

Preparation and properties of isotactic polypropylene obtained from MgCl_2 -supported TiCl_4 catalyst bearing bifunctional internal donor

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Abstract In this research, a novel MgCl_2 -supported TiCl_4 catalyst in conjunction with bifunctional internal donor was synthesized. The effects of internal donor on propylene polymerization behaviors and polymer properties (morphology, M_w and MWD) were investigated. It was found that the activity of novel catalyst was higher than that of the traditional DIBP-based Ziegler–Natta catalyst, while the catalyst activity was less influenced by the ether group length of the bifunctional internal donor. It was also observed that the MWD of PP obtained by bifunctional internal donor-based catalyst was broader than that of PP made by DIBP-based Ziegler–Natta catalyst.

Keywords Ziegler–Natta catalyst · Polypropylene · Molecular weight distribution · Bifunctional internal donor

Introduction

The polyolefin industries began in the 1950s because of discoveries of Ziegler–Natta catalyst. All of the common polyolefins led to births in the industries by their discoveries [1, 2]. Over the years, Ziegler–Natta catalysts have evolved from simple TiCl_3 crystals to the multi-component MgCl_2 /donor/ TiCl_4 catalyst systems, where

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the donor was a Lewis base that can be added during catalyst preparation (the so-called internal donor) [3]. 1,3-Diether [4, 5], aromatic ester (benzoate and phthalate) [3, 6, 7], and aliphatic ester (succinate) [8, 9] were widely used as internal donors. The internal donor plays its role during the preparation of the solid catalyst when it competes with TiCl_4 for coordination to the MgCl_2 support and shields the faces of the support where only specific centers could be formed from TiCl_4 coordination [10]. During polymerization, internal donor was removed from catalyst due to complex formation with the alkyl-aluminium cocatalyst, so that external donor was needed to supply for high isotacticity [4, 11]. The presence of donor was essential to affect the performance of the Ziegler–Natta catalyst, since they can strongly modify the catalyst activity, stereoselectivity, regioselectivity and molecular weight distribution. However, the discovery of 1,3-diethers has made it possible to obtain highly active and stereospecific catalysts using only an internal donor.

It was well known that molecular weight and molecular weight distribution were very important factors in determining the physical, mechanical, and rheological properties of polymers [12]. The molecular weight controls the mechanical properties of polymers and molecular weight distribution mainly controls the rheological properties [13]. It was highly desirable to have for many applications, such as an extrusion and molding processes, polymer which have a broad molecular weight distribution. Therefore, it was necessary to provide a high performance catalyst system which can be usefully employed in highly efficient production of polymers which have a broad molecular weight distribution. Therefore, the aim of the present work was to study the effect of novel bifunctional donor (ether and ester group) on catalyst activity, isospecificity, molecular weight and molecular weight distribution of PP.

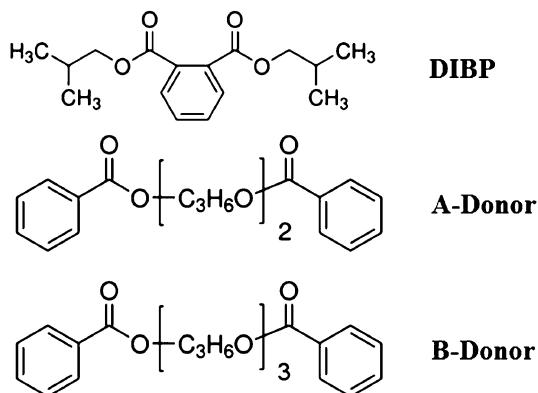
Experimental

Materials

$\text{MgCl}_2 \cdot 2.8\text{C}_2\text{H}_5\text{OH}$, TiCl_4 , dimethoxydiphenylsilane (DDS), di(propylene glycol) dibenzoate (A-Donor) and tri(propylene glycol) dibenzoate (B-Donor) were supplied by Yingkou xiangyang Chemicals Group and used as received. Diisobutyl phthalate (DIBP) was purchased from Aldrich and dried with CaH_2 . The structures of internal donor were given in Scheme 1. Hexane was dried with Na/K alloy with benzophenone. Triethyl aluminium (TEA, 1.0 M solution in *n*-hexane) was purchased from Tosoh Akzo Co., Ltd., Japan.

Preparation of catalyst

A Schlenk type reactor was used to prepare the catalysts. A large excess of TiCl_4 was introduced into the reactor and kept at -20°C . An amount of micro-spherical $\text{MgCl}_2 \cdot 2.5\text{C}_2\text{H}_5\text{OH}$ was added slowly, with agitation and maintained at this temperature for 30 min. The suitable internal electron donors (DIBP, A-Donor or

Scheme 1 Structure of internal donor

B-Donor) were added after the temperature was raised to 60 °C. The reactor mixture was allowed to react at 110 °C for 2 h. The resulting solid was filtered and washed with hexane 5 times at 60 °C and 2 times at room temperature. The final catalysts dried under vacuum were $MgCl_2/TiCl_4/DIBP$, $MgCl_2/TiCl_4/A-Donor$ and $MgCl_2/TiCl_4/B-Donor$.

Polymerization procedure

The bulk polymerization of propylene was carried out in a 2-L stainless steel autoclave. The reactor was back-filled three times with nitrogen and charged with 0.8 L liquid propylene. After 0.8 L liquid propylene was added, the cocatalyst, DDS, and catalyst were transferred into the autoclave with 0.6 L liquid propylene and then the polymerization started. The polymerization temperature was brought to 80 °C. After 2 h, the unreacted monomer was released and the obtained polymer was dried under vacuum at 60 °C to its constant weight.

Characterization

The obtained polymers were fractionated by extraction with boiling *n*-heptane for 8 h to determine the isotactic index (II) and the II values reported for each samples were the weight percentage of *n*-heptane insoluble polymer.

The inductively coupled plasma mass spectrometry (ICP-MS) used in this work was provided by Thermo Jarrell-Ash Corporation, Franklin, MA, USA.

The melting temperature (T_m) of the obtained polymer was determined by differential scanning calorimetry (DSC, Perkin-Elmer Pyris) operating at a heating rate of 10 °C/min. The PP cooled down from melt (200 °C) to 30 °C at a rate of 10 °C/min, and the melting point was determined in the second scan.

The molecular weight and PDI of the obtained polymers were determined by GPC measurement with 1,2,4-trichlorobenzene as solution at 135 °C using a PL-220 (Polymer Laboratories) equipped with a refractive-index detector.

Results and discussion

Effect of internal donor on polymerization behaviors

The contents and structure of internal donors have a significant effect on the polymerization behaviors and polymer properties. The polymerization was carried out using three kinds of $\text{MgCl}_2/\text{ID}/\text{TiCl}_4$ catalysts in conjunction with TEA in the presence of DDS as external donor. The experimental results were given in Table 1.

It was found that the titanium content of the catalyst with DIBP as internal donor was higher than that of the catalyst contains bifunctional internal donor. With regards to the polymerization results, the lowest catalyst activity was obtained by DIBP as internal donor and the catalyst with A-Donor and B-Donor as internal donor have a similar catalyst activity toward propylene polymerization. It means that the catalyst activity was strongly affected by the type of internal donor, while less affected by the ester group length of the bifunctional internal donor. Among the catalyst used in the present research (run 2, 4 and 5), the catalyst with A-Donor and B-Donor as internal donor showed a slightly higher II value than that of the catalyst with DIBP (phthalate) as internal donor in the presence of DDS as external donor. The higher II could correspond to the higher content of internal donor remained in the solid catalyst after treated with TEA cocatalyst. As reported by Correa et al. [10], the donor coordination with MgCl_2 fragment reflects the relative Lewis base strength of oxygen atom and the coordination energies of the oxygen atoms were in the order of: ether > carboxyl \gg ester. It means that the coordination strength of different internal donor to the solid catalyst was in the following order: B-Donor \approx A-Donor > DIBP. In addition, Albizzati et al. [14] found that only trace amount of internal donor was extracted from the catalyst with diether as internal donor after treated with TEA, while near 70 wt% of internal donor was extracted from the $\text{MgCl}_2/\text{DiBP}/\text{TiCl}_4$ catalyst system.

The T_m of PP were slightly influenced by the kind of internal donor in the solid catalyst, while the T_m increased with the increasing II.

Effect of internal donor on polymer morphology

The morphology of the MgCl_2 , catalyst and polymer was examined by SEM and the results were given in Figs. 1, 2, 3.

Table 1 Influence of ID structure and contents on propylene polymerization

Run	ID	ID/ MgCl_2 feed ratio (mol/mol)	Ti wt%	Mg wt%	ID wt%	Activity (kg/mol-Ti-h)	II (%) ^a	T_m (°C)
1	A-Donor	0.06	2.97	18.2	8.4	14,222	97.4	161.8
2	A-Donor	0.10	2.65	17.8	9.8	16,845	98.8	162.3
3	B-Donor	0.06	2.91	17.2	10.5	14,185	97.3	161.5
4	B-Donor	0.10	2.88	15.7	12.6	16,166	98.5	162.3
5	DIBP	0.1	3.84	17.2	10.2	14,125	98.2	162.2

Polymerization conditions: bulk polymerization; $[\text{Al}]/[\text{Si}] = 6$; Time = 2 h; Temp = 80 °C

^a Isotacticity index: insoluble fraction in boiling *n*-heptane after extraction for 8 h

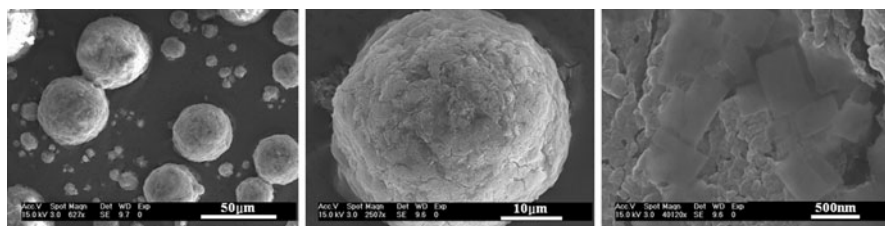


Fig. 1 External morphology of MgCl_2 support at different magnification

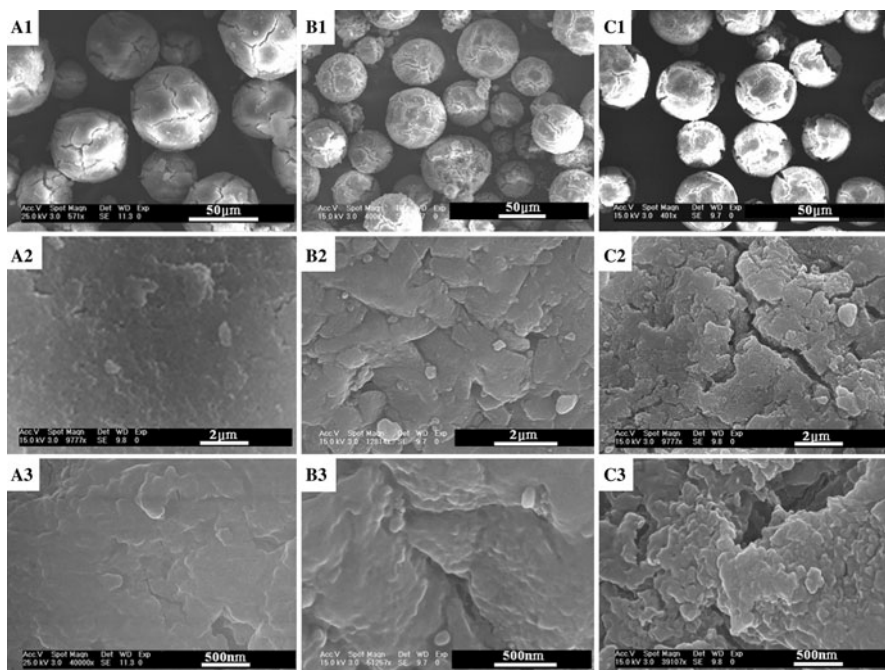


Fig. 2 SEM micrographs of the morphologies of catalysts with DIBP (A1–A3), A-Donor (B1–B3) and B-Donor (C1–C3) as internal donor

It can be seen that the MgCl_2 particles were very spherical in shape, ca. 30 ~ 50 μm in diameter. At higher magnifications, the nature of the particle surface was more clearly illustrated. Most of the spherical MgCl_2 particle surface was amorphous, but small portions of the crystal were still visible.

Figure 2 shows the morphologies of the catalyst with DIBP (A1–A3), A-Donor (B1–B3), and B-Donor (C1–C3), respectively. It was found that all the catalysts were free-flowing, spherical in shape, whose diameters were about 50 μm . A lot of micro-cracks were observed on the surface of the catalyst due to the violent reaction between support and TiCl_4 . In addition, the catalyst with A-Donor or B-Donor shows a loose structure as compared to the catalyst with DIBP as internal donor.

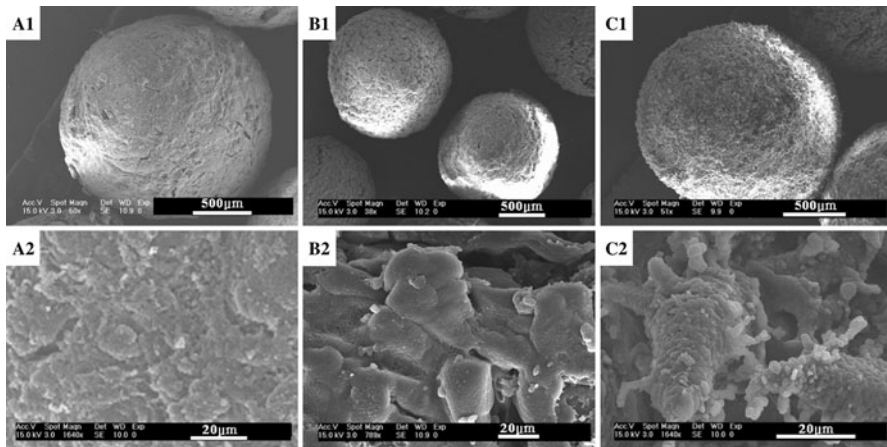


Fig. 3 SEM micrographs of the morphologies of PP particles obtained by DIBP (A1–A2), A-Donor (B1–B2) and B-Donor (C1–C2)-based catalyst

This may be attributed to the flexibility of the molecular chain in the A-Donor and B-Donor.

The morphologies of the PP particles were shown in Fig. 3. With the aid in morphological replication of the Ziegler–Natta catalyst, the obtained PP particles were spherical-shaped with diameter of 1,500 ~ 1,800 μm . Out of question, in contrast with the PP particles obtained by the catalyst with DIBP as internal donor, the PP particles obtained by bifunctional internal donor-based catalysts show a loose structure.

Effect of internal donor on M_w and MWD

Figure 4 showed the molecular weight distribution curves of the *n*-heptane insoluble fractions and the M_w and MWD results were given in Table 2.

The internal donor shows strong effect on the M_w and MWD of the PP product. The GPC curves of the obtained PP samples were all unimodal with broad MWD. As given in Table 2, the polymers produced from the catalyst with A-Donor and B-Donor as internal donor systems have similar molecular weight values, which were much lower than the one for the polymer obtained from DIBP-based catalyst system. Important observation related to the MWD of the PP products was that the MWD of PP obtained by catalyst with bifunctional internal donor broader than that of the PP made by catalyst with DIBP as internal donor, while the M_w decreased and MWD broadened with the increase of the number of ether group in bifunctional internal donor. This may be attributed to the more active sites were generated for catalyst consist of bifunctional internal donor. As seen in our previous research [15, 16], the catalyst consists of phthalate internal donor leads to produce PP with higher M_w than that of the PP obtained by the catalyst consists of diether internal donor.

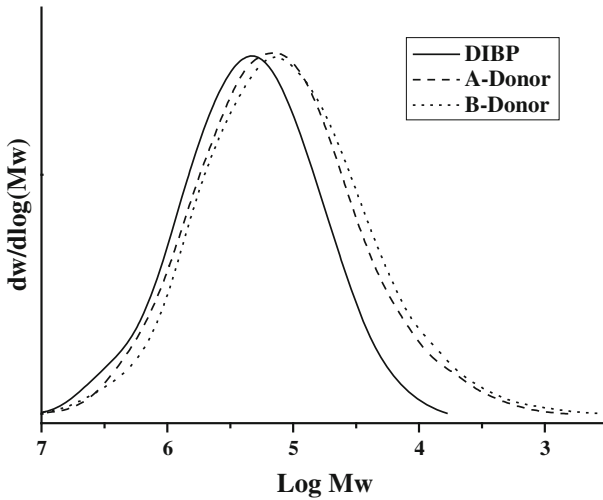


Fig. 4 GPC curves of PP obtained by DIBP, A-Donor and B-Donor-based catalyst

Table 2 Effect of internal donor on M_w and MWD of PP

ID	ID/MgCl ₂ feed ratio (mol/mol)	M_w ($\times 10^{-4}$)	MWD
DIBP	0.10	47.9	4.4
A-Donor	0.10	34.1	8.1
B-Donor	0.10	31.2	9.5

Conclusions

The activity of catalyst consists of bifunctional internal donor was higher than that of the catalyst with DIBP as internal donor. The catalyst activity with different internal donor decreases in the following order: A-Donor \approx B-Donor > DIBP. The obtained PP particles were spherical-shaped with diameter of 1,500 ~ 1,800 μm . In contrast with the PP particles obtained by the catalyst with DIBP as internal donor, the PP particles obtained by bifunctional internal donor show a loose structure. Among the three catalysts, the DIBP-based catalyst has the highest molecular weight and narrow MWD. The M_w and MWD of PP obtained with catalyst of bifunctional internal donor was dependent on the number of ether groups. In essence, increasing the number of ether groups leads to a decreased M_w and a broader MWD.

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