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Physical property and chemical composition distribution of ethylene–hexene copolymer produced by metallocene/Ziegler–Natta hybrid catalyst

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Abstract

Silica–magnesium bisupport (SMB) was prepared by a sol–gel method for use as a support for metallocene and metallocene/Ziegler–Natta hybrid catalysts. SMB was treated with methylaluminoxane (MAO) prior to catalyst immobilization. The supported heterogeneous catalysts were applied to the ethylene copolymerization with 1-hexene. The h-copolymer (ethylene–hexene copolymer produced by metallocene/Ziegler–Natta hybrid catalyst) showed two melting points and broad molecular weight distribution. The differences in physical properties between h-copolymer and m-copolymer (ethylene–hexene copolymer produced by metallocene catalyst) could be explained by the differences in chemical composition and side chain distributions of the produced copolymers.

Keywords: Ethylene–hexene copolymer; Metallocene; Ziegler–Natta; Hybrid catalyst; Chemical composition distribution; Stepwise crystallization

1. Introduction

Linear low-density polyethylene (LLDPE), typically obtained by copolymerization of ethylene with various alpha olefins such as 1-butene, 1-hexene, and 1-octene, is an important chemical product in the petrochemical industry. LLDPE has similar properties to LDPE, but has better strength properties in film applications [1]. The mechanical, optical, and rheological properties of LLDPE are strongly affected by chemical composition distribution (CCD) (also referred to as side chain distribution), molecular weight (M_w), and molecular weight distribution (MWD) [2,3]. Although LLDPE produced by metallocene catalyst shows excellent mechanical and optical properties due to narrow MWD and CCD, it also has limitation in polymer processing due to narrow MWD [4]. Metallocene catalyst systems are basically homogeneous systems. Therefore, major studies on the metallocene catalysts have been done to heterogenize in order for use in the existing commercial gas or slurry phase processes [5,6]. On the other hand, LLDPE produced by Ziegler–Natta catalyst shows broad MWD and CCD due to the irregularity of catalytic active sites.

In order to take advantage of both metallocenes and Ziegler–Natta catalysts, the blending of polyethylenes produced in two different reactors containing different metallocene catalysts or the combination of metallocene and Ziegler–Natta catalysts in a single reactor has been reported [7–11]. However, the physical blending of two different polyethylenes might be limited in the polymer processing because they could not be mixed on a molecular level. Another report to hybridize metallocene catalyst with Ziegler–Natta catalyst is to use a silica–magnesium bisupport (SMB). It was prepared by a sol–gel method in order to immobilize both metallocene and Ziegler–Natta catalysts on the same support [12]. It was reported that both silica and magnesium chloride species were dispersed on the surface and inside of SMB, and therefore, SMB served as an excellent support for the preparation of metallocene/Ziegler–Natta hybrid catalyst. HDPE [13] and LLDPE [14,15] produced by metallocene/Ziegler–Natta hybrid catalysts showed broad and

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bimodal molecular weight distributions, leading to improved processability of the polymer [16,17].

In this work, silica–magnesium bisupport (SMB) was prepared by a sol–gel method for use as a support for metallocene and metallocene/Ziegler–Natta hybrid catalysts. The prepared catalysts were applied to the ethylene copolymerization with 1-hexene. The effects of hybridization of Ziegler–Natta catalyst with metallocene catalyst on the molecular weight (M_w), molecular weight distribution (MWD), melting temperature (T_m), and chemical composition distribution (CCD) of the produced ethylene–hexene copolymer were investigated.

2. Experimental

2.1. Materials

High purity ethylene (World Gas) and nitrogen (Daesung Gas) were further purified by sequential passage through columns containing molecular sieve 5A (Kokusan Chemical Works) and anhydrous P_2O_5 (Yakuri Chemicals). Toluene (Samjun Chemicals) and 1-hexene (Aldrich) were purified by distillation over sodium metal. $MgCl_2$ (Junsei Chemical), colloidal SiO_2 (LUDOX HS-40, Aldrich), *rac*-Et(Ind)$_2$ZrCl$_2$ (Strem), $TiCl_4$ (Aldrich), methylaluminoxane (MAO, Albermale), and triethylaluminum (TEA, Aldrich) were used without further purification.

2.2. Preparation of silica–magnesium bisupport (SMB) treated with methylaluminoxane (MAO)

Silica–magnesium bisupport (SMB) treated with methylaluminoxane (MAO) was prepared according to the similar method in a previous report [12]. $MgCl_2$ was dissolved in distilled water (100 ml), and pH of the solution was adjusted at 6.4 by adding H_2SO_4. The resulting solution was introduced into corn oil (2.5 l), and it was stirred at 2000 rpm for uniform dispersion. Colloidal silica (80 ml) was then introduced into the mixed solution of corn oil and $MgCl_2$. The agglomerated particles separated from the solution were washed seven times with *n*-heptane, and they were dried at 110 °C in a nitrogen stream to yield silica–magnesium bisupport. Silica–magnesium bisupport (SMB) (6 g) was suspended in toluene (100 ml), and then methylaluminoxane (MAO, 10 wt.% in toluene) (100 ml) was introduced into the slurry for 2 h at 0 °C. The mixture was stirred at 0, 20, 40, and 60 °C for 30 min each, and then finally at 80 °C for 2 h. SMB treated with MAO was washed seven times with toluene and dried under vacuum.

2.3. Preparation of supported catalyst

MAO-treated SMB (MAO/SMB, 5 g) was suspended in toluene (100 ml), and it was reacted with $TiCl_4$ (5 ml) or *rac*-Et(Ind)$_2$ZrCl$_2$ (0.5 g) at 50 °C for 2 h. The resulting slurry was washed seven times with toluene (100 ml) and dried under vacuum to obtain $TiCl_4$/MAO/SMB or *rac*-Et(Ind)$_2$ZrCl$_2$/MAO/SMB. $TiCl_4$/MAO/SMB was further reacted with *rac*-Et(Ind)$_2$ZrCl$_2$ (0.5 g) dissolved in toluene (20 ml), and the resulting slurry was washed seven times with toluene (100 ml) and dried under vacuum to yield *rac*-Et(Ind)$_2$ZrCl$_2$/$TiCl_4$/MAO/SMB.

2.4. Copolymerization of ethylene with 1-hexene

Toluene (500 ml), supported catalyst (0.04 g), 1-hexene (5 ml), and prescribed amount of cocatalyst (triethylaluminum (TEA) and/or methylaluminoxane (MAO)) were introduced into a glass reactor (1000 ml) equipped with a magnetic stirrer under the nitrogen flow. Cocatalyst ratio with respect to transition metal was fixed at Al/Ti = 300 (TEA) and Al/Zr = 3000 (MAO). After nitrogen in the reactor was evacuated, the temperature of reactor was maintained at 55 °C. Copolymerization was initiated by introducing ethylene at a constant pressure of 1.3 atm. After 40 min reaction, the polymerization was stopped by adding methanol.

2.5. Characterization of supported catalyst and ethylene–hexene copolymer

Elemental analysis of supported catalyst was done by ICP-AES (ICPs-10001V). Melting point of ethylene–hexene copolymer was determined by DSC (differential scanning calorimeter, TA 2010) with a heating rate of 10 °C/min. Molecular weight (M_w) and molecular weight distribution (MWD) were determined by GPC (gel permeation chromatography, SSC-7100) at 135 °C using *o*-dichlorobenzene as a solvent. The GPC column was calibrated with standard polystyrene. 1-Hexene content and triad sequence in ethylene–hexene copolymer were analyzed by 125 MHz ^{13}C NMR (nuclear magnetic resonance spectrometer, Avance 500) at 125 °C on the basis of Randall method [18].

A stepwise annealing procedure was conducted to analyze the chemical composition distribution (CCD) of ethylene–hexene copolymer [19–21]. As shown in Fig. 1, temperature was increased up to 160 °C with a rate of 10 °C/min and maintained for 2 h for complete melting. The melted polymer was slowly cooled at 137, 130, 123, 116, 109, 102, 95, 88, 81, and 74 °C for 2 h, respectively, and was finally cooled to 30 °C with a rate of 10 °C/min. And then the chemical composition distribution of ethylene–hexene copolymer was determined using

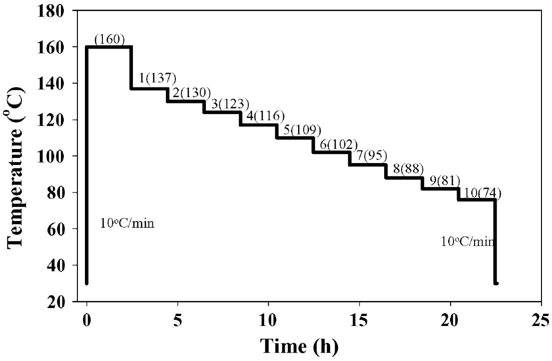

Fig. 1. Stepwise annealing procedure for chemical composition distribution analysis of ethylene–hexene copolymer.