Olefins Terpolymerization with Ziegler-Natta Catalysts of Different Stereoregularity

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ABSTRACT: Terpolymerizations of propylene/1-hexene/1-hexadecene had been carried out with high-isospecific and nonisospecific catalysts. For high-isospecific Solvay TiCl3-Cp2TiMe2 catalyst system, polymerization rate accelerated and incorporation of 1-hexene and 1-hexadecene in terpolymer increased when feed ratio of 1-hexene and/or 1-hexadecene increased. In contrast, catalyst activity and comonomers content decreased with addition of comonomers for nonisospecific MgCl2/TiCl3-TEA catalyst system. These phenomena might be explained with the concept of monomer diffusion limitation.

Keywords: terpolymerization, Solvay TiCl3-Cp2TiMe2, MgCl2/TiCl3-TEA.

INTRODUCTION

Copolymerization and terpolymerization of olefins are important methods in the manufacturing of polyolefin products. For copolymerization of olefins, it was well-known that rate enhancement can be observed due to the presence of a small amount of comonomer, which is called as "comonomer effect" by Chien et al. The reason of rate enhancement is one of the unsolved problems in the fields of Ziegler-Natta polymerization of olefins, but one possible explanation is based on the monomer diffusion limitation through high crystalline polymer layer to active site.

If monomer diffusion limitation is one reason of rate enhancement, the effect of comonomer could be dependent on the crystallinity (i.e., tacticity) of polymers produced by catalysts of different isotacticity. In other words, not only catalyst activity but polymer composition may be depen-
dent on stereoregularity of catalysts.

From the previous studies, it had been found that Solvay TiCl₃-Cp₂TiMe₂ catalyst system⁹ gave very high isotactic ([mmmnn] = 98.7) polypropylene (PP) while MgCl₂/TiCl₃-triethylaluminum (TEA) catalyst system¹⁰ produced totally atactic PP.

In this study, terpolymerizations of propylene/1-hexene/1-hexadecene were carried out with high-isospecific Solvay TiCl₃-Cp₂TiMe₂ and nonisospecific MgCl₂/TiCl₃-TEA catalyst systems. The catalyst activity and polymer composition were examined, and results were correlated with the isospecificity of catalyst systems.

**EXPERIMENTAL**

**Materials.** Propylene was purified by passing through NaOH and P₂O₅ columns. Commercial 1-hexene and 1-hexadecene were purified by the usual procedures. Solvay TiCl₃ (from Showa Denko Co.) was used without further treatment. Cp₂TiMe₂ was prepared according to the reported procedures,¹¹ diluted into 0.25 mol/dm³ of heptane and stored as stock solution. Nonisospecific MgCl₂/TiCl₃ catalyst was obtained with the method described previously.¹⁰

**Terpolymerization.** Terpolymerization was carried out in a 200 cm³ glass reactor equipped with a magnetic stirrer. 1.0 mol of TiCl₃ was suspended in 92 cm³ of heptane and comonomer (1-hexene and/or 1-hexadecene) under nitrogen atmosphere. After the temperature was raised to 40 °C, propylene was saturated with continuous flow under a total pressure of 1 atm and 2.0 mmol of Cp₂TiMe₂ (8 cm³ of heptane solution) was added to start the polymerization. The concentration of propylene in heptane was calculated according to Henry's equation quoted by Kissin.¹² Polymerization was conducted at 40 °C for 15 min and terminated by adding a dilute hydrochloric acid solution in methanol. The precipitated polymer was adequately washed and dried in vacuum.

**Characterization of Polymers.** The composition of polymers were determined by¹³¹³C-NMR, according to the method reported by Randall et al.¹³¹³C-NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 25.14 MHz or JEOL GX-270 spectrometer operating at 67.20 MHz under proton decoupling in the Fourier Transform (FT) mode. Instrument conditions were π/4 pulse of 9.0 s, 8.0 s repetition time. Sample solution of polymer was prepared at a concentration of 10 g/dL in 1,2,4-trichlorobenzene/benzene-d₆ (vol. ratio 3:1) mixture with internal hexamethyldisiloxane.

**RESULTS AND DISCUSSION**

To study the comonomer effect for catalysts having different isospecificity, terpolymerization of propylene (C₃)/1-hexene (C₆)/1-hexadecene (C₁₆) had been carried out with high-isospecific Solvay TiCl₃-Cp₂TiMe₂ and nonisospecific MgCl₂/TiCl₃-TEA catalyst systems. The catalyst activity and polymer composition had been examined and correlated with isospecificity of catalysts.

With high-isospecific Solvay TiCl₃-Cp₂TiMe₂ catalyst system, catalyst activity and polymer composition for terpolymerization of C₃/C₆/C₁₆ were compared with those of C₃/C₆ copolymer as shown in Table 1.

As shown in Table 1, the catalyst activity of C₃/C₁₆ copolymer was smaller than that of C₃ homopolymer due to the presence of C₁₆ and content of C₁₆ in copolymer was found to be small. For 1.00/0.22 feed mole ratio of C₃/C₁₆, the catalyst activity decreased in a great extent and comonomer effect could not be observed due to the same amount of C₆. The rate enhancement could be observed in the presence of only a small amount of C₆ (0.04 mole/L).⁷
Table 1. Catalyst Activity and Polymer Composition for High-isospecific Solvay TiCl₃-Cp₂TiMe₂ Catalyst System

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Concentration (mol/L)</th>
<th>Feed ratio (mole ratio)</th>
<th>Activity (g-polymer/ g-Ti/hr)</th>
<th>Polymer (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃</td>
<td>0.45</td>
<td>1.00/0.22</td>
<td>111.9</td>
<td>-</td>
</tr>
<tr>
<td>C₃/C₁₅</td>
<td>0.45/0.10</td>
<td>1.00/0.22</td>
<td>134</td>
<td>99.5/0.5</td>
</tr>
<tr>
<td>C₃/C₃/C₁₅</td>
<td>0.45/0.04/0.10</td>
<td>1.00/0.09/0.22</td>
<td>22.1</td>
<td>97.3/1.2/1.5</td>
</tr>
<tr>
<td></td>
<td>0.45/0.10/0.10</td>
<td>1.00/0.22</td>
<td>134.0</td>
<td>93.3/3.1/3.6</td>
</tr>
<tr>
<td></td>
<td>0.45/0.04/0.20</td>
<td>1.00/0.09/0.44</td>
<td>160.3</td>
<td>94.9/1.2/3.9</td>
</tr>
</tbody>
</table>

With more addition of a small amount of C₃ to the C₃/C₁₅ copolymerization system, catalyst activity increased more than half to show the comonomer effect. Surprisingly C₁₅ content became 3 times larger than that in C₃/C₁₅ copolymer.

By increasing C₃ feed ratio more than 2.5 times, catalyst activity increased up to 6 times and C₃ content increased up to 2.5 times as expected. In addition, C₁₅ content increased more than double in spite of unchanged feed ratio of C₁₅.

On the other hand, double increment of C₁₅ with fixed amount of C₃ resulted in remarkable increase of catalyst activity as well as unexpected high C₁₅ content while C₃ content is almost unchanged.

The above unexpected results could be explained with consideration that the higher α-olefin comonomer has the less diffusivity through crystalline polymer layer to active site due to its bulkiness.

For noncrystalline polymer layer produced by nonisospecific catalyst, it could be expected that monomer diffusion limitation may be less serious and the comonomer effect is not observed.

To check the above expectation, terpolymerization was also carried out with nonisospecific catalyst system and the results were shown in Table 2.

Compared with copolymerization behaviors of

Table 2. Catalyst Activity and Polymer Composition for Nonisospecific MgCl₂/TiCl₃-TEA Catalyst System

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Concentration (mol/L)</th>
<th>Feed ratio (mole ratio)</th>
<th>Activity (g-polymer/ g-Ti/hr)</th>
<th>Polymer (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃</td>
<td>0.45</td>
<td>1.00/0.22</td>
<td>6000</td>
<td>-</td>
</tr>
<tr>
<td>C₃/C₁₅</td>
<td>0.45/0.10</td>
<td>1.00/0.22</td>
<td>1169</td>
<td>99.5/0.5</td>
</tr>
<tr>
<td>C₃/C₃/C₁₅</td>
<td>0.45/0.04/0.10</td>
<td>1.00/0.09/0.22</td>
<td>459</td>
<td>96.2/2.4/1.4</td>
</tr>
</tbody>
</table>

high-isospecific catalyst system, the catalyst activity decreased in a great extent by adding C₁₅ comonomer while comonomer content was larger due to its less diffusion limitation. By further addition of C₃, the catalyst activity decreased remarkably and C₁₅ content became less due to its lower reactivity. In addition, C₆ content was larger than C₁₅ content due to its smaller size even if the feed ratio of C₃ was smaller.

To confirm the rate enhancement of comonomer, C₃ feed flow rates corresponding to polymerization rates had been measured for different C₆ and/or C₁₅ contents with high-isospecific catalyst system and given in Fig. 1.

The polymerization rate increased slightly with addition of small amount of C₆ and/or C₁₅ and

![Figure 1. Effect of feed olefin compositions on rate profile of polymerization using high-isospecific Solvay TiCl₃-Cp₂TiMe₂ catalyst system.](image-url)
rate enhancement was profound for larger addition of comonomers. The polymerization rate profile was found to be decay-type and the decay was accelerated by the more addition of C₈ and/or C₁₆. The reason of accelerated decay with addition of C₈ and/or C₁₆ is not clear yet, but this phenomenon might be a supporting evidence for the idea of monomer diffusion limitation.

CONCLUSION

For terpolymerizations of propylene/1-hexene/1-hexadecene with high-isospecific Solvay TiCl₃-Cp₂TiMe₂ catalyst system and nonisospecific MgCl₂/TiCl₃-TEA catalyst system, the followings had been found: (1) For high-isospecific catalyst system, catalyst activity and incorporation of 1-hexene and 1-hexadecene in terpolymer increased with feed ratio of 1-hexene and/or 1-hexadecene. (2) For nonisospecific catalyst system, catalyst activity and comonomers content decreased with addition of comonomers. (3) For high-isospecific catalyst system, polymerization rate increased and rate decay accelerated with addition of 1-hexene and/or 1-hexadecene.

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REFERENCES