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Materials Letters 59 (2005) 3771 – 3774
materials letters
www.elsevier.com/locate/matlet

Impact of diene addition on properties for ethylene–propylene copolymerization with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst

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Received 20 May 2005; accepted 7 July 2005
Available online 28 July 2005

Abstract

In the present study, the impact of diene addition during copolymerization of ethylene and propylene using a metallocene/MAO catalyst was investigated. It showed that with a small amount of diene added, the dienes (except for ENB) did not incorporate in the polymer backbone pronouncedly. However, the addition of dienes can alter the incorporation of ethylene and propylene in the polymer backbone according to different types of dienes used. The catalytic behaviors and yields were not significant changes with the addition of dienes. The characteristics of polymer obtained using ^{13}C NMR, SEM, and DSC were also further discussed in more detail.

Keywords: Polymerization; Metallocene; Catalyst; Elastomers; Methylaluminoxane

1. Introduction

It is known that the copolymerization of ethylene (E) and propylene (P) can result in a production of rubbery materials called EP elastomers [1–3]. Because there are no double bonds in the backbone of polymer chain, they are usually insensitive to oxygen, ozone, acids, and alkaline. It was found that addition of the third monomer such as dienes could be applied in order to escalate the properties of EP elastomers, the so-called EPDM elastomers. As known, EPDM can be widely used in many applications so far [4–6]. Currently, EPDM is synthesized using vanadium-based catalysts. With the presence of dienes, it was found that the vanadium-based catalysts exhibited low activities along with toxicity concerns due to the residual vanadium remains in the polymer [7]. Thus, in order to overcome those problems, an alternative way of using the homogeneous metallocene catalysts has been substantially investigated by many authors [8–10]. Nevertheless, the production of EPDM is considered to be an important matter, the approach of our present study was apparently different from the

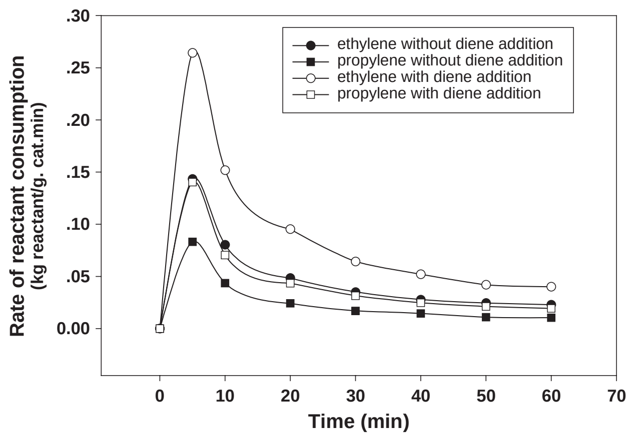

Fig. 1. Activity profiles based on ethylene (E) and propylene (P) consumption with and without diene addition.

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doi:10.1016/j.matlet.2005.07.014

Table 1
Yields and activities of EP elastomers produced from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst; [Zr] = 30 μM in toluene, [Al]/[Zr] = 2000, [diene] = 0.1 M, E/P molar ratio = 75/25, polymerization temperature = 40 °C, and polymerization time = 1 h

Sample	Types of diene	Polymer yield (g)	Activity (kg polymer/mol Zr h)
EP (0)	None added	2.88	3198
EP(1)	ENB	2.40	2671
EP(2)	VCH	2.60	2887
EP(3)	HD	2.54	2824

Table 2
Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced

Sample	Types of diene	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (0)	None added	0.502	0.187	0.045	0.122	0.032	0.112
EP (1)	ENB	0.604	0.191	0.023	0.107	0.024	0.051
EP (2)	VCH	0.505	0.205	0.056	0.114	0.088	0.032
EP (3)	HD	0.609	0.210	0.032	0.118	0.031	–

others. Hereby, only a small amount of various dienes was introduced into the system during EP copolymerization, not for the purpose of synthesizing the EPDM as in general, but specifically for altering the behaviors of EP copolymerization. Thus, in our present study, the small amount of various dienes added did not incorporate into the polymer backbone, which can be determined using ^{13}C NMR measurement.

2. Experimental

In this study, EP copolymerization was performed using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst. All chemicals were manipulated under purified argon using a vacuum atmosphere glove boxes and/or Schlenk techniques. Polymerization was carried out in 100-ml stainless steel reactor with magnetic stirrer. First, 30 ml of toluene used as a solvent was added to the reactor. Then, methylaluminoxane (MAO) solution was added according to the specified ratio to the catalyst concentration ([Al]/[Zr] = 2000) followed by the addition of 0.1 M of a selected diene [dienes used were 5-ethylidene-2-norbonene (ENB);(1), 4-vinylcyclohexene (VCH);(2), and 1,4-hexadiene (HD);(3)]. Then, the catalyst was injected into the system. The reactor was immediately put into liquid nitrogen to stop the reaction between the catalyst and cocatalyst (MAO). After the reaction mixture was frozen for 15 min, the reactor was evacuated for 3 min to remove argon then filled with the gaseous monomers (ethylene/propylene with a molar ratio of 75/25) while the reactor was still frozen in liquid nitrogen. Then, the reactor was taken out of liquid nitrogen and heated up to polymerization temperature (40 °C) to start the polymerization reaction. The polymerization time was kept for 1 h. In order to stop the reaction, the gaseous monomers were released and the reaction mixture was washed with acidic methanol. The polymer (white rubbery powder) obtained was filtered and dried overnight at ambient condition. Technically, for each diene, the polymerization was run at least three times to ensure the results obtained. The average values were reported. Characterization of the polymer obtained was performed using the ^{13}carbon nuclear magnetic resonance, ^{13}C NMR (JEOL JMR-A500 operating at 125 MHz), differential scanning calorimetry, DSC (Perkin-Elmer DSC 7), and scanning electron microscopy, SEM (JSM-5800 LV).

3. Results and discussion

The present research indicated that a small amount of dienes (ENB, VCH, and HD) added could have impact on behaviors of ethylene–propylene (EP) copolymerization with a metallocene/MAO catalyst. In fact, a large amount of diene addition could result in a decreased activity of polymerization as reported by Malmberg et al. [5]. However, it should be noted that the large amounts (~10–16 mol%) of diene were technically required in order to produce the terpolymer of EPDM. In particular, only a small amount (~3.6 mol%) of each diene was added during EP copolymerization in this study in order to maintain high activity of polymerization at this specified condition.

The rates of consumption for E and P with and without the diene addition are shown in Fig. 1. It was found that the

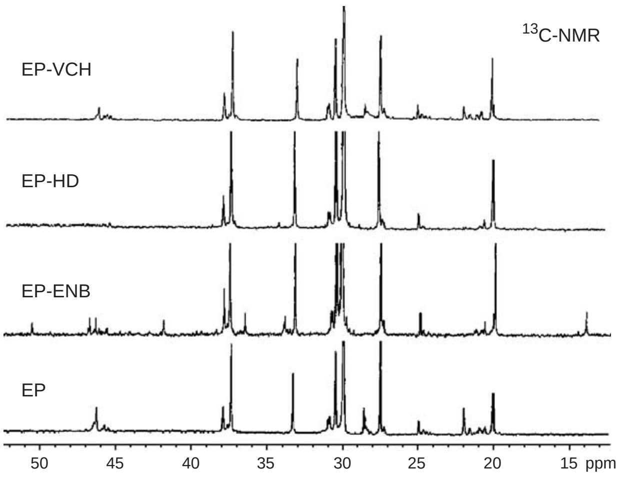

Fig. 2. ^{13}C NMR spectra of various EP elastomers with and without diene addition.

Table 3
Incorporation of ethylene (E), propylene (P) and reactivity ratios of ethylene (r_E) and propylene (r_P) calculated from ^{13}C NMR measurement

Sample	Types of diene	Incorporation (%)		Reactivity ratios		
		E	P	r_E	r_P	r_Er_P
EP (0)	None added	73	27	5.3	1.9	10.1
EP (1)	ENB[a]	80	18	6.9	1.5	10.4
EP (2)	VCH	76	24	4.8	1.5	7.2
EP (3)	HD	85	15	6.2	1.1	6.8

[a] ENB incorporation ca. 2%.