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ORIGINAL PAPER

A novel effect of bis(6-heptenyl)zinc on the molecular weight and rheologic performance of polypropylene produced by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$/MAO

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Abstract The polymerization of propylene combined with bis(6-heptenyl)zinc (BHZ) catalyzed by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$/MAO was investigated. BHZ acts as both a comonomer and a chain transfer reagent, which was verified by ^1H NMR and ^{13}C NMR spectra. A novel effect of BHZ on the molecular weight and rheologic properties of the product was explained by the production of LCB.

Keywords Propylene polymerization · Metallocene catalysts · Alkylzinc compounds · Copolymerization · Chain transfer

Introduction

Chain transfer to alkylzinc compounds, often referred as [1–9], has recently raised rejuvenated interest in olefin coordination polymerization, presumably because of the recent discovery of diethylzinc ($ZnEt_2$) as a "chain shuttling" agent causing a unique effect of chain shuttling between two distinctively different catalyst active sites, resulting in the preparation of multiblock, "blocky" poly(ethylene-co-1-octene) materials by virtue of differing capabilities for 1-alkene incorporation between the two active propagating centers, and these highly valued polyolefin materials are not accessible through the traditional methods [10, 11]. In fact, even before pronouncement of the concept of chain shuttling, many researchers have reported the production of blocky polypropylene (PP) by binary catalysts in combination with alkylaluminum as chain transfer agent to obtain i-PP-b-a-PP [12]

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and i-PP-b-s-PP [13–15], although PP mixtures (besides stereoblock PP) that contain simple isotactic and atactic polymers were usually reported due to the relatively slow chain transfer rate of alkylaluminum in contrast to diethylzinc. The driving force behind this scientific renaissance is certainly the rapid developing olefin coordination polymerization catalyst technologies, especially those of the well-defined single site catalysts (e.g., metallocene and non-metallocene catalysts) that allow good understandings of the catalyst properties so as to manipulate polymerization process to accomplish specific goals. In fact, it was the ingenious combination of single site catalysts based on a bis(phenoxyimine)-based Group 4 complex (FI catalysts) [16–20] and a hafnium pyridylamide complex [21, 22] to carry out the chain shuttling polymerization, which was based on the concept of the well-known "catalyzed chain growth" [23–25] and "coordinative chain-transfer" [26] reaction.

Reviewing the not-so-abundant literatures on Zn-based chain transfer reaction, we have found that, as far as single site catalysts are concerned, no matter they are metallocene- or non-metallocene-type, the past reports were overwhelmed by ethylene, or ethylene-rich polymerization reactions. As for α-olefin polymerizations, only very recently Sita [27] reported the first example of living coordinative chain-transfer polymerization of propylene, in which a-PP was produced using $Cp^*HfMe_2[N(Et)C(Me)N(Et)]/[PhNMe_2H][B(C_6F_5)_4]$ in the presence of varying amounts of $ZnEt_2$ as a chain transfer agent.

Shiono [7] have used two bis(ω-alkenyl)zinc compounds bis(3-butenyl)zinc (BBZ) and bis(7-octenyl)zinc (BOZ) in propylene polymerization catalyzed by the conventional catalyst $TiCl_3$, and the latter compound acts as a chain transfer agent and a copolymerization monomer. As for metallocene catalysts, with their outstanding abilities of copolymerization in contrast to $TiCl_3$, they were anticipated to have a different behavior in the presence of bis(ω-alkenyl)zinc compounds. Herein, we report the polymerization of propylene combined with BHZ catalyzed by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$/MAO, and the rheologic properties of the products were investigated.

Experimental section

Materials and instruments

All O_2- and moisture-sensitive manipulations were carried out inside an argon-filled vacuum atmosphere dry-box equipped with a dry train. 3-bromo-1-propene and 1,4-dibromobutane were bought from Sinopharm Chemical Reagent Beijing Co., Ltd. of China, and were used without further purification. $ZnCl_2$ was dried by refluxing in $SOCl_2$ for 24 h. Toluene (Sinopharm Chemical Reagent Beijing Co., Ltd. of China) was distilled over sodium and benzophenone under nitrogen before use. Methylaluminoxane (MAO) (1.4 M in toluene) was kindly supplied by CNPC Lanzhou Chemical Company and was depleted of free trimethylaluminum (TMA) by drying in vacuum to a free-flowing powder, and then dissolved in toluene before use. *Rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$ was prepared according to the procedures described in Spaleck et al. [28]. Polymerization grade propylene was supplied by Yanshan Petrochemical Co. of China.

Room temperature ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 instrument. High temperature ^{1}H and ^{13}C NMR spectra were carried out in 1,2,4-trichlorobenzene at 390 K using a Bruker DMX 300 spectrometer. Differential scanning calorimetry (DSC) measurements were made on a PE Diamond DSC. Molecular weight and molecular weight distribution were determined by a Waters alliance GPC 2000 at 150 °C in 1,2,4-trichlorobenzene as solvent using polystyrene calibration. Rheologic testing were carried out on a Rheometrics SR 200 dynamic stress rheometer using parallel plates with a diameter of 25 mm and a gap height of 1 mm. The samples were prepared by compression molding at 190 °C, followed by cut from the sheet. The frequency range was 0.07–600 rad/s, and the maximum strain was fixed at 3%. All measurements were carried out under a nitrogen atmosphere to limit degradation and the absorption of moisture.

Synthesis of BHZ

7-Bromo-1-heptene was synthesized by the coupling reaction of allylmagnesium bromide with 1,4-dibromobutane [29]. BHZ was prepared from the Grignard agent and anhydrous $ZnCl_2$ in a procedure similar to the literature [7]. ^{1}H NMR of BHZ ($CDCl_3$) 5.72–5.94 (2H, m, $-CH=$), 4.88–5.09 (4H, q, $=CH_2$), 1.95–2.17 (4H, q, $-CH_2-CH=$), 1.52–1.65 (4H, m, $Zn-CH_2-CH_2-$), 1.20–1.50 (8H, m, $-CH_2-CH_2-CH_2-CH=$), 0.33–0.45 (4H, t, $Zn-CH_2-$).

Polymerization

In a typical reaction, a Parr 450 mL stainless steel autoclave reactor equipped with a mechanical stirrer was charged with 3 bar propylene. Toluene (150 mL) was introduced into the propylene purged reactor and stirred vigorously (600 rpm). The toluene was kept at 40 °C and then MAO in toluene was injected. After stirring for 5 min, a prescribed amount of BHZ in toluene was added and stirred for another 5 min. Then the polymerization was initiated by the addition of a toluene solution of the prescribed catalyst. After 30 min of reaction at 50 °C, the reactor pressure was released. The reaction solution was discharged from the reactor and quenched with acidified ethanol. The precipitated polymer was isolated and dried at 50 °C for 12 h in a vacuum oven.

Results and discussions

The polymerization results are summarized in Table 1. Both of the molecular weight of PP [7] prepared in the presence of BBZ and BOZ catalyzed by $TiCl_3$ decreased with the increasing concentration of alkylzinc compounds, which was attributed to the effective chain transfer rate of aklylzinc. What is interesting in our polymerization is the increasing molecular weight of the products in a certain concentration of BHZ, and molecular weight begins to decrease above the critical

Table 1 Polymerization of propylene catalyzed by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$/MAO/BHZ

Run	Zn/Cat	Yield/g	$A/10^6$ g PP·mol Zr^{-1} h^{-1}	T_m^a/°C	$M_n \times 10^{-4}$	M_w/M_n^b	$-CH{=}CH_2^c$/mmol/mol monomer
1	0	14.223	28.45	155.0	7.6	3.3	0.13
2	10	7.435	14.87	155.8	16.6	2.9	0.18
3	20	5.378	10.76	156.5	23.0	2.3	0.17
4	40	4.659	9.32	155.8	12.3	2.6	0.19
5	100	2.739	5.48	154.3	5.9	2.2	0.25

Polymerization conditions: 50 °C, 30 min, propylene pressure = 3 atm; cat. 1 μ; Al/Zr = 2,000, toluene = 150 mL

[a] Melting point determined by a PE Diamond DSC

[b] In run 1 and 2, M_w/M_n is a bit high due to the violent exothermal reaction at the initial step

[c] Determined by ^1H NMR

concentration. In Shiono's polymerization, bis(ω-alkenyl)zinc compounds just filled the role of copolymerization and chain transfer, both of which contributed to the reduction of molecular weight. However, due to the excellent copolymerization capability of metallocene catalysts in combination with the efficient chain transfer rate of alkylzinc compounds, there must be a third role for BHZ in metallocene catalysts catalyzed propylene polymerization, which was the key point for the novel change of molecular weight.

We proposed that a vinyl-terminated polymer chain can be prepared after the chain transfer of the small molecule BHZ (Scheme 1), indicating a gradually increase vinyl content with the increasing concentration of BHZ. However, ^1H NMR spectra (Table 1) indicates that no significant changes on the concentration of the corresponding vinyl group in polymers are detected while increasing the amount of BHZ, which is in accordance with Shiono's results [7] in the presence of BBZ.

To investigate the structure of the chain ends in more detail, ^{13}C NMR spectra of the product from run 5 was measured (Fig. 1) (With regard to this catalyst and its preferred chain termination mechanisms, see ref. [30, 31]; Peaks were attributed according to [32] and references therein). Typical resonances attributable to isobutyl end group are observed, which were generally attributed to the aluminum-ended polymer chain arising from chain transfer to the free TMA in MAO. However, dried MAO depleted of free TMA was used in our experiment, and the isobutyl group must be from Zn-terminated polymer chains upon hydrolytic workup, in other words, chain transfer to BHZ affirmatively occurred, which was in contradiction to the mechanism we proposed before. As a result, we supposed that a cyclization around the active site might take place after chain transfer to BHZ, and then a stable six-membered ring formed (Scheme 2).

In addition, some resonances assigned to the pendant pentyl group are observed in the ^{13}C NMR spectra (Fig. 1), which indicates that BHZ can copolymerize with propylene to form the pendant pentylzinc group too.

$$\mathrm{Zr{-}P} \xrightarrow{\text{chain transfer to BHZ}} \mathrm{Zr\text{-}(CH_2)_5CH_2{=}CH_2} \xrightarrow{\text{chain propagation}} \mathrm{P\text{-}CH_2{=}CH_2}$$

Scheme 1 A proposed mechanism when BHZ was introduced into the polymerization reaction

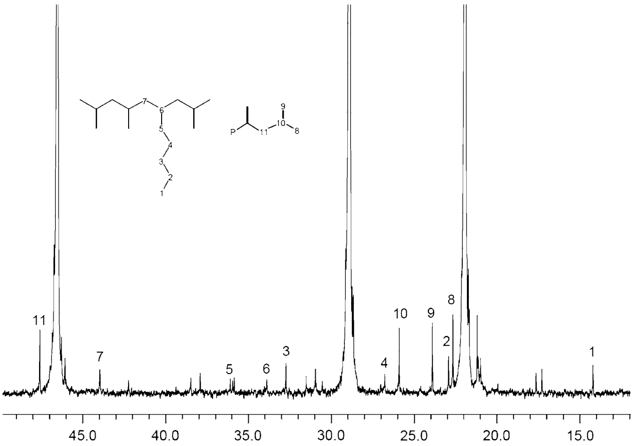
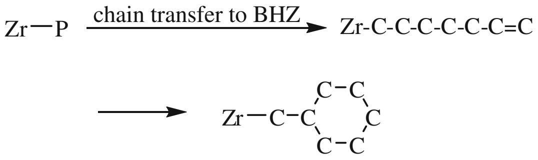


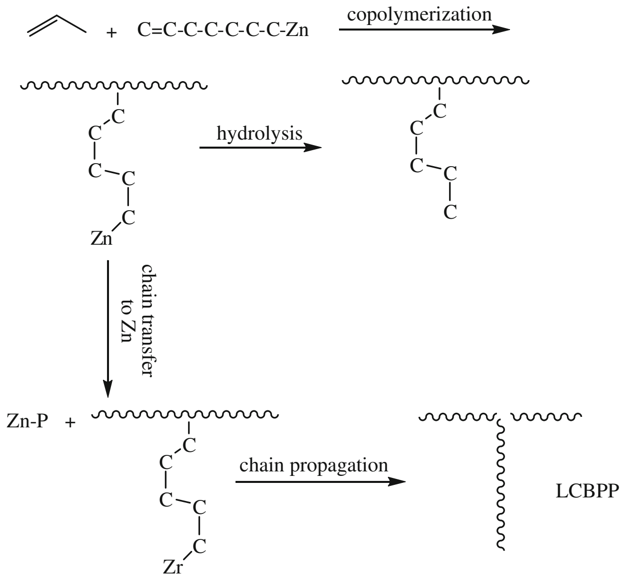
Fig. 1 ^{13}C NMR spectra of PP of run 5



Scheme 2 A plausible mechanism of cyclization after chain transfer to BHZ

Scheme 3 depicts a plausible mechanism during polymerization. The first route is the direct hydrolysis of the pentylzinc group to produce the pendant pentyl group; and considering the increased molecular weight of run 2–4 and the fact that alkylzinc compounds are among the most efficient chain transfer reagents for single-site catalysts across the transition series [33], we suppose that the second route is a chain transfer reaction of the copolymerized pentylzinc group, after which the active site moves to the side chain. The following propagation of the active site can produce long-chain branched PP (LCBPP), and hence the molecular weight of the product increases. But when the concentration of BHZ is high, chain transfer reaction becomes dominant and the molecular weight decreases. Long-chain-branching density depends on the copolymerization ability of BHZ and chain transfer rate of the copolymerized pentylzinc group. The length of the branched chain is determined by the propagation rate of the active site.

Rheology is a convenient and sensitive method to detect long-chain branching (LCB) [34–40]. A comparative molecular weight linear PP sample ($M_w = 5.4 \times 10^5$, $M_w/M_n = 3.4$) was prepared in contrast with the product of run 3. Figure 2 compares the storage moduli and complex viscosity versus angular frequency curves for the linear PP sample and the samples of run 3. The latter shows an



Scheme 3 A plausible mechanism for the production of LCBPP

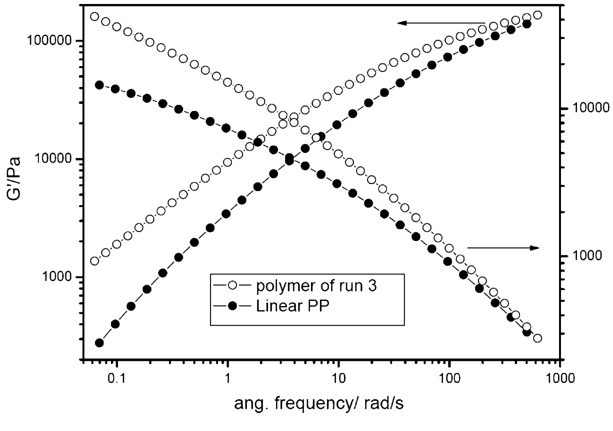


Fig. 2 Master curves of storage moduli and complex viscosities for linear PP and the polymer of run 3 with comparable molecular weight

evident shear thinning behavior and exhibits much higher viscosity in the low frequency region, which indicates a LCB structure.

Conclusions

In conclusion, the polymerization of propylene combined with BHZ catalyzed by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2/MAO$ was reported. BHZ acts as both a comonomer and a chain transfer reagent, which was verified by ^{1}H NMR and ^{13}C NMR spectra. A novel effect of BHZ on the molecular weight and rheologic properties of the product was explained by the production of LCB. Detailed work was in progress in our laboratory for the further confirmation of LCB and the elaborate structure of LCB.

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