Synthesis of Isotactic Polypropylene Containing a Terminal Cl, OH, or NH_2 Group via Metallocene-Mediated Polymerization/Chain Transfer Reaction

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ABSTRACT: This paper discusses a direct (one-pot) polymerization process to prepare isotactic polypropylene (i-PP) having a terminal functional group including Cl, OH, and NH_2. The chemistry involves metallocene-mediated propylene polymerization using *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO complex in the presence of styrene derivatives (St−f), carrying a Cl (St−Cl) or a silane-protected OH (St−OSi) or a silane-protected NH_2 (St−NSi_2), followed by hydrogenation. Apparently, the propylene propagating chain end engages in a facile consecutive chain transfer reaction, reacting with St−f and then hydrogen, with high catalyst reactivity under the proper St−f and hydrogen concentrations. The polymer molecular weight was inversely proportional to the molar ratio of [St−f]/[propylene] with a chain transfer constant (k_{tr}/k_p) of 1/21 for St−Cl, 1/34 for St−NSi_2, and 1/48 for St−OSi, respectively. Both silane protecting groups were hydrolyzed in acidic aqueous solution during the sample workup step to obtain the desirable i-PP polymers with a terminal OH and NH_2 group (i.e., PP-*t*-St−OH and PP-*t*-St−NH_2). The terminal functional group was confirmed by end group analysis and chain extension reaction. Despite the high molecular weight, the terminal functional group in PP engages a coupling reaction with polycapolactone (PCL) in solution and melt to form PP-*b*-PCL diblock copolymers that are very effective compatibilizers in PP/PCL polymer blends.

Introduction

Hydrocarbon polymer with a terminal functional group[1] is a very attractive material that possesses 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,[2] formation of graft and block copolymers,[3] and reactive blending[4] to improve the compatibility of two dissimilar polymer blends. This chain end functionalized polymer structure is particularly useful in polyolefins (PE, PP, EP, s-PS, etc.), whose lack of functionality and poor compatibility with other materials has imposed limitations on its applications[5] in many areas, especially in polymer blends and alloys.

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[6] or a control termination (functionalization) reaction[7] 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.[8] 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 our recent papers,[9] we have reported a new chemical route to prepare polyolefin (including PE, PP, 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−BR_2)[10] and *p*-methylstyrene/hydrogen (*p*-MS/H_2),[11] 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 convertion 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 Cl, OH, and NH_2. In other words, the ideal reaction is a one-pot process,[12] and no chain end functionalization would be needed after the polymerization/chain transfer reaction. Both phenol and primary amine are very interesting terminal groups with good chemical reactivity in many applications. As will be discussed later, they can engage 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.

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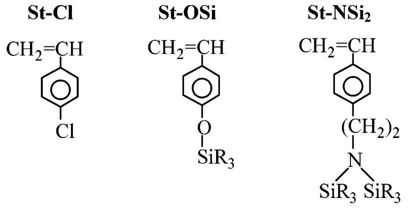
Chart 1

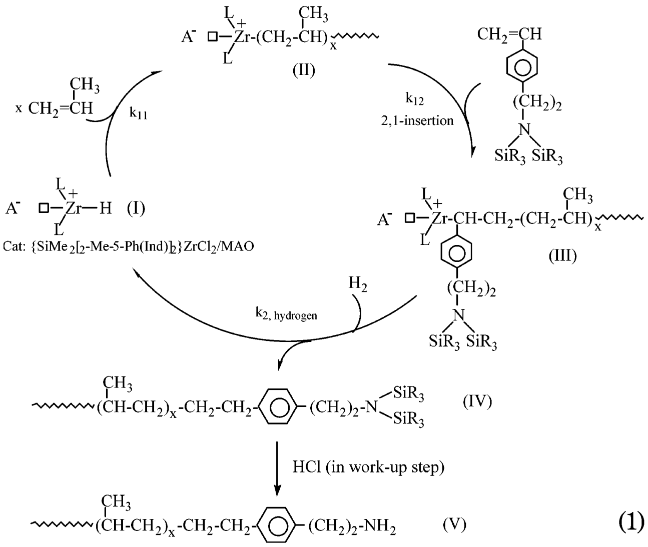


Results and Discussion

The basic idea in the direct preparation of the chain functionalized PP was to use a functionalized styrenic chain transfer agent (St−f) that could engage in similar metallocene-mediated propylene polymerization/chain transfer reaction under some reaction conditions. Three St−f molecules were investigated, including *p*-chlorostyrene (St−Cl), dimethylisopropylsilane protected *p*-vinylphenol (St−OSi), and bis(trimethylsilane) protected *p*-ethylaminostyrene (St−NSi_2), as illustrated in Chart 1.

No external protection agent is needed for St−Cl in metallocene/MAO systems. However, both the OH and NH_2 groups are very sensitive to the metallocene cationic site. The silane groups not only provide effective protection for both the OH and NH_2 functional groups during the metallocene catalysis but also can be completely deprotected by aqueous HCl solution during the sample workup procedure. 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_2Si[2-Me-4-Ph-(Ind)]$_2$$ZrCl_2$/MAO complex[13] 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[11] 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 a St−NSi_2 unit (k_{12}) (via 2,1-insertion) to form a St−NSi_2-capped propagating site (**III**) with an adjacent phenyl group interacting with metal cation. The new propagating site (**III**) is incapable of continuing the insertion of St−NSi_2 (k_{22}) or propylene (k_{21}) due to the steric jamming. However, it can react with hydrogen to complete the chain transfer reaction. This consecutive reaction with St−NSi_2 and hydrogen results in a PP-*t*-St−NSi_2 polymer chain (**IV**), and a regenerated Zr−H species (**I**) reinitiates the polymerization of propylene and continues the polymerization cycles. After the polymerization is complete, the desirable NH_2 terminal group in PP-t-NH_2 (**V**) can be easily recovered during the sample workup step using HCl aqueous solution. Theoretically, the PP-*t*-NH_2 molecular weight should be linearly proportion to the molar ratio of [propylene]/[St−NSi_2].



(1)

Tables 1 and 2 summarize the experimental results involving three chain transfer agents—St−Cl/H_2, St−OSi/H_2, and St−NSi_2/H_2, respectively—in *rac*-Me_2Si[2-Me-4-Ph(Ind)]$_2$$ZrCl_2$/MAO catalyzed polymerization of propylene. In all control reactions, a small amount of any styrene derivative (St−f) 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 from A4 to A6, and runs A7 and A8 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. A sufficient quantity of hydrogen, proportional to the St−Cl concentration, is needed to maintain high catalyst activity. In run A3, with 0.144 M St−Cl and 20 psi H_2, the catalyst exhibits about 85% of the catalyst activity seen in the regular propylene polymerization (control 1). Overall, the catalyst activity was also proportionally depressed with the concentration of St−Cl, which reflects the competitive coordination at metallocene active sites between monomer and chain transfer agents.

The general trend of hydrogen effects was also observed in both the St−OSi/H_2 and St−NSi_2/H_2 chain transfer runs in Table 2. Hydrogen is clearly needed to complete the chain transfer cycle in all the polymerization reactions. Compared to the corresponding St−Cl cases, the consistently lower catalyst activity may imply an effect (steric and/or electronic ones) from the bulky protected functional group at the active site to slow the completion of the chain transfer reaction. Fortunately, this effect is small, especially in the preparation of high polymer that only requires a small concentration of chain transfer agent. Overall, the PP molecular weight is governed by the chain transfer agent − the higher the concentration of the St−f, the lower the molecular weight of the resulting polymer. Figure 1 shows the plot of the polymer molecular weight (M_n) vs the molar ratio of [propylene]/[St−f], including all three St−Cl/H_2, St−OSi/H_2, and St−NSi_2/H_2 chain transfer agents. In general, the polymer molecular weight and molar ratio of [propylene]/[St−f] are linearly proportional. It is clear that the chain transfer reaction to St−f (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 eq $X_n = k_p[\text{olefin}]/k_{tr}[p\text{-MS}]$ with a chain transfer constant k_{tr}/k_p of 1/21 for St−Cl/H_2, 1/48 for St−OSi/H_2, and 1/34 for St−NSi_2/H_2, respectively. It is intriguing that the k_{tr}/k_p values are significantly lower than those seen in

Table 1. Summary of PP-*t*-St−Cl Polymers Prepared by the Combination of *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO Catalyst and St−Cl/$H_2$ Chain Transfer Agents

	polymerization conditions[a]									
run	propylene (psi)	St−Cl (mol/L)	H_2 (psi)	yield (g)	catal activity[b]	St−Cl in PP (mol %)	St−Cl convn (%)	M_n ($\times 10^{-3}$)	PDI (M_w/M_n)	T_m (°C)
control 1	100	0	0	26.90	86 208	0		77.6	2.9	159.6
control 2	100	0.144	0	0.11	352	0.12	0.028	54.6	1.9	158.3
A1	100	0.144	6	1.36	4402	0.13	0.42	45.3	1.9	159.0
A2	100	0.144	12	7.56	24 192	0.13	2.21	47.5	2.0	158.2
A3	100	0.144	20	21.8	70 435	0.12	6.57	46.1	2.1	158.1
control 3	100	0.289	0	~0	~0					
A4	100	0.289	6	1.24	4388	0.23	0.46	18.5	2.2	156.8
A5	100	0.289	14	4.44	15 712	0.23	1.62	19.1	2.1	157.1
A6	100	0.289	20	12.91	45 673	0.22	4.80	18.7	2.1	156.9
control 4	100	0.433	0	~0	~0					
A7	100	0.433	27	8.49	27 200	0.39	4.79	8.2	1.9	155.3
A8	100	0.433	35	11.27	36 106	0.39	6.21	8.4	1.9	155.4
A9[c]	20	0.144	20	4.74	7593	1.20	18.8	3.5	1.6	154.8
A10[c]	20	0.433	20	3.66	5862	2.08	7.70	2.2	1.5	154.1
A11[c]	20	0.866	20	2.22	3556	3.40	3.67	1.4	1.4	153.2

[a] Reaction conditions (unless otherwise specified): 50 mL toluene, [Zr] = 1.25×10^{-6} mol, [MAO]/[Zr] = 3000, temperature = 30 °C, and time = 15 min. [b] Catalyst activity = kg of PP/mol of catalyst·h. [c] Reaction time = 30 min.

Table 2. Summary of PP-*t*-St−OH and PP-*t*-St−NH_2 Polymers[a] Prepared by the Combination of *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO Catalyst and St−OSi/H_2 or St−NSi_2/H_2 Chain Transfer Agents

run	St−OSi or St−NSi_2 (mol/L)	H_2 (psi)	yield (g)	catal activity[b]	St−OH or St−NH_2 in PP (mol %)	M_n ($\times 10^{-3}$)	PDI (M_w/M_n)	T_m (°C)
control 5	St−OSi/0.198	0	~0	~0				
B1	St−OSi/0.198	6	0.36	1165	0.09	52.1	2.3	159.1
B2	St−OSi/0.198	12	2.36	7637	0.08	53.4	2.4	158.4
B3	St−OSi/0.198	20	8.34	26 995	0.10	52.5	2.2	158.2
control 6	St−OSi/0.396	0	~0	~0				
B4	St−OSi/0.396	6	~0	~0				
B5	St−OSi/0.396	12	0.63	2039	0.18	23.4	2.5	157.4
B6	St−OSi/0.396	20	2.57	8318	0.20	22.0	2.0	156.3
control 7	St−NSi_2/0.125	0	~0	~0				
C1	St−NSi_2/0.125	6	0.41	1327	0.07	56.3	2.1	159.1
C2	St−NSi_2/0.125	12	2.62	8480	0.06	55.4	2.5	158.4
C3	St−NSi_2/0.125	20	9.78	31 655	0.08	58.9	2.3	158.2
control 8	St−NSi_2/0.250	0	~0	~0				
C4	St−NSi_2/0.250	12	0.81	2622	0.18	25.3	2.2	156.3
C5	St−NSi_2/0.250	20	3.11	10 066	0.19	24.2	2.3	155.9

[a] Reaction conditions: 50 mL toluene, [Zr] = 1.25×10^{-6} mol, [MAO]/[Zr] = 3000, temperature = 30 °C, and time = 15 min. [b] Catalyst activity = kg of PP/mol of catalyst·h.

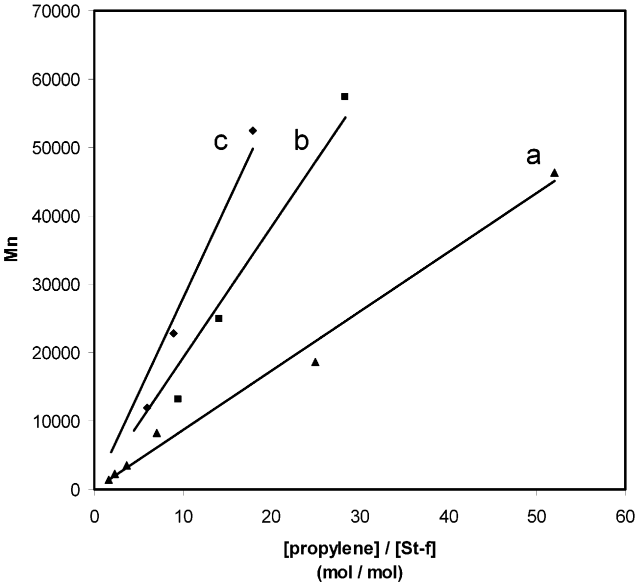


Figure 1. Plots of number-average molecular weights (M_n) of PE-*t*-St−f polymers vs the mole ratio of [propylene]/[St−f] prepared by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO complex and chain transfer agents of (a) St−Cl, (b) St−OSi, and (c) St−NSi_2, respectively.

styrene and *p*-MS cases[11] under similar reaction conditions. The bulky protected functional groups may reduce the frequency of chain transfer reaction.

Polymers with very low molecular weights (a few thousand) have been obtained, and the molecular weight distributions are quite narrow, which are generally consistent with single site polymerization processes. Some low molecular weight polymers with exceptionally low $M_w/M_n < 2$ (despite extra efforts to recover all polymers) may be associated with the sensitivity of GPC at very low molecular range.

End Group Analysis. The terminal functional group at the polymer chain end provides direct evidence for the chain transfer reaction. Figure 2 shows the ^1H NMR spectra (with an inset of the expanded region and the chemical shift assignments) of two resulting PP-*t*-St−Cl polymers ($M_n = 47.5 \times 10^3$, $M_w/M_n = 2.0$ and $M_n = 8.2 \times 10^3$, $M_w/M_n = 1.9$). In addition to three major peaks (δ = 0.95, 1.35, and 1.65 ppm) corresponding to the C$\mathbf{H}_3$, C$\mathbf{H}_2$, and C$\mathbf{H}$ groups in the PP backbone, there are two sets of weak chemical shifts at 2.64 and 7.05−7.28 ppm corresponding to $-C\mathbf{H}_2-C_6H_4-Cl$ and $-CH_2-C_6\mathbf{H}_4-Cl$, respectively. The terminal group concentration is inversely proportional to the polymer molecular weight, which is in good agreement with estimated value by the GPC curve. Figure 3 shows the ^{13}C NMR

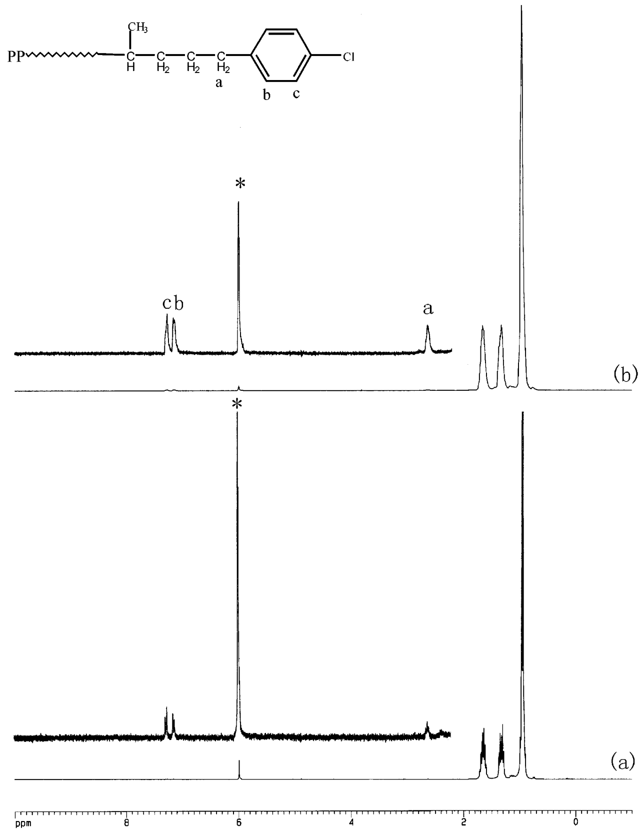


Figure 2. ^1H NMR spectra of two PP-*t*-St−Cl polymers, including (a) sample A2 ($M_n = 47\,500$ g/mol, $M_w/M_n = 2.0$) and sample A7 ($M_n = 8200$ g/mol, $M_w/M_n = 1.9$) in Table 1 (solvent, $C_2D_2Cl_4$; temperature, 110 °C).

spectrum (with an inset of the expanded region and the chemical shift assignments) of a PP-*t*-St−Cl polymer ($M_n = 1.4 \times 10^3$, $M_w/M_n = 1.4$). Both polymer chain ends ($-CH_2-C_6H_4-Cl$ and $-CH_3$) were clearly observed with about a 1/1 molar ratio. It was interesting to find that there is no detectable vinyl group associated with the conventional chain transfer process (via β-H elimination), nor any chemical shifts for $-\mathbf{CH}\text{-}C_6H_4-Cl$ associated with the copolymerization reaction. In addition, the St−Cl/H_2 chain transfer agents showed no effect on the stereospecific insertion of propylene monomers, even with this high degree of chain transfer reaction. As shown in Tables 1 and 2, all the functional group terminated PP polymers appear to have melting temperatures similar to that of the corresponding unfunctionalized PP. Similar results were observed in St−OSi/H_2 and St−NSi_2/H_2 cases. Figure 4 shows the ^1H NMR spectra (with inset of magnified region and chemical shift assigments) of PP-*t*-St−OSi polymer ($M_n = 22.0 \times 10^3$, $M_w/M_n = 2.0$) and the corresponding PP-*t*-St−OH. In addition to three major peaks ($\delta = 0.95$, 1.35, and 1.65 ppm) for the $C\mathbf{H}_3$, $C\mathbf{H}_2$, and $C\mathbf{H}$ groups in the PP backbone, there are three minor chemical shifts at 0.25, 2.61, and 6.75−7.18 ppm (with an intensity ratio near 6/2/4) shown in Figure 4a, corresponding to $-OSi(C\mathbf{H}_3)_2$(*t*-Bu), $-C\mathbf{H}_2-Ph$, and $-CH_2-C_6\mathbf{H}_4-OSi$, respectively. The chemical shift for the silane protecting group completely disappears in Figure 4b, indicating the occurrence of a very effective deprotection reaction during the sample workup step by using HCl solution. The equally split chemical shifts for the phenyl protons, combined with no detectable side product, further indicate the terminal *p*-alkylphenol moiety. Figure 5 compares the ^1H NMR spectra of PP-*t*-St−NSi_2 polymer ($M_n = 24.2 \times 10^3$, $M_w/M_n = 2.3$) and the corresponding PP-*t*-St−NH_2. In addition to the chemical shifts for PP polymer, Figure 5a shows all of the chemical shifts associated with the protecting bis(trimethylsily)amino terminal group that is connected to the symmetrical *p*-dialkylbenzene moiety. In fact, all four phenyl protons

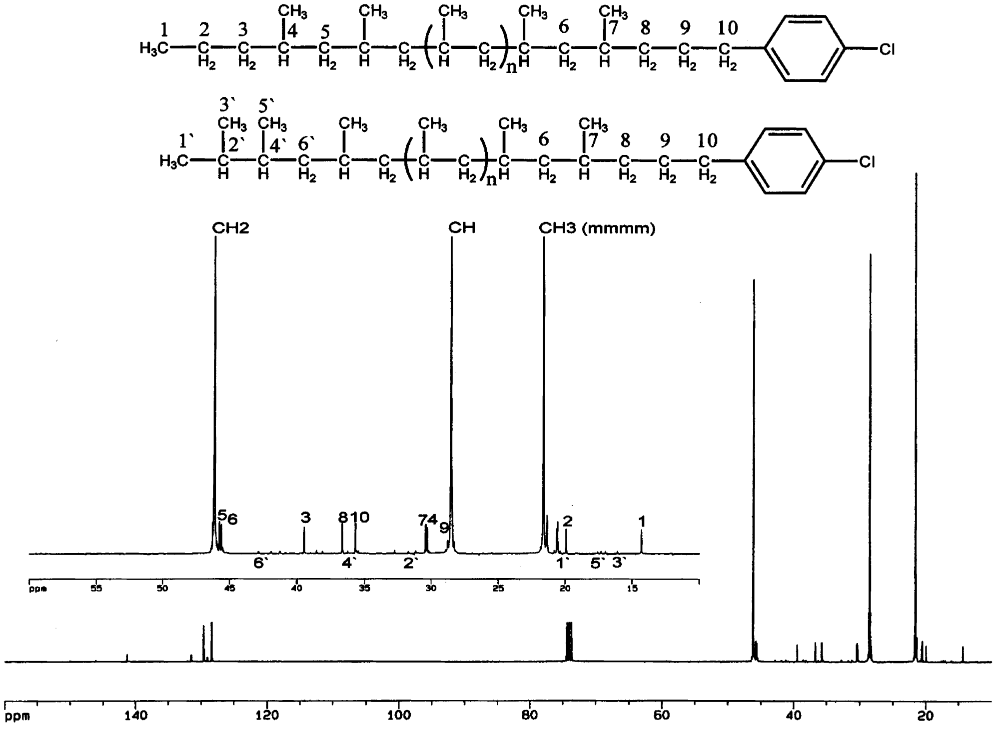


Figure 3. ^{13}C NMR spectrum of a PP-*t*-St−Cl polymer (sample A11; $M_n = 1400$ g/mol, $M_w/M_n = 1.4$), with an inset showing the expanded the aliphatic region and another insert showing the chemical shift assignments (solvent, $C_2D_2Cl_4$; temperature, 110 °C).

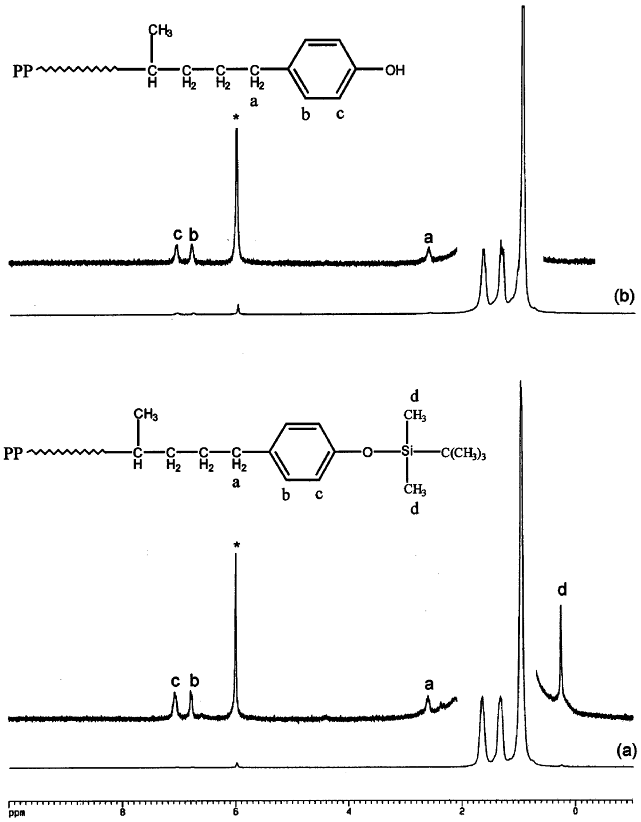


Figure 4. ^{1}H NMR spectra of (a) a PP-*t*-St−OSi polymer (sample B6) and its corresponding PP-*t*-St−OH ($M_n = 22\,000$ g/mol, $M_w/M_n = 2.0$) (solvent, $C_2D_2Cl_4$; temperature, 110 °C).

merge into a single chemical shift at 7.22 ppm. Figure 5b shows an almost identical spectrum, except for the disappearance of the silane protecting group at 0.24 ppm.

Overall, the combined experimental results strongly indicate a clean and effective reaction scheme, as illustrated in eq 1. The combination of the facile in situ chain transfer to St−f/H_2 during the catalytic polymerization of propylene and the subsequent complete deprotection reaction during the sample workup step affords a very interesting reaction scheme in the preparation of the chain end functionalized i-PP with a Cl, OH, or NH_2 terminal group via a one-pot reaction process.

Coupling Reaction. The existence of a terminal functional group in PP was further examined by chain extension reaction using the terminal functional group as the reaction site. Specifically, we investigated the coupling reactions between the terminal OH (phenol) and NH_2 in PP and the terminal COOH group in polyesters and polyamides in melt or solution. The in situ formed diblock copolymers were used as the compatibilizers in PP/polyester and PP/polyamide blends. One example is a coupling reaction between PP-*t*-St−NH_2 ($M_n = 110 \times 10^3$, $M_w/M_n = 2.0$) and polycarpolactone (PCL; $M_n = 50 \times 10^3$, $M_w/M_n = 2.0$) containing a terminal COOH group in the refluxing toluene solution. The resulting PP-*b*-PCL diblock copolymer (with an amide linkage) was subjected to a vigorous Soxhlet extraction by boiling acetone to remove any unreacted PCL homopolymer. The purification was continued until the composition of the insoluble portion became constant. The insoluble fraction (soluble in 1,1,2,2-tetrachloroethane at elevated temperatures) is PP-*b*-PCL diblock copolymer, which is evidenced by both intrinsic viscosity and NMR spectrum. The intrinsic viscosity changes from 1.03 dL/g for PP-*t*-St−NH_2 to 1.42 dL/g

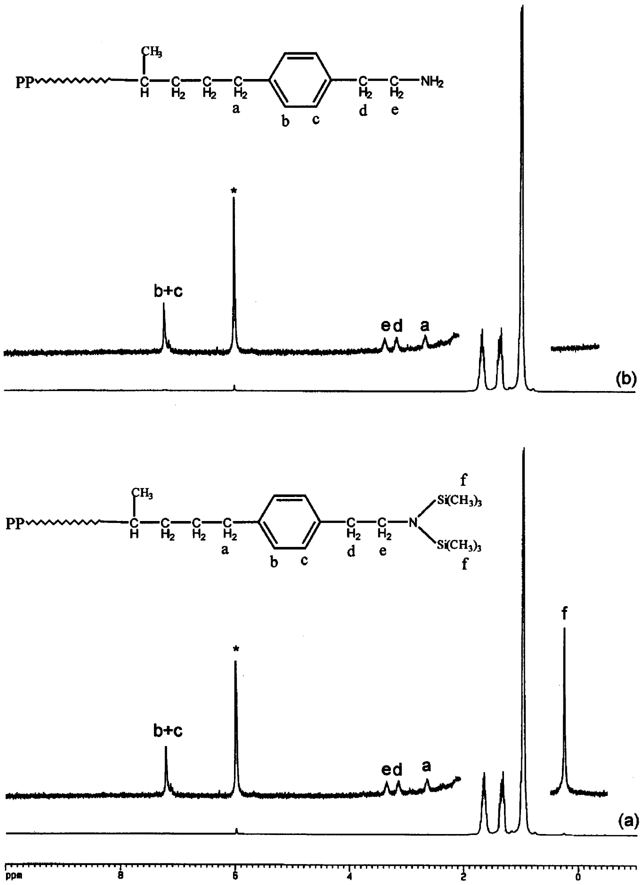


Figure 5. ^{1}H NMR spectra of (a) a PP-*t*-St−NSi_2 polymer (sample C5) and (b) its corresponding PP-*t*-St−NH_2 (M_n = 24,200 g/mol, $M_w/M_n = 2.3$) (solvent, $C_2D_2Cl_4$; temperature, 110 °C).

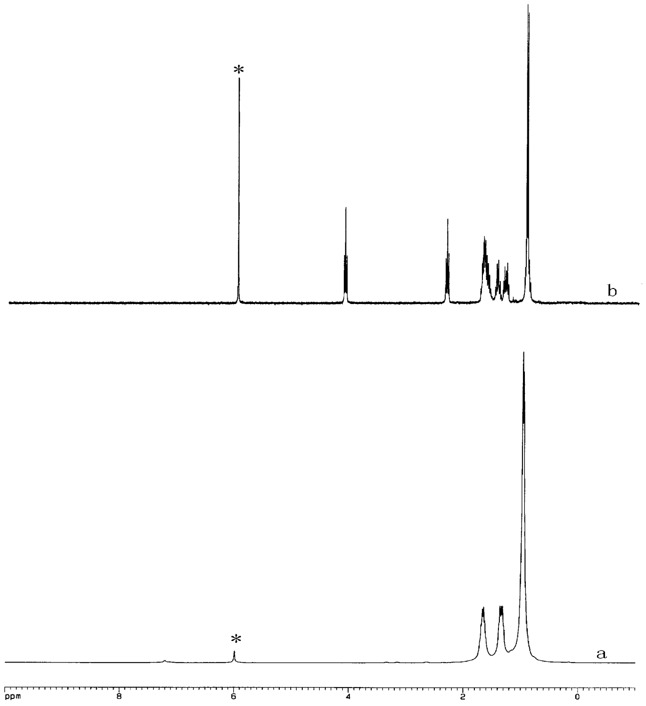


Figure 6. ^{1}H NMR spectra of (a) PP-*t*-St−NH_2 and (b) PP-*b*-PCL samples (solvent, $C_2D_2Cl_4$; temperature, 110 °C).

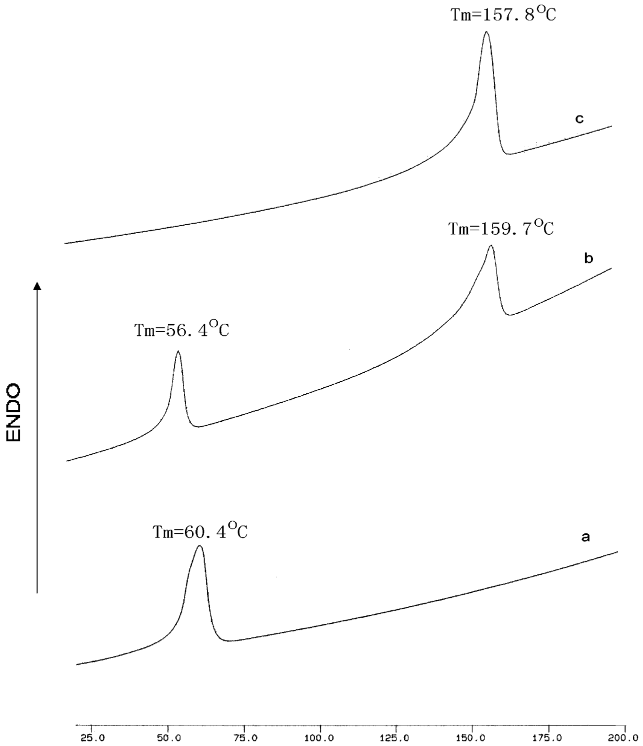


Figure 7. The DSC curve comparison between (a) PCL (M_n = 42 500 g/mol, $M_w/M_n = 1.5$) and (b) PP-*b*-PCL (M_n = 150 000 g/mol, $M_w/M_n = 2.9$), and (c) PP-*t*-St-NH$_2$ (M_n = 100 000 g/mol, $M_w/M_n = 2.4$).

for PP-*b*-PCL diblock copolymer. Figure 6 compares the ^{1}H NMR spectra of the starting PP-*t*-St−NH$_2$ and the resulting PP-*b*-PCL diblock copolymer. In addition to the chemical shifts at 1.9, 1.6, and 1.1 ppm, corresponding to methine, methylene, and methyl groups in polypropylene, the new chemical shifts at 4.1 and 2.3 ppm correspond to methylene groups (C**H**$_2$−O) and (C**H**$_2$−C=O) in the PCL block, respectively. The quantitative analysis of the copolymer composition was calculated by the ratio of two integrated intensities between $\delta = 4.1$ and $\delta = 2.0-1.0$ ppm and the number of protons both chemical shifts represent, which indicates about 30 mol % of PCL in the PP-*b*-PCL diblock copolymer. 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. It is interesting to note that, under similar coupling reaction conditions, PP-*t*-St−OH ($M_n = 97 \times 10^3$, $M_w/M_n = 2.0$) containing a terminal phenol group only showed about 60% of the coupling efficiency with PCL. The estification reaction requires a much longer reaction time. Figure 7 compares the DSC curves of the PP-*b*-PCL diblock copolymer containing 30 mol % 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 form in the diblock copolymer and exhibit melting temperatures (159 and 56 °C) that are similar to those seen in the corresponding PP and PCL homopolymers. The resulting PP-*b*-PCL diblock copolymer containing 30 mol % of PCL was used as a compatibilizer in PP/PCL polymer blends. Two polymer blends—PP/PCL (70/30 weight ratio) homopolymer blend and a blend comprised of a 70/30/10 weight ratio of PP, PCL, and PP-*b*-PCL, respectively—were prepared by homogeneous mixing in dichlorobenzene solution at 180 °C before precipitating in hexane at ambient temperature. Films were then press-molded at 180 °C. Figure 8 compares SEM images of the cross section of two cryofractured films. In the homopolymer blend (Figure 8a), the polymers are grossly phase separated, as can be seen by a minor component PCL that exhibits nonuniform, poorly dispersed domains and voids at the fracture surface. This “ball and socket” topography is indicative of poor interfacial adhesion between the PP and PCL domains and represents PCL domains that are pulled out of the PP matrix. Such pull out indicates that no stress transfer takes place between the phases during fracture. Upon blending PP and PCL with the PP-*b*-PCL compatibilizer, a drastic change in the morphology occurs. The compatibilized blend shown in Figure 8b no longer displays the distinct PCL globules and has a rather flat, featureless surface, indicating very small domain size. The addition of the diblock copolymer must stabilize the interfaces and increase the interfacial adhesion between the PP and PCL microdomains.

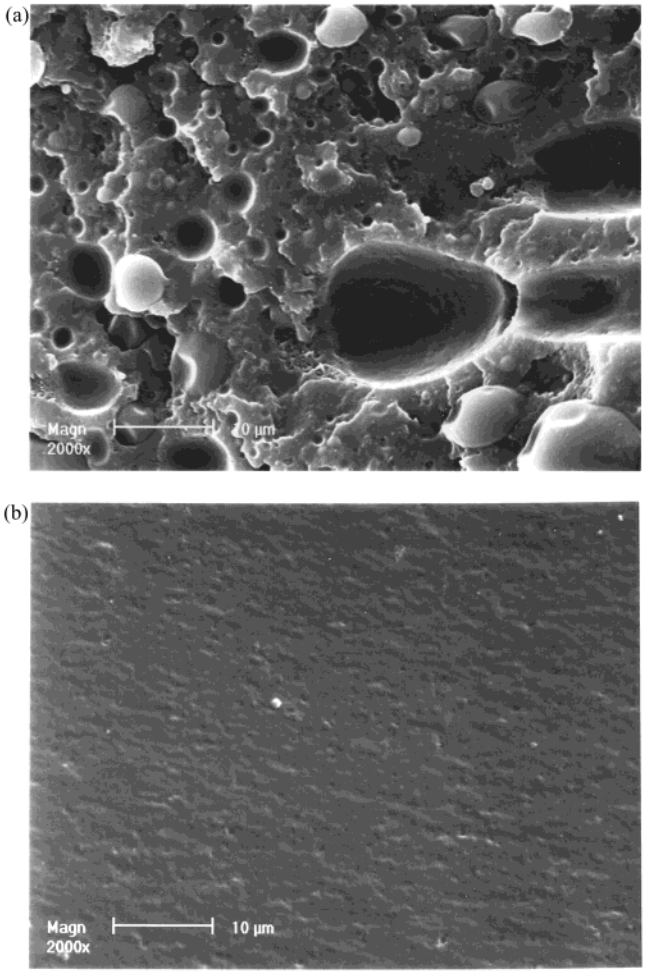


Figure 8. SEM micrographs of (a) two homopolymer blend with i-PP/PCL = 70/30 (1000×) and (b) two homopolymers with PP-*b*-PCL, i-PP/PP-*b*-PCL/PCL = 70/10/30 (1000×).

Similar PP-*b*-polyamide (Nylon 11) compatibility was also observed in the PP/Nylon 11 blends. In fact, PP-*t*-St−NH$_2$ was directly used in the reactive blending between PP and Nylon 11 in a melt mixer (Brabender). The in situ formed PP-*b*-Nylon 11 diblock copolymer reduces the domain size and improves the morphology in PP/Nylon 11 blends. Results from the systematic study of reactive melt blending using these well-defined chain end functionalized PP polymers as compatibilizers, especially the effects on polymer molecular weight, will be discussed in the near future.

Experimental Detail

Instrumentation and Materials. All ^{1}H 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 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. 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 carbon 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 48 h and then distilled over sodium. 4-Chlorostyrene, 4-vinylbenzyl chloride, 4-hydroxybenzaldehyde, acetic acid, *n*-butyllithium (2.5 M in hexane), *tert*-butyldimethylsilyl chloride, lithium bis(trimethylsilyl)amide, methyltriphenylphosphonium bromide, imidazolechloromethyl methyl ether, magnesium chips, methylaluminoxane (MAO) (10 wt % in toluene), tetrabutylammonium fluoride, butylated hydroxytoluol (BHT), and polycaprolactone (PCL) were purchased from Aldrich Chemical Co. 4-Chlorostyrene and 4-vinylbenzyl chloride were distilled over CaH$_2$ prior to use. High purity grade propylene (MG Industries) was used as received. The *rac*-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$ catalyst was prepared by the published procedures.[13]

Synthesis of 4-(*tert*-Butyldimethylsilyloxy)styrene (St−OSi). 4-(*tert*-Butyldimethylsilyloxy)styrene was synthesized in two steps, following the literature.[14] In a 500 mL flask equipped with a magnetic stirring bar was mixed 70.4 g (1.02 mol) of imidazole with 52.4 g (0.42 mol) of 4-hydroxybenzaldehyde and 77.4 g (0.52 mol) of *tert*-butyldimethylsilyl chloride in THF solution. The mixture was stirred at ambient temperature for 4 h before being poured into cold water. The organic layer was separated and extracted with ether and then dried with magnesium sulfate. After the solvent was evaporated off, 94 g of 4-(*tert*-butyldimethylsilyloxy)benzaldehyde (90% yield), a deep yellow color liquid, was obtained. The second reaction step was performed under nitrogen atmosphere. In a 500 mL flask equipped with a magnetic stirring bar, 123.6 g (0.38 mol) of methyltriphenylphosphonium bromide suspended in THF was treated with 149.6 mL (0.19 mol) of *n*-butyllithium(2.5 M in hexane). After 1 h, 80.0 g (0.34 mol) of 4-(*tert*-butyldimethylsilyloxy)benzaldehyde was introduced dropwise into the red solution. The mixture was stirred overnight at room temperature and then poured into cold water. The organic layer was separated by ether extraction and dried with magnesium sulfate. Further purification was performed by distillation under vacuum (10 Torr) at elevated temperature (80 °C). Then 65 g of 4-(*tert*-butyldimethylsilyloxy)styrene was obtained with a yield of more than 90%. Its structure was confirmed by ^{1}H NMR spectrum.

Synthesis of 4-{**2-[***N*,*N*-bis(trimethylsilyl)amino]ethyl}-styrene (**St—N**Si$_2$*)*. 4-{2-[*N*,*N*-Bis(trimethylsilyl)amino]ethyl}-styrene was prepared in two reaction steps.[15] Into a 500 mL flask equipped with a magnetic stirring bar was slowly added 100 g (0.598 mol) of lithium bis(trimethylsilyl)amide dissolved in 200 mL of THF into a mixture of 50 mL (0.658 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 for 2 h before evaporating the excess chloromethyl methyl ether and THF solvent. *N*,*N*-Bis(trimethylsilyl)methoxymethylamine (80% yield) was isolated by distillation. In the second step, 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene was prepared by treating 4-vinylbenzylmagnesium chloride with *N*,*N*-bis(trimethylsilys)methoxymethylamine. In a 500 mL flask equipped with a magnetic stirring bar and a condenser was suspended 15.2 g (0.62 mol) of magnesium in 50 mL dry ether, and 80 mL (0.57 mol) of 4-vinylbenzyl chloride diluted with 50 mL dry ether was then introduced dropwise through the condenser. The solution was refluxed for 4 h before the addition of 117 g (0.57 mol) of *N*,*N*-bis(trimethylsilys)methoxymethylamine over a period of 2 h. The reaction was allowed to proceed at room temperature for another 2 h before adding 100 mL of aqueous NaOH solution (30%). The organic layer was separated and dried, and the residual was then distilled over CaH$_2$ to obtain 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene in 70% yield.

Synthesis of PP-*t*-St—Cl Polymers. In a typical reaction (run A3 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 (20 psi). Then 1.0 mL (0.144 M) of 4-chlorostyrene was injected into the reactor and 100 psi (3.24 M) of propylene was charged, bringing the total pressure to 120 psi at ambient temperature (30 °C). About 1.25×10^{-6} mol of *rac*-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$ 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 (120 psi) during the course of the polymerization. After 15 min of reaction at 30 °C, the reaction solution was quenched with acidic methanol and filtered, washed extensively with THF, and dried under vacuum at 50 °C for 8 h. About 21.8 g of PP-*t*-ClSt was obtained with a catalyst activity of 70 435 kg of PP/mol of Zr·h.

Synthesis of PP-*t*-St—OSi and PP-*t*-Si—OH Polymers. PP-*t*-St−OSi polymers were synthesized by using 4-(*tert*-butyldimethylsilyloxy)styrene as a chain transfer agent in propylene polymerization. In a typical reaction (run B3 in Table 2), 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 (20 psi). Then 1.0 mL (0.125 M) of 4-(*tert*-butyldimethylsilyloxy)styrene was injected into the reactor and 100 psi (3.24 M) of propylene was charged, bringing the total pressure to 120 psi at ambient temperature (30 °C). About 1.25×10^{-6} mol of *rac*-Me$_2$Si[2-Me-4-Ph(Ind)]$_2$ZrCl$_2$ 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 (120 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 4-(*tert*-butyldimethylsilyloxy)styrene homopolymer, and then dried under vacuum at 50 °C for 8 h. About 8.34 g of PP-*t*-St−OSi polymer was obtained with a catalyst activity of 26 995 kg of PP-*t*-St−OSi/mol of Zr·h.

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

Synthesis of PP-*t*-St—*Si*$_2$ and PP-*t*-**St—N**H$_2$ Polymers. Following the same procedures for the synthesis of PP-*t*-St−OSi polymers, PP-*t*-St−NSi$_2$ polymers were prepared by using 4-{2-[*N*,*N*-bis(trimethylsilyl)amino]ethyl}styrene as a chain transfer agent in propylene polymerization.

PP-*t*-St−NH$_2$ polymers were prepared from PP-*t*-St−NSi$_2$ polymers by treating them with hydrogen chloride, which can be accomplished during the sample workup step. Alternatively, the isolated PP-*t*-St−NSi_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-polycarpolactone (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 dry agent. About 2 g of PP-*t*-St−NH_2 ($M_n = 110 \times 10^3$, $M_w/M_n = 2.0$) 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, 2.85 g of PP-*b*-PCL diblock copolymer was obtained.

Conclusion

All of the experimental results support the formation of chain end functionalized PP polymers during direct (one-pot) metallocene-mediated propylene polymerization/chain transfer reaction. With the proper 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 styrenic unit containing either a Cl, OH, or NH_2 group. This reaction scheme is especially useful in the preparation of chain-end functionalized PP with high molecular weight. Almost the same reaction procedures used in regular PP polymerization can be directly applied, except for the addition of a small amount of chain transfer agent. In turn, the PP polymer with a reactive functional group is a useful material that can be used to prepare diblock copolymers by coupling reactions, and can serve as a reactive compatibilizer in solution and melt blends.

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