen, in metallocene-catalyzed propylene polymerization. With the proper choice of reaction conditions and catalyst system, it is very effective for preparing polyolefin polymer with a terminal styrenic unit. The *p*-MS terminal group provides an efficient route for preparing

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polyolefin diblock copolymers, such as PP-*b*-PS, that would be very difficult to obtain using other existing methods.

Experimental Details:

Instrumentation and Materials. All ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 instrument in 1,1,2,2-tetrachloroethane- d_2 at 110 °C. The molecular weight and molecular weight distribution of the polymers were determined by Gel Permeation Chromatography (GPC) using a Waters 150 C with a refractive index (RI) detector and a set of u-Styragel HT columns of 10^6 , 10^5 , 10^4 , and 10^3 pore size in series. The measurements were taken at 140 °C using 1,2,4-trichlorobenzene (TCB) as solvent and a mobile phase of 0.7 mL/min flow rate. Narrow molecular weight PS samples were used as standards for calibration. 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 30 to 180 °C with a heating rate of 20 °C/min.

All O_2 and moisture sensitive manipulations were carried out inside an argon filled Vacuum Atmosphere drybox. Toluene, cyclohexane, and *p*-methylstyrene (Wiley Organics) were distilled over CaH_2 under argon. High purity grade propylene (MG Industries), methanol, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *s*-BuLi (Aldrich), and methylaluminoxane (MAO) (Ethyl) were purchased and used as received. The *rac*- $\text{Me}_2\text{Si}[2\text{-Me-4-Ph(Ind)}]_2\text{ZrCl}_2$ catalyst was prepared by the published procedures.⁸

Chain Transfer Reaction in Metallocene-Mediated Propylene Polymerization. In a typical reaction (run A-1 in Table 1), a Parr 450 mL stainless autoclave equipped with a mechanical stirrer was charged with 50 mL of toluene and 1.5 mL of MAO (30 wt % in toluene) before purging with hydrogen (28 psi). The reactor was then injected with 0.2 g (0.0305 M) of *p*-methylstyrene and charged with 100 psi (3.24 M)¹³ of propylene to a total pressure of 128 psi at ambient

temperature. About 1.25×10^{-6} mol of *rac*- $\text{Me}_2\text{Si}[2\text{-Me-4-Ph(Ind)}]_2\text{ZrCl}_2$ in toluene solution was then syringed into the rapidly stirring solution under propylene pressure to initiate the polymerization. Additional propylene was fed continuously into the reactor to maintain a constant pressure (128 psi) during the course of the polymerization. To minimize mass-transfer and to maintain the constant feed ratio, the reactions were carried out by rapid mixing and short reaction time. After 15 min of reaction at 30 °C, the polymer solution was quenched with methanol. The resulting *p*-MS-terminated polypropylene (PP-*t-p*-MS) was washed with THF to remove excess styrene and then vacuum-dried at 50 °C. About 23.25 g of PP-*t-p*-MS polymer was obtained with a catalytic activity of 73 760 kg of PP/mol of Zr·h.

Synthesis of PP-*b*-PS Diblock Copolymer. The first reaction step is a lithiation reaction of PP-*t-p*-MS polymer. In an argon filled drybox, 5 g of PP-*t-p*-MS (sample B-1 in Table 1) was suspended in 80 mL of cyclohexane in a 250 mL air-free flask with a magnetic stirrer bar. Next, 1 mL (1.3 mmol) of 1.3 M *s*-BuLi solution and 0.2 mL (1.3 mmol) of TMEDA were added to the flask, and the flask was brought out of the drybox and heated to 60 °C for 4 h under N_2 . The reaction was then cooled to room temperature and moved back to the drybox. The resulting lithiated PP-*t-p*-MS polymer was filtered and washed with cyclohexane a few times to remove excess *s*-BuLi and TMEDA.

The lithiated PP-*t-p*-MS polymer (3 g) was then again suspended in 100 mL of anhydrous cyclohexane, and the anionic polymerization was carried out at ambient temperature in a slurry solution by introducing 5 mL of styrene. After 5 h, 10 mL of methanol was added to terminate the reaction. The precipitated polymer was filtered and then subjected to fractionation. A good solvent (THF) for PS side chain polymers was used in a Soxhlet apparatus under N_2 for 24 h, resulting in almost no soluble fractions. The THF-insoluble fraction was a PP-*b*-PS diblock copolymer that was completely soluble in 1,1,2,2-tetrachloroethane at elevated temperatures.

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