Stereoblock Polypropylenes Prepared by Efficient Chain Shuttling Polymerization of Propylene with Binary Zirconium Catalysts and iBu$_3$Al

Xiao Yin$^a$, Huan Gao$^a$, Fei Yang$^a$, Li Pan$^a$, Bin Wang$^a$, Zhe Ma$^a$, and Yue-Sheng Li$^{a,b}$

$^a$ Tianjin Key Lab of Composite & Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China
$^b$ Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

**Abstract** Stereoblock polypropylenes bearing isotactic, atactic, and syndiotactic polypropylene segments were successfully prepared by dry methyl aluminoxane activated binary catalysts system, Ph$_2$CFluCpZrCl$_2$ and (Me$_5$Si(2,5-Me$_2$-3-(2-MePh)-cyclopentol(2,3-b)thiophen-6-yl))ZrCl$_2$, in the presence of iBu$_3$Al as a chain shuttling agent. By studying the catalyst activity, chain transfer efficiency, and reversibility of chain transfer reaction of each catalyst system, as well as the molecular weight and polydispersity of the resulting polymers, the alkyl exchange reactions between the zirconium catalyst and different main-group metal alkyl were estimated, respectively. Based on the optimized react condition, the chain shuttling polymerization was conducted by binary catalyst system in the presence of iBu$_3$Al under both atmospheric and high pressure. Resultant polymers were identified as stereoblock polypropylenes according to microstructure and physical properties analyses by $^{13}$C($^1$H)-NMR, DSC, and GPC.

**Keywords** Stereoblock polypropylene; Chain shuttling polymerization; Zirconium catalyst; Chain transfer reaction

**Citation:** Yin, X.; Gao, H.; Yang, F.; Pan, L.; Wang, B.; Ma, Z.; Li, Y. S. Stereoblock polypropylenes prepared by efficient chain shuttling polymerization of propylene with binary zirconium catalysts and iBu$_3$Al. *Chinese J. Polym. Sci.* **2020**, *38*, 1192–1201.

**INTRODUCTION**

Polypropylene (PP), as one of the important families of polyolefin resins, can be molded or extruded into many plastic products in which toughness, flexibility, light weight, and heat resistance are required. Essentially, the pendant methyl group (CH$_3$) can adopt a number of tacticities, or spatial arrangements in relation to the carbon main-chain, but in practice only the isotactic form is marketed in significant quantities.$^{[1]}$ Since its discovery in 1954 by Giulio Natta and co-workers,$^{[2]}$ as a crystalline thermoplastic with a melting point of approximately 170 °C, isotactic polypropylene (iPP) keeps on sparking the curiosity of chemists on account of its strong tensile strength and low cost. However, the poor impact strength and brittleness greatly limit the application of iPP. Therefore, modification of iPP with improved physical performance has attracted wide attention.$^{[3,4]}$ Considering that the stereochemistry of polyolefins strongly influences their properties, PP consisting of blocks of low-isotactic (soft block) and high-isotactic/syndiotactic (hard block) will be a promising thermoplastic elastomer with improved toughness. Benefitting from the invention of very efficient catalyst systems and development of polymerization techniques, the syntheses of novel polyolefins with various stereoblocks and peculiar physical properties have been realized via different ways. As a representative example, Sita et al. provided different tactics that used living catalyst with sequential monomer feed or carried out degenerative chain transfer polymerization to gain the well-controlled isotactic-atactic stereoblock architecture.$^{[5]}$ A strategy entails the use of unbridged “oscillating” metallocene catalysts, which causes reversible isomerization between different coordination geometries, leading to corresponding changes of chemical selectivity.$^{[6−11]}$ However, achieving precise control of the molecular structure via this approach turned out to be tremendously difficult.$^{[12]}$ Homogeneous binary catalyst systems have also been investigated to prepare blend that contained the stereoblock fraction.$^{[13−17]}$ As the most efficient and economic approach, chain shuttling polymerization for syntheses of various copolymers containing alternating soft and hard segments which can complement each other’s advantages was reported by Arriola and co-worker in 2006.$^{[18]}$ The olefin block copolymers produced by this approach exhibit excellent elastomeric properties and have been continuously industrialized. In addition to regulating the molecular weight of the polymer and achieving atom economy, chain transfer polymerization with alkyl metal compounds can also perform functionalization of the products and control the
insertion rate of comonomer. In the past ten years or so, the endeavor to generate olefin multiblock copolymer via chain shuttling polymerization has been burgeoning, in which unrepresented block copolymers based on linear and branched polyethylene, regio/stereo-selective polystyrene, and conjugated dienes have been easily obtained. To date, only several stereoblock PPs have been obtained by chain shuttling polymerization with two specific catalysts in the presence of trimethyl aluminum (TMA), triethyl aluminum (TEA), or diethylzinc (DEZ) as a chain shuttling agent (CSA), respectively. However, the intriguing stereoblock PPs are still sought after because of their outstanding properties, great application potential, and attractive cost advantage.

In this work, on the base of previous literatures on the chain transfer reaction of propylene polymerization, the effect of various chain transfer agents on catalyst activities, chain transferability, molecular weight, and molecular weight distribution in stereospecific polymerization of propylene were studied. Two catalysts, Ph₂C(Flu)ZrCl₂ (Cat. 1) and (Me₃Si)(2,5-Me₂-3-(2-MePh)-cyclopentono[2,3-b]-thiophen-6-yl)₂-ZrCl₂ (Cat. 2), were selected to produce stereoselective PPs. A detailed and systematic study on chain shuttling polymerization of the above mentioned dual catalyst system was carried out.

EXPERIMENTAL

General Considerations

All water- and air-sensitive operations were performed under nitrogen with standard Schlenk techniques or in a MBraun glovebox. Toluene was purified by Etelux solvent purification system. Commercial propylene (99.99%) for polymerization was purified by a gas purification system (O₂ ≤ 0.1 ppm, H₂O ≤ 0.1 ppm). Methylaluminoxane (MAO, 10 wt% in toluene) was purchased from Acros and the free trimethyl aluminum was removed prior to polymerization. Trimethylaluminum (Me₃Al), triisobutyl aluminum (iBu₃Al), and diethylzinc (Et₂Zn) were obtained from Acros and used as received. Cat. 1 was purchased from Innochem, and Cat. 2 was synthesized according to literature.

Propylene Polymerization

Coordination chain transfer polymerizations of propylene were carried out in a 150 mL glass reactor equipped with a magnetic stirrer under atmospheric pressure or in a 250 mL autoclave under high pressure. Under propylene atmosphere, prescribed volume of toluene, dry methylalumoxanene (dMAO), and chain transfer agents were sequentially added to the reaction bottle filled with propylene. After stirring for 5 min, the polymerization reaction was initiated by the addition of a catalyst solution. After a required period, ethanol was added to terminate the polymerization. Then, the polymers were precipitated from acidified ethanol, filtered, washed repeatedly with ethanol, and dried to constant weight in vacuum at 70 °C.

Characterization

The high-temperature ¹³C(¹H)-NMR and ¹H-NMR data of polymers were collected by a Bruker AM-400 spectrometer at 120 °C with 1,1,2,2-tetrachloroethane-d₂ as a solvent; the d₁ time for instance was 4. The glass transition temperature (Tg) and melting point (Tm) were determined from the second heating and the first cooling curves obtained by the differential scanning calorimetry (DSC), on a TA Instruments Q2000 calorimeter under a nitrogen atmosphere, at a heating or cooling rate of 10 °C/min under a nitrogen atmosphere. The molecular weights (Mn) and the molecular weight distributions (Mw/Mn) of the polymer samples were determined by a PL-GPC 220 type high-temperature gel permeation chromatography apparatus at 150 °C. The elute solvent was 1,2,4-trichlorobenzene (TCB) stabilized with 0.0125% BHT at a flow rate of 1.0 mL/min and the standard sample was Easi-Cal PS-1 (PL Ltd.). Tensile property of samples was tested by an Instron 5969 Machine using ISO 527-1 as a standard with a tensile rate of 50 mm/min. The polypropylene cut into dumbbell-shaped samples was hot-compressed into the sheets with a thickness of 0.5 mm. To ensure accurateness and repeatability, five duplicate experiments were performed.

RESULTS AND DISCUSSION

As shown in Scheme 1, two zirconium complexes with different stereoselectivities toward propylene polymerization were first synthesized according to previous literatures. The commercially available Cat. 1, Ph₂CF₆u/ZrCl₂, was reported to be temperature sensitive that gave syndiotactic PP at low reaction temperature and yielded amorphous PP at elevated temperature. This catalyst was chosen to synthesize a relatively soft PP segment. On the other hand, Cat. 2, (Me₃Si)(2,5-Me₂-3-(2-MePh)-cyclopentono[2,3-b]-thiophen-6-yl)₂-ZrCl₂, was proved to be an isospecific catalyst for producing iPP with strong crystallization ability. It is noteworthy that both the catalysts are non-living catalysts with myriad of chain transfer reactions. Before the chain transfer agent was added, terminal double bonds formed by both β-β-hydride elimination and β-methyl elimination to metal or to monomer were identified from ¹H-NMR spectra of PP obtained by the dMAO activated Cat. 1 (entry 1 in Table 1) and 2 (entry 2 in Table 2), respectively, as shown in Fig. 54 (in the electronic supplementary information, ESI). The portion of terminal alkenyl group for each catalyst system could be easily calculated based on previously reported method, which is 1.3 mol% and 2.0 mol% for PP system.
from Cat. 1 and Cat. 2, respectively. Similar to the previous reports, chain transfer to alkyl aluminum overwheels other chain transfer modes in presented propylene polymerization using individual catalyst systems.\cite{39,40} Once a large amount of chain transfer agent was added, chain transfer to the alkyl metal would certainly be the dominant chain transfer mode. According to previous reports, the steric repulsion and relative strength of metal-carbon bond play vital roles in the chain transfer efficiency, catalytic activity, reversibility of the transfer reaction, and molecular weight of the resulting polymers.\cite{41,42} To probe the potential of constructing the stereoblock polypropylenes by Cat. 1 and Cat. 2, chain transfer reactions of each catalyst were conducted and estimated as follows.

### Chain Transfer in Polymerization of Propylene by Using a Single Catalytic System

Activated with 1500 equivalents of dried MAO (dMAO), propylene polymerization was conducted at 70 °C in the presence of different main group alkyl metals, including Me$_3$Al, Et$_2$Zn, and iBu$_3$Al. Results of polymerization are summarized in Tables 1 and 2.

In the absence of a chain transfer agent, Cat. 1 activated by dMAO showed high activity for the polymerization of propylene, giving PP with a glass transition temperature ($T_g$) around $-2.3$ °C and weight-average molecular weight ($M_w$) of $8.1 \times 10^4$ (Table 1). The low $T_g$ of PP reflected a low tacticity of the resulting PP, as reported previously in literature.\cite{43,44} $M_w$ decreased to $3.2 \times 10^4$ when 10 equivalents of Et$_2$Zn was added and further decreased to $2.2 \times 10^4$ as the dosage of Et$_2$Zn was doubled, indicating that a significant chain transfer reaction occurred. However, the productivity also drastically decreased with the increasing amounts of Et$_2$Zn, showing that the rather strong action between Et$_2$Zn and the active species affected the chain propagation.\cite{44,45}

Differently, the polymerization activity was enhanced by addition of 50 equivalents of Me$_3$Al, and only slight decrease in activity was observed even the dosage of Me$_3$Al was increased to 100 equivalents of the catalyst. A similar decrease in $M_w$ was observed, while the polydispersity index (PDI) remained almost unchanged, indicative of a successful chain transfer to Me$_3$Al. Chain transfer reaction in the presence of iBu$_3$Al was quite similar to that of Me$_3$Al, where an evident increase in activity and reduction in molecular weight could be observed as the dosage of iBu$_3$Al increased. Compared with the result of entry 1, the number of chains initiated by per Zr catalyst molecule (calculated based on Hong and co-workers\cite{45} was remarkably increased by adding different chain transfer agents. Among these three CTAs, iBu$_3$Al was the best candidate because of its best chain transfer efficiency (efficiency of entry 7 is almost 7 folds higher than that of entry 1 in Table 1) and ability to maintain a much higher catalytic activity (entry 7 is one time higher than entry 1). This result is similar to what has been stated previously, namely the alkyl aluminum compounds have an influence on the activity of zirconium metalloence catalysts in olefin polymerization.\cite{46,47}

Under similar reaction conditions, propylene polymerizations promoted by Cat. 2 were also conducted and the results are summarized in Table 2. As observed, Cat. 2 displayed similar high activity to that of Cat. 1, but gave PP with much lower $M_w$. A melting point of 153.8 °C can be detected, indicating an isotactic structure of the obtained PP ($[\text{mmm}] = 72$%, Fig. S1 in ESI).\cite{40} $M_w$ was decreased to $3.2 \times 10^4$ when 10 equivalents of Et$_2$Zn was added, and further decreased to $2.2 \times 10^4$ as the dosage of Et$_2$Zn was doubled, indicating that a significant chain transfer reaction occurred. However, the productivity also drastically decreased with the increasing amounts of Et$_2$Zn, showing that the rather strong action between Et$_2$Zn and the active species affected the chain propagation.\cite{43,44}
Et₂Zn was efficient (Table 2, entries 2 and 3 versus 1). When Me₃Al or iBu₃Al was used as chain transfer agents, the higher chain transfer agent dosage led to much higher activities and efficiencies. Besides, the molecular weight of the polymer decreased significantly but the molecular weight distribution remained rather narrow (2.1–2.7, Table 2). According to these observations, both Me₃Al and iBu₃Al were very good CTA candidates for the chain transfer reaction during propylene polymerization promoted by Cat. 2. It is worth noting that both the $T_0$ of atactic polypropylene (aPP) obtained by Cat. 1 and the $T_m$ of iPP from Cat. 2 were affected by the addition of different chain transfer agents. Following two reasons could account for it: one is the significant decline in $M_w$ of the polypropylene, and the other is the slight decrease in regularity led by the presence of a CTA (Table S1 in ESI). The first one is believed to play a vital role.

As a reversible chain transfer reaction is required for a successful chain shuttling polymerization, we therefore further study the reversibility of propylene chain transfer polymerization in the presence of iBu₃Al. As shown in Table 3, as the polymerization time was extended from 10 min to 40 min, the yield of PP was increased for both Cat. 1 and Cat. 2. More remarkably, an evident increase in molecular weight of the PP by Cat. 1 and Cat. 2 could be seen in Figs. 1 (a) and 1(b), respectively, while the molecular weight distribution values remained basically unchanged. This phenomenon was an evident signal of a reversible chain transfer polymerization. In other words, Zr-polymerly exchanged with an isopropyl group in iBu₃Al, and then the chains could also transfer from Al to Zr active site and continued to grow on Cat. 1 or Cat. 2, which corresponded to the mechanism of reversible chain transfer as proposed. A reduced rate in increase of $M_w$ and the slight increase in PDI (from 2.3 to 2.8) of iPP from Cat. 2 suggested a relatively low chain propagation rate compared to the chain transfer.

### Chain Shutting Polymerization of Propylene by Using Dual Complex System

Since Cat. 1 and Cat. 2 could prepare amorphous PP and isotactic PP via the reversible chain transfer polymerization under very similar conditions, the possibility of obtaining the stereoblock PP materials with alternating hard and soft blocks by chain shuttling polymerization is very high. Therefore, the chain shuttling polymerizations of the dual catalyst system with different chain transfer agents, [CTA]/[Zr] ratios, and reaction time were studied exhaustively. When propylene polymerization was carried out at a desired temperature (70 °C), the polymerization system was homogeneous and there was no precipitation of the polymer in toluene before quenching. Without the presence of Et₃Zn, Me₃Al, or iBu₃Al, the polymerization activity of the mixed Cat. 1 and Cat. 2 decreased slightly compared to that of the single catalyst system, indicating that a possible interaction between the two catalysts might occur and thus inhibited the catalytic activity. $T_m$ of 157 °C of the polymer can be observed, which is very close to that of iPP obtained by Cat. 2. When Et₃Zn, Me₃Al, or iBu₃Al was separately introduced, the polymerization activity of the system

| Entry | Cat. | Time (min) | Yield (g) | Act. $× 10^{-4}$ | $T_0^\circ$ (°C) | $T_m^\circ$ (°C) | $M_w^a × 10^{-4}$ | PDI $^d$ | Efficiency $^a$ |
|-------|------|-----------|-----------|-----------------|----------------|----------------|----------------|--------|---------------|
| 1     | 1    | 10        | 1.7       | 2.0             | −4.0           | 157            | 3.3            | 2.2    | 23            |
| 2     | 1    | 20        | 2.8       | 1.7             | −4.3           | 157            | 3.8            | 2      | 29            |
| 3     | 1    | 30        | 3.6       | 1.4             | −3.6           | 157            | 4              | 2.2    | 40            |
| 4     | 1    | 40        | 4.1       | 1.2             | −3.7           | 157            | 4.7            | 1.8    | 31            |
| 5     | 2    | 10        | 1.9       | 2.3             | 148            | 157            | 1.1            | 2.3    | 79            |
| 6     | 2    | 20        | 2.7       | 1.6             | 153            | 157            | 1.6            | 2.4    | 81            |
| 7     | 2    | 30        | 3.2       | 1.3             | 155            | 157            | 1.8            | 2.6    | 92            |
| 8     | 2    | 40        | 3.9       | 1.1             | 151            | 157            | 1.9            | 2.8    | 115           |

$^a$Polymerization conditions: $n_{Zr} = n_{CTA} = 5$ μmol, [dMAO]/[Zr] = 1500, V$_{solvent}$ = 50 mL, 70 °C, propylene pressure = $1.01 \times 10^5$ Pa. $^b$Chain shuttling polymerization. $^c$Measured by differential scanning calorimetry. $^d$Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-C₆H₄Cl₂. $^e$The number of chains initiated per catalyst.

---

**Fig. 1** Plots of $M_w$ and PDI of polymers prepared by single (a) Cat. 1/iBu₃Al catalytic system and (b) Cat. 2/iBu₃Al catalytic system against polymerization time.

https://doi.org/10.1007/s10118-020-2446-2
was much improved and comparable with that of PP obtained by the individual catalyst. In addition, the obtained products exhibited two melting points (see Fig. S17 in ESI), which were similar to those of PP obtained by single catalyst as shown in Table 2. Presence of two melting points should be ascribed to the iPP segments with different length synthesized by Cat. 2.

As evidenced by GPC traces in Fig. S18 (in ESI), a broad and bimodal molecular weight distribution of the polymers was obtained with no chain shuttling agent. It could be seen from the peak fitting that $M_w$ of peak 1 was almost the same with $M_w$ of the PP obtained by Cat. 1, but the content of high molecular weight in the mixture was low. On the other hand, peak 2 was practically the same as the GPC trace of the product gained by Cat. 2. This observation further reveals that the product obtained in the absence of chain shuttling agent was a mixture of amorphous PP and iPP (Fig. 2). Similarly, a broader, bimodal molecular weight distribution could also be observed even 10 equivalents of Et$_2$Zn was added. The two peaks obtained by the peak-separation treatment were consistent with the molecular weight and molecular weight distribution of the single catalyst system in the presence of Et$_2$Zn, indicating that no effective chain shuttling occurred between the two active species upon Et$_2$Zn (Fig. S19 in ESI).

When 50 equivalents of Me$_3$Al was added as a CSA, the molecular weight distribution changed from bimodal to unimodal, and a PDI of 3.3 was presented. According to the results of chain transfer polymerization as shown in Tables 1 and 2, as well as the identified good reversibility of chain transfer reaction as revealed by the data collected in Table 3, iBu$_2$Al was expected to show better performance as a CSA. To our delight, as observed in Fig. S18 (in ESI), only a mono-modal, narrow molecular weight distribution (PDI = 2.8) was presented. Chen et al.\cite{19} reported that the PDI is approximately equal to (1 + $k_p$/2) for the single catalyst system, where $k_p$ and $k_t$ are representative of the rate constant of propagation and transfer, respectively. Faster transfer produces polymer with PDI close to 1. The observed relatively broad molecular weight distribution (1.8–2.8) of product is mainly due to a lower chain exchange rate in the chain transfer process,$^{[19,31,50]}$ and the presence of very small amount of free Me$_3$Al originated from dMAO. Me$_3$Al may also participate in the chain transfer reaction, but show different influence on the chain transfer rate ($R_t$) and the chain propagation rate ($R_p$) compared with iBu$_2$Al.$^{[51,52]}$ When more dosage of iBu$_2$Al was adopted, $M_w$ of the obtained PP was slightly decreased, while the PDI became lower, as compared in Table 4 (entry 4 versus 5), suggesting a higher chain transfer efficiency.

Subsequently, the polymerization behavior as a function of polymerization time of Cat. 1/Cat. 2/100 equivalents of iBu$_2$Al system was studied (entries 4 and 6–8 in Table 4). As observed, the yield of PP was increased to almost two folds higher as the reaction time extended from 10 min to 40 min. It is noteworthy that $T_m$ of the polymers were also enhanced from 150 °C and 157 °C along with the extension of reaction time, which might be ascribed to an increase in the molecular weight of the obtained iPP segments. It could also be seen from Table 4 and Fig. 3 that $M_w$ of resulting polymers was increased from 1.8 × 10$^4$ to 3.1 × 10$^4$, while the PDI values remained lower than 2.9 with a unimodal distribution regardless of the extension in polymerization time. Evidently, as the reaction time increased, the low-$M_w$ portion of the polymer gradually decreased while the high-$M_w$ portion enhanced. Both the increases in $T_m$ and $M_w$ demonstrate that an effective chain shuttling occurred in this catalytic system.

To further enhance the molecular weight of resulting PP, the polymerization was also conducted under higher propylene pressure (6.06 × 10$^3$ Pa). As shown in Table 5, besides the high yields as expected, $M_w$ of the obtained PP was significantly enhanced to 17 × 10$^4$ and 12 × 10$^4$, respectively. However, the tacticity of PP catalyzed by Cat. 1 was also improved, as a $T_m$ of 111 °C could be observed. This is because of the syndiotactic PP (sPP) segment increased by the high polymerization conditions: $n_{cat, 1} = n_{cat, 2} = 2.5$ μmol, [dMAO]/[Zr] = 1500, $V_{solvent} = 50$ mL, 70 °C, propylene pressure = 1.01 × 10$^5$ Pa. a $g_{polymer}/(mol_{cat}·h)$.

Table 4 Chain shuttling polymerization using two Zr catalysts with different CSA.\textsuperscript{a}.

| Entry | Time (min) | CSA | CSA/Zr | Yield (g) | Act. $k \times 10^{-4}$ | $T_m$ (°C) | $M_w$ $\times 10^{-4}$ | PDI $^d$ |
|-------|------------|-----|--------|-----------|----------------------|-------------|---------------------|--------|
| 1     | 30         | −   | −      | 2.3       | 2.9                  | 157         | 4.8                 | 3.4    |
| 2     | 30         | Et$_2$Zn | 10     | 2.6       | 1.0                  | 144/151     | 2.3                 | 5.6    |
| 3     | 30         | Me$_3$Al | 50     | 3.0       | 1.2                  | 146/153     | 2.4                 | 3.3    |
| 4     | 30         | iBu$_2$Al | 100    | 3.9       | 1.6                  | 147/155     | 2.2                 | 2.8    |
| 5     | 30         | iBu$_2$Al | 250    | 3.5       | 1.4                  | 149/155     | 2.0                 | 2.3    |
| 6     | 10         | iBu$_2$Al | 100    | 2.2       | 2.6                  | 150         | 1.8                 | 2.3    |
| 7     | 20         | iBu$_2$Al | 100    | 2.9       | 1.7                  | 147/154     | 2.0                 | 2.5    |
| 8     | 40         | iBu$_2$Al | 100    | 4.2       | 1.3                  | 150/157     | 3.1                 | 2.9    |

\textsuperscript{a} Polymerization conditions: $n_{cat, 1} = n_{cat, 2} = 2.5$ μmol, [dMAO]/[Zr] = 1500, $V_{solvent} = 50$ mL, 70 °C, propylene pressure = 1.01 × 10$^5$ Pa. b $g_{polymer}/(mol_{cat}·h)$.

\textsuperscript{b} Measured by DSC. \textsuperscript{c} Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-C$_6$H$_3$Cl$_2$.

https://doi.org/10.1007/s10118-020-2446-2
points can be observed for entries 3–5, which are very similar to those of entries 1 and 2, respectively. Compared with the single catalyst system, the sPP portion of the polymers obtained by dual catalytic system had an identical melting enthalpy, certifying a similar low crystallization degree. On the contrary, the melting enthalpy of the iPP portion became much lower due to the hindered crystallization led by the changes in segments distribution, although the $T_m$ values became a little higher. Additionally, besides an increase in $M_w$ compared with those PPs from individual catalist, the molecular weight distribution curve of entry 4 was still unimodal with a PDI of 1.8. A further increase in molecular weight could be observed when extending the reaction time to 45 min, while the PDI remained as low as 1.9 (entry 5). All these observations prove that the stereoblock PPs have been successfully obtained via an efficient chain shuttling polymerization (CSP) process.

### Characterization of the Microstructure of Stereoblock Polypropylenes

To further verify the component of PPs, masses of fractions of the PP samples were analyzed by a fractionation experiment as shown in Table 6. The PP obtained by Cat. 1 under high pressure was completely dissolved in tetrahydrofuran solution after being refluxed for 12 h, which was the same as the polymer prepared under atmospheric pressure conditions. Moreover, the tetrahydrofuran-soluble (THF-soluble) fractions of iPP obtained under high pressure and atmospheric pressure were only 9% and 16%, respectively, indicating that tetrahydrofuran could be used as the solvent for extraction. The product obtained by Cat. 1/Cat. 2/iBu3Al system under atmospheric pressure comprised of 44% of THF-soluble portion ($M_w = 2.8 \times 10^4, M_n/M_w = 2.2$) and 56% of THF-insoluble portion ($M_w = 1.9 \times 10^4, M_n/M_w = 2$). Differences in solubility of the PP obtained by single catalyst and CSP system can further certify an absolutely different microstructure feature of these two kinds of PPs. Representative PPs were further analyzed by $^{13}$C($^1$H)-NMR spectroscopy.

### Table 5 Chain shuttling polymerization of propylene under high pressure.

| Entry | Cat. | Time (min) | iBu3Al/Zr | Yield (g) | Act. $\times 10^{-6}$ | $\Delta H$ ($J/g$) | $T_m$ (°C) | $M_w \times 10^4$ | PDI a |
|-------|------|------------|-----------|-----------|----------------------|----------------|----------|----------------|-------|
| 1     | 1    | 30         | 100       | 12.2      | 24.4                 | 13             | 111      | 17             | 1.7   |
| 2     | 2    | 30         | 100       | 13.6      | 27.2                 | 71.5           | 156      | 12             | 2.0   |
| 3     | 1+2  | 30         | 0         | 4.1       | 8.2                  | 12/35          | 111/158  | 23             | 2.0   |
| 4     | 1+2  | 30         | 100       | 7.1       | 14.2                 | 13/26          | 110/159  | 19             | 1.8   |
| 5     | 1+2  | 45         | 100       | 9.8       | 13.1                 | 13/28          | 114/161  | 19.5           | 1.9   |

Polymerization conditions: $n_{\text{cat.1}} = n_{\text{cat.2}} = 1 \mu$ mol, dMAO [Al]/[Zr] = 1500, $V_{\text{toluene}} = 100 \text{ mL}, 70 ^\circ\text{C}$, propylene pressure = $6.06 \times 10^5 \text{ Pa}$. a $n_{\text{cat.1}} = n_{\text{cat.2}} = 0.5 \mu$ mol, dMAO [Al]/[Zr] = 1500, $V_{\text{toluene}} = 100 \text{ mL}, 70 ^\circ\text{C}$, propylene pressure = $6.06 \times 10^5 \text{ Pa}$. b Measured by DSC. c Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-C$_6$H$_4$Cl$_3$.

### Table 6 Summary of results of the fractionation experiment.

| Entry | Cat. | CSA | Time (min) | THF-Sol. (%) | THF-Insol. (%) | THF-Sol. [mm] (%) | THF-Insol. [mmm] (%) |
|-------|------|-----|------------|--------------|---------------|-----------------|---------------------|
| 1     | 1    | iBu3Al | 30         | 1            | 0             | 70              | 91                  |
| 2     | 2    | iBu3Al | 30         | 0.09         | 0.91          | 7               | 88                  |
| 3     | 1+2  | iBu3Al | 30         | 0.66         | 0.34          | 72              | 86                  |
| 4     | 1+2  | iBu3Al | 45         | 0.70         | 0.30          | 63              | 76                  |
| 5     | 1    | –    | 30         | 1            | 0             | –               | –                   |
| 6     | 2    | iBu3Al | 30         | 0.16         | 0.84          | 46              | 89                  |
| 7     | 1+2  | iBu3Al | 30         | 0.44         | 0.56          | 43              | 80                  |

Fractionation conditions: tetrahydrofuran (150 mL), polymer sample of 1 g, reflux for 12 h in tetrahydrofuran; a PP prepared at high pressure; b PP prepared at atmospheric pressure; c Integral percentage, determined by $^{13}$C($^1$H)-NMR spectroscopy.

https://doi.org/10.1007/s10118-020-2446-2
spectra to identify their microstructure. As shown in Fig. 4(a), compared with the THF-insoluble sample (red line) obtained by chain shuttling polymerization with those from Cat. 1 and Cat. 2, respectively, it is apparent that a new pentad signal (δ 20.2 ppm) referring to rrr originated from shorter sPP segments appeared. As compared in Fig. 4(b), the resonance of other pentads also became stronger relative to the PP obtained from single catalyst system. These facts suggest that a stereoblock copolymer has been really produced by the chain shuttling polymerization.

Similar THF-extraction and characterization were also conducted on the chain shuttling product under high pressure condition (entries 1–4 in Table 6). The PP obtained via chain shuttling polymerization comprised of 66% of THF-soluble and 34% of THF-insoluble portion. These two portions showed a completely same molecular weight distribution curves with that of the crude PP product as shown in Fig. 5(a), with a perfectly unimodal distribution, suggesting that the fractions of molecular weight with different solubility were uniform. As shown in Fig. 5(b), besides the evident T_m of 160 °C for the THF-insoluble fraction (black line), a small melting peak at 110 °C corresponding to sPP is also presented, proving that this fraction contained both sPP and iPP segments. Moreover, two T_g at 104 and 115 °C and a T_r around 0.6 °C originated from the sPP and iPP could be easily observed for the THF-soluble portion, showing that this THF-soluble sample was composed by both kinds of PP segments. As the chain shuttling reaction time was extended, the sPP fraction in the stereoblock PP was proved to be increased accordingly in Fig. 6(a).

As can be observed in Fig. 6(b), the THF-soluble portion of the PPs obtained from Cat. 1/Bu_3Al show no resonance of mmmr pentad and a very tiny signal of mmmr pentad (black line), but it can be clearly observed that the signals of mmmr and mmmr pentads become stronger for the chain shuttling polymerization (red line). Moreover, as the chain shuttling reaction time was extended, the signals of mmmr appear and those of the mmmr pentads originated from the iPP segment become stronger (blue line), indicating that the presence of isotactic PP segments in the THF-soluble products and its portion can be enhanced. Notably, increase in the intensities of mmmr, mmrr, and mrrr pentads, which is relative to the junctions between isotactic and amorphous stereoblocks, can also clearly identify the existence of stereo-block segments. Therefore, analyses by 13C{(H)}-NMR spectra (Fig. 6) further identified that both the THF-insoluble and THF-soluble portion of PPs obtained from the chain shuttling polymerization simultaneously contained syndiotactic, isotactic, and atactic PP segments. Above experimental and characterization proved that Bu_3Al could serve as an excellent chain shuttling agent for promoting the efficient chain shuttling polymerization, in which stereoblock PPs were obtained.

![Figure 4](https://doi.org/10.1007/s10118-020-2446-2)  
*Fig. 4* (a) 13C{(H)}-NMR spectra in the methyl region δ = 19.5–22 ppm of the extracted products compared with PP obtained by Cat. 1; (b) Pentad distribution for the extracted products. The abscissa indicates the content ratio between other pentads and mmmm.

![Figure 5](https://doi.org/10.1007/s10118-020-2446-2)  
*Fig. 5* (a) Molecular weight distributions of the polymers extracted; (b) DSC of heating scans of the polymers extracted.
Stereoblock polypropylene could be used as heterophase compatibilizer or thermoplastic elastomer. To further confirm the existence of stereoblock architecture, the tensile properties of stereoblock PPs were tested and are presented in Fig. 7. A blended sample composed by 70% of PP obtained from Cat. 1 and 30% of PP from Cat. 2 (similar to the ratio of THF soluble and insoluble fraction of entries 3 and 4 in Table 6), respectively, was also prepared in boiling toluene as control (dark green dotted line). Because of the very poor compatibility between the two neat PPs, this blended sample exhibited the lowest tensile properties, while the PP obtained by Cat. 2 displayed the best tensile strength and elongation among all samples. Although the stereoblock segments might be formed by the free Me3Al for entry 3 in Table 5 (dark green line), the tensile strength and elongation to break of this sample were remarkably reduced relative to those of entry 1 (black line) and entry 2 (blue line), indicating that the compatibility of the two components was very limited. As observed, the tensile properties of the PPs prepared via the chain shuttling polymerization (red and pink lines) were better than those of the product obtained by Cat. 1 alone or Cat. 1 and Cat. 2 together without iBu3Al. Such improvements in stiffness, tensile strength, and toughness should be ascribed to the incorporation of stronger IPP segments in the mainchain.

Fig. 6 13C(1H)-NMR spectra in the methyl region δ = 18.5–22 ppm of (a) THF-insoluble and (b) THF-soluble polymer isolated from the high pressure chain shuttling polymerization of propylene.

**CONCLUSIONS**

In summary, efficient chain transfer polymerization of propylene promoted by Cat. 1 and Cat. 2 with dMAO as co-catalyst, respectively, was achieved in the presence of Me3Al or iBu3Al. Good reversibility was identified when iBu3Al served as the chain transfer agent. More remarkably, in the presence of both catalysts and iBu3Al as a chain shuttling agent, stereoblock polypropylenes were obtained via the chain shuttling polymerization. Clear proofs of stereoblock microstructure were obtained by GPC, DSC, NMR characterization, and tensile test. How to tune the content of the desired stereo-segment and improve the physical performance of the resulting stereoblock polypropylene deserves further investigation and is ongoing in our group.

**Electronic Supplementary Information**

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2446-2.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (No. 21574097).

**REFERENCES**

1. Coates, G. W. Precise control of polyolefin stereochemistry using single-site metal catalysts. *Chem. Rev.* 2000, 100, 1223–1252.
2. Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. Crystalline high polymers of α-olefins. *J. Am. Chem. Soc.* 1955, 77, 1708–1710.
3. Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D. Homogeneous binary zirconocenium catalysts for propylene polymerization. II.
Mixtures of iso- and syndiospecific zirconocene systems. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 2439−2445.

4. Zhang, W.; Sita, L. R. Highly efficient, living coordinative chain-transfer polymerization of propylene with ZnEt₂: practical production of ultra-high to very low molecular weight amorphous atactic polypropylenes of extremely narrow polydispersity. J. Am. Chem. Soc. 2008, 130, 442−443.

5. Harney, M. B.; Zhang, Y. H.; Sita, L. R. Discrete, multiblock isotactic-atactic stereoblock polypropylene microstructures of differing block architectures through programmable stereoregulated living Ziegler-Natta polymerization. Angew. Chem. Int. Ed. 2006, 118, 2400−2404.

6. Coates, G. W.; Waymouth, R. M. Oscillating stereocentrality: a strategy for the synthesis of thermoplastic elastomeric polypropylene. Science 1995, 267, 217−219.

7. Busico, V.; Cipullo, R.; Segre, A. L.; Talarico, G.; Vacatello, M.; Castelli, V. V. A. “Seeing” the stereoblock junctions in polypropylene made with oscillating metallocene catalysts. Macromolecules 2001, 34, 8412−8415.

8. Cohen, A.; Goldberg, I.; Venditto, V.; Kol, M. Oscillating non-metallocenes-from stereoblock-isotactic polypropylene to isotactic polypropylene via zirconium and hafnium diiodophenylate catalysts. Eur. J. Inorg. Chem. 2011, 2011, 5219−5223.

9. De Rosa, C.; Auriemma, F.; Circelli, T. Stereoblock polypropylene from a metallocaent catalyst with a haptio-flexible naphthyl-indenyl ligand. Macromolecules 2003, 36, 3465−3474.

10. Miller, S. A.; Berca, J. E. Isotactic-hemiisotactic polypropylene from C₅-symmetric aniso-metallocene catalysts: A new strategy for the synthesis of elastomeric polypropylene. Organometallics 2002, 21, 934−945.

11. Gauthier, W. J.; Collins, S. Elastomeric polypropylene: propagation models and relationship to catalyst structure. Macromolecules 1995, 28, 3779−3786.

12. Cai, Z. G.; Nakayama, Y.; Shiono, T. Synthesis of stereoblock polypropylene by change of temperature in living polymerization. Macromol. Res. 2010, 18, 737−741.

13. Lieber, S.; Brintzinger, H. H. Propylene polymerization with catalyst mixtures containing different ansa-zirconocenes: chain transfer to alkylaluminox cocatalysts and formation of stereoblock polymers. Macromolecules 2000, 33, 9192−9199.

14. Marques, M. D. V.; Chaves, E. G. Polypropylene fractions produced by binary metallocene catalysts. J. Polym. Sci., Part A: Polym. Chem. 2003, 41, 1478−1485.

15. Ye, Z. B.; Zhu, S. P. Synthesis of branched polypropylene with isotactic backbone and atactic side chains by binary iron and zirconium single-site catalysts. J. Polym. Sci., Part A: Polym. Chem. 2003, 41, 1152−1159.

16. Vaezi, J.; Nekoomanesh, M.; Khonakdar, H. A.; Jafari, S. H.; Mojarrad, A. Correlation of microstructure, rheological and morphological characteristics of synthesized polypropylene (PP) reactor blends using homogeneous binary metalloccent catalyst. Polymers 2017, 9, 75−89.

17. Chien, J. C. W.; Iwamoto, Y.; Rausch, M. D.; Wedler, W.; Winter, H. H. Homogeneous binary zirconocene catalyst systems for propylene polymerization. I. isotactic/atactic interfacial compatibilized polymers having thermoplastic elastomeric properties. Macromolecules 1997, 30, 3447−3458.

18. Arriola, D. J.; Carnahan, E. M.; Hestad, P. D.; Kuhlman, R. L.; Wenzel, T. T. Catalytic production of olefin block copolymers via chain shuttling polymerization. Science 2006, 312, 714−719.

19. Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative chain transfer polymerization. Chem. Rev. 2013, 113, 3836−3857.

20. Zintl, M.; Rieger, B. Novel olefin block copolymers through chain-shuttling polymerization. Angew. Chem. Int. Ed. 2007, 46, 333−335.

21. Xiao, A. G.; Wang, L.; Liu, Q. Q.; Yu, H. J.; Wang, J. J.; HUo, J.; Tan, Q. H.; Ding, J. H.; Ding, W. B.; Amin, A. M. Novel linear-hyperbranched multiblock polyethylene produced from ethylene monomer alone via chain walking and chain shuttling polymerization. Macromolecules 2009, 42, 1834−1837.

22. Pan, L.; Zhang, K. Y.; Nishiura, M.; Hou, Z. M. Chain-shuttling polymerization at two different scandium sites: regio- and stereospecific “one-pot” block copolymerization of styrene, isoprene, and butadiene. Angew. Chem. Int. Ed. 2011, 50, 12012−12015.

23. Valente, A.; Stoclet, G.; Bonnet, F.; Mortreux, A.; Visseaux, M.; Zinck, P. Isoprene-styrene chain shuttling copolymerization mediated by a lanthanide half-sandwich complex and a lanthanidocene: straightforward access to a new type of thermoplastic elastomers. Angew. Chem. Int. Ed. 2014, 53, 4638−4641.

24. Liu, B.; Cui, D. M. Regioselective chain shuttling polymerization of isoprene: an approach to access new materials from single monomer. Macromolecules 2016, 49, 6226−6231.

25. Phuphuak, Y.; Bonnet, F.; Stoclet, G.; Bria, M.; Zinck, P. Isoprene chain shuttling polymerisation between ciss and trans regulating catalysts: straightforward access to a new material. Chem. Commun. 2017, 53, 5330−5333.

26. Dai, Q. Q.; Zhang, X. Q.; Hu, Y. M.; He, J. Y.; Shi, C. L.; Li, Y. Q.; Bai, C. X. Regulation of the cis-1,4- and trans-1,4-polybutadiene multiblock copolymers via chain shuttling polymerization using a ternary neodymium organic sulfonate catalyst. Macromolecules 2017, 50, 7887−7894.

27. Childers, M. I.; Vitek, A. K.; Morris, L. S.; Coates, G. W.; Widger, P. C. B.; Ahmed, S. M.; Zimmerman, P. M. Isospecific, chain shuttling polymerization of propylene oxide using a bimetallic chromium catalyst: a new route to semicrystalline polyols. J. Am. Chem. Soc. 2017, 139, 11048–11054.

28. Tynys, A.; Eilertsen, J. L.; Seppala, J. V.; Ryttie, E. Propylene polymerizations with a binary metalloccen system-chain shuttling caused by trimethylaluminium between active catalyst centers. J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 1364−1376.

29. Alfano, F.; Boone, H. W.; Busico, V.; Cipullo, R.; Stevens, J. C. Polypropylene “chain shuttling” at enantiomorphous and enantiopure catalytic species: direct and quantitative evidence from polymer microstructure. Macromolecules 2007, 40, 7736−7738.

30. Descour, C.; Macko, T.; Cavallo, D.; Parkinson, M.; Hubner, G.; Spoelsstra, A.; Villani, M.; Duchateau, R. Synthesis and characterization of iPP-sPP stereoblock produced by a binary metalloccen system. J. Polym. Sci., Part A: Polym. Chem. 2014, 52, 1422−1434.

31. Hestad, P. D.; Kuhlman, R. L.; Carnahan, E. M.; Wenzel, T. T.; Arriola, D. J. An exploration of the effects of reversibility in chain transfer to metal in olefin polymerization. Macromolecules 2008, 41, 4081−4089.

32. Quevedo-Sanchez, B.; Nimmons, J. F.; Coughlin, E. B.; Henson, M. A. Kinetic modeling of the effect of MAO/Zr ratio and chain transfer to aluminum in zirconocene catalyzed polypropylene polymerization. Macromolecules 2006, 39, 4306−4316.

33. Lin, W.; Niu, H.; Chung, T. C. M.; Dong, J. Y. Borane chain transfer reaction in olefin polymerization using trialkylboranes as chain transfer agents. J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 3534−3541.

34. Zhang, C. H.; Niu, H.; Dong, J. Y. A novel effect of bis(6-heptenyl) zinc on the molecular weight and rheologic performance of polypropylene produced by rac-Me₅Si[2-Me-4-Ph-Ind]₂ZrCl₂/MAO. Polym. Bull. 2010, 65, 779−786.

35. Fan, G. Q.; Dong, J. Y. An examination of aluminum chain transfer
reaction in rac-Me$_2$Si[2-Me-4-Naph-Ind]ZrCl$_2$/MAO catalyzed propylene polymerization and synthesis of aluminum-terminated isotactic polypropylene with controlled molecular weight. J. Mol. Catal. A: Chem. 2005, 236, 246–252.

36 Naga, N.; Mizunuma, K. Chain transfer reaction by trialkylaluminum (AlR$_3$) in the stereospecific polymerization of propylene with metallocene-alkyl (AlR$_3$/Ph$_3$CB(C$_3$F$_7$)$_3$). Polymer 1998, 39, 5059–5067.

37 Ni Bhriain, N.; Brintzinger, H. H.; Ruchatz, D.; Fink, G. Polymery exchange between ansa-zirconocene catalysts for norbornene-ethene copolymerization and aluminum or zinc alkyls. Macromolecules 2005, 38, 2056–2063.

38 Ewen, J. A.; Elder, M. J.; Jones, R. L.; Rheingold, A. L.; Liable-Sands, L. M.; Sommer, R. D. Chiral ansa metalloccenes with Cp ring-fused to thiophenes and pyrroles: syntheses, crystal structures, and isotactic polypropylene catalysts. J. Am. Chem. Soc. 2001, 123, 4763–4773.

39 Tynys, A.; Eilertsen, J. L.; Rytter, E. Zirconocene propylene polymerisation: controlling termination reactions. Macromol. Chem. Phys. 2006, 207, 295–303.

40 Li, Y. L.; Song, D. P.; Pan, L.; Ma, Z.; Li, Y. S. Facile functionalization of isotactic propylene copolymers via click chemistry. J. Polym. Sci., Part A: Polym. Chem. 2019, 10, 6368–6378.

41 Britovsek, G. J. P.; Cohen, S. A.; Gibson, V. C.; van Meurs, M. Iron catalyzed polyethylene chain growth on zinc: a study of the factors delineating chain transfer versus catalyzed chain growth in zinc and related metal alkyl systems. J. Am. Chem. Soc. 2004, 126, 10701–10712.

42 Cueny, E. S.; Johnson, H. C.; Lands, C. R. Selective quench-labeling of the hafnium-pyridyl amido-catalyzed polymerization of 1-octene in the presence of trialkyl-aluminum chain-transfer reagents. ACS Catal. 2018, 8, 11605–11614.

43 Zhang, C. H.; Dong, J. Y. Dialkyltitanic compounds as chain transfer agents in ethylene and propylene polymerizations catalyzed by metallocene catalysts. J. Macromol. Sci., Part A-Pure Appl. Chem. 2010, 47, 452–456.

44 van Meurs, M.; Britovsek, G. J. P.; Gibson, V. C.; Cohen, S. N. Polyethylene chain growth on zinc catalyzed by olefin polymerization catalysts: a comparative investigation of highly active catalyst systems across the transition series. J. Am. Chem. Soc. 2005, 127, 9913–9923.

45 Hue, R. J.; Ciobuzar, M. P.; Tonks, I. A. Analysis of polyethyl chain transfer between group 10 metals and main group alkyls during ethylene polymerization. ACS Catal. 2014, 4, 4223–4231.

46 Santamaki, S.; Aitolta, E.; Kokko, E.; Repo, T.; Leskela, M.; Seppala, J. Activation of hafnocene catalyzed polymerization of 1-hexene with MAO and borane. Eur. Polym. J. 2009, 45, 863–869.

47 Fryga, J.; Bialek, M. Effect of AlR$_3$ (R = Me, Et, iBu) addition on the composition and microstructure of ethylene-1-olefin copolymers made with postmetallocene complexes of group 4 elements. Polym. J. 2018, 51, 19–29.

48 Rouholahnejad, F.; Mathis, D.; Chen, P. Narrowly distributed polyethylene via reversible chain transfer to aluminum by a sterically hindered zirconocene/MAO. Organometallics 2010, 29, 294–302.

49 Jeon, J. Y.; Park, S. H.; Kim, D. H.; Park, S. S.; Park, G. H.; Lee, B. Y. Synthesis of polyolefin-block-polystyrene through sequential coordination and anionic polymerizations. J. Polym. Sci., Part A: Polym. Chem. 2016, 54, 3110–3118.

50 Lee, H. J.; Baek, J. W.; Kim, T. J.; Park, H. S.; Moon, S. H.; Park, K. L.; Bae S. M.; Park, J.; Lee, B. Y. Synthesis of long-chain branched polyolefins by coordinative chain transfer polymerization. Macromolecules 2019, 52, 9311–9320.

51 Zhang, C. H.; Huang, H. H.; Niu, H.; Dong, J. Y. Alkyl exchange reaction between dialkylzinc compounds and methylaluminoxane and the effect on propylene polymerization. Appl. Organomet. Chem. 2010, 24, 641–645.

52 Ehn, C.; Cipullo, R.; Budzelaa, P. H. M.; Busico, V. Role(s) of TMA in polymerization. Dalton Trans. 2016, 45, 6847–6853.

https://doi.org/10.1007/s10118-020-2446-2