Assessing 1,9-Decadiene/Ethylene Copolymerization with Ziegler–Natta Catalyst to Access Long Chain-Branched Polyethylene

Yang Liu, Yawei Qin, and Jin-Yong Dong*

ABSTRACT: 1,9-Decadiene/ethylene copolymerization is assessed as a way for Ziegler–Natta catalysts to access long chain-branched polyethylene (PE). A MgCl2/9,9-bis-(methoxymethyl)-fluorine/TiCl4 catalyst with triethylaluminium as a cocatalyst is exemplified for the task. 1,9-Decadiene was found to induce a substantial comonomer effect on catalyst activity and continuing decreases of PE molecular weight. Both the double bonds of 1,9-decadiene were poorly reactive during polymerization, of which the polymer chain-attached was even much less reactive than the original one. As a consequence, at decreased feeds, 1,9-decadiene gave small amounts (<0.1 mol %) of pendant vinyl groups to PE without prompting the formation of long-chain branches. Long chain-branching was realized at increased 1,9-decadiene feeds, which was however accompanied by proportional gelation.

1. INTRODUCTION

Polyethylene (PE) is ranked no.1 in volume in the whole of polymer materials.1 Because of its versatile polymerization chemistry and production processes, PE is rich in resin grades. Among them, free radical polymerization-produced PE resins, commercially dubbed low-density PE (LDPE), contain substantial comonomer eect on catalyst activity and continuing decreases of PE molecular weight. Among them, free radical polymerization-produced PE resins, commercially dubbed low-density PE (LDPE), contain significant amounts of short- and long-chain branches (SCBs and LCBs).2 The LCBs render LDPE resins with high melt strength and enhanced shear-thinning behavior and thus good processability.3 On the other hand, chromium (Cr)-based Philips catalysts and titanium (Ti)-based Ziegler–Natta catalysts produce high-density PE (HDPE) under much milder conditions (much lower temperature and pressure).4 Ziegler–Natta catalysts also produce linear low-density PE (LLDPE) by copolymerization with small amounts of 1-olefins (usually 1-butene, 1-hexene, or 1-octene). However, both HDPE and LLDPE resins from Ziegler–Natta catalysts lack LCBs, which must resort to broadening molecular weight distribution for bettering melt processability.5 Metallocene catalysts with constrained geometry configurations in situ incorporate vinyl-terminated polymer chains into chain propagation (macromonomer copolymerization), producing long chain-branched PE.5 However, the use of molecular hydrogen (H2) for control of polymer molecular weights has the collateral effect of suppressing the terminal vinyl group formation and thus inhibits the occurrence of long-chain-branching7. An effective solution for that is copolymerization with linear nonconjugated α,ω-diolefin, such as 1,9-decadiene, which increases the vinyl group concentration and synthesizes long chain-branched PE with concomitant control of molecular weight and long chain-branching structure.8−10

Despite the success in the synthesis of long chain-branched PE with metallocene catalysts, it is still a pending issue as to how HDPE and LLDPE by Ziegler–Natta catalysts could be rendered controllability on long chain-branching structure. In this paper, an attempt of using 1,9-decadiene to prompt long chain-branching structure formation in ethylene polymerization with Ziegler–Natta catalyst is reported (Figure 1). 1,9-Decadiene has been widely used in ethylene and propylene polymerization with metallocene catalysts, eliminating the cyclization tendency that as a major side reaction reduces the LCB efficiency of a nonconjugated α,ω-diolefin.8−12 In a recent report, we assessed the synthesis of long chain-branched polypropylene through 1,9-decadiene/propylene copolymerization with Ziegler–Natta catalysts,13 which was specifically tasked to a MgCl2/9,9-bis-(methoxymethyl)fluorine/TiCl4 catalyst with triethylaluminium (TEA) as a cocatalyst that has long been known as a higher α-olefin-capable Ziegler–Natta catalyst system. The results nevertheless indicated that the catalyst system exhibited a poor incorporation efficiency...
for 1,9-decadiene, with meaningful incorporations being realized only at greatly increased concentrations, and that the formation of LCB structure was much delayed relative to 1,9-decadiene incorporation, making the synthesis of gel-free LCB-PP rather difficult.

In this paper, with the same MgCl2/9,9-bis-(methoxymethyl)fluorene/TiCl4 catalyst and TEA cocatalyst, 1,9-decadiene/ethylene copolymerization was conducted in the presence of varied amounts of 1,9-decadiene. The polymerization was evaluated by the effect of 1,9-decadiene additions on catalyst activity and PE molecular weight. The chain structures of the polymer samples were assessed by 1H NMR, gel permeation chromatography (GPC), and melt rheology measurements.

2. RESULTS AND DISCUSSION

2.1. Effect of 1,9-Decadiene on Catalyst Activity and PE Molecular Weight. The conditions and results of ethylene polymerization in the presence of varied amounts of 1,9-decadiene are summarized in Table 1. It can be seen that 1,9-decadiene induced a substantial comonomer effect on the catalyst activity. The catalytic activities in the polymerization runs with the engagement of 1,9-decadiene were increased greatly and were systematical as compared to those in the control run. The activity dropped from 6 × 103 g mol⁻¹ Ti h⁻¹ when the 1,9-decadiene feed in the polymerization was increased to 0.19 mmol/L, inching even closer to the catalyst activity regime of metallocene catalysts. On the other hand, it is noticed that 1,9-decadiene caused continuing decreases of PE molecular weight (Figure 2). In terms of effects on catalyst activity and PE molecular weight, 1,9-decadiene behaved similar to higher α-olefins, such as 1-hexene.14

2.2. Pendant Vinyl Group Incorporation. The microstructures of the PE samples were examined by 1H NMR. The spectra are shown in Figure 3. With the increase of 1,9-decadiene feed in polymerization, the samples were gradually incorporated with pendant vinyl groups from 1,9-decadiene. The resonant signals at 4.9 and 5.8 ppm are the characteristic chemical shifts of −CH==CH2 and −CH==CH2, respectively. The incorporation data are given in Table 1. Much bulkier than 1-hexene, 1,9-decadiene displayed a rather sluggish incorporation into PE chains. Even at an increased concentration of 0.19 mmol/L, the content of the pendant vinyl groups was no more than 0.30 mol %, suggesting a much lower reactivity of 1,9-decadiene as compared to ethylene.

Despite the low polymerization reactivity, samples prepared with the engagement of 1,9-decadiene were detected through proportional gelation by solvent (xylene) extraction, indicating that PE chain binding by 1,9-decadiene would be possible.

2.3. Identification of Long Chain Branching. Melt rheological properties of the PE samples were examined by a small amplitude oscillating shear (SAOS) rheometer in the linear viscoelastic regime (180 °C, 0.05–500 rad/s, 3.0% strain). As shown in Figure 4, due to a decrease of Mw, sample run 1 with the smallest 1,9-decadiene feed was quickly reduced of storage modulus (G′), loss modulus (G″), and complex viscosity (η*) at the low frequency (ω) end as compared to the control sample. Nevertheless, it can be observed that, against a continuing decrease of Mw samples from run 1 through run 5 show a progressive increase of G′ at the low frequency end (Figure 3A).

The η* = ω|η*| curves can be simulated with the Cross equation:15

\[
\eta^* = \frac{\eta_0}{1 + (\lambda \omega)^n}
\]

Table 1. Conditions and Results of Ethylene Polymerization with MgCl2/BMMF/TiCl4-TEA

| run | 1,9-decadiene (mmol/L) | catalyst activity | [pendant vinyl] (mol %) | Mw (10^4 g/mol) | D^* | Gel (wt %) | Tm (°C) |
|-----|------------------------|-------------------|-------------------------|-----------------|-----|-----------|---------|
| control | 0 | 27.2 | 0.01 | 15.7 | 6.5 | 0 | 135.0 |
| 1 | 0.02 | 34.6 | 0.03 | 14.7 | 6.6 | 0 | 133.5 |
| 2 | 0.04 | 45.7 | 0.09 | 11.6 | 10.2 | 0.9 | 132.8 |
| 3 | 0.08 | 48.2 | 0.16 | 9.3 | 5.9 | 8.4 | 130.7 |
| 4 | 0.13 | 61.1 | 0.28 | 9.7 | 5.9 | 8.6 | 130.6 |
| 5 | 0.19 | 53.8 | 0.30 | 7.7 | 6.9 | 15.3 | 131.5 |

*Polymerization conditions: catalyst, ∼15.0 mg, TEA (1.8 M), 0.6 mL; n-hexane, 100 mL; ethylene, 0.53 MPa, H2, 0.20 MPa, total polymerization pressure 0.73 MPa; polymerization temperature, 80 °C; polymerization duration, 30 min. 1,9-Decadiene: 10^-3 mol^-1 Ti h^-1. Determined from 1H NMR spectra. Determined by GPC with polystyrene as standard. Determined by boiling xylene extraction.
where $\eta_0$ is the zero-shear viscosity, $\lambda$ the characteristic relaxation time, and $n$ the shear thinning index. The data are summarized in Table 2.

As shown in Table 2, for the control sample, which has a $M_w$ of 157,000 g/mol and $D$ of 6.5, $\eta_0$, $\lambda$, and $n$ are given at $3.24 \times 10^4$ Pa s, 2.67 s, and 0.47, respectively, typical for a linear PE. Sample run 1, with a reduced $M_w$ of 147,000 g/mol and similar $D$ (6.6), is significantly reduced on $\eta_0$ and $\lambda$, which is explained by the reduced intermolecular forces due to shortened molecular chains. However, though continuously decreasing in $M_w$ from sample run 1 through run 4, both $\eta_0$ and $\lambda$ take an unmistakably increasing trend, suggesting that these samples exhibit increased intermolecular forces and thus lengthened relaxation process. Sample run 1 was not detected in gelation. Sample run 2 was determined to contain a mere 0.9 wt % of the gel. The latter had a lower $M_w$ but much broader $D$. The increases in $\eta_0$ and $\lambda$ should be ascribed to the formation of LCBs by 1,9-decadiene. Increasing 1,9-decadiene feeds in sample runs 3 through 5 led to continuously increased $\eta_0$ and $\lambda$, due to increased long chain-branches with proportional gelation. Sample run 5 contained 15.3 wt % of gel, the $|\eta'|=\omega$ curve of which is thus off the legitimate range of Cross equation.

2.4. PE Structure Evolution. Based on the above experimental results, the evolution of the PE structure as affected by 1,9-decadiene in ethylene polymerization with the Ziegler–Natta catalyst in the presence of H$_2$ can be summarized as follows, along the line of increasing 1,9-decadiene feed. Similar to regular higher $\alpha$-olefins, such as 1-hexene, 1,9-decadiene causes PE to reduce molecular weight, and the reduction degrees increase with its feeds. The two double bonds of 1,9-decadiene are both fairly reactive in polymerization, only that the derived polymer chain-attached double bond is much less reactive as compared with the original one. As a result, with decreased feed, 1,9-decadiene forms pendant vinyl groups on PE chains of reduced $M_w$. Increasing the feed in turn increases the concentration of the polymer chain-attached double bond, which promotes its reaction in polymerization and enables the formation of LCBs. The LCB portion has higher molecular weights, thus broadening the molecular weight distribution. The increased double bond concentrations of PE make chain crosslinking inevitable, and the gelation degrees (gel contents) increases with 1,9-decadiene feeds.

3. CONCLUSIONS

In summary, we assessed 1,9-decadiene/ethylene copolymerization as a way for Ziegler–Natta catalysts to access long chain-branched PE. 1,9-Decadiene was found to induce a substantial comonomer effect on the catalyst activity and continuing decreases of PE molecular weight, similar to a regular higher $\alpha$-olefin, such as 1-hexene. Both double bonds of 1,9-decadiene were poorly reactive in polymerization, of which the polymer chain-attached was even much less reactive than the original one. This led to the formation of two distinct PE structures depending on 1,9-decadiene feeds. At decreased feeds, 1,9-decadiene gave pendant vinyl groups to PE on a very small scale (<0.1 mol %) without prompting formation of LCBs. On the other hand, long chain-branching was realized at increased 1,9-decadiene feeds, which was however accompanied by proportional gelation.

4. EXPERIMENTAL SECTION

4.1. Materials. MgCl$_2$/9,9-bis(methoxymethyl)fluorene (BMMF)/TiCl$_4$ catalyst was provided by Yingkou Xiangyang Chemical Co., China, which contains 3.8 wt % of Ti and 11.2 wt % of BMMF. TEA from Albemarle was diluted to 1.8 M in n-heptane. AR grades of heptane and hexane from Beijing Chemical Company were refluxed over Na before use. After stirring CaH$_2$ for 2 days, 1,9-decadiene (98%) purchased from J&K Chemical was purified by distilling under reduced pressure before use. Ethylene (polymerization grade) was from Sinopec YanShan Petrochemical Co. of China.

4.2. Copolymerization. Ethylene polymerization was carried out in a 450 mL stainless steel autoclave reactor. In a typical polymerization run (run 5 in Table 1), having been...
vacuumed and dried at 80 °C for 1 h beforehand, the reactor was fed with ethylene at atmospheric pressure, followed by addition of 100 mL of hexane, 0.6 mL (1.8 M in n-heptane) of AlEt₃, and 3.5 mL of (18.9 mmol) of 1,9-decadiene via a syringe in a row. Then, 0.2 MPa of hydrogen was followed into the reactor. The contents of the reactor were mixed for 2 min with stirring, after which 15 mg of MgCl₂/BMMF/TiCl₄ catalyst was added dropwise to start the polymerization. The ethylene pressure was quickly brought up to 0.73 MPa, and the polymerization temperature kept at 80 °C. The polymerization was allowed to proceed for 30 min before 100 mL of acidic ethanol (10%) was introduced to terminate the polymerization. The final product was poured into 300 mL of ethanol and stirred vigorously, after which the product was retrieved by filtration and repeatedly washed with ethanol and water. It was then vacuum-dried overnight at 60 °C, after which 32.0 g of the product as a white powder was obtained.

### 4.3. Characterization

A bruker DMX 300 spectrometer operating at 300 MHz and 110 °C was used to acquire the 1H NMR spectra. 0.5 mL of o-dichlorobenzene-d₄ was used to dissolve the samples. The highest peak of o-dichlorobenzene-d₄ (δ ¹H 7.26) was used as the reference. Other parameters were set as follows: 30° pulse angle, 2 s recycle delay, 0.8 s acquisition time, 15.50 μs pulse width, 22,675 Hz spectral width, and 1000 scans.

The molecular weight and molecular weight distribution of the polymer were analyzed by a Waters Alliance PL-GPC 220 instrument equipped with three PL-gel Mixed-B (10 μm) columns and a refractive index detector. 1,2,4-Trichlorobenzene was used as the eluent at a flow rate of 1.0 mL/min at 150 °C. For samples containing the gel, the on-line filter would impede the gel from entering the columns and exclude it from measurement.

A Pyris 1 PerkinElmer DSC-7 instrument was used to study the crystallizing and melting behaviors, which was calibrated with indium and tin under an ultra-high purity nitrogen atmosphere prior to the measurement. The samples were sealed in aluminum pans. For the experiment, the sample was first heated to 200 °C at 50 °C/min and maintained at that temperature for a period of 5 min for the thermal history to be released. It was then cooled down to 30 °C at a rate of 10 °C/min and reheated to 200 °C at the same rate to obtain the melting profile.

A strain-controlled AR 2000 rheometer (TA Instruments) with a Peltier temperature control system was employed to carry out the small-amplitude oscillatory shear (SAOS) experiment using parallel-plate geometry (diameter of 25 mm). Samples were fabricated by injection molding at 200 °C into cylindrical specimens of 25 mm in diameter and 1 mm in thickness. The frequency range and the measurement temperature were between 0.05 and 500 rad/s and 180 °C, respectively. The measurement was conducted in a linear viscoelastic regime (3.0% strain). During the experiment, dry nitrogen was used to constantly purge the rheometer oven lest the samples were degraded.

Boiling xylene extraction was used to determine the gel contents (percentage of insoluble portion).

### Table 2. Cross Equation Parameters for Samples in Table 1

| entry | η₀ (× 10⁴ Pa s) | λ (s) | N   |
|-------|----------------|------|-----|
| control | 3.24 | 2.67 | 0.47 |
| 1     | 1.30 | 0.98 | 0.45 |
| 2     | 1.34 | 3.01 | 0.42 |
| 3     | 1.99 | 11.8 | 0.39 |
| 4     | 4.22 | 41.8 | 0.41 |
| 5     |      |      |     |

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**Figure 4.** Sample characterization with SAOS at 180 °C. (A) Storage modulus (G’) vs angular frequency (ω); (B) loss modulus (G’’) vs ω; and (C) complex viscosity (|η*|) vs ω. (a) Control run, (b) run 1, (c) run 2, (d) run 3, (e) run 4, and (f) run 5.

**Table 2. Cross Equation Parameters for Samples in Table 1**

- **η₀** (× 10⁴ Pa s): Viscosity at 0.1% strain
- **λ**: Relaxation time
- **N**: Decay exponent

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**Notes**

The authors declare no competing financial interest.

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