

Stereoblock Polypropylenes Prepared by Efficient Chain Shuttling Polymerization of Propylene with Binary Zirconium Catalysts and *i*Bu₃Al

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 Electronic Supplementary Information

Abstract Stereoblock polypropylenes bearing isotactic, atactic, and syndiotactic polypropylene segments were successfully prepared by dry methyl aluminoxane activated binary catalysts system, Ph₂CFluCpZrCl₂ and {Me₂Si(2,5-Me₂-3-(2-MePh)-cyclopento[2,3-*b*]thiophen-6-yl)₂}ZrCl₂, in the presence of *i*Bu₃Al 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 *i*Bu₃Al under both atmospheric and high pressure. Resultant polymers were identified as stereoblock polypropylenes according to microstructure and physical properties analyses by ¹³C{¹H}-NMR, DSC, and GPC.

Keywords Stereoblock polypropylenes; Chain shuttling polymerization; Zirconium catalyst; Chain transfer reaction

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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 (CH₃) 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 (*i*PP) 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 *i*PP. Therefore, modification of *i*PP with improved physical performance has attracted wide attention.^[3] 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 effi-

ent 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.^[4,5] 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

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insertion rate of comonomer.^[19] In the past ten years or so, the endeavor to getting 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.^[20–27] 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.^[28–31] 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,^[32–37] 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(Cp)FluZrCl₂ (Cat. 1) and {Me₂Si(2,5-Me₂-3-(2-MePh)-cyclopento[2,3-*b*]-thiophen-6-yl)₂}-ZrCl₂ (Cat. 2), were selected to produce stereoselective PPs.^[38,39] 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 MBraum 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 (*i*Bu₃Al), 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.^[38]

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 methylaluminoxane (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. Chain shuttling polymerizations of propylene were performed *via* a similar procedure, with prescribed amount of catalyst mixture of 1 and 2.

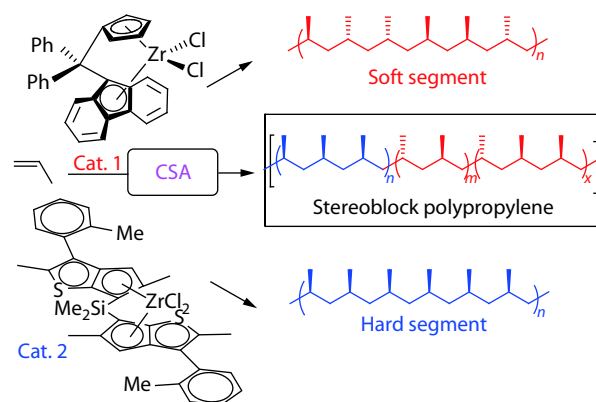
Characterization

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 (*T*_g) and melting point (*T*_m) 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 (*M*_w) and the molecular weight distributions (*M*_w/*M*_n) 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.^[38,39] The commercially available Cat. 1, Ph₂CFluZrCl₂, was reported to be temperature sensitive that gave syndiotactic PP at low reaction temperature and yielded amorphous PP at elevated temperature.^[39] This catalyst was chosen to synthesize a relatively soft PP segment. On the other hand, Cat. 2, {Me₂Si(2,5-Me₂-3-(2-MePh)-cyclopento[2,3-*b*]thiophen-6-yl)₂}-ZrCl₂, was proved to be an isospecific catalyst for producing *i*PP with strong crystallization ability.^[38] 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-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. S4 (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,^[35] which is 1.3 mol% and 2.0 mol% for PP



Scheme 1 Chain shuttling polymerization of propylene in this study.

Table 1 Polymerization of propylene catalyzed by Cat. 1 with different CTA.^a

Entry	CTA	CTA/Zr	Yield (g)	Act. ^b × 10 ⁻⁶	T _g ^c (°C)	M _w ^d × 10 ⁻⁴	PDI ^d	Efficiency ^e	[rrrr] ^f (%)
1	–	–	3.7	1.5	–2.3	8.1	1.9	17	46
2	Et ₂ Zn	10	2.9	1.2	–4.6	3.2	2.0	36	44
3	Et ₂ Zn	20	1.5	0.6	–5.3	2.2	1.9	26	
4	Me ₃ Al	50	4.5	1.8	–3.2	4.0	2.0	45	40
5	Me ₃ Al	100	3.6	1.4	–4.5	2.6	2.1	58	
6	<i>i</i> Bu ₃ Al	100	3.6	1.4	–3.6	4	2.2	40	44
7	<i>i</i> Bu ₃ Al	250	5.6	2.2	–7.3	1.8	2.6	160	

^a Polymerization conditions: $n_{(\text{Cat. 1})} = 5 \mu\text{mol}$, $[\text{dMAO}]/[\text{Zr}] = 1500$, $V_{\text{toluene}} = 50 \text{ mL}$, $70 \text{ }^\circ\text{C}$, 30 min, propylene pressure = $1.01 \times 10^5 \text{ Pa}$. ^b $g_{\text{polymer}}/(\text{mol}_{\text{Cat. h}})$.

^c Measured by differential scanning calorimetry. ^d Weight-average molecular weights and polydispersity indices determined by GPC at $150 \text{ }^\circ\text{C}$ in $1,2,4\text{-C}_6\text{H}_3\text{Cl}_3$.

^e The number of chains initiated per catalyst: $\text{chains}_{\text{initiated}} = \text{yield}_{\text{polymer}}/(M_n \cdot \text{moles}_{\text{catalyst}})$. ^f Integral percentage, determined by $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy.

Table 2 Polymerization of propylene catalyzed by Cat. 2 with different CTA.^a

Entry	CTA	CTA/Zr	Yield (g)	Act. ^b × 10 ⁻⁶	T _m ^c (°C)	M _w ^d × 10 ⁻⁴	PDI ^d	Efficiency ^e	[mmmm] ^f (%)
1	–	–	2.8	1.1	153.8	2.4	2.5	58	72
2	Et ₂ Zn	10	3.0	1.2	146.4	0.9	2.6	171	81
3	Et ₂ Zn	20	1.1	0.4	144.4	0.4	2.1	116	
4	Me ₃ Al	50	2.8	1.1	151.6	1.3	2.4	104	67
5	Me ₃ Al	100	3.6	1.4	148.3	0.9	2.4	189	
6	<i>i</i> Bu ₃ Al	100	3.2	1.3	155	1.8	2.6	92	71
7	<i>i</i> Bu ₃ Al	250	5.2	2.1	146.8	1.4	2.7	200	

^a Polymerization conditions: $n_{(\text{Cat. 2})} = 5 \mu\text{mol}$, $[\text{dMAO}]/[\text{Zr}] = 1500$, $V_{\text{toluene}} = 50 \text{ mL}$, $70 \text{ }^\circ\text{C}$, 30 min, propylene pressure = $1.01 \times 10^5 \text{ Pa}$. ^b $g_{\text{polymer}}/(\text{mol}_{\text{Cat. h}})$.

^c Measured by differential scanning calorimetry. ^d Weight-average molecular weights and polydispersity indices determined by GPC at $150 \text{ }^\circ\text{C}$ in $1,2,4\text{-C}_6\text{H}_3\text{Cl}_3$.

^e The number of chains initiated per catalyst. ^f Integral percentage, determined by $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy.

from Cat. 1 and Cat. 2, respectively. Similar to the previous reports, chain transfer to alkyl aluminum overwhelms other chain transfer modes in presented propylene polymerization using individual catalyst systems.^[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.^[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 $70 \text{ }^\circ\text{C}$ in the presence of different main group alkyl metals, including Me₃Al, Et₂Zn, and *i*Bu₃Al. 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 $-2.3 \text{ }^\circ\text{C}$ and weight-average molecular weight (M_w) of 8.1×10^4 (Table 1). The low T_g of PP reflected a low tacticity of the resulting PP, as reported previously in literature ([rrrr] = 46%, Fig. S1 in ESI).^[39] M_w was decreased to 3.2×10^4 when 10 equivalents of Et₂Zn was added, and further decreased to 2.2×10^4 as the dosage of Et₂Zn was doubled, indicating that a significant chain transfer reaction occurred. However, the productivity also drastically decreased with the increasing amounts of Et₂Zn, showing that the rather strong action between Et₂Zn and the active species affected the chain

propagation rate.^[43,44]

Differently, the polymerization activity was enhanced by addition of 50 equivalents of Me₃Al, and only slight decrease in activity was observed even the dosage of Me₃Al 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 Me₃Al. Chain transfer reaction in the presence of *i*Bu₃Al was quite similar to that of Me₃Al, where an evident increase in activity and reduction in molecular weight could be observed as the dosage of *i*Bu₃Al increased. Compared with the result of entry 1, the number of chains initiated by per Zr catalyst molecule (calculated based on Tonks *etc.*)^[45] was remarkably increased by adding different chain transfer agents. Among these three CTAs, *i*Bu₃Al 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 metallocene catalysts in olefin polymerization.^[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 $153.8 \text{ }^\circ\text{C}$ can be detected, indicating an isotactic structure of the obtained PP ([mmmm] = 72%, Fig. S2 in ESI). The catalytic activity was slightly enhanced by adding 10 equivalents of Et₂Zn, but it was remarkably decreased by further adding another 10 equivalents of Et₂Zn. The molecular weight was also decreased from 2.4×10^4 to 0.4×10^4 , while the efficiency of each Zr active species enhanced evidently, indicating that the chain transfer to

Et_2Zn was efficient (Table 2, entries 2 and 3 versus 1). When Me_3Al or $i\text{Bu}_3\text{Al}$ 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 Me_3Al and $i\text{Bu}_3\text{Al}$ 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_g of atactic polypropylene (*a*PP) obtained by Cat. 1 and the T_m of *i*PP 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 $i\text{Bu}_3\text{Al}$. 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-polymeryl exchanged with an isopropyl group in

$i\text{Bu}_3\text{Al}$, 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 *i*PP from Cat. 2 suggested a relatively low chain propagation rate compared to the chain transfer.

Chain Shuttling 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 Et_2Zn , Me_3Al , or $i\text{Bu}_3\text{Al}$, 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 *i*PP obtained by Cat. 2. When Et_2Zn , Me_3Al , or $i\text{Bu}_3\text{Al}$ was separately introduced, the polymerization activity of the system

Table 3 Dependence of M_w on reaction time in the chain transfer polymerization of propylene by Cat. 1 and Cat. 2.^a

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

^a Polymerization conditions: $n_{(\text{Cat. 1})} = n_{(\text{Cat. 2})} = 5 \mu\text{mol}$, $[\text{dMAO}]/[\text{Zr}] = 1500$, $V_{\text{toluene}} = 50 \text{ mL}$, 70 °C, propylene pressure = $1.01 \times 10^5 \text{ Pa}$. ^b $g_{\text{polymer}}/(\text{mol}_{\text{Cat.}} \cdot \text{h})$.

^c Measured by differential scanning calorimetry. ^d Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$.

^e The number of chains initiated per catalyst.

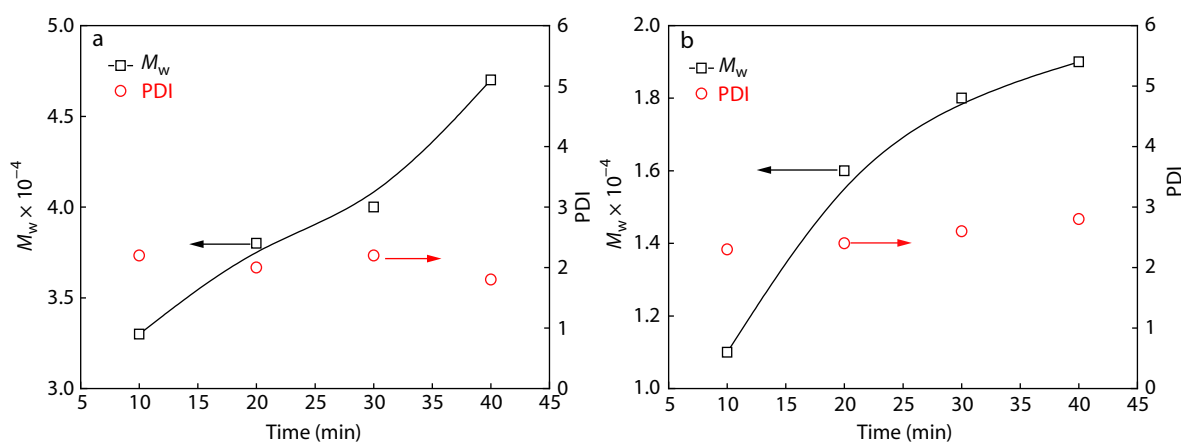


Fig. 1 Plots of M_w and PDI of polymers prepared by single (a) Cat. 1/ $i\text{Bu}_3\text{Al}$ catalytic system and (b) Cat. 2/ $i\text{Bu}_3\text{Al}$ catalytic system against polymerization time.

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 *i*PP 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 *i*PP (Fig. 2). Similarly, a broader, bimodal molecular weight distribution could also be observed even 10 equivalents of Et_2Zn 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_2Zn , indicating that no effective chain shuttling occurred between the two active species upon Et_2Zn . (Fig. S19 in ESI)

When 50 equivalents of Me_3Al 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

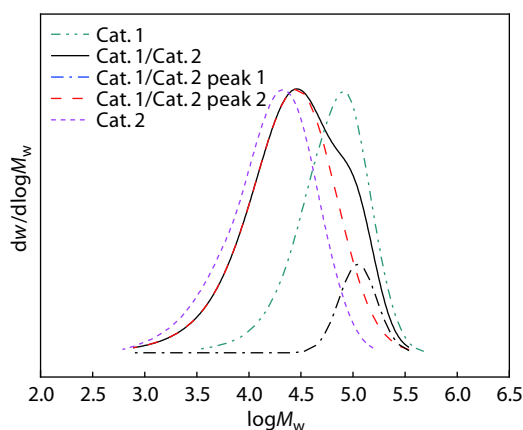


Fig. 2 Molecular weight distribution curves of the polymers prepared by Cat. 1/Cat. 2 with no chain transfer agent (black line), Cat. 1 (green line) and Cat. 2 (pink line). Cat. 1/Cat. 2 peak 1 and Cat. 1/Cat. 2 peak 2 were obtained by fitting and dividing peak of GPC curve of polymer catalyzed by Cat. 1/Cat. 2.

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, *i*Bu₃Al 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.*^[48] reported that the PDI is approximately equal to $(1 + k_p/k_t)$ 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,^[49,31,50] and the presence of very small amount of free Me_3Al originated from dMAO. Me_3Al 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 *i*Bu₃Al.^[51,52] When more dosage of *i*Bu₃Al 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 *i*Bu₃Al 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 s 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 *i*PP 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 (6.06×10^5 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 (*s*PP) segment increased by the high

Table 4 Chain shuttling polymerization using two Zr catalysts with different CSA.^a

Entry	Time (min)	CSA	CSA/Zr	Yield (g)	Act. ^b $\times 10^{-6}$	T_m ^c (°C)	M_w ^d $\times 10^{-4}$	PDI ^d
1	30	–	–	2.3	0.9	157	4.8	3.4
2	30	Et_2Zn	10	2.6	1.0	144/151	2.3	5.6
3	30	Me_3Al	50	3.0	1.2	146/153	2.4	3.3
4	30	<i>i</i> Bu ₃ Al	100	3.9	1.6	147/155	2.2	2.8
5	30	<i>i</i> Bu ₃ Al	250	3.5	1.4	149/155	2.0	2.3
6	10	<i>i</i> Bu ₃ Al	100	2.2	2.6	150	1.8	2.3
7	20	<i>i</i> Bu ₃ Al	100	2.9	1.7	147/154	2.0	2.5
8	40	<i>i</i> Bu ₃ Al	100	4.2	1.3	150/157	3.1	2.9

^a Polymerization conditions: $n_{(\text{Cat. 1})} = n_{(\text{Cat. 2})} = 2.5 \mu\text{mol}$, $[\text{dMAO}]/[\text{Zr}] = 1500$, $V_{\text{toluene}} = 50 \text{ mL}$, 70 °C, propylene pressure = 1.01×10^5 Pa. ^b $g_{\text{polymer}}/(\text{mol}_{\text{Cat.}} \cdot \text{h})$. ^c Measured by DSC. ^d Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4- $\text{C}_6\text{H}_3\text{Cl}_3$.

pressure as further revealed by $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (Fig. S20 in ESI). Different from the observation of entry 1 in Table 4 under atmospheric pressure, the polypropylene obtained by dual catalytic system in the absence of *i*Bu₃Al exhibited a higher molecular weight ($M_w = 23 \times 10^4$) and a lower, monomodal molecular weight distribution (PDI = 2). This result might be originated from the presence of free Me₃Al derived from dMAO, which played a role as a chain transfer and chain shutting agent between the two catalytic sites. Although the reaction temperature was also set at 70 °C for the polymerization under 6.06×10^5 Pa, temporary temperature was detected to be about 10 °C higher because of the enhanced reaction rate, and therefore more Me₃Al was presented in the polymerization mixture compared to the reaction that proceeded under atmospheric pressure. However, a lower yield compared with that of entry 4 (4.1 g versus 7.1 g) with 100 equivalents of *i*Bu₃Al suggests that the role of Me₃Al as a chain shuttling agent was relatively inferior. Two melting

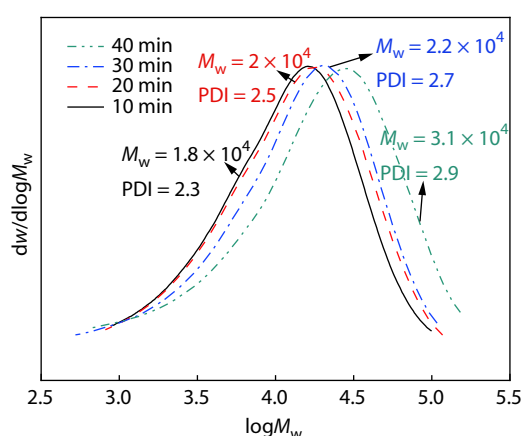


Fig. 3 Molecular weight distributions of PPs obtained by catalysts 1 and 2 with 100 equivalents of *i*Bu₃Al at 10 min, 20 min, 30 min, and 40 min.

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 *i*PP 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 catalyst, 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 *i*PP 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/*i*Bu₃Al system under atmospheric pressure comprised of 44% of THF-soluble portion ($M_w = 2.8 \times 10^4$, $M_w/M_n = 2.2$) and 56% of THF-insoluble portion ($M_w = 1.9 \times 10^4$, $M_w/M_n = 2$). 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 $^{13}\text{C}\{^1\text{H}\}$ -NMR

Table 5 Chain shuttling polymerization of propylene under high pressure.

Entry	Cat.	Time (min)	<i>i</i> Bu ₃ Al/Zr	Yield (g)	Act. ^c × 10 ⁻⁶	ΔH ^d (J/g)	T_m^d (°C)	M_w^e × 10 ⁻⁴	PDI ^e
1	1 ^a	30	100	12.2	24.4	13	111	17	1.7
2	2 ^a	30	100	13.6	27.2	71.5	156	12	2.0
3	1+2 ^b	30	0	4.1	8.2	12/35	111/158	23	2.0
4	1+2 ^b	30	100	7.1	14.2	13/26	110/159	19	1.8
5	1+2 ^b	45	100	9.8	13.1	13/28	114/161	19.5	1.9

^a Polymerization conditions: $n_{(\text{Cat. 1})} = n_{(\text{Cat. 2})} = 1 \mu\text{mol}$, dMAO [Al]/[Zr] = 1500, $V_{\text{toluene}} = 100 \text{ mL}$, 70 °C, propylene pressure = $6.06 \times 10^5 \text{ Pa}$. ^b $n_{(\text{Cat. 1})} = n_{(\text{Cat. 2})} = 0.5 \mu\text{mol}$, dMAO [Al]/[Zr] = 1500, $V_{\text{toluene}} = 100 \text{ mL}$, 70 °C, propylene pressure = $6.06 \times 10^5 \text{ Pa}$. ^c $g_{\text{polymer}}/(\text{mol}_{\text{Cat.}} \cdot \text{h})$. ^d Measured by DSC. ^e Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-C₆H₃Cl₃.

Table 6 Summary of results of the fractionation experiment. ^a

Entry	Cat.	CSA	Time (min)	THF-Sol. (g)	THF-Insol. (g)	THF-Sol. [rrrr] ^d (%)	THF-Insol. [mmmm] ^d (%)
1	1 ^b	<i>i</i> Bu ₃ Al	30	1	0	70	
2	2 ^b	<i>i</i> Bu ₃ Al	30	0.09	0.91		91
3	1+2 ^b	<i>i</i> Bu ₃ Al	30	0.66	0.34	72	88
4	1+2 ^b	<i>i</i> Bu ₃ Al	45	0.70	0.30	63	76
5	1 ^c	–	30	1	0	46	
6	2 ^c	<i>i</i> Bu ₃ Al	30	0.16	0.84		89
7	1+2 ^c	<i>i</i> Bu ₃ Al	30	0.44	0.56	43	80

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

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 rrrr 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_m s at 104 and 115 °C and a T_g around 0.6 °C originated from the sPP and iPP could be easily observed for the THF-sol-

uble 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/*i*Bu₃Al show no resonance of mmmm pentad and a very tiny signal of mmmr pentad (black line), but it can be clearly observed that the signals of mmmr and mmrr pentads become stronger for the chain shuttling polymerization (red line). Moreover, as the chain shuttling reaction time was extended, the signals of mmmm appear and those of the mmmr pentads originated from the *i*PP 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[¹H]-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 *i*Bu₃Al could serve as an excellent chain shuttling agent for promoting the efficient chain shuttling polymerization, in which promising stereoblock PPs were obtained.

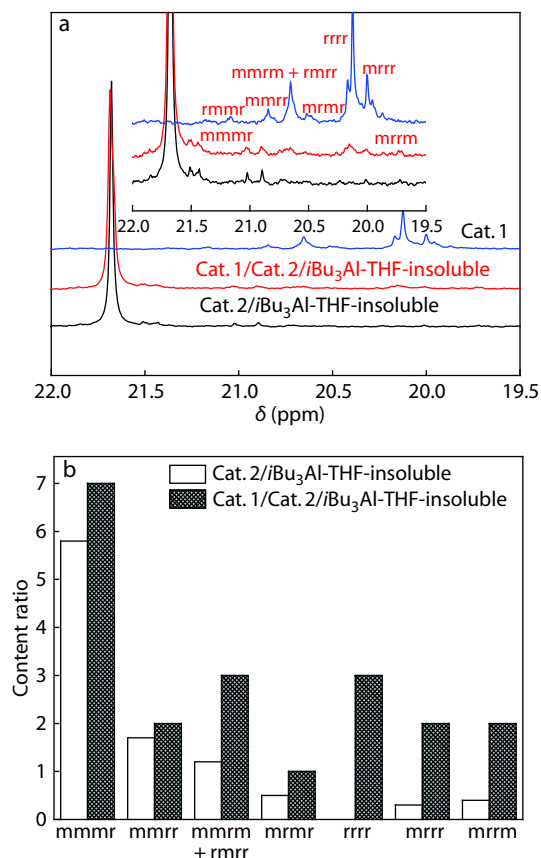


Fig. 4 (a) ¹³C[¹H]-NMR spectra in the methyl region $\delta = 19.5$ – 22 ppm of the extracted products compared with PP obtained by Cat. 1; (b) Pentad distribution for the extracted products. The abscissa indicates the content ratio between other pentads and mmmm.

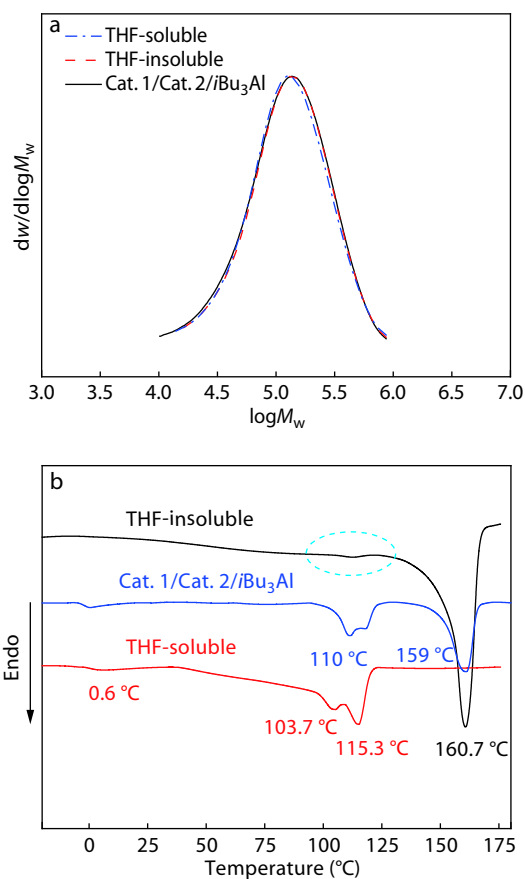


Fig. 5 (a) Molecular weight distributions of the polymers extracted; (b) DSC of heating scans of the polymers extracted.

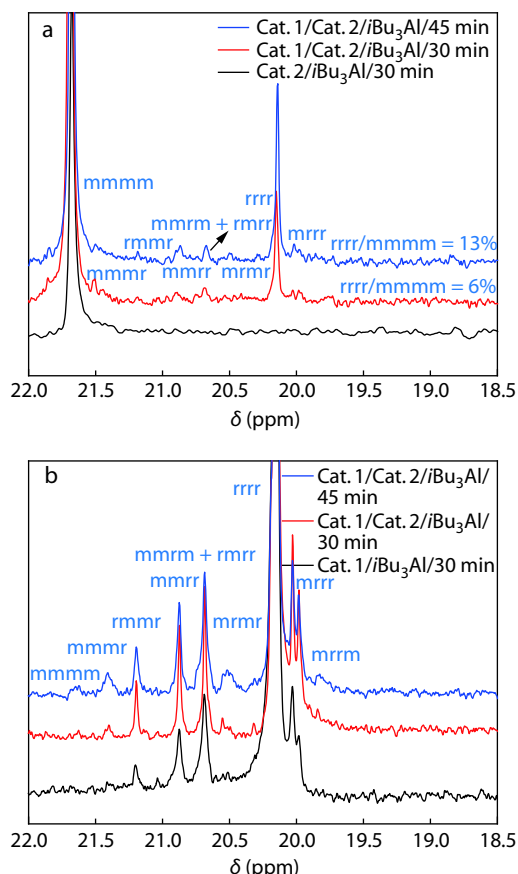


Fig. 6 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra in the methyl region $\delta = 18.5\text{--}22$ ppm of (a) THF-insoluble and (b) THF-soluble polymer isolated from the high pressure chain shuttling polymerization of propylene.

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 Me_3Al 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 $i\text{Bu}_3\text{Al}$. Such improvements in stiffness, tensile strength, and toughness should be ascribed to the incorporation of stronger *i*PP segments in the mainchain.

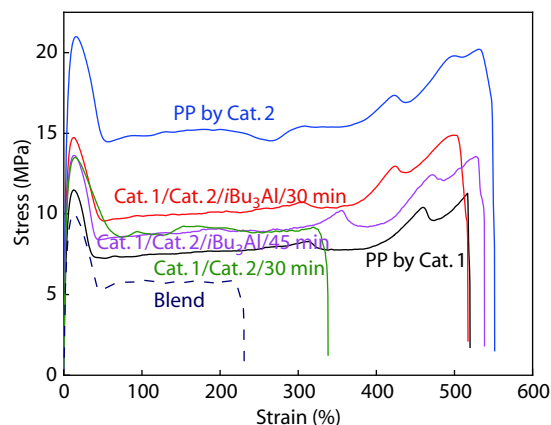


Fig. 7 Stress-strain curves of representative polymers obtained by Cat. 1 (black line), Cat. 2 (blue line), Cat. 1/Cat. 2/30 min (dark green line), Cat. 1/Cat. 2/ $i\text{Bu}_3\text{Al}$ /30 min (red line), Cat. 1/Cat. 2/ $i\text{Bu}_3\text{Al}$ /45 min (pink line) (entries 1–5 in Table 5), and blend sample composed of two neat polypropylenes (dotted line), at a stretching rate of 50 mm/min under room temperature. At least 5 specimens were tested for each polymer.

CONCLUSIONS

In summary, efficient chain transfer polymerization of propylene promoted by Cat. 1 and Cat. 2 with $d\text{MAO}$ as co-catalyst, respectively, was achieved in the presence of Me_3Al or $i\text{Bu}_3\text{Al}$. Good reversibility was identified when $i\text{Bu}_3\text{Al}$ served as the chain transfer agent. More remarkably, in the presence of both catalysts and $i\text{Bu}_3\text{Al}$ 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>.

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