Effect of Triethylaluminum/Transition-Metal Ratio on the Physical Properties and Chemical Composition Distributions of Ethylene-Hexene Copolymers Produced by a rac-Et(Ind)_2ZrCl_2/TiCl_4/MAO/SMB Catalyst

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Received November 13, 2006; Revised February 7, 2007

Abstract: A silica-magnesium bisupport (SMB) was prepared by a sol-gel method for use as a support for a metalloene/Ziegler-Natta hybrid catalyst. The prepared rac-Et(Ind)_2ZrCl_2/TiCl_4/MAO(methylaluminoxane)/SMB catalyst was applied to the copolymerization of ethylene with 1-hexene using a variable triethylaluminum (TEA)/transition-metal (Ti) ratio and fixed MAO/transition-metal (Zr) ratio. The effect of the Al(TEA)/Ti ratio on the physical properties and chemical composition distributions (CCDs) of the ethylene-hexene copolymers produced by the hybrid catalyst was investigated. In the ethylene-hexene copolymers, two melting temperatures attributed to the metalloene and Ziegler-Natta catalysts were clearly observed. The number of CCD peaks was increased from six to seven and the temperature region in which the peaks for the short chain branches of the ethylene-hexene copolymer were distributed became lower as the Al(TEA)/Ti ratio was increased from 300 to 400. Furthermore, the temperature regions corresponding to the lamellas in the copolymer became lower and those corresponding to the small lamellas in the copolymer became higher as the Al(TEA)/Ti ratio was increased from 300 to 400. In the copolymer produced with Al(TEA)/Ti = 500, however, only four CCD peaks were observed and the short chain branches were poorly distributed.

Keywords: Ziegler-Natta, metalloene, hybrid catalyst, ethylene-hexene copolymerization.

Introduction

Metalloene catalysts have attracted much attention as next generation catalysts because of their high activity and excellent ability of comonomer incorporation. However, polymers produced by a metalloene catalyst have limitations in polymer processing because of their narrow molecular weight distribution. Ziegler-Natta catalysts used in commercial slurry and gas phase processes are heterogeneous catalyst systems. Therefore, it is desirable to heterogenize the metalloene catalyst in order for use in the existing commercial processes.

A mixture of metalloene and Ziegler-Natta catalysts has been employed to improve the physical properties of polymers. It was also reported that a polyethylene produced by a metalloene/Ziegler-Natta hybrid catalyst supported on MgCl_2 showed a bimodal molecular weight distribution and two melting temperatures, indicating the existence of two different active sites on the support. A silica-magnesium bisupport (SMB) prepared by a sol-gel method was also used to impregnate both metalloene and Ziegler-Natta catalysts on the single support.

In this work, a silica-magnesium bisupport (SMB) was prepared by a sol-gel method for use as a support for a metalloene/Ziegler-Natta hybrid catalyst. The prepared rac-Et(Ind)_2ZrCl_2/TiCl_4/MAO(methylaluminoxane)SMB catalyst was applied to the ethylene copolymerization with 1-hexene under the conditions of variable triethylaluminum (TEA)/transition-metal (Ti) ratio and fixed MAO/transition-metal (Zr) ratio. The effect of Al(TEA)/Ti ratio on the physical properties and chemical composition distributions of ethylene-hexene copolymers produced by the hybrid catalyst was investigated.

Experimental

The SMB treated with MAO was prepared according to the similar method in a previous report. MgCl_2 was dis-
solved in distilled water (100 mL), and pH of the solution was adjusted at 6.4. The solution was introduced into 2.5 liter of corn oil, and it was stirred at 2,000 rpm for uniform dispersion. Colloidal silica (LUDOX, HS-40) (80 mL) was then introduced into the mixed solution of corn oil and MgCl₂. The agglomerated particles separated from the solution were washed with toluene, and they were dried at 110°C in a nitrogen stream. The SMB was treated with MAO prior to the immobilization of Ziegler-Natta and metallocene catalysts. The MAO-treated SMB (MAO/SMB) (2 g) was suspended in toluene (100 mL) and it was reacted with TiCl₄ (2 mL) at 50°C for 2 h. After washing the slurry several times with toluene, it was finally dried under vacuum to yield rac-Et(Ind)₂ZrCl₂ dissolved in toluene (10 mL) at 50°C for 2 h. After washing the slurry several times with toluene, it was finally dried under vacuum to yield rac-Et(Ind)₂ZrCl₂/ TiCl₄/MAO/SMB. The contents of Al, Ti, and Zr were 10.67, 4.86, and 0.55 wt%, respectively.

Toluene (300 mL), supported catalyst (0.04 g), 1-hexene (6 mL), and known amounts of cocatalysts (MAO and TEA) were introduced into a glass reactor (1,000 mL) equipped with a magnetic stirrer under a flow of nitrogen. The molar ratio of MAO with respect to transition-metal (Zr) was fixed at Al(MAO)/Zr = 300 based on preliminary experimental results, while that of TEA with respect to transition-metal (Ti) was varied (Al(TEA)/Ti = 300, 400, and 500). After evacuating the nitrogen in the reactor by a vacuum pump, hydrogen was fed into the reactor at a pressure of 0.2 atm. The polymerization was initiated by introducing ethylene at a constant pressure of 1.3 atm. The copolymerization of ethylene with 1-hexene was conducted at 55°C for 60 min. The copolymerization was terminated by adding an excess amount of hydrochloric acid solution diluted with methanol.

The melting temperature ($T_m$) of ethylene-hexene copolymer was measured using a DSC (TA 2010) with a heating rate of 10°C/min. The comonomer content of the ethylene-hexene copolymer was analyzed using a 100 MHz ¹³C-NMR spectrometer (Avance 500) at 130°C on the basis of Randall method. The chemical composition distribution (CCD) of ethylene-hexene copolymer was determined by a stepwise annealing method. The lamella thickness of fractionated ethylene-hexene copolymer was determined using the Thomson-Gibbs equation.

**Results and Discussion**

The physical properties of ethylene-hexene copolymers produced by individual metallocene and Ziegler-Natta catalysts supported on SMB were reported in a previous work. Figure 1 shows the DSC profiles of ethylene-hexene copolymers produced with a variation of Al(TEA)/Ti ratio. The melting temperatures ($T_m$) of ethylene-hexene copolymers are also summarized in Table I. As shown in Figure 1, two melting temperatures were clearly observed in the ethylene-hexene copolymers. The melting points appearing at around 110°C are attributed to active sites of metallocene catalyst, while those appearing at around 130°C are due to active sites of Ziegler-Natta catalyst. This result indicates that metallocene and Ziegler-Natta components successfully contributed to the ethylene-hexene copolymerization. The melting point caused by Ziegler-Natta catalyst shifted from 130.3 to 134.8°C with increasing Al(TEA)/Ti ratio from 300 to 500. The melting points of the copolymer produced with Al(TEA)/Ti = 500 were observed at 111.8 and 134.8°C. These melting points were similar to those of the copolymer produced by the individual metallocene and Ziegler-Natta catalysts supported on SMB. Additionally, the peak intensity of melting point caused by Ziegler-Natta catalyst became stronger with increasing Al(TEA)/Ti ratio, contrary to that caused by metalloocene catalyst. This means that the catalytic activity contributed by Ziegler-Natta component was increased with increasing Al(TEA)/Ti ratio.

Table I shows the catalytic activities of hybrid catalyst and physical properties of ethylene-hexene copolymer with a variation of Al(TEA)/Ti ratio. The maximum catalytic activity contributed by Ziegler-Natta component was increased with increasing Al(TEA)/Ti ratio.
Effect of Al/Ti on Ethylene-Hexene Copolymerization

The catalytic activity was small when Al(TEA)/Ti = 400. Although the reason for this result is not still clear, it is believed that TEA inhibited the catalytic function of metalloene component on SMB at a certain Al(TEA)/Ti ratio. However, the catalytic activity was increased with increasing Al(TEA)/Ti ratio from 400 to 500, because of the increasing catalytic activity of Ziegler-Natta catalyst at high Al(TEA)/Ti ratio.

Figure 2 shows the chemical composition distributions (CCDs) of ethylene-hexene copolymers analyzed by a step-wise annealing method. Six peaks were observed in the copolymer produced with Al(TEA)/Ti = 300. When Al(TEA)/Ti ratio was increased to 400, one additional peak (seven peaks in total) appeared and CCD peaks shifted to lower temperature region. It is believed that the increase in comonomer content from 7.2 to 7.7 (Table I) caused the shift of CCD peaks and peak temperature ranges. In the copolymer produced with Al(TEA)/Ti = 500, on the other hand, only four CCD peaks were observed and the short chain branches were poorly distributed. This indicates that the active sites of metalloene catalyst were interfered by those of Ziegler-Natta catalyst when Al(TEA)/Ti was 500.

Table II shows the lamella thickness of fractionated ethylene-hexene copolymer and its distribution determined on the basis of Thomson-Gibbs equation. The lamella thickness of fractionated ethylene-hexene copolymer produced with Al(TEA)/Ti = 300 were distributed in the range of 76-59 Å, while 42.8 wt% of lamellas in the copolymer produced with Al(TEA)/Ti = 400 showed small lamellas with a thickness of 33 Å. The copolymer produced with Al(TEA)/Ti = 500 showed 36.0 wt% of extremely large lamellas with a thickness of 536 Å, which were not found in the other copolymers. It is believed that these large lamellas were responsible for the increase in melting temperature attributed to Ziegler-Natta catalyst in the copolymer produced with Al(TEA)/Ti = 500.

Conclusions

A silica-magnesium bisupport (SMB) was prepared by a sol-gel method, and then it was treated with MAO prior to the impregnation of TiCl₄ and rac-Et(Ind)₂ZrCl₂. The prepared rac-Et(Ind)₂ZrCl₂/TiCl₄/MAO/SMB catalyst was applied to the ethylene-hexene copolymerization under the conditions of variable Al(TEA)/Ti ratio and fixed Al(MAO)/Zr. Two melting temperatures attributed to metalloene and Ziegler-Natta catalysts were clearly observed in the ethylene-hexene copolymers. The melting point caused by Ziegler-Natta catalyst shifted from 130.3 to 134.8°C with increasing Al(TEA)/Ti ratio from 300 to 500. The number of the CCD peaks was increased from six to seven.
and the short chain branches of ethylene-hexene copolymer were distributed over lower temperature region with increasing Al(TEA)/Ti ratio from 300 to 400. Additionally, the lamellas in the copolymer were distributed over lower temperature region and the small lamellas in the copolymer were increased with increasing Al(TEA)/Ti ratio from 300 to 400. In the copolymer produced with Al(TEA)/Ti = 500, however, only four CCD peaks were observed and the short chain branches were poorly distributed. Furthermore, the copolymer produced with Al(TEA)/Ti = 500 showed extremely large lamellas with a thickness of 536 Å, which were responsible for the increase in melting temperature attributed to Ziegler-Natta component.

Acknowledgments. The authors wish to acknowledge support from the Taeyoung Industry Corporation (Grant No. 0458-200600008).

References