Synthesis of New Dendritic Titanium Catalysts and Catalytic Ethylene Polymerization

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ABSTRACT: The 1.0G dendrimer polyamidoamine (PAMAM), 3,5-dichlorosalicylaldehyde, and TiCl₄·2THF were used as synthetic materials, and the dendritic salicylaldehyde imide ligand with substituent hindrance and its titanium catalyst were synthesized by the condensation reaction of Schiff base. The structure of the synthesized products was characterized by infrared spectroscopy, nuclear magnetic resonance hydrogen spectroscopy, ultraviolet spectroscopy, electrospray mass spectrometry, and inductively coupled plasma-mass spectrometry. Activated methylaluminoxane (MAO) was used as a catalyst precursor for ethylene polymerization in the process of ethylene catalytic. The effects of ethylene polymerization were studied in terms of the Al/Ti molar ratio, reaction time, reaction temperature, polymerization pressure, and ligand structure of the catalyst. The results show good catalytic performance (70.48 kg PE/mol Ti·h) for ethylene polymerization because of the existence of ortho substituent hindrance on the salicylaldehyde skeleton. Furthermore, high-temperature gel permeation chromatography (GPC)-IR, differential scanning calorimetry (DSC), and torque rheometer were used to characterize the microstructure, thermal properties, and viscoelastic state of the polyethylene samples obtained. The results showed that the product was ultrahigh-molecular-weight polyethylene.

1. INTRODUCTION
Polyolefin materials have aroused much attention of the people. The development of the polyolefin industry can greatly promote the development and progress of all related fields. However, the development of polyolefin industry is dependent with that of the catalysts. The renewal of the catalysts often leads to the revolution of the polyolefin industry. The development of catalysts is mainly carried out through several stages, such as Ziegler−Natta catalyst, metallocene catalyst, and nonmetallocene catalyst. Nonmetallocene catalysts have attracted increasing attention because of their advantages of simple synthesis and high catalytic efficiency. Many scientists are involved in the research on the synthesis and catalytic performance of nonmetallocene catalysts. The FI catalyst was developed by Fujita’s team in Japan, and it was designed with ligand as the central concept characterized by simple synthesis, mild reaction conditions, and very high activity against ethylene polymerization. Ligand structure with rich electronic properties is the key to achieve high catalytic activity. New polyolefin materials such as ultrahigh-molecular-weight polyethylene (UHMWPE), polyolefin particles, monodisperse polyethylene, and olefin block copolymers can be catalyzed by changing the ligand structure.

Among the FI catalysts, dendritic macromolecular catalysts are relatively special. This series of catalysts can accurately control the number and position of catalytic active points. However, most of them are studies on ethylene oligomerization studies on homogeneous polymerization of ethylene catalyzed are limited. Zhao conducted preliminary studies on the titanium-catalyzed ethylene polymerization of polyamides dendrimers, but they did not evaluate the effects of core ligand structure changes on the activity and product properties. In recent years, the author’s research group synthesized a series of transition-metal catalysts with dendrimers as the skeleton to catalyze ethylene polymerization. These catalysts have good...
catalytic ethylene polymerization performance. Moreover, the alkyl chain length at the end of the catalyst and the molecular hole can directly affect the catalytic activity of the catalyst.27−32 In this paper, poly(amidoamine) dendrimer-supported titanium catalyst was synthesized. Dendritic salicylaldehyde imine ligands with steric hindrance were designed and synthesized, and the corresponding complexes were obtained after coordination with titanium. The effects of steric hindrance of ligand on catalytic activity and product performance were investigated.

2. RESULTS AND DISCUSSION

2.1. Fourier Transform Infrared Spectrometer (FTIR) Analysis of the Ligand and the Metal Catalyst. Adopt Vector 22 Fourier Transform of Swiss Bruker Company Infrared spectroscopy was used for the analysis of dendritic 3,5-dichlorosalicylaldehyde ligand and catalyst. As shown in Figure 1, the peak at 3425 cm$^{-1}$ can be assigned to the $\text{O\text{H}}$ stretching vibrations. The characteristic absorption peak at 2922 cm$^{-1}$ can be assigned to the $\text{CH}_2$ vibration of the ligand skeleton. A sharp peak was observed near 1208 cm$^{-1}$ and can be assigned to the $\text{C\text{O}}$ vibration. In addition, the absorption peak near 1453 cm$^{-1}$ can be assigned to the $\text{C=}$ of the benzene ring skeleton in ligand L. The absorption peak near 740 cm$^{-1}$ can be assigned to the $\text{C-Cl}$ vibration. The sharp peak observed at 1642 cm$^{-1}$ can be assigned to the $\text{C=N}$ vibration of the dendritic 3,5-dichlorosalicylaldehyde ligand, indicating that the terminal amine group of 1G polyamidoamine (PAMAM) underwent the Schiff base reaction with the aldehyde group of salicylaldehyde to form a dendritic 3,5-dichlorosalicylaldehyde ligand.33 Moreover, the comparison of the infrared spectra of ligand L and complex C shows that after the dendritic 3,5-dichlorosalicylaldehyde ligand is coordinated with metallic titanium, the stretching vibration absorption peak of the catalyst C=$\text{N}$ shifted to the low displacement direction and appeared at 1637 cm$^{-1}$.

2.2. Nuclear Magnetic Resonance Hydrogen Spectrum ($^1$H NMR) Analysis of the Ligand and Metal Catalyst. As shown in Figure 2, the INOV-400 MHz nuclear magnetic vibration instrument was used to characterize the $^1$H NMR of the synthesized dendritic salicylaldimine ligands and catalysts.

![Figure 1. IR spectra of 3,5-dichlorosalicylaldehyde ligands and titanium complexes.](image)

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![Figure 2. $^1$H NMR spectra of (a) dendritic 3,5-dichlorosalicylaldehyde ligand and (b) titanium metal catalyst.](image)

Figure 2. $^1$H NMR spectra of (a) dendritic 3,5-dichlorosalicylaldehyde ligand and (b) titanium metal catalyst.
2.3. $^{13}$C NMR Analysis of the Ligand and Metal Catalyst. Figure 3 shows the $^{13}$C NMR spectrum of the dendritic 3,5-dichlorosalicylaldehyde ligand and catalyst. The chemical shifts corresponding to various carbon atoms are basically the same. $^{13}$C NMR (CDCl$_3$, 400 MHz): $\delta$ ppm = 176.21, 132.18, 127.45, 61.49, 56.65, 53.54, 48.87, 42.24, and 32.65. This is due to the fact that the carbon atoms in the ligand skeleton are connected to atoms with different electrical absorption capabilities, resulting in different electron cloud densities around each carbon atom and therefore different chemical shifts; because the benzene ring is an electron-deficient group, it has a high chemical shift, and the multiple-peak chemical shift $\delta = 132.18$ and $\delta = 127.45$ are caused by the benzene ring in the ligand structure; because the carbon atom of the carbonyl group in −CONH− is connected to the oxygen atom, the electron cloud density around the carbon atom is the lowest. The chemical shift is the highest, so a corresponding single peak appeared at the chemical shift $\delta = 176.21$; the other single peaks at low chemical shifts are all caused by the carbon atoms in the alkyl chain of the ligand structure.

2.4. Mass Spectrometry (MS) Analysis of Synthetic Ligands and Metal Catalysts. The mass spectra of the synthesized dendritic 3,5-dichlorosalicylaldehyde ligand and its titanium metal catalyst were characterized by a Bruker’s micro-OTOF-Q II electrospray ionization mass spectrometer. The result is shown in Figure 4. The quasi-molecular ion peaks of the dendritic 3,5-dichlorosalicylaldehyde ligand and its titanium metal catalyst can be observed in the mass spectrum, where the quasi-molecular ion peak of ligand L [M]$^+$ appears at $m/z = 1209.18$. In addition, the mass spectrum peaks $m/z$ 701.4030 and 588.4091 can be assigned to [M-C$_{20}$H$_{18}$C$_4$N$_4$O$_3$]$^+$ and [M-C$_{26}$H$_{30}$C$_4$N$_5$O$_4$]$^+$, respectively. The quasi-molecular ion peak [M]$^+$ of the catalyst C appeared at $m/z = 1441.86$, and the mass spectrum peaks $m/z$ 559.3956 and 493.3781 can be assigned to [M-C$_{32}$H$_{38}$Cl$_6$N$_8$O$_6$Ti]$^+$ and [M-C$_{36}$H$_{46}$Cl$_6$N$_8$O$_6$Ti]$^+$, respectively.

2.5. UV Spectra Analysis of the Ligands and Metal Catalyst. The UV−vis spectra of the dendritic 3,5-dichlorosalicylaldehyde ligand and its titanium metal catalyst were characterized using a UV-1700 PharmaSpec ultraviolet−visible spectrophotometer. The results are shown in Figure 5. Three absorption bands were observed at approximately 224.5, 258.5, and 333.5 nm in dendritic 3,5-dichlorosalicylaldehyde ligand L. The band at 224.5 nm can be assigned to the $\pi \rightarrow \pi^*$ transition of the C=O of the ligand skeleton. The K band at
258.5 nm can be assigned to the conjugation of the benzene ring and C=N. The B band of the benzene ring was masked by the K band. The band around 333.5 nm can be assigned to the $\pi \rightarrow \pi^*$ transition R of C=N generated after the reaction. In comparison with the three absorption bands of L near 224.5, 258.5, and 333.5 nm, the K band representing the $\pi \rightarrow \pi^*$ transition of C=N in the ultraviolet spectrum of the titanium complex C was very weakened and cannot be observed. The K band (258.5 nm) of the benzene ring conjugated with C=N was also blue-shifted. This phenomenon occurred because the coordination of the titanium atom with the N atom destroyed the conjugated system formed by the C=N bond and the benzene ring. Subsequently, the maximum absorption wavelength decreased, the molar absorption coefficient decreased, and the band intensity weakened or even disappeared.

2.6. Catalytic Ethylene Polymerization. Toluene was used as a solvent, and methylaluminoxane (MAO) was used as a cocatalyst in the ethylene polymerization. To probe the effect of reaction parameters on the ethylene polymerization behaviors, we investigated the complexes by changing the catalytic system.

Based on the catalytic antisense of entries 1–5 in Table 1, the Al/Ti molar ratio has a greater influence on ethylene polymerization. Without MAO, the catalytic system had no activity. As the Al/Ti molar ratio increased, the catalytic activity and the viscosity average molecular weight of polyethylene gradually increased. When $n(\text{Al})/n(\text{Ti})$ was 1000, the catalytic activity reached the maximum value of 70.48 kg PE/(mol·h). However, when $n(\text{Al})/n(\text{Ti})$ increased to 1500, both the activity and molecular weight decreased. This finding was recorded possibly because of the increase. This is because when the addition amount of MAO is relatively low, part of the MAO reacts with the impurities in the system and the remaining MAO is insufficient to fully activate the metal active sites in the system. MAO continues to grow, increase the chain transfer rate, and thus decreasing the molecular weight of the polymerized product. Therefore, the maximum $n(\text{Al})/n(\text{Ti})$ should be set to 1000.

Based on entries 4, 6, 7 in Table 1, with the increase of polymerization time, the activity of the catalytic system decreased, whereas the viscosity average molecular weight increased, but the change was not large. This is because, as the polymerization time extends, there are more and more polymers in the system, which may not only embed part of the active center but also affect the diffusion of monomers in the solvent and reduce the concentration of monomers around the active center, so the polymerization activity becomes lower and lower. Therefore, the polymerization time is preferably 30 min.

Based on entries 4, 8, and 9 in Table 1, as the polymerization temperature increased, the activity of the catalytic system decreased, and the viscosity average molecular weight gradually decreased. The best catalytic activity was observed at 25 °C. This phenomenon occurred possibly because as the reaction temperature rises, the rate of motion between molecules of the system will also increase, and the possibility of a collision between ethylene monomer and the active site will also increase. Meanwhile, the catalytic activity will also increase. When the reaction temperature reaches a certain critical point, too high a temperature will make ethylene monomer difficult to dissolve in the solvent, so the activity of the catalyst will decrease with the increase of the reaction temperature. Hence, both the catalytic activity and molecular weight decreased.

Based on entries 4, 10, 11, and 12 in Table 1, the activity of the catalytic system first increases and then decreases. This finding occurred because of the concentration of ethylene in the system and the remaining MAO is insufficient to fully activate the metal active sites in the system. MAO continues to grow, increase the chain transfer rate, and thus decreasing the molecular weight of the polymerized product. Therefore, the maximum $n(\text{Al})/n(\text{Ti})$ should be set to 1000.

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Table 1. Results of Ethylene Polymerization Catalyzed by Catalyst

| entry | catalyst | $n(\text{Al})/n(\text{Ti})$ | time (min) | temperature (°C) | Pc2h4 (MPa) | activity (kg PE·mol⁻¹·h⁻¹) | $10^{-4}M_4$ |
|-------|----------|-----------------|------------|------------------|-------------|-----------------------------|------------|
| 1     | C        | 0               | 30         | 25               | 1.0         | 3.23                        | 1.39       |
| 2     | C        | 500             | 30         | 25               | 1.0         | 12.26                       | 1.42       |
| 3     | C        | 800             | 30         | 25               | 1.0         | 70.48                       | 1.46       |
| 4     | C        | 1000            | 30         | 25               | 1.0         | 52.21                       | 1.38       |
| 5     | C        | 1500            | 60         | 25               | 1.0         | 44.46                       | 1.49       |
| 6     | C        | 1000            | 120        | 25               | 1.0         | 30.21                       | 1.51       |
| 7     | C        | 1000            | 45         | 25               | 1.0         | 50.35                       | 1.42       |
| 8     | C        | 1000            | 65         | 25               | 1.0         | 40.36                       | 1.38       |
| 9     | C        | 1000            | 30         | 25               | 0.3         | 20.34                       | 1.29       |
| 10    | C        | 1000            | 30         | 25               | 0.5         | 47.88                       | 1.38       |
| 11    | C        | 1000            | 30         | 25               | 1.2         | 60.46                       | 1.38       |
| 12    | C        | 1000            | 30         | 25               | 1.0         | 56.56                       | 1.28       |
| 13    | C⁰       | 1000            | 30         | 25               | 1.0         | 1                           | 0.08       |

**Table 1. Results of Ethylene Polymerization Catalyzed by Catalyst**

- Reaction conditions: 8 μmol catalyst and 50 mL of toluene.
the catalytic system, the probability of ethylene colliding with the catalytic active center, and the chain growth rate all increased. Moreover, the chain transfer was effectively inhibited, thus increasing the catalytic activity and viscosity average molecular weight; however, the viscosity of the system will increase with the increase of the content of higher olefin, and when the viscosity reaches a certain value, the chain growth reaction will be hindered, thus resulting in the declined content of the higher olefin.

The titanium catalysts C, C1,26 and C235 were used as the research objects (Figures 6 and 10) to investigate the effect of the catalyst structure on the performance of ethylene polymerization. Under the optimal reaction conditions, three kinds of salicylaldimine titanium were obtained. The results of the ethylene polymerization catalyzed by the catalyst are shown in Table 1. Entries 4, 13, and 14 show that dendritic titanium catalysts C and C1 have much higher activity for polymerizing ethylene than nondendritic titanium catalyst C2 because of the dendritic structure in the same molecule. This is because the local concentration of the active sites of the macromolecular catalyst precursor is high. The activity of the dendritic catalyst C with large volume hindrance and electron-withdrawing group and the molecular weight of the resulting polyethylene were higher than those of the dendritic catalyst C2. This is because the 3,5-dichlorosalicylaldehyde complexes with the larger steric hindrance can effectively inhibit the β−H elimination reaction during the catalysis of ethylene. The bulky substituents shield the axial plane and prevent chain termination. Moreover, chlorine substituents are electron-absorbing groups, which can increase the electrostatic charge of the active center, promote the ethylene insertion process, and finally make the chain growth rate greater than the chain transfer rate, which is beneficial to the production of polymers. The catalyst easily causes a chain termination reaction. The dendritic titanium-based catalyst had a good catalytic activity for ethylene, and the steric hindrance and electron absorption function of the substituents can largely control the activity of the catalytic system and the molecular weight of the polymerized product.

2.7. Characterization of Polyethylene Structure. Figure 7 shows the high-temperature gel permeation chromatography (GPC) spectrum of the polyethylene sample obtained by catalyst C. The molecular weight of polyethylene sample overall distribution is unimodal, showing that the polyethylene sample characteristics of narrow overall molecular weight distribution, reflecting the characteristics of the corresponding single-component catalyst for ethylene polymerization.

Figure 8 shows the differential scanning calorimetry (DSC) curve of the polyethylene sample obtained from catalyst C. Figure 8 indicates that the melting peak of the obtained polyethylene is relatively narrow, thus supporting its high-temperature GPC data. The melting point of the sample reached 136 °C, which is in line with the thermal performance characteristics of the linear low-density polyethylene.36

2.8. Viscoelasticity of Polyethylene. At 220 °C, the dynamic storage and loss modulus (G’ and G″), complex viscosity (η∗), and dynamic viscosity (η′) of polyethylene as a function of frequency (f) are shown in Figure 9a,b. In the entire frequency range of the study, the storage modulus was higher than the loss modulus, showing the high elasticity of polyethylene. The dynamic viscous flow properties of polyethylene are consistent with the characteristics of ultrahigh-molecular-weight polyethylene37 which is caused by the entanglement between macromolecular chains. The higher the molecular weight of the polymer, the easier it is for the polymer chains to entangle and interact. The high elasticity of polyethylene shows that polyethylene is an ultrahigh-molecular-weight polyethylene. This result is consistent with the result of viscosity average molecular weight determination.
3. CONCLUSIONS

In summary, dendritic 3,5-dichlorosalicylic aldehyde ligand and its titanium metal catalyst were synthesized, and the structure was characterized by FTIR, $^1$H NMR, UV−vis, electrospray ionization mass spectrometry (ESI-MS), and inductively coupled plasma-mass spectrometry (ICP-MS). The actual structure is consistent with the theoretical design structure. This titanium metal catalyst was used as the catalyst system precursor, under the activation of MAO, the catalyst system under different polymerization conditions (e.g., Al/Ti molar ratio, reaction time, reaction temperature, and polymerization pressure). The results show that the dendritic 3,5-dichlorosalicylaldehyde titanium metal catalyst has good catalytic performance in ethylene polymerization. At the reaction temperature of 25 °C, the reaction time was 30 min and the ethylene pressure was 1.0. When the ratio of the amount of MPa and Al/Ti was 1000, the catalytic activity can reach 70.48 kg PE/(mol Ti·h), which is much higher than that of the monomolecular catalysts with similar structures and dendrimers with low steric hindrance of steric substituents. The catalyst proves that the steric hindrance of the end group of catalyst substituent and electron-absorbing ability have a significant effect on the dendritic titanium catalyst catalyzing ethylene. As the steric hindrance and electron-absorbing groups of the substituent increased, the catalytic activity and the molecular weight of the product also increased. In addition, the thermal properties and viscoelastic state of the catalyzed polyethylene samples were analyzed and characterized, and the
results showed that the product was ultrahigh-molecular-weight polyethylene.

4. EXPERIMENTAL SECTION

4.1. Reagents and Instruments. 3,5-Dichlorosalicylaldehyde (analytical grade, Aladdin Co., Ltd.), tetrahydrofuran, toluene, n-hexane, dichloromethane (analytical grade, Tianjin Comiou Co., Ltd.) were used as reagents. Tetrahydrofuran and toluene were dried by refluxing sodium wire/benzophenone under the protection of argon before use. Dichloromethane was used after drying with CAH2. MAO (10% toluene solution), Aladdin Co., Ltd., TiCl4 (analytically grade, Tianjin Kemeiou Chemical Reagent Co., Ltd.), and ethylene (polymerization grade, Sinopec Daqing Petrochemical Co., Ltd.) were used after the 4A zeolite drying treatment. 1.0G dendritic macromolecules were synthesized in the laboratory.38 All operations were carried out in an argon atmosphere using the standard Schlenk technology, where the solvent was steamed.

The equipment used included a Fourier transform infrared spectrometer (Vector 22, Bruker, Switzerland), a Micr OTOF-Q Q II electro spray ionization mass spectrometer (ESI-MS, Bruker), an Inov-400 MHz NMR instrument (Varian Corporation), an UV-1700 PharmaSpec type UV-vis spectrophotometer (Shenzhen Comija Instrument and Equipment Co., Ltd.), an Agilent 8800 inductively coupled plasma-mass spectrometer (Agilent), and a H NMR, Bruker AVANCE spectrometer (Agilent), an Agilent 8800 inductively coupled plasma-mass spectrometer (Agilent), and a H NMR, Bruker AVANCE spectrometer with TMS as an internal table standard and scanning frequency of 500 MHz. Elemental analysis, EA-1106 analyzer (PerkinElmer); PI-GPC220 high-temperature gel chromatograph (Beijing Pulitech Co., Ltd.); CL800S glovebox, Chengdu Delis Industrial Co., Ltd. The melting and crystallization temperatures were determined using a STA 449 F3 Jupiter differential scanning thermal analyzer (DSC). The heating rate was 10 K/min under a nitrogen atmosphere. The viscoelasticity of polyethylene was measured using a Thermo Haake Rheostress 600 torque rheometer at 220, with a frequency of 1 Hz and a maximum swing stress of 10 kPa.

4.2. Synthesis of Dendritic Salicylaldimine Titanium Catalyst. 4.2.1. Synthesis of Ligand. The synthetic route and the structure of the ligand are shown in Figure 10.

A magnetic stirring bar was placed in a 250 mL three-necked flask in a glovebox. The flask was added with anhydrous sodium sulfate (3.0 g) and slowly with 3,5-dichlorosalicylic aldehyde (4.44 g, 28.34 mmol). Under a nitrogen atmosphere, the flask was connected to the double-row tube and pumped thrice, and absolute ethanol (20 mL) was injected into it. Then, the mixture was stirred and heated. When the temperature reached 78 °C, ethanol (50 mL) and 1.0G PMAM (2.3 g, 4.46 mmol) were injected for 12 h, followed by filtration. The obtained liquid was precipitated using ether as the precipitant, and the yellow solid precipitate was collected and dried in a vacuum at 50 °C. A light-yellow solid powder, which is the dendritic salicyladimine ligand, was obtained in a yield of 68%. ESI-MS (me, relative strength, %): 1209.1808 (M+), M-elemental analysis C_{50}H_{36}C_{10}N_{10}O_{8} (1209.87): C, 49.69; H, 4.67; N, 11.59; O, 10.59. Elemental analysis: C, 49.25; H, 4.58; N, 11.46; O, 10.62.

4.2.2. Synthesis of Dendritic Titanium Catalyst. In a vacuum glovebox, ligand (1.3 mmol) was added to tetrahydrofuran (THF) (100 mL). After full dissolution, NAH (5.2 mmol) was added to the mixture and stirred for 24 h at 25 °C. A yellow solid powder was precipitated in the solution. TiCl4·2THF (2.45 mmol) was added to this solution and stirred continued at 25 °C for 24 h. Then, the mixture was filtered, and the precipitate was extracted and purified with dichloromethane, washed with toluene, and finally added with n-hexane to precipitate a light-yellow solid powder. The yield after vacuum drying was 40%. ESI-MS (me, relative strength, %): 1442.18 (M+). C_{60}H_{52}C_{11}N_{10}O_{8}Ti_{2} (1442.18): Elemental analysis: Ti, 6.64, ICP-AES: Ti 6.67.

The synthesis route and the structure of the titanium catalyst are shown in Figure 10.

4.2.3. Ethylene Polymerization. The ethylene polymerization reaction was carried out in a 250 mL stainless steel reactor with magnetic stirring. The reactor was heated under a vacuum for 2 h at 160 °C and subsequently allowed to cool to room temperature. The reactor was flushed with ethylene three times. Solvent, the desired amount of cocatalyst, and solution of the metal complex (0.8 μmol/mL, 10 mL) (the total volume was 50 mL) were added to the reactor in this order under an ethylene atmosphere, filled with ethylene to the set pressure, and subjected to polymerization reaction at the specified temperature. The reaction was continued for the expect time, the temperature was reduced, the pressure was relieved, and the polymerization reaction was terminated using acidified ethanol with a mass fraction of 10%. Then, the mixture was filtered and the white solid powder was washed with ethanol. The obtained polyethylene was vacuum-dried at 50 °C, and the catalyst activity of the catalyst was calculated. The molecular weight of polyethylene was determined using the viscosity method and gel chromatography (GPC). The former used decalin as a solvent at 140 ± 0.1 °C using an Uzbekistan viscometer, where η = 6.77 × 10^{-4} (Mg)^0.67. The viscosity average molecular weight Mn of polyethylene was calculated. The latter was measured on a PL-220 high-temperature GPC at 140 °C with 1,2,4-trichlorobenzene as the mobile phase.

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All authors have given approval to the final version of the manuscript. T.L. performed the conceptualization, methodology, software, investigation, and writing of the original draft.
The authors declare no competing financial interest.

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**ABBREVIATIONS**

| Abbreviation | Definition |
|--------------|------------|
| PE           | Polypropylene |
| PAMAM        | Polyamidoamine |
| MAO          | Methylaluminoxane |
| FTIR         | Fourier transform infrared spectrometer |
| 1H NMR       | Nuclear magnetic resonance hydrogen spectrum |
| UV-Vis       | Ultraviolet-visible spectrophotometry |
| ESI-MS       | Electrospray ionization ion trap mass spectrometry |
| ICP-MS       | Inductively coupled plasma-mass spectrometry |
| GPC          | Gel permeation chromatography |
| DSC          | Differential scanning calorimetry |
| THF          | Tetrahydrofuran |

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