Study on Copolymerization of Ethylene/1-Hexene Catalyzed by a Novel Polystyrene-Supported Metallocene Catalyst

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ABSTRACT: Ethylene/1-hexene copolymerization was carried out with polystyrene-supported metallocene catalyst. It was found that the kinetic of the copolymerization was strongly influenced by the steric hindrance of carrier. The influences of 1-hexene concentration in the feed on catalyst productivity and comonomer reactivity were investigated. The microstructure of resultant copolymer was analyzed by ^{13}C NMR. It was found that the different carriers have slight effect on the composite of copolymer. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1574–1577, 2006

Key words: polystyrene-supported metallocene; ethylene/1-hexene; copolymerization; kinetics

INTRODUCTION

Copolymer of ethylene/α-olefin such as 1-hexene is a very important commercial products classified as linear low density polyethylene (LLDPE). Usually, Ziegler-Natta catalysts produce copolymers with a wide molecular weight distribution (MWD) and comonomer distribution (CCD) because of multiple active sites.[1–2] In Contrast, homogeneous metallocene are single-site catalysts and produce very uniform copolymers with narrow MWD and CCD.

Ethylene/1-hexene copolymerization processes have been mainly investigated in the presence of homogeneous metallocene catalysts. However, industrial processes inquired that metallocene catalysts can be immobilized on carriers. Therefore, heterogeneous polymerization for ethylene/α-olefin copolymerization becomes a hot subject in the polyolefin field.[3–4] Marques[5] studied the Zeolite–supported metallocene for ethylene/1-hexene copolymerization. The results showed that the T_m and crystallization of copolymer were strongly influenced by the cononomer. Czaja[6] investigated bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2)/MAO anchored on $MgCl_2(THF)_2$ support for ethylene/1-hexene copolymerization. The MWD of the copolymers obtained over the supported zirconocene catalysts was higher than that obtained by homogeneous polymerization.

In this article, the ethylene/1-hexene copolymerization catalyzed by polystyrene-supported metallocene was studied. The concentration of 1-hexene on the effect of catalyst productivity and copolymer composition were investigated.

EXPERIMENTAL

Materials

All the operations were carried out under argon atmosphere, using the standard Schlenk techniques. Methylaluminoxane (MAO) was obtained from ACROs (Fairlawn, NJ). Polymerization-grade ethylene was further purified by passing over 4 Å molecular sieves. 1-Hexene was purified by refluxing over Na under nitrogen atmosphere.

Polystyrene-supported metallocene catalysts PSM-1 and PSM-2 with different crosslinked structure were synthesized in our previous work.[7] The crosslinked density of PSM-2 is higher than that of PSM-2.

Copolymerization

Ethylene/1-hexene copolymerization was carried out in a 100-mL glass flasks equipped with an ethylene inlet, a magnetic stirrer, and a vacuum line outlet. The reactor was filled with 50 mL toluene and certain quantities of 1-hexene. The mixture was stirred at fixed temperature and then saturated with ethylene (1 atm). Certain amount of MAO was added into the
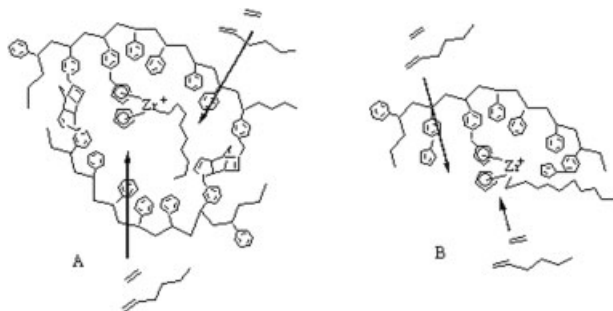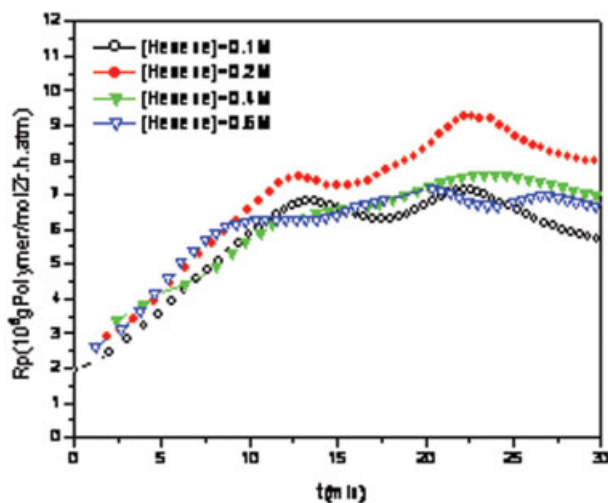
Figure 1 Model of polymer growth for ethylene/1-hexene copolymerization with polystyrene-supported metallocene.

TABLE I
The Results of Ethylene/1-hexene Copolymerization Catalyzed by Supported Catalysts

Catalyst	1-Hexene in the feed (M)	Activity (10^5 g Polymer/ mol Zr. h)	T_m (°C)	M_w (10^3)	PDI
PSM-1	0.1	6.04	115.2	80	3.52
PSM-1	0.2	6.77	107.5	50	2.56
PSM-1	0.4	6.18	99.6	22	3.96
PSM-1	0.6	6.03	88.9	15	3.98
PSM-2	0.1	3.95	116.0	74	2.27
PSM-2	0.2	6.96	108.7	54	2.57
PSM-2	0.4	5.83	97.4	28	2.95
PSM-2	0.6	5.26	88.9	20	3.45

Polymerization condition: Tp = 50°C, 50 mL toluene, [Al]/[Zr] = 1000.

(a)
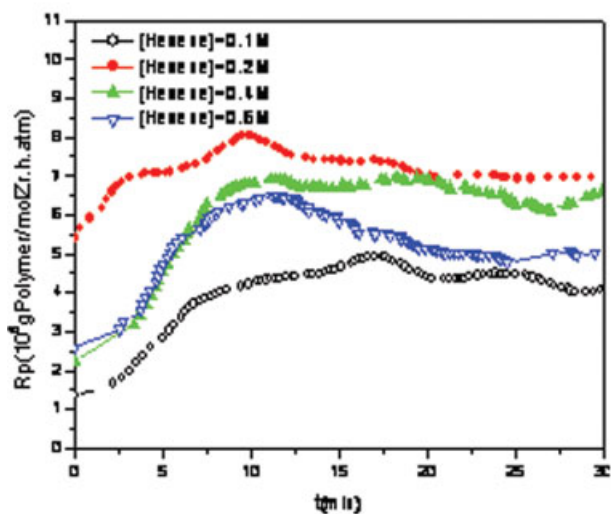
(b)

Figure 2 Kinetic curves of ethylene/1-hexene copolymerization catalyzed by polystyrene-supported metallocene catalyst: (a) PSM-1 catalyst and (b) PSM-2 catalyst. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

above system. The reaction was initiated by adding the catalyst. After 30 min, the polymerization was terminated by the addition of acidified ethanol. The resulting polymer was separated by filtration and dried at 50°C.

Characterization of the copolymers

A high-temperature gel permeation chromatograph was used for the MWD analysis with 1,2,4-trichlorobenzene as solvent at 150°C. The universal calibration curve, based on polystyrene standards, was used to determine the molecular weight of the linear polyethylene chains. The ^{13}C NMR spectra of the ethylene/1-hexene copolymers were recorded on a Vnily400 spectrometer at 120°C. The differential scanning calorimetry (DSC) analysis of the polymer was carried out on PerkinElmer DSC-7 calorimeter at a heating rate of 10°C/min, and the second scan was recorded. The previous thermal history in the sample was eliminated by the specimen being heated to 150°C, maintained at this temperature for 1 min, and then cooled down to 50°C. Crystallization were calculated from Xc = 100 × ΔH_f/290.[8]

RESULTS AND DISCUSSION

The synthesis of the catalyst is based on the soluble polystyrene, bearing cyclopentadiene groups. Some of cyclopentadiene groups in polystyrene chain are used to yield a biscyclopentadiene zirconium dichloride bond covalently to polystyrene and the other cyclopentadiene groups to form insoluble carrier by a Diels–Alder crosslinked reaction. The Model of crosslinked polystyrene-supported metallocene for ethylene/1-hexene copolymerization was shown in Figure 1. Insoluble A catalyst with crosslinked network could convert to soluble B catalyst with long linear chains via MAO.[9]

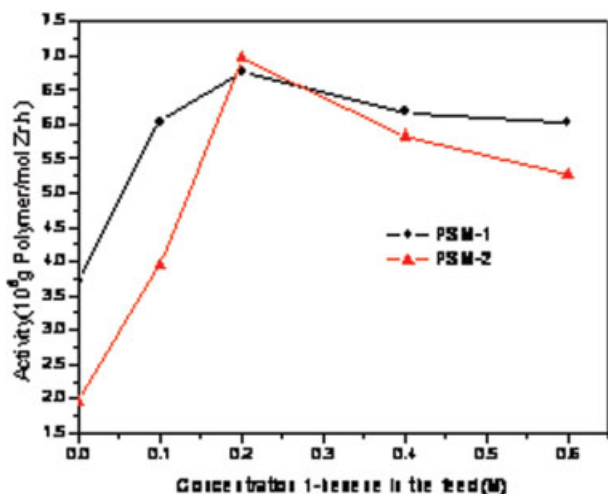Figure 2 showed the kinetic curves of ethylene/1-

Figure 3 Relationship between the activity and 1-hexene molar concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

metallocene catalysts. The results indicated that the molecular weight decreased with the increase of comonomer content. This behavior attributed to the fact that α-olefin could act as chain-transfer agents in the system. The α-olefin incorporated into the polymer chain favored the chain-ending reactions through β-hydrogen transfer or through a transfer reaction to the comonomer, thereby reducing the polymer molecular.[10–11] Moreover, the copolymer had narrow MWD (M_w/M_n = 2–4).

Figure 3 showed the effect of comonomer on the activity of the copolymerization. It was found that there was a maximum value of activity at 1-hexene = 0.2M. The phenomena could be attributed to an increase in the polymer solubility. For an increase in monomer, diffusion through the reaction medium would increase its concentration around the active centers.[12] At same time, the presence of the comonomer in the polyethylene chain would make it difficult to form the crystalline shell of polyethylene around the active sites.[13]

For the higher crosslinked, density of PSM-2 would not convert effectively to B catalyst, so the PSM-1 catalyst has higher activity than PSM-2 catalyst.

The typical ^{13}C NMR spectrum of the copolymers of ethylene/1-hexene was shown in Figure 4, the chemical shift assignments in the ^{13}C NMR spectrum, according to the literature.[14] Dyad sequence distributions, triad sequence distributions, and comonomer mole fractions of the copolymers estimated by ^{13}C NMR are listed in Table II. No copolymer showed HHE or HHH triad sequences. This indicates that

hexene copolymerization. The mild copolymerization kinetic curves implied that the carrier had great influence on the copolymerization kinetic. The crosslinked network of A catalyst has greater steric hindrance to block the monomer to the active sites, which lead to mild copolymerization process. However, A catalyst was gradually converted to B catalyst with less steric hindrance to monomer, which increased the activity and performed stable copolymerization.

Table I showed the results of ethylene/1-hexene copolymerization catalyzed by polystyrene supported
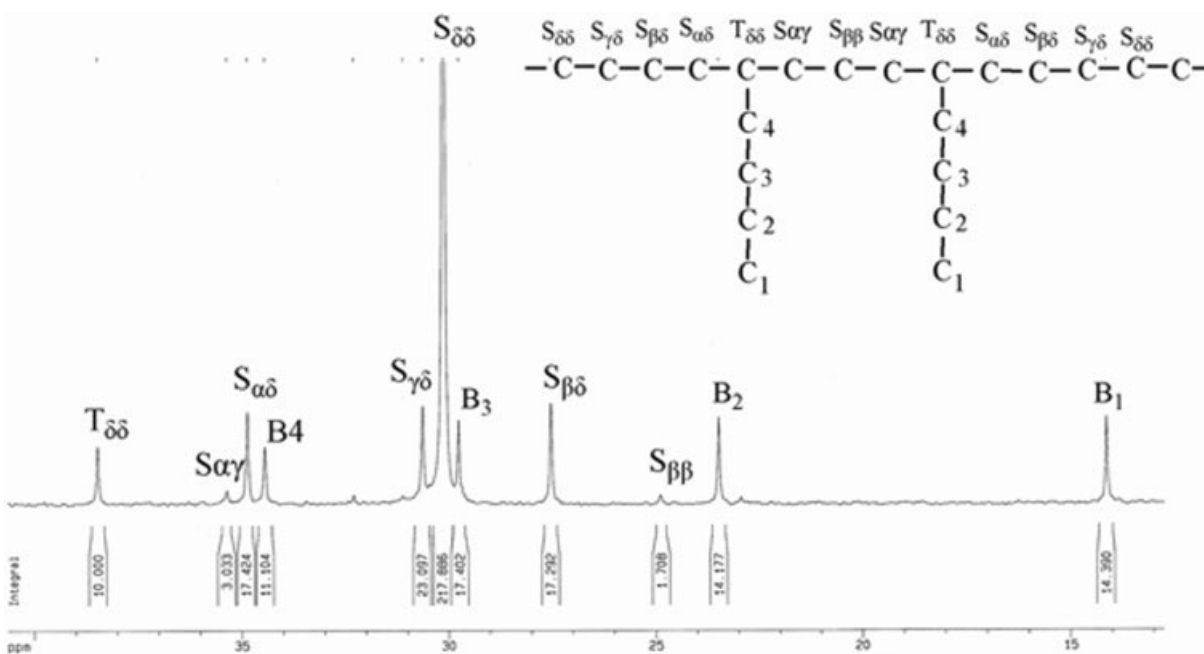

Figure 4 ^{13}C NMR spectrum of ethylene/1-hexene copolymer.

1-hexene does not form blocks with these catalysts. The 1-hexene units are all "isolated" as ethylene-1-hexene-ethylene sequences.

Figure 5 exhibited the amount of the comonomer incorporated into the copolymer with the increase of 1-hexene concentration in the feed. The incorporation of comonomer was nearly the same and increase with the increase of the comonomer concentration in the feed. Therefore, the reactivity of comonomer was similar in the presence of the two kinds of catalysts. This indicated that the carrier do not influence strongly on the microstructure of copolymer. Additionally, the melting point (shown in Table I) decreased markedly with the increase of comonomer concentration in the feed.

CONCLUSIONS

Metallocene catalysts supported on polystyrene with different crosslinked density were used for ehtylene/1-hexene copolymerization. The results showed that the kinetics of copolymerization was strongly influenced by the carrier. And the molecular weight of copolymer was influenced markedly by the concentration of comonomer. The microstructure of copolymer was analyzed by ^{13}C NMR spectra. The result indicated that most of the 1-hexene units were isolated in the copolymer.

TABLE II
Comonomer Mole Fractions and Driad of Ethylene/1-hexene Copolymers Obtained by Polystyrene-Supported Catalyst

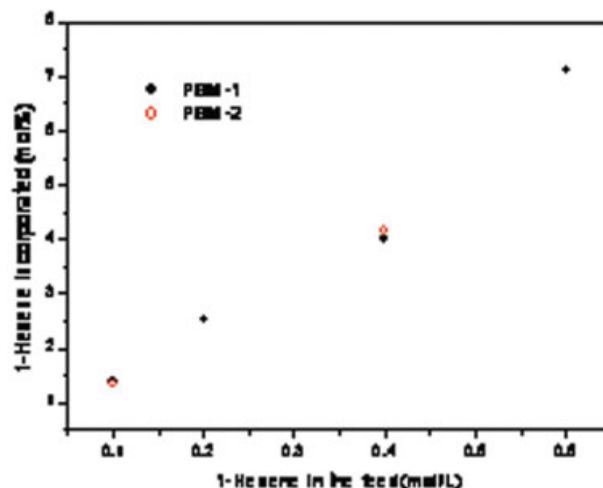| Catalyst	1-Hexene (M)	Mole fractions		Diad distributions	
		H	E	HE	EE
PSM-1	0.1	0.014	0.986	0.028	0.972
PSM-1	0.2	0.025	0.975	0.050	0.950
PSM-1	0.4	0.040	0.960	0.080	0.920
PSM-1	0.6	0.071	0.929	0.142	0.858
PSM-2	0.1	0.014	0.987	0.027	0.973
PSM-2	0.4	0.042	0.959	0.083	0.917

Figure 5 The concentration of 1-hexene in the feed against 1-hexene content in the copolymer for ethylene/1-hexene copolymerization with PSM-1 and PSM-2 catalysts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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