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# Syntheses of Stereoregular Amorphous−Crystalline Diblock Copolymers and Their Self-Assembly Studies

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ABSTRACT: The syndiotactic polypropylene-*block*-atactic polystyrene (sPP-*b*-aPS), a novel crystalline−amorphous stereoregular diblock copolymer, is prepared in two steps. First, *p*-methylstyrene-capped syndiotactic polypropylene (pMS-capped sPP), which served as an end-functionalized prepolymer, can be successfully prepared by conducting propylene polymerization in the presence of *p*-methylstyrene and hydrogen using $Me_2C(Cp)(Flu)ZrCl_2$ as the catalyst. Second, the resulting end-functionalized prepolymer is linked to polystyrene (aPS) to provide the stereoregular crystalline−amorphous diblock copolymer, sPP-*b*-aPS, with a narrow range of molecular weight distribution (MWD). The resulting stereoregular crystalline−amorphous diblock copolymer, sPP-*b*-aPS, is able to self-organize into ordered nanopatterns in bulk as revealed by bright field transmission electron microscopy analyses.

## Introduction

Block copolymers[1] are characterized by their chemical structures of combining two or more polymers that are joined from end to end. Because of these unique structures, block copolymers are able to self-organize, in bulk or in solvent, into ordered nanopatterns. For amorphous diblock copolymers, ordered phase morphologies originate largely from the tendency of blocks to segregate. In contrast, crystalline−amorphous diblock copolymers possess a more complicated phase behavior due to the crystallization of the crystallizable block. Controlling the crystallization process of crystalline−amorphous block copolymers can lead to the formation of long-range nanopatterns,[2] as commonly applied in modern devices. Recent studies further reveal that the self-assembly of stereoregular crystalline−amorphous diblock copolymers can result in the formation of unusual nanopatterns[3] (e.g., nanohelical structure) due to the stereo-interactions between stereoregular entities. Despite this, simultaneous investigations of stereo-interactions and crystallization behaviors in the molecular level by using stereoregular crystalline−amorphous diblock copolymers have been quite limited due to the difficulties in preparing stereoregular block copolymers, especially those which can be used in self-assembly studies that display ordered microstructures.

To date, the diblock copolymers used in self-assembly studies are mostly prepared by living polymerizations (e.g., living anionic,[4] living free radical,[5] living cationic,[6] living group transfer polymerization,[7] and living ring-opening metathesis polymerization[8]), as these polymerizations offer a direct linking method for connecting different blocks and provide perfect controls in the chain propagation step to give block copolymers with a narrow range of molecular weight distribution (MWD). However, living polymerizations are typically unable to provide effective stereoregularity controls in the polymerization of α-olefins; thus, these commonly used methods for the syntheses of block copolymers cannot be directly used for preparations of stereoregular block copolymers. Evidently, new synthetic methods have to be developed for the preparations of stereoregular block copolymers, which are able to self-organize into nanopatterns in self-assembly studies.

## Experimental Section

**General Procedure.** All reactions and manipulations were conducted under a nitrogen atmosphere using the standard Schlenk line or drybox techniques. Solvents and common reagents were obtained commercially and were used either as received or purified by distillation with sodium/benzophenone. Propylene (purity >99.9%) and hydrogen (purity >99.9%) were obtained from Matheson and were used as received. *p*-Methylstyrene (pMS; purity >97%), *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA; purity >99%), and methyl ethyl ketone (MEK; purity >99%), which were commercially obtained from Aldrich, were dried over calcium hydride and distilled under reduced pressure. The 2-butyllithium (12% in cyclohexane) was obtained from Lancaster and was used as received. The $Me_2C(Cp)(Flu)ZrCl_2$ [9] and 2-butyllithium/TMEDA[10] were prepared by methods described in the literature. Methylaluminoxane (MAO, 14% in toluene), which was purchased from Albemarle, was dried under vacuum to remove trimethylaluminum (TMA).[11] The resulting TMA-free MAO was diluted in toluene to the desired concentration before use.

Synthesis of *p*-Methylstyrene End-Capped Syndiotactic Polypropylene (pMS-Capped sPP). Representative Experiment (for the Preparation of Sample $A_3$ in Table 1**)**. A 100 mL stainless steel reactor, equipped with a magnetic stirrer, was allowed to dry at 80 °C under vacuum. The reactor was cooled to 0 °C in an ice bath and was then charged sequentially with 50 mL of toluene, 2.0 mL of pMS (15.1 mmol), 2.5 mmol of MAO (in toluene), and 2.5 $\mu$mol of zirconium catalyst. After allowing the reactor to stir at 0 °C for 5 min, the reactor was charged with a premixed gas mixture containing 8 atm of propylene and 1.5 atm of hydrogen from a 5 L stainless steel reservoir to initiate the polymerization. As such, polymerization was conducted at 0 °C for 1 h, and the polymerization solution was then quenched with excess (ca. 15 mL) acidic methanol (1 N HCl solution in methanol), which led to the deposition of the polymerization product as a white precipitate. After isolation by filtration, the resulting polymer was purified by extracting it with boiling acetone in a Soxhlet extractor to remove

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**Table 1. Preparations of *p*-Methylstyrene-Capped Syndiotactic Polypropylene by $Me_2C(Cp)(Flu)ZrCl_2$/Methylaluminoxane (MAO) at Various Polymerization Conditions**[a]

| pMS-*t*-sPP sample | propylene (atm) | *p*MS (mmol) | $H_2$ (atm) | syndio-tacticity[b] (%) | $M_n$[c] ($\times 10^3$) | PDI[c] ($M_w/M_n$) | $T_m$[d] (°C) | cat. activity[e] |
|---|---|---|---|---|---|---|---|---|
| $A_0$ [f] | 8 | 0 | 1.5 | 92 | 59.1 | 2.97 | 145 | 2420 |
| $A_1$ [f] | 8 | 3.76 | 1.5 | 92 | 32.0 | 2.58 | 143 | 1860 |
| $A_2$ [f] | 8 | 7.53 | 1.5 | | 19.6 | 2.33 | 142 | 1230 |
| $A_3$ [f] | 8 | 15.1 | 1.5 | 92 | 11.0 | 2.07 | 141 | 1060 |
| $A_4$ [f] | 8 | 30.2 | 1.5 | 90 | 7.83 | 1.89 | 137 | 745 |
| $B_1$ [f] | 8 | 15.1 | 1 | | 11.2 | 2.18 | 141 | 974 |
| $B_2$ [f] | 8 | 15.1 | 3 | | 11.2 | 2.07 | 141 | 1120 |
| $B_3$ [f] | 8 | 15.1 | 6 | 92 | 11.0 | 2.12 | 140 | 1150 |
| $C_1$ [f] | 4 | 3.76 | 1.5 | | 24.5 | 2.46 | 142 | 846 |
| $C_2$ [f] | 4 | 7.53 | 1.5 | | 14.2 | 2.25 | 140 | 725 |
| $C_3$ [f] | 4 | 15.1 | 1.5 | 92 | 8.7 | 1.94 | 138 | 638 |
| $C_4$ [f] | 4 | 30.2 | 1.5 | | 6.2 | 1.82 | 136 | 554 |
| $D_1$ [f] | 4 | 15.1 | 3 | 92 | 8.5 | 1.96 | 138 | 712 |
| $D_2$ [f] | 4 | 15.1 | 6 | | 8.4 | 1.91 | 138 | 718 |
| $E_0$ [g] | 8 | 0 | 1.5 | 88 | 37.3 | 3.27 | 143 | 3150 |
| $E_1$ [g] | 8 | 3.76 | 1.5 | 87 | 26.4 | 3.10 | 141 | 2110 |
| $E_2$ [g] | 8 | 7.53 | 1.5 | | 15.6 | 2.83 | 140 | 1970 |
| $E_3$ [g] | 8 | 15.1 | 1.5 | | 9.2 | 2.56 | 139 | 1760 |
| $E_4$ [g] | 8 | 30.2 | 1.5 | 87 | 6.8 | 2.27 | 136 | 1440 |
| $F_1$ [g] | 8 | 15.1 | 1 | | 9.4 | 2.54 | 139 | 1660 |
| $F_2$ [g] | 8 | 15.1 | 3 | | 9.0 | 2.43 | 138 | 1730 |
| $F_3$ [g] | 8 | 15.1 | 6 | 86 | 8.9 | 2.50 | 138 | 1880 |
| $G_1$ [f] | 8 | 15.1 | 0 | | | | | ~0 |
| $G_2$ [g] | 8 | 15.1 | 0 | | | | | ~0 |

[a] Polymerization conditions: 50 mL of toluene, 2 μmol of zirconium catalyst, 2.5 mmol of MAO, reaction time = 1 h. [b] Syndiotacticity (rrrr) was determined by $^{13}C$ NMR analyses. [c] $M_n$ (number-average molecular weight), $M_w$ (weight-average molecular weight), and PDI (polydispersity, $M_w/M_n$) were determined by high-temperature GPC (solvent, trichlorobenzene; temperature, 135 °C). [d] $T_m$ (melting temperature) was determined by DSC. [e] Catalyst activity = kg of PP/(mol of catalyst h). [f] Polymerization temperature = 0 °C. [g] Polymerization temperature = 40 °C.

the atactic polypropylene. The resulting insoluble fraction of the polymer was dried under vacuum to provide the pMS-capped sPP as an off-white powder. Yield: 2.12 g. The syndiotacticity (rrrr) is 92% by $^{13}C$ NMR (in 1,1,2,2-tetrachloroethane-$d_2$, at 110 °C). $M_n$ = 11 000, $M_w$ = 22 800 by GPC (in 1,2,4-trichlorobenzene, at 135 °C).

**Soxhlet Extraction of pMS-Capped sPP in MEK.** On a vacuum line, 1.50 g of the pMS-capped sPP ($M_n$ = 11 000, $M_w$ = 22 800) was placed in a Soxhlet extractor and was allowed to undergo Soxhlet extraction in boiling MEK (50 mL) under nitrogen for 24 h. The resulting MEK solution was collected and was allowed to concentrate under vacuum to 15 mL. The resulting solution was then charged with excess methanol (ca. 20 mL), which in turn resulted in the deposition of the MEK soluble polymer as a white precipitate. The resulting MEK soluble polymer was isolated by filtration and dried under high vacuum to provide 0.82 g of the lower molecular weight pMS-capped sPP. The syndiotacticity (rrrr) is 82% by $^{13}C$ NMR (in 1,1,2,2-tetrachloroethane-$d_2$, at 110 °C). $M_n$ = 8900, $M_w$ = 14 800 by GPC (in 1,2,4-trichlorobenzene, at 135 °C).

**Preparation of sPP-*b*-aPS (2).** On a vacuum line, 0.50 g of the lower molecular weight pMS-capped sPP ($M_n$ = 8900, $M_w$ = 14 800) was dissolved in 15 mL of boiling cyclohexane. The solution was then allowed to cool to room temperature and was charged with the excess of 2-butyllithium/TMEDA (0.11 mmol in cyclohexane). The solution gradually turned into a light brown solution after the addition of the 2-butyllithium/TMEDA, indicating the successful functionalization of the pMS-capped sPP. The solution was stirred at room temperature for 6 h, and the excess of dimethylsilyl dichloride (15 mmol) was added. This resulted in the immediate formation of a light yellow solution. Volatiles were then removed under vacuum (to remove the excess dimethylsilyl dichloride) to provide the silyl chloride end-capped sPP. The resulting polymer was suspended in 15 mL of cyclohexane and was then charged with the excess amount (ca. 0.1 mmol) of freshly prepared living anionic polystyrene ($M_n$ = 7400, $M_w$ = 7800) to undergo the anionic coupling reaction. After overnight stirring of the solution at room temperature, the polymer solution was quenched with excess methanol (20 mL), which resulted in the deposition of the polymer mixture as a white precipitate. The resulting polymer mixture (containing pMS-capped sPP, sPP-*b*-aPS, and the excess aPS) was isolated after filtration and dried under vacuum. The purification of sPP-*b*-aPS diblock was completed in two steps. First, the excess polystyrene (soluble in boiling acetone) was removed by extracting it with boiling acetone in a Soxhlet extractor. The resulting acetone insoluble fraction was collected, dried, and allowed to undergo the second Soxhlet extraction with heptane to remove the unused pMS-capped sPP (soluble in heptane). The resulting heptane insoluble fraction was collected and dried under vacuum overnight to give 0.23 g of sPP-*b*-PS as a white solid. $M_n$ = 16 700, $M_w$ = 21 500 by GPC (in 1,2,4-trichlorobenzene, at 135 °C).

**Polymer Analysis.** The molecular weight and molecular weight distribution were determined by means of high-temperature gel permeation chromatography (Waters 150-CALAC/GPC) 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 sizes in series. The measurements were taken at 135 °C using 1,2,4-trichlorobenzene as solvent. PS samples with narrow MWDs were used as the standards for calibration. The standards were in the range of absolute molecular weight which is from 980 to 2 110 000, and the *R* square of the ideal calibrated line was limited to up to 0.999.

All $^1H$ (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were recorded on a Bruker AMX-400 NMR spectrometer. The PS−sPP samples were dissolved in 1,1,2,2-tetrachloroethane-$d_2$ as solvent, and the recorded temperature was at 110−130 °C.

Bright field transmission electron microscopy (TEM) images were obtained using the mass−thickness contrast with a JEOL TEM-1200x transmission electron microscope (at an accelerating voltage of 120 kV). Staining was accomplished by exposing the samples to the vapor of a 4% aqueous $RuO_4$ solution for 30 min.

## Results and Discussion

In this report, we aim at developing a synthetic method for preparations of stereoregular crystalline−amorphous diblock copolymers, which are suitable for self-assembly studies. Thereby, the stereoregular diblock copolymer not only need to have, at least, one crystallizable stereoregular block but also need to have a well-defined chemical structure (e.g., uniform chemical structure with narrow MWDs[12]). Evidently, these requirements create synthetic problems and difficulties because a stereoregular poly-α-olefin block cannot be prepared directly using the known living polymerization method. Recently, Marks[13] and Chung[14,15] demonstrated the successful preparations of utilizations of metallocene catalysts to induce the selective chain transfer reactions to silanes, boranes, and *p*-methylstyrene (pMS) for providing the functional group end-capped stereoregular poly-α-olefin, including functional group end-capped isotactic PP (iPP) and syndiotactic PS (sPS). Consequently, these end-functionalized prepolymers were used for successful preparations of stereoregular block copolymer by subsequent block copolymerization reactions. These results clearly indicate that the preparations of stereoregular block copolymers may inevitably start from a functional group end-capped stereoregular prepolymer since it requires a nonliving stereospecific catalyst to induce the stereoregularity control during the preparation of the stereoregular block. Although these synthetic routes provide useful synthetic tools for constructing stereoregular diblock copolymers, the stereoregular block copolymers prepared by these methods are not suitable for self-assembly studies because of their broad MWDs. Evidently, the successful preparations of a suitable stereogular block copolymer for self-assembly studies may depend on if the stereoregular block copolymer can be precisely prepared with uniform chemical structure and narrow MWD. In this paper the preparation of the novel stereoregular block copolymer (sPP-*b*-aPS), which can be used in the self-assembly studies for displaying consistent nanopatterns, is reported. Our selection of sPP-based diblock copolymers stems from two considerations: the first is simply because sPP-based diblock copolymers has never been prepared before, in addition, sPP offers a low crystallization temperature for conducting crystallization behavior examinations and for controlling the crystallizable phase during self-assembly studies. The synthesis of sPP-*b*-aPS will start from our efforts to prepare the pMS-capped sPP, which acts as the functional group end-capped sPP prepolymer for constructing diblock copolymers.

**Preparation of pMS-Capped sPP by Selective Chain Transfer to pMS and Hydrogen.**[16,17] The preparation of the pMS-capped sPP was conducted by using a syndiospecific catalyst,[18] namely $Me_2C[(Cp)(Flu)]ZrCl_2$, for conducting the propylene polymerization in the presence of different concentrations of pMS, at different pressures of hydrogen, and at different polymerization temperatures. As shown in the comparison results listed in Table 1, the molecular weight of the pMS-capped sPP is strongly dependent on the concentration of pMS (entries $A_0-A_4$, $C_1-C_4$, and $E_0-E_4$) added in the polymerization solution, but it shows only an insignificant influence by the hydrogen pressure (entries $B_1-B_3$, $D_1-D_2$, and $F_1-F_2$). However, in the absence of $H_2$, the polymerization of propylene and the presence of pMS lead to a detrimental effect on catalyst activity (entries $G_1-G_2$). These results clearly indicate that the incorporation of pMS leads to the generation of a dormant propagating chain, that the presence of hydrogen is essential for completing the chain transfer reaction and to reactivate the dormant active site (by hydrogen addition), and that the syndiospecific catalyst, $Ph_2C[(Cp)(Flu)]ZrCl_2$, is able to induce the selective chain transfer reaction to pMS and $H_2$ to produce the pMS-capped sPP. As shown in Table 1, the syndiotacticity (rrrr)[19] of the pMS-capped sPP is dependent on the polymerization temperature, but it shows only an insignificant influence by the concentrations of pMS and $H_2$. The molecular weight of the pMS-capped sPP is strongly dependent on propylene pressure (an increase in $M_n$ with an increasing propylene pressure) and polymerization temperature (an increase in $M_n$ with a reducing polymerization temperature). An increase in the polymerization temperature leads to the MWD broadening in the resulting pMS-capped sPP should be noted. These results clearly indicate that a lower polymerization temperature, lower propylene pressure, and a higher concentration of pMS are the more preferable polymerization conditions since these reaction conditions lead to the generation of the pMS-capped sPP prepolymer, which have the desired chemical structures, including a narrower MWD, lower molecular weight, and higher syndiotacticity to be used in the subsequent block copolymerizations for the preparation of the suitable sPP-*b*-aPS sample for self-assembly studies.

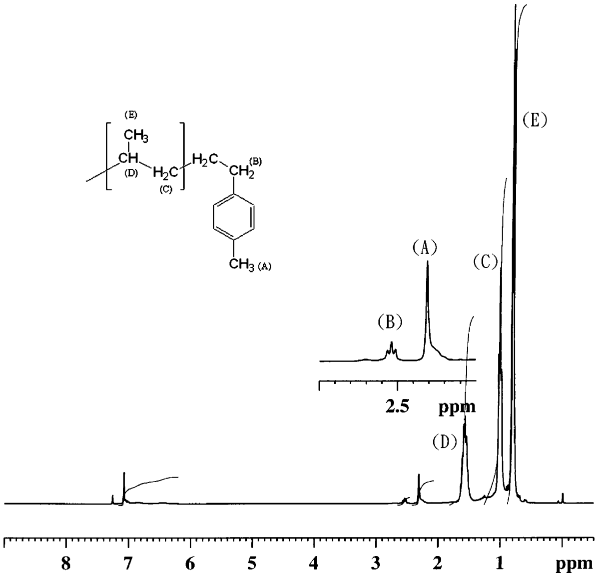


**Figure 1.** $^1H$ NMR spectrum (400 MHz) of a pMS-capped sPP sample ($M_n$ = 1900 g/mol, prepared by conducting propylene polymerization in the presence of *p*-methylstyrene, hydrogen, and $Me_2C(Cp)(Flu)ZrCl_2$ catalyst at 60 °C) (solvent, $CDCl_3$; temperature 60 °C).

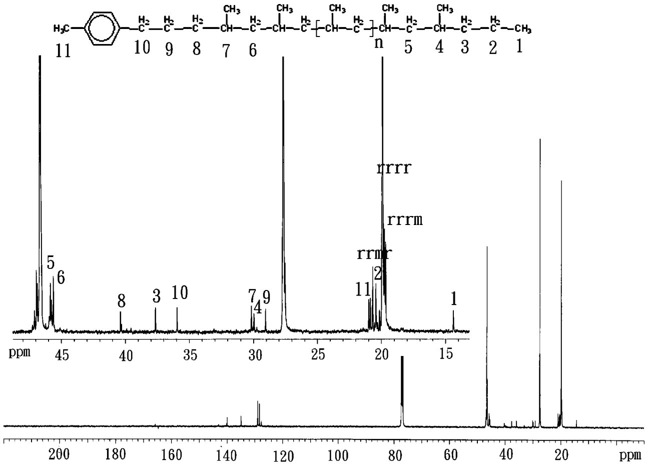


**Figure 2.** $^{13}C$ NMR spectrum (100 MHz) of a pMS-capped sPP sample ($M_n$ = 1900 g/mol, prepared by conducting propylene polymerization in the presence of *p*-methylstyrene, hydrogen, and $Me_2C(Cp)(Flu)ZrCl_2$ catalyst at 60 °C) (solvent, $CDCl_3$; temperature 60 °C).

**End-Group Analyses of the pMS-Capped sPP.** End-group analyses provide the direct evidence for the successful preparation of pMS-capped sPP. Figure 1 shows the $^1H$ NMR spectrum (with an inset of the expanded region and chemical shift assignments) of a low molecular weight sample of pMS-capped sPP[20] ($M_n$ = 1900, $M_w/M_n$ = 1.62). As shown in Figure 1, in addition to three major peaks ($\delta$ = 0.80, 1.01, and 1.58) corresponding to $CH_3$, $CH_2$, and $CH$ proton absorptions of the sPP backbone, there are three sets of weak chemical absorptions at 2.31, 2.53, and 7.08 ppm, which correspond to the $-CH_2-C_6H_4-CH_3$, $-CH_2-C_6H_4-CH_3$, and $-CH_2-C_6H_4-CH_3$ absorptions of the pMS end group, respectively. The triplet coupling pattern of benzylic proton absorption ($-CH_2-CH_2-C_6H_4-CH_3$) at 2.53 ppm directly indicates the following facts. First, the pMS is situated at the chain end position as a terminal group. Second, the incorporation of pMS is via a 2,1-insertion pathway. If the incorporation of pMS were by 1,2-insertion or by copolymerization, the resulting benzylic proton absorption should appear as a much more complicated coupling pattern. Figure 3 shows the $^{13}C$ NMR spectrum (with an inset of the expanded upfield region and chemical shift assignments) of a low molecular weight pMS-capped sPP sample ($M_n$ = 1900, $M_w/M_n$ = 1.62). The detailed $^{13}C$ chemical shift assignments are based on the structural information revealed in 2-D $^1H$ and $^{13}C$ NMR (Figure 3) and $^{13}C$ (DEPT 135) NMR spectra (Figure 4) and by comparison with prior NMR analyses of sPP.[21] In addition to three strong absorptions ($\delta$ = 19.9, 27.6, and 46.4) corresponding to $CH_3$ (rrrr), $CH$, and $CH_2$ absorptions of the sPP backbone, the chain end structures have been fully identified (Figure 2). These NMR spectra clearly reveal that the pMS-capped sPP has an aromatic chain end ($-CH_2-CH_2-C_6H_4-$

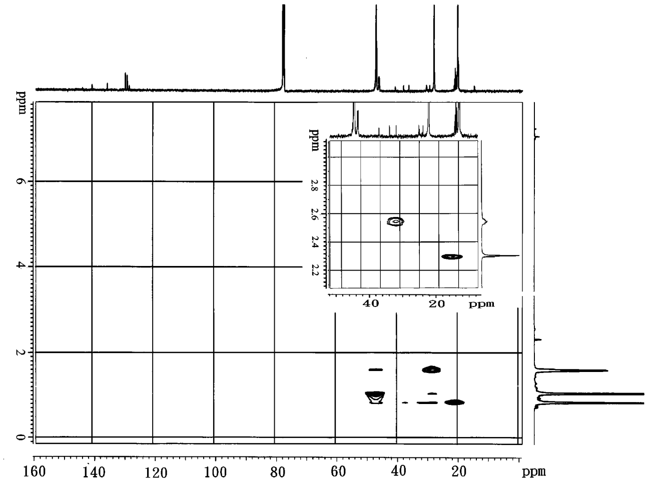


**Figure 3.** 2-D $^{1}H$ (400 MHz) and $^{13}C$ (100 MHz) NMR of a pMS-capped sPP sample ($M_n$ = 1900 g/mol, prepared by conducting propylene polymerization in the presence of *p*-methylstyrene, hydrogen, and $Me_2C(Cp)(Flu)ZrCl_2$ catalyst at 60 °C) (solvent, $CDCl_3$; temperature 60 °C).

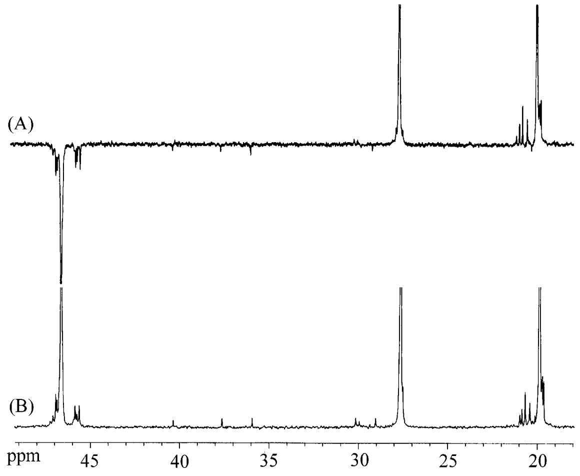
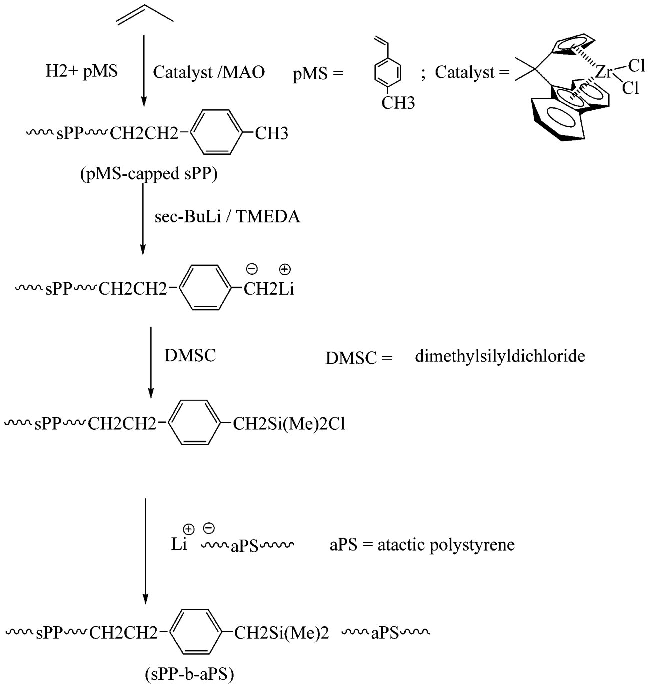


**Figure 4.** $^{13}C$ and $^{13}C$ (DEPT 135) NMR spectra (100 MHz) of a pMS-capped sPP sample ($M_n$ = 1900 g/mol, prepared by conducting propylene polymerization in the presence of *p*-methylstyrene, hydrogen, and $Me_2C(Cp)(Flu)ZrCl_2$ catalyst at 60 °C) (solvent, $CDCl_3$; temperature 60 °C).

$CH_3$) which is generated in the chain-transfer reaction by the 2,1-insertion of pMS followed by hydrogen addition and an aliphatic chain end ($-CH_2-CH_2-CH_3$) which is generated in the chain-initiation reaction by hydride 1,2-insertion to propylene. Theses results clearly reveal that using $Me_2C[(Cp)(Flu)]ZrCl_2$ as catalyst for the preparation of pMS-capped sPP not only facilitates the successful control in stereoregularity but also give pMS-capped sPP with specific chain end structures because the pMS-capped sPP has been prepared by involving a clean chain-initiation reaction, a clean chain-termination reaction, and a syndiospecific chain-propagation reaction.

**Preparations of Diblock Copolymers and Their Self-Assembly Studies.** The terminal pMS of the pMS-capped sPP can be used as a reactive functional group for preparations of block copolymers, since it can be treated with strong bases to provide the highly reactive lithiated anion ($sPP-CH_2-CH_2-C_6H_4-CH_2Li$); thus, the lithiated anion can be used directly for conducting anionic polymerizations for preparations of diblock copolymers. However, living block copolymerization by directly using the insoluble lithiated anion to conduct heterogeneous copolymerization would result in the generation of block copolymers with undesired broad MWDs.[15] To overcome this problem, the nucleophilic lithiated anion was converted to an electrophilic functional group by reacting with $Me_2SiCl_2$ (DMSC); thus, the silyl chloride-capped sPP [$sPP-CH_2-CH_2C_6H_4-CH_2-Si(Me)_2Cl)$] can be generated accordingly and be used to couple with living anionic polystyrene, which can be easily prepared with a predetermined chain length and a narrow MWD by living anionic polymerization, to provide the block copolymer. Consequently, sPP-*b*-aPS with a narrow MWD aPS block can be precisely prepared. The detailed synthetic route for preparations of sPP-based diblock copolymers is illustrated in Scheme 1. In our preparation of the sPP-*b*-PS (**1**), a sPP-*t*-pMS sample [$M_n$ = 11 000, $M_w/M_n$ = 2.07, syndiotacticity[19] (rrrr) = 92%; entry $A_3$ in Table 1] was treated with 2-BuLi/TMEDA in cyclohexane at room temperature to produce the highly reactive lithiated anion. Accordingly, the generated lithiated anion was allowed to react with excess DMSC to produce the silyl chloride end-capped sPP. After removing the volatile DMSC under vacuum, the silyl chloride end-capped sPP was charged with the excess of the freshly prepared living anionic polystyrene for conducting coupling reaction. The resulting polymer mixture was extracted first with boiling acetone to remove the excess polystyrene. The acetone insoluble fraction was collected and allowed to undergo the second Soxhlet extraction with heptane for removing the unused pMS-capped sPP (soluble in heptane) to provide the pure sPP-*b*-aPS copolymer **1** ($M_n$ = 18 500, $M_w/M_n$ = 1.38). Proton NMR analyses of different fractions of extraction products can be found in the Supporting Information. Figure 5 compares the GPC elution curves of the starting pMS-capped sPP ($M_n$ = 11 000, $M_w/M_n$ = 2.07) and polystyrene ($M_n$ = 9800, $M_w/M_n$ = 1.05) with the diblock copolymer **1** ($M_n$ = 18 500, $M_w/M_n$ = 1.38). Interestingly, the resulting sPP-*b*-aPS (**1**) has a relatively narrower MWD ($M_w/M_n$ = 1.38) as compared to the starting pMS-capped sPP ($M_w/M_n$ = 2.07). Evidently, the coupling between the broad MWD pMS-capped sPP and the narrow MWD living aPS ($M_w/M_n$ = 1.05) results in averaging out the MWD between the crystalline sPP block and the amorphous aPS block to give diblock copolymer **1** with a relatively narrow MWD. These results clearly indicate that using the synthetic

**Scheme 1**



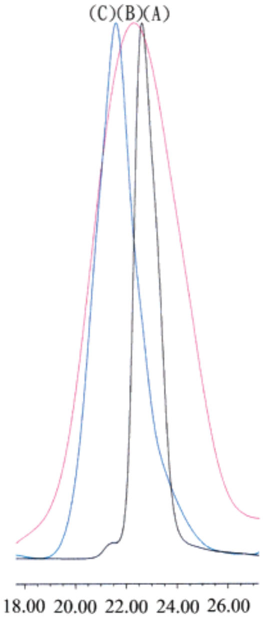


**Figure 5.** GPC curve comparison between (A) atactic polystyrene (aPS, $M_n$ = 9800 g/mol, $M_w/M_n$ = 1.05), (B) *p*-methylstyrene-capped syndiotactic polypropylene (pMS-capped sPP, $M_n$ = 11 000 g/mol, $M_w/M_n$ = 2.07), and (C) syndiotactic polypropylene-*block*-atactic polystyrene [sPP-*b*-aPS (**1**), $M_n$ = 18 500 g/mol, $M_w/M_n$ = 1.38) (solvent trichlorobenzene; temperature 135 °C).

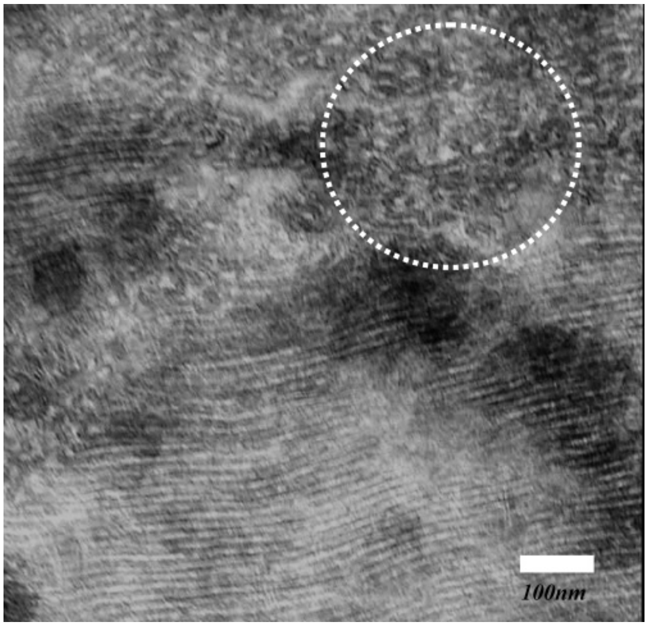


**Figure 6.** TEM micrograph of $RuO_4$-stained syndiotactic polypropylene-*block*-atactic polystyrene [PP-*b*-aPS (**1**)]: dark and white domains are for aPS and sPP, respectively. The morphology is mainly lamellar, but unidentified morphology is also found as shown in the marked circle.

methods (as illustrated in Scheme 1) can result in the successful preparations of stereoregular diblock copolymers which have narrower MWDs. Although diblock block copolymer **1** has the narrow MWD, the self-assembly of **1** (prepared by solution casting to provide a thin film which was sectioned by ultramicrotome at room temperature and examined by TEM) results in the formation of inconsistent morphologies. As shown in Figure 6, the TEM image shows the formation of the lamellar morphology as the major microstructure, but inconsistent morphologies are also present as shown in the area of the marked circle. We believe that the formation of inconsistent microstructures is due to the fact that the starting pMS-capped sPP has a broad range of molecular weight distribution ($M_w/M_n$ = 2.07); thus, copolymer **1** is unable to self-organize into a consistent nanopattern, since it does not have a uniform block length in the sPP block for providing uniform domain sizes and morphological boundaries.[12]

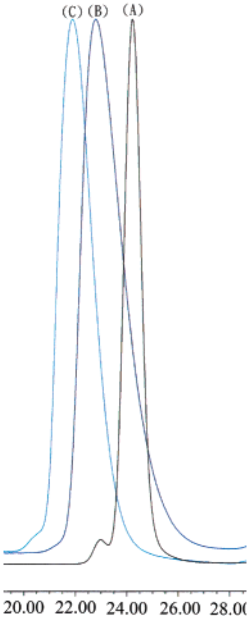


**Figure 7.** GPC curve comparison between (A) atactic polystyrene (aPS, $M_n$ = 7400 g/mol, $M_w/M_n$ = 1.06), (B) *p*-methylstyrene-capped syndiotactic polypropylene (pMS-capped sPP, $M_n$ = 8900 g/mol, $M_w/M_n$ = 1.66), and (C) syndiotactic polypropylene-*block*-atactic polystyrene [sPP-*b*-aPS (**2**), $M_n$ = 16 700 g/mol, $M_w/M_n$ = 1.29) (solvent trichlorobenzene; temperature 135 °C).

Fortunately, a narrower MWD pMS-capped sPP can be obtained by conducting Soxhlet extraction of the original pMS-capped sPP in various solvents.[22] For example, Soxhlet extraction of the pMS-capped sPP sample ($M_n$ = 11 000, $M_w/M_n$ = 2.07; entry $A_3$ of Table 1) in MEK provides a lower molecular weight pMS-capped sPP sample with a narrower range of MWD ($M_n$ = 8900, $M_w/M_n$ = 1.66, rrrr = 82%) in the MEK soluble fraction. Although we can isolate different pMS-capped sPP samples by subsequent extraction of the MEK insoluble fraction using different solvents (e.g., THF, cyclohexane, heptane, etc.), we typically use the sample isolated in the MEK soluble fraction because it has a narrower MWD and a higher solubility in common organic solvents for conducting subsequent reactions. Thus, by using this narrower MWD pMS-capped sPP sample as the starting material to conduct block copolymerization by following the synthetic procedures elucidated in Scheme 1, we have successfully prepared sPP-*b*-aPS (**2**) ($M_n$ = 16 700, $M_w/M_n$ = 1.29). Figure 6 compares the GPC elution curves of the starting pMS-capped sPP ($M_n$ = 8900, $M_w/M_n$ = 1.66) and polystyrene ($M_n$ = 7400, $M_w/M_n$ = 1.06) with **2**. The successful preparation of **2** can be further elucidated by NMR analyses. Figure 7 compares the $^1$H NMR spectra of the pMS-capped sPP with **2**. As in Figure 7b, new resonances at chemical shifts between 6.3 and 7.2 ppm and between 1.4 and 1.9 correspond to the aromatic and aliphatic protons of the PS block; meanwhile, new resonances at chemical shift around 0.05 ppm correspond to the methyl protons of the dimethylsilane linkage [$-Si(CH_3)_2-$]. Figure 8 shows the TEM image of nanopatterns formed by the self-assembly of diblock copolymer **2** in bulk. Unlike **1**, diblock copolymer **2** successfully self-organizes into a consistent lamellar structure as revealed by the TEM image (small-angle X-ray studies on the crystallization behavior of the

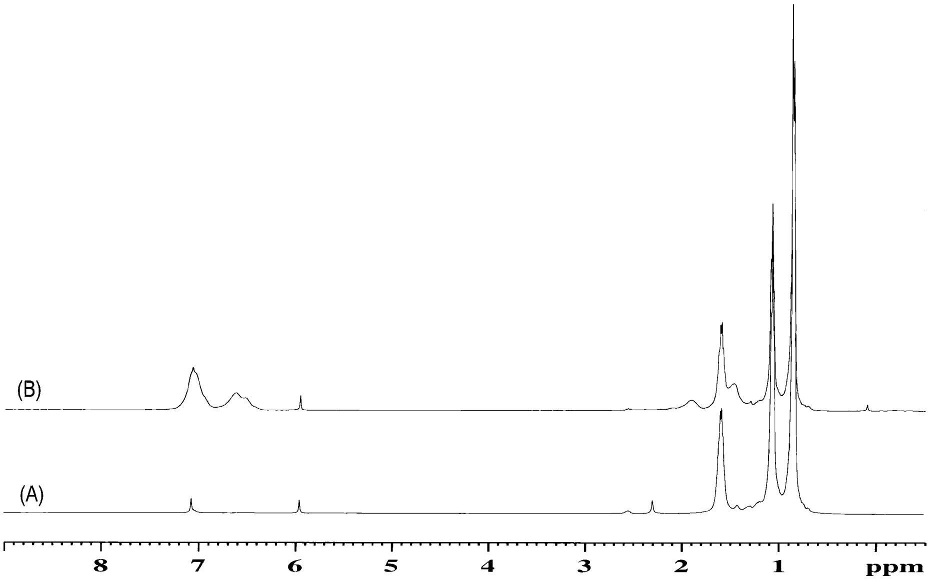


**Figure 8.** $^1$H NMR spectra (400 MHz) of (A) *p*-methylstyrene-capped syndiotactic polypropylene (pMS-capped sPP, $M_n = 8900$ g/mol, $M_w/M_n = 1.66$) and (B) syndiotactic polypropylene-*block*-atactic polystyrene [sPP-*b*-aPS (**2**), $M_n = 16\,700$ g/mol, $M_w/M_n = 1.29$) (solvent, $C_2D_2Cl_4$; temperature 110 °C).

**Table 2. Syntheses and Self-Assembly Studies of Syndiotactic Polypropylene-*block*-Atactic Polystyrene (sPP-*b*-aPS) Diblock Copolymers with Different Volume Fractions[a]**

| sPP-*b*-aPS | pMS-*c*-sPP Mn (PDI)[b] | aPS $M_n$ (PDI) | block $M_n$ (PDI) | volume fraction (sPP) | morphology[c] |
|---|---|---|---|---|---|
| **1** | 11000 (2.07) | 9800 (1.05) | 18500 (1.38) | 0.56 | lamellar |
| **2** | 8900 (1.66) | 7400 (1.06) | 16700 (1.29) | 0.58 | lamellar |
| **3** | 8500 (1.96) | 17600 (1.03) | 25400 (1.33) | 0.35 | cylindrical |
| **4** | 6400 (1.30) | 12900 (1.03) | 20200 (1.08) | 0.35 | cylindrical |

[a] sPP-*b*-aPS samples were prepared by the method illustrated in Scheme 1. [b] $M_n$ (number-average molecular weight), $M_w$ (weight-average molecular weight), and PDI (polydispersity, $M_w/M_n$) were determined by high-temperature GPC (solvent, trichlorobenzene; temperature, 135 °C). [c] Morphologies of the self-organized nanopatterns were determined by TEM.

sPP block of copolymer **2** can be found in the Supporting Information). We have to point out that both copolymers **1** and **2** were prepared by similar reaction procedures; they were even prepared from the same pMS-capped sPP sample ($A_3$, Table 1). The detailed structural differences between copolymers **1** and **2** are summarized in Table 2. As shown in Table 2, the most prominent difference between **1** and **2** is that diblock copolymer **1** was directly prepared from a broad MWD metallocene-mediated reaction product ($A_3$), and in contrast, diblock copolymer **2** was prepared from a narrower MWD pMS-capped sPP sample which was isolated from the MEK soluble fraction of $A_3$. These results clearly reveal that a narrow MWD block copolymer (e.g., diblock copolymer **1**) may not be good enough for displaying consistent nanopatterns because it requires each block within the block copolymer to have uniform chemical structures and narrow MWDs to display consistent nanopatterns. In other words, we need to ensure that each individual block of the block copolymer has been precisely prepared (uniform chemical structures and narrow MWDs) if the resulting block copolymer will be used in self-assembly studies.

The importance of precisely preparing the diblock copolymer with both a narrow MWD sPP block and a narrow MWD aPS block can be further demonstrated in our effort to prepare sPP-*b*-aPS (**3**) and (**4**), which were designed and synthesized to have lower volume fractions (i.e., 35%) in the sPP blocks for displaying cylindrical morphology. The detailed structural information on copolymers **3** and **4** are summarized in Table 2. In the preparation of diblock copolymer **3** ($M_n = 25\,400$, $M_w/M_n = 1.33$), a broad MWD pMS-capped sPP sample ($M_n = 8500$, $M_w/M_n = 1.96$; entry $D_1$ of Table 1) was used to conduct the coupling reaction with living anionic polystyrene ($M_n = 17\,600$, $M_w/M_n = 1.03$). In contrast, in the preparation of **4** ($M_n = 20\,200$, $M_w/M_n = 1.08$), a narrower MWD pMS-capped sPP ($M_n = 6400$, $M_w/M_n = 1.30$), which was isolated from the MEK soluble fraction of $D_1$, was used to conduct the coupling reaction with living anionic polystyrene ($M_n = 12\,900$, $M_w/M_n = 1.03$). Although both **3** and **4** have been prepared by identical methods, both have similar volume fractions in the sPP and aPS blocks and both have narrow MWDs; they display different nanopatterns in the self-organized microphase separation. Thus, self-assembly of sPP-*b*-aPS **4** leads to the formation of the continuous cylindrical morphology as revealed by TEM analyses. In contrast, diblock copolymer **3** only displays inconsistent microstructures (as shown in the Supporting Information). Consequently, we prove that the stereoregular crystalline−amorphous diblock copolymer, sPP-*b*-aPS, prepared by using metallocene catalyst to induce the stereoregularity control, is able to self-organize into ordered nanopatterns if the copolymer is precisely prepared to have a uniform chemical structure and narrow MWDs in both the crystalline sPP and the amorphous aPS blocks.

## Conclusion

Our results demonstrate that the $[Ph_2C(Cp)(Flu)ZrCl_2]$ catalyst induces the syndiospecific propylene polymerization as well as the selective chain transfer reaction to pMS and hydrogen, and this leads to the successful preparation of the pMS-capped sPP as an end-functionalized prepolymer. The pMS functional group of the prepolymer can undergo subsequent deprotonation and silylation reactions to produce the silyl chloride-end capped sPP. Consequently, coupling the silyl chloride end-capped sPP with living anionic polystyrene produces the novel sPP-based diblock copolymer (sPP-*b*-aPS). Although the sPP-*b*-aPS prepared by the method described in this report typically shows a narrow range of molecular weight distribution, it may not be suitable for self-assembly studies because the sPP block of the diblock copolymer was prepared using a nonliving metallocene catalyst that typically leads to the generation of the sPP prepolymer with a broad range of molecular weight distribution. To obtain a

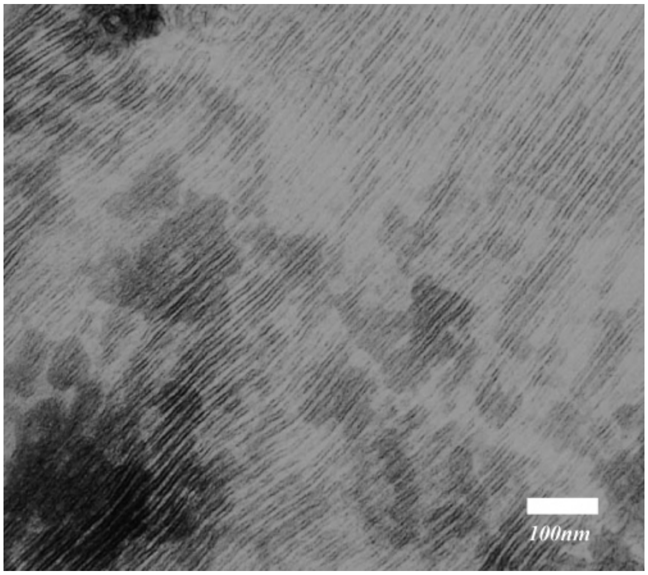


**Figure 9.** TEM micrograph of $RuO_4$-stained syndiotactic polypropylene-*block*-atactic polystyrene [sPP-*b*-aPS (**2**)]: dark and white domains are for aPS and sPP, respectively. The morphology is consistently lamellar.

suitable sample for self-assembly studies, precise control in molecular weight distribution for providing uniform domain sizes in the sPP block is required. Fortunately, a narrow MWD pMS-capped sPP sample can be isolated by physical separation method (Soxhlet extraction); thus, using the narrow MWD pMS-capped sPP prepolymer to undergo the subsequent block copolymerization provides a successful sPP-*b*-aPS sample for self-assembly studies. These results open the opportunity for preparations of various architectures of block copolymers, which are able to self-organize into ordered nanopatterns, using the versatile metallocene synthetic tools. Efforts for preparations of other stereoregular crystalline−amorphous diblock copolymers by methods developed in this research are currently underway.

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**Supporting Information Available:** $^1$H NMR spectra of pMS-capped sPP, SAXS profiles of PS−sPP, and TEM micrographs of sPP-*b*-aPS. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Recent reviews about block copolymers: (a) Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block Copolymers: Synthetic Strategies, Physical Properties and Applications*; John Wiley and Sons: New York, 2003. (b) Alexandridis, P.; Lindman, B. *Amphiphilic Block Copolymers: Self-Assembly and Applications*; Elsevier: Amsterdam, 2000. (c) Calleja, F. J. B.; Roslaniec, J. *Block Copolymers*; Marcel Dekker: New York, 2000.

(2) (a) Ho, R. M.; Chung, T. M.; Tsai, J. C.; Kuo, J. C.; Hsiao, B. S.; Sics, I. *Macromol. Rapid Commun.* **2005**, *26*, 107−111. (b) Zhu, L.; Mimnaugh, B. R.; Ge, Q.; Quirk, R. P.; Cheng, S. Z. D.; Thomas, E. L.; Lotz, B.; Hsiao, B. S.; Yeh, F.; Lin, L. *Polymer* **2001**, *42*, 9121−9131. (c) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525−557. (d) Ryan, A. J.; Hamley, I. W.; Bras, W.; Bates, F. S. *Macromolecules* **1995**, *28*, 3860−3868. (e) Zhu, L.; Chen, Y.; Zhang, A.; Calhoun, B. H.; Chun, M.; Quirk, R. P.; Cheng, S. Z. D.; Hsiao, B. S.; Yeh, F.; Hashimoto, T. *Phy. Rev. B* **1999**, *60*, 10022−10031.

(3) (a) Ho, R. M.; Chiang, Y. W.; Tsai, C. C.; Lin, C. C.; Ko, B. T.; Huang, B. H. *J. Am. Chem. Soc.* **2004**, *126*, 2704−2705.

(4) (a) Morton, M. *Anionic Polymerization: Principle and Practice*; Academic Press: New York, 1983. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principle and Practical Applications*; Marcel Dekker: New York, 1996.

(5) (a) Matyjaszewski, K. *Control Radical Polymerization*; ACS Symposium Series Vol. 685; American Chemical Society: Washington, DC, 1998. (b) Davis, K. A.; Matyjaszewski, K *Statistical, Gradient, Block and Graft Copolymerization by Controlled/Living Radical Polymerizations*; Springer: New York, 2002.

(6) (a) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265−272. (b) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 2228−2230. (c) Matyjaszewski, K. *Cationic Polymerization: Mechanism, Synthesis and Application*; Marcel Dekker: New York, 1996.

(7) Webster, O. W.; Anderson, B. C. Group Transfer Polymerization. In *New Methods for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum Press: New York, 1992; pp 1−32.

(8) (a) Gillion, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733−742. (b) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907−915. (c) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346−6347.

(9) (a) Razavi, A.; Ferrara, J. *J. Organomet. Chem.* **1992**, *435*, 299−310. (b) Resconi, L.; Piemontesi, F.; Gamurati, I.; Sudmeijer, O.; Nifant'ev, I. E.; Ivchenko, P. V.; Kuz'mina, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 2308−2321.

(10) Brandsma, L.; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: Berlin, 1987; Vol. 1, pp 3−18.

(11) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142−3145.

(12) Lynd, N. A.; Hillmyer, M. A. *Macromolecules* **2005**, *38*, 8803−8810.

(13) (a) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4019−4020. (b) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 8791−8802.

(14) (a) Lu, B.; Chung, T. C. *Macromolecules* **1999**, *32*, 2525−2533. (b) Xu, G.; Chung, T. C. *Macromolecules* **1999**, *32*, 8689−8692. (c) Lu, B.; Chung, T. C. *Macromolecules* **1998**, *31*, 5943−5946.

(15) (a) Dong, J. Y.; Chung, T. C. *J. Am. Chem. Soc.* **2001**, *123*, 4871−4876. (b) Dong, J. Y.; Manias, E.; Chung, T. C. *Macromolecules* **2002**, *35*, 3439−3447.

(16) *p*-Methylstyrene end-capped isotactic PP has been prepared by T. C. Chung and co-workers (see refs 14, 15, and 17).

(17) Kandil, U.; Chung, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1858−1872.

(18) In our efforts to synthesize the *p*-methylstyrene end-capped sPP (by selective chain transfer reaction), several syndiospecific metallocene catalysts, including $Me_2Si(Cp)(Flu)ZrCl_2$, $Ph_2Si(Cp)(Flu)ZrCl_2$, $Me_2C(Cp)(Flu)ZrCl_2$, and $Ph_2C(Cp)(Flu)ZrCl_2$, have been tested. Our experimental results indicate that the selective chain transfer reaction, which leads to the generation of pMS-capped sPP, is highly dependent on the bridging atom of the metallocene catalysts. For example, both of the silicon-bridged metallocene catalysts are unable to provide any pMS incorporated sPP polymer. In contrast, both of the carbon-bridged metallocene catalysts are capable of inducing the selective chain transfer reaction for generation of the pMS-capped sPP. Our report is based on the polymerization product generated by using $Me_2C(Cp)(Flu)ZrCl_2$, since the catalyst has a higher polymerization activity for the production of pMS-capped sPP.

(19) (a) Zambelli, A.; Locatelli, T.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267−270. (b) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 564−573.

(20) This low molecular weight pMS-capped sPP was prepared at a higher polymerization temperature (60 °C) and under higher concentration of pMS (50 mmol) and lower propylene pressure (2 atm) comparing with the polymerization conditions (e.g., entry $A_3$) listed in Table 1.

(21) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.

(22) Fractionation of PP by extraction with different solvents has been reported before: Hu, Y.; Krejchi, M. T.; Shah, C. D.; Myers, C. L.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 6908−6916.

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