The Effects of Prepolymerization on Propylene Polymerization with Mg (OC\textsubscript{2}H\textsubscript{5})\textsubscript{2} Supported Catalyst

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(Received August 3, 1995, Accepted October 6, 1995)

Abstract: Prepolymerization with Mg(OC\textsubscript{2}H\textsubscript{5})\textsubscript{2}/phenyl triethoxy silane (PTES)/TiCl\textsubscript{4}/diisobutyl phthalate (DIBF)-Al(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}/PTES catalyst system was carried out under conditions of relatively low temperature and low pressure for a short time before the main polymerization. The effects of prepolymization on the yield, tacticity and morphology of polypropylene were examined under various prepolymization conditions using propylene as the prepolymization monomer. Prepolymization improved polymer morphology and enhanced the yield and isotactic index (I.I.). To obtain high performance polymers such as high-modulus polypropylene (HMPP), two-stage polymerization and prepolymization using vinyl cyclohexane (VCH) and divinyl benzene (DVB) as the prepolymization monomer were also investigated.

1. Introduction

Polypropylene is a versatile plastic material applied in the form of fibers and films. Ziegler-Natta is a common catalyst used in producing polypropylene. In spite of the enormous number of papers[1] and patents issued on Ziegler-Natta catalyst for polymerization of propylene, there are few publications dealing with in the effects of prepolymization parameter on the yield, tacticity and properties of the polymer. In the literature, a few publications[2-6] reported the effect of prepolymization on polymer morphology and rate enhancement. The prepolymization could reduce the catalyst fragmentation and thereby improve the polymer morphology.

The catalysts used in producing polyolefin are frequently prepolymized[7-9] by applying a thin coating of olefin on the catalyst in the presence of an alkyl aluminum compound, but the nature and mechanism of prepolymization have still not been well elucidated and required further attention[6].

Prepolymization means that a prepolymization step is carried out under mild conditions before the polymerization step is carried out. Non prepolymerization means that the polymerization step is carried out without the prepolymization step.

It was reported that straight-chain monoolefins (ethylene and propylene), branched monoolefins (4-methyl-1-pentene, VCH) and aromatic compounds (DVB) were frequently used as the prepoly-
merization are monomer. Especially, aromatic compounds are used to obtain HMPP[10-13]. The effects of prepolymerization with \( \text{TiCl}_3 \) catalyst on the morphology of the polymer were reported by Xu et al.[6] and Coutinho et al.[12].

In this study, prepolymerization with the \( \text{Mg} (\text{OC}_2\text{H}_5)_2 / \text{PTES} / \text{TiCl}_4 / \text{DIBP} - \text{Al} (\text{C}_3\text{H}_8)_3 / \text{PTES} \) catalyst system patented by Lee et al.[14] was carried out under various prepolymerization conditions, and then the effects of prepolymerization on the yield, tacticity and morphology of polypropylene were examined. In addition to propylene, DVB and VCH were used as the prepolymerization monomer.

2. Experimental

2.1. Materials and Equipment

Propylene (Honam Petrochemical Co.) was purified by passing through 5Å molecular sieve columns. Nitrogen was passed through deoxygenation columns and a molecular sieve bed to remove moisture and oxygen. Hexane and heptane were also purified by distillation with sodium for 12 hrs. \( \text{Mg} (\text{OC}_2\text{H}_5)_2 \), DVB, PTES, ethylene dichloride (EDC), VCH, DIBP, \( \text{Al} (\text{C}_3\text{H}_8)_3 \) and \( \text{TiCl}_4 \) were commercially obtained from Aldrich chemical Co. and used without further purification.

The equipment used in this study was: autoclave (Ernest Haage Co.), UV-visible spectro photometer (Milton Roy, Spectronic 300), gel permeation chromatography (GPC) (Waters Associates, Model GPC-150C), scanning electron microscope (SEM) (CSI Co., Model SX-30A), test machine for flexural modulus (FM) (Instron Co., Model 6022) and particle size analyzer (Malvern Instruments, Particle size 2600).

2.2. Preparation of Catalyst

Catalyst preparation was carried out under dry nitrogen in a four-necked flask (500 mL) equipped with an agitator and a reflux condenser. The catalyst used in this study was prepared by a method described in the patent literature[14]. The steps in the procedure for catalyst preparation are as follows: suspending 3 g of \( \text{Mg} (\text{OC}_2\text{H}_5)_2 \) in the mixtures of decane (100 mL) and EDC (50 mL); adding 6.9 mL of PTES as an internal donor; increasing the temperature to 80°C; stirring at 80°C for 2 hrs; adding 28.9 mL of \( \text{TiCl}_4 \) over 1 hr; increasing the temperature to 120°C; stirring at 120°C for 30 minutes; adding 3.4 mL of DIBP as an internal donor over 1 hr; stirring at 120°C for 2 hrs; cooling the temperature to room temperature; filtering the solid precipitate; suspending the solid component in n-hexane (100 mL); adding 170 mL of \( \text{TiCl}_4 \) at room temperature over 2 hrs for the second treatment; increasing the temperature to 120°C over 1 hr; stirring at 120°C for 2 hrs; cooling to room temperature; removing the supernatant by decantation; washing the solid catalyst with n-hexane five times. The Ti content of catalyst was determined by a UV-visible spectrophotometer using absorbance at 406 nm[15]. The Ti-content of catalyst was 34 mg Ti/g catalyst.

2.3. Polymerization

The autoclave (2 L, 18 cm I. D.) equipped with a stirrer of anchor type (17 cm I. D.) was used for polymerization as shown in Fig. 1. After the autoclave was purged by nitrogen, n-heptane (1 L), catalyst (0.03 mmol Ti), \( \text{Al} (\text{C}_3\text{H}_8)_3 \) as cocatalyst, and PTES as an external electron donor at room temperature were added, stirred for 10 minutes, then increased to reaction temperature. Subsequently, up to the operation pressure, the prepolymerization monomer was fed; prepolymerization was carried out for the given time; the reaction was stopped; unreacted prepolymerization monomer was removed. This prepolymerization step was carried out at various conditions (Al/Ti mole ratio, donor/Al mole ratio, pressure, time, temperature, etc.).

The polymerization step was carried out as follows: feeding n-heptane (1 L) and catalyst
percentage of the total amount of powder after extracting for 15 hrs. by boiling n-heptane using a soxhlet extractor; the T-II (total isotactic index, %) was taken as the amount of insoluble polymer as a percentage of the sum of the amount (P) of powder and the amount (A) of soluble fractions existing in the reaction medium withdrawn from reactor. The yield (kg-PP/g-Ti) of IPP (isotactic polypropylene), the yield of WPP (whole polypropylene) and the APP per unit mass of catalyst were calculated from the following equations:

\[
\text{Yield of IPP} = \frac{[PxP-II/100]}{g-\text{Ti}} \\
\text{Yield of APP} = \frac{[Px(I-P-II/100)+A]}{g-\text{Ti}} \\
\text{Yield of WPP} = \frac{[A+P]}{g-\text{Ti}} \\
\text{T-II} = \frac{[P-II x P]/(A+P)}
\]

The molecular weight distribution (MWD) of polymers was determined by GPC at 135°C with 1,2,4-trichlorobenzene as solvent, and standard polystyrene was employed to construct a calibration curve. The morphology of polymer and catalyst were examined by SEM. The bulk density (BD, g/cc) and melt index (MI, g/10min) of polymer were measured according to ASTM D1895 and ASTM D1238, respectively. Flexural modulus (FM, kg/cm²) of polymer was measured by bending-moment technique according to ASTM D790. The particle-size distribution of catalyst was measured by particle-size analyzer.

3. Results and Discussion

3.1. The Changes of Al/Ti Mole Ratio

The roles of alkyl aluminum in the polymerization have been reported as follows[16-18]: Gate et al.[16] reported that the rate of polymerization initially increases as the ratio of alkyl aluminum to titanium increases. However, as the ratio of alkyl aluminum to titanium increases over an optimum value the polymerization rate decreases and the stero-
Fig. 3. Effect of donor/Al mole ratio on the yield, IL, and BD of polymer produced. Prepolymerization conditions: Al/Ti=150, Press=2 atm, time=20 min, temp=70°C. Donor/Al mole ratio

Fig. 2. Effect of Al/Ti mole ratio on the yield, IL, and BD of polymer produced. Prepolymerization conditions: donor/Al=1, press=2 atm, time=20 min, temp=70°C. Donor/Al mole ratio

Donor/Al mole ratio

Yield of WPP and IPP(Kg-PP/g-Ti)

Yield of IPP and WPP(Kg-PP/g-Ti)
to over-reduction of titanium from Ti$^{3+}$ to Ti$^{2+}$.

To illustrate the effects of alkyl aluminum in the prepolymerization step, the prepolymerization step was carried out at various Al/Ti mole ratios; the polymerization step was carried out subsequently. The effects of the Al/Ti mole ratio on the yield, II and BD of produced polypropylene are shown in Fig. 2.

On increasing the Al/Ti mole ratio, the yield of IPP initially increases but decreases as the mole ratio increases over an Al/Ti mole ratio of 150; also the yield of WPP shows the same trend as the yield of IPP given in Fig. 2(A). The yield of WPP with prepolymerization is higher than that for nonprepolymerization: about 20% at an Al/Ti mole ratio of 150. On the other hand, the yield of APP initially decreases with increase in the mole ratio, but increases as the mole ratio increases over an Al/Ti mole ratio of 150.

As indicated in Fig. 2(B), the II increases rapidly when the Al/Ti mole ratio is less than 150, where as the II decreases relatively when the Al/Ti mole ratio is more than 150. The T-II with prepolymerization is higher than that for nonprepolymerization: about 2% at an Al/Ti mole ratio of 150.

Fig. 2(C) shows that BD increased slightly with prepolymerization.

From the above results it can be assumed that excess trialkyl aluminum above an Al/Ti mole ratio of 150 extracts internal donor from the catalyst, so the formation of APP is enhanced and the BD of polymer is decreased due to aggregation of polymer particles.

3.2. The Changes of Donor/Al Mole Ratio

An electron donor plays an important role in propylene polymerization. The addition of an external donor to Al(C$_2$H$_5$)$_3$ increases the isotacticity of polymer, but the activity of catalyst usually decreases. The roles of an external donor in the polymerization have been reported[19] to be as follows: selective poisoning of atactic centers, transformation of atactic centers to isotactic ones, increase in propagation-constant rate for isotactic centers, complexing and removal by donor of inhibitors of active sites, reduction in reducing power of alkyl aluminum, stabilization of active-center structure by an electron donor, etc. Alkoxysilanes are widely used as an external donor for Ziegler-Natta catalyst systems. PTES was used here as the external electron donor.

The prepolymerization step were carried out at various donor/Al mole ratios, after which the polymerization step was carried out. The effects of donor/Al mole ratio on the yield, II and BD of produced polypropylene are shown in Fig. 3.

On increasing the donor/Al mole ratio, the yield of IPP increased slightly, but decreased again as the mole ratio increased over a donor/Al mole ratio of 0.1; also the trend of APP yield is similar to that of IPP yield shown in Fig. 3(A). On the other hand, the yield of APP initially decreases with increase in the mole ratio but then increases as the mole ratio increases over a donor/Al mole ratio of 0.1.

The effects of donor/Al mole ratio on the II are shown in Fig. 3(B). The T-II and P-II increased rapidly up to a donor/Al mole ratio of 0.1, but decreased gradually as the mole ratio increased over a donor/Al mole ratio of 0.1 in the case of both nonprepolymerization and prepolymerization. Thus we could assume that the excess donor to alkyl aluminum is adsorbed isotactic site as well as atactic site and the reduction of II is caused by this adsorption over a donor/Al mole ratio of 0.1 as was reported by Keii[18] for polymerization. The difference between prepolymerization and nonprepolymerization is that the declination of II of the former is smaller than that of the latter over donor/Al mole ratio of 0.1.

The BD of polymer initially increases with increase in the mole ratio, but decreases as the mole ratio increases over a donor/Al mole ratio of 0.1 as shown in Fig. 3(C).
Fig. 4. Effect of prepolymerization press. on the yield, II, and BD of polymer produced. prepolymerization conditions; Al/Ti=150, donor/Al=0.1, time=20min., temp=30℃, polymerization conditions; temp.=70℃, time=2hrs, press.=8atm (H₂press.=2atm). (prepolymerization pressure=0; nonprepolymerization).

Fig. 5. Effect of prepolymerization time on the yield, II, and BD of polymer produced. prepolymerization conditions; Al/Ti=150, donor/Al=0.1, press.=2atm. polymerization conditions; temp.=70℃, time=2hrs, press.=8atm (H₂press.=2atm). (prepolymerization time=0; nonprepolymerization).

These results indicate that stabilization of the active-center structure by electron donor in the case of prepolymerization is higher than that in the case of nonprepolymerization.

3.3. The Effects of Prepolymerization Pressure

The prepolymerization pressure is related to the amount of polymer prepolymerized onto the surface of catalyst. To illustrate the effects of the pressure of monomer on the prepolymerization, the prepolymerization pressure is adjusted up to the pressure of polymerization (8 atm).

Fig. 4(A) shows the effects of prepolymerization pressure on the yield. The yields of WPP and IPP increase with increase in the prepolymerization pressure, but the yield of APP indicates minimum formation at 2 atm and increases rapidly when the prepolymerization pressure is more than 2 atm.

The T-II and P-II in the case of prepolymerization decrease more than those for nonprepolymerization under 2 atm as shown in Fig. 4(B). These results show that the rate of APP formation is higher than that of IPP formation over 2 atm.

The BD of polymer increases up to a pressure of 2 atm; prepolymerization over 2 atm has little effect compared to nonprepolymerization, as shown in Fig. 4(C).

Therefore prepolymerization is more effective in relatively low pressures than polymerization.

3.4 The Effects of Prepolymerization Time

Fig. 5(A) shows the dependence of the yield of IPP, WPP and APP on the prepolymerization time. On increasing the prepolymerization time, the yields of IPP and WPP initially increase, but decrease as the prepolymerization time exceeds 20 minutes. On the other hand, the yield of APP initially decreases with prepolymerization time increase, and then increases as the prepolymerization time exceeds 20 minutes. This experiment shows that the
optimum time is 20 minutes and the yield of IPP in the case of prepolymerization is about 16% higher than the yield of IPP in the case of nonprepolymerization. When the prepolymerization time is about 50 minutes, the yield of APP is similar to the yield of APP in the case of nonprepolymerization.

Fig. 5(B) shows that the T-II and P-II increase as prepolymerization time increases, and the T-II for prepolymerization is about 2% higher than that for nonprepolymerization at optimum condition.

The BD of polymer increases generally compared to that of nonprepolymerization in the range 20 to 50 minutes and the optimum condition is 20 minutes as shown in Fig. 5(c).

Therefore prepolymerization is more effective in a relatively short time than polymerization.

3.5. The Effects of Prepolymerization Temperature

Fig. 6(A) shows the dependence of the yield of IPP, WPP and APP on the prepolymerization temperature. On increasing the prepolymerization temperature, the yield of IPP increases steadily, but the yield of APP initially decreases with increase in the temperature and rapidly increases as the temperature increases over 30°C. Thus the yield of WPP is nearly same in the range 20 to 30°C, but the yield of WPP increases rapidly over 30°C due to the formation of APP.

The T-II and P-II increase within the range 20 to 30°C, but decrease rapidly over 30°C due to the formation of APP as shown in Fig. 6(B).

Fig. 6(C) shows the dependence of BD on the prepolymerization temperature. It seems that BD decreases over 30°C due to the formation of APP. Prepolymerization is an effective means for improving the bulk density as reported by Tang et al.[20].

3.6. Morphology

The morphological control of polymer has many advantages concerning the polymerization process. Actually, controlling the particle mor-

![Graph](image)

Fig. 7. Particle-size distribution curves of catalyst and prepolymerized catalyst.

phology such as particle size, shape and bulk density improve productivity.

In Fig. 7, the average particle size of catalyst is about 21 μm, that of prepolymerized catalyst is about 48 μm. Fig. 8 shows SEM photographs of catalyst and prepolymerized catalyst. The prepolymerized catalyst consists of some particle agglomerations, each sub-particle of which is considered to be a catalyst particle coated by prepolymer. It is assumed that the yield of prepolymerized catalyst increases due to the increase in the number of active centers caused by cleavage of catalyst particles in the prepolymerization step, and the polymer morphology of prepolymerization is improved due to a reduction in catalyst fragmentation.

SEM photographs of polymer particles prepared with and without prepolymerization are shown in Fig. 9. The average particle size of polymer obtained by nonprepolymerized catalyst is about 110 μm and the particles have irregular shapes, while the average particle size of polymer obtained by prepolymerized catalyst is about 300 μm and the particles have uniform shapes. It seems that the prepolymer coated as an amorphous phase improves the mechanical
stability of catalyst during polymerization and the polymer morphology.

From these results, it can be assumed that the nature of the active centers formed by the prepolymerization is different from that of non-prepolymerization, and that the polymer morphology may be attributed to the polymer coating on the catalyst, as reported by Coutinho[12].

3.7. The Effects of Modified Prepolymerization

Since the Ziegler-Natta catalyst started to be used for the production of polypropylene, numerous improvements have been made in the performance of catalysts. Nowadays, the studies of catalysts and polymerization seem to concentrate on producing high-performance polymer such as HMPP. This polymer has
excellent properties, such as mechanical properties (stiffness), optical properties (transparency and gloss), heat resistance, etc. These properties contribute to the result of improvements in tacticity, crystallinity and molecular-weight distribution of polymer.

Among the methods for HMPP, i.e. method using nucleating agent, modification of catalyst, etc. Two methods are chosen. One method is two-stage polymerization and another method is prepolymerization using VCH, DVB as the prepolymerization monomer. In the case of two-stage polymerization, the catalyst is only fed in the first reaction without further addition in the second reaction. The polymer portion with high MI is produced in the first reaction; thereafter the reactor is flushed, then the polymerization in the second reaction is carried out to produce the polymer portion with low MI under the conditions indicated in Table 1.

The properties (MI, MWD and FM) of polymer obtained from various polymerization conditions are given in Table 1. The polymer of nonprepolymerization (division 4 in Table 1) has a flexural modulus of 13000 kg/cm² and 1,3-dibenzylidene sorbitol is added as a nucleus-creating agent to the polymer of non-prepolymerization (division 4 in Table 1). The polymer (division 5 in Table 1) treated by nucleus-creating agent has a FM of 18000 kg/cm². In the case of two-stage polymerization, the FM (18100 to 18800 kg/cm², division 1-3 in Table 1) of the polymer obtained is higher than that of the polymer of nonprepolymerization (13000 kg/cm²). The FM (17000 to 17200 kg/cm², division 6-7 in Table 1) of polymer produced by prepolymerization using VCH, DVB as the prepolymerization monomer is higher than that (13000 kg/cm²) of the polymer for nonprepolymerization. Also, two-stage polymerization is more effective than prepolymerization using VCH or DVB.

4. Conclusions

Prepolymerization improved the morphology of polymer and increased the yield, and the IL and reduced the formation of APP. These results might be attributed to the stability of the catalyst and the change of the catalyst structure resulting from prepolymerization. The optimum conditions for prepolymerization were as follows: Al/Ti mole ratio of about 150, donor/Al mole ratio of about 0.1, pressure of about 2 atm, temperature of 20°C and time of about 20 minutes.

<table>
<thead>
<tr>
<th>Division</th>
<th>First reaction</th>
<th>Second reaction</th>
<th>MI (g/10min.)</th>
<th>MWD (Mw/Mn)</th>
<th>FM (kg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Propylene(g)</td>
<td>H2(mL) 3rd component</td>
<td>Propylene(g)</td>
<td>H2 (mL)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>2100</td>
<td>285</td>
<td>350</td>
<td>5.3</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2100</td>
<td>270</td>
<td>350</td>
<td>5.8</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>2100</td>
<td>255</td>
<td>350</td>
<td>5.2</td>
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<tr>
<td>4</td>
<td>262</td>
<td>350</td>
<td>0</td>
<td>0</td>
<td>5.2</td>
</tr>
<tr>
<td>5**</td>
<td>262</td>
<td>350</td>
<td>0</td>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>6</td>
<td>262</td>
<td>350</td>
<td>1.0(DVB)</td>
<td></td>
<td>7.7</td>
</tr>
<tr>
<td>7</td>
<td>262</td>
<td>350</td>
<td>1.5(VCH)</td>
<td></td>
<td>4.7</td>
</tr>
</tbody>
</table>

* Polymerization conditions: 70°C, 8atm, 2hr, Ti=0.03mmol, Al/Ti=150 mole ratio, donor/Al=0.1 mole ratio
** No 4 was treated with nucleating agent(1,3-dibenzylidene sorbitol).
Both two-stage polymerization and prepolymerization using VCH, DVB as the prepolymerization monomer were also investigated, the results showing that flexural modulus of polymer was improved. From the results of prepolymerization, it is understood that prepolymerization is an important tool for the improvement of catalyst performance and the properties of the polymer.

References