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Norbornene copolymerization with α-olefins using methylene-bridged *ansa*-zirconocene

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Abstract

Copolymers of norbornene with 1-hexene or 1-octene were prepared using the *ansa*-metallocene [methylene(bis(2,5-dimethylcyclopentadienyl))]zirconium dichloride (**1**) in the presence of MAO. The α-olefin content in the copolymer was determined by ^{13}C NMR spectroscopy and resulted in a dramatic decrease in polymer T_g and M_w. The catalyst activity was determined to be 1.0 ± 0.1 kg (polymer)/mmol(Zr) h at 70 °C.

Keywords: *ansa*-Metallocene catalysts; Zirconocene; Copolymerization; Norbornene; Propylene; α-olefins

1. Introduction

The discovery of metallocene catalysts that excel in olefin-addition polymerization of cycloolefins such as norbornene have led to numerous studies of ethylene/cycloolefin copolymerization [1]. *Ansa*-metallocenes have demonstrated catalytic ability to polymerize bulky olefins or cycloolefins with greater activity and stereoregularity than the corresponding non *ansa*-metallocenes, mainly due to a wider open coordination site and easy modification of catalyst symmetry with facile Cp ring substitution [2]. Besides metallocene catalyst systems, copolymerizations have recently been expanded to late transition metals such as neutral nickel catalysts bearing anionic P–O chelate ligands [3] to facilitate chain termination which in turn effects low molecular weight polymers [4]. Among the cyclic olefin copolymers (COC's), ethylene/norbornene copolymer (ENC) is recognized as a promising new class of commercial technical thermoplastic for materials in packaging, medical equipment, optics, capacitors, digital data storage devices (CD-ROM), and binder in printer toner [5].

The production of ENC aided by a metallocene catalyst, especially an *ansa*-metallocene catalyst, is advantageous in industry because of its mechanistic simplicity, compared to ring opening metathesis polymerization followed by hydrogenation to achieve the corresponding copolymer [6]. In addition, the mechanical and structural properties of the cyclic olefin copolymers (COCs) can be modulated primarily with an *ansa*-metallocene and further controlled by polymerization conditions [7]. Besides these, replacement of ethylene by other olefins such as propylene or α-olefins, 1-hexene (AO's) is promising in modifying ENC properties [8]. As recently reported, substitution of ethylene for propylene in the copolymerization diminishes the activity of the metallocene catalyst and results in lower polymer yield [8b]. Even the use of an AO such as 1-hexene gives only a trace of polymer [9]. No reports on 1-hexene or 1-octene AO/norbornene by metallocene copolymerization have been reported, to the best of our knowledge. Although in the polyethylene industry an AO such as 1-hexene and 1-octene is frequently used as the co-monomer to

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control properties such as density of polyethylene [10], AO was used in a ternary system with ethylene/norbornene/AO only for enhancement of norbornene insertion [11] or alternatively as a chain transfer agent to introduce terminal vinyl groups [12].

Recently, we reported the novel *ansa*-zirconocene catalyst, [methylenebis(2,5-dimethylcyclopentadienyl)]zirconium dichloride $[H_2C(Me_2C_5H_2)_2]ZrCl_2$ (**1**), which demonstrated excellent ENC activity. Thus, the careful catalyst design with permethylation adjacent to the *ansa*-bridge lowered the steric hindrance while retaining electronic properties [13]. We have performed preliminary studies on copolymerization of norbornene with AO, revealing that catalyst **1** has adequate activity despite substrate bulkiness. More importantly, this was the first time the AO content in the AO/norbornene copolymer, was calculated using the extended calculation method for ENC [14].

2. Experimental

2.1. Materials

Catalyst **1** was prepared according to the literature procedure [13a]. The cocatalyst methylaluminoxane (MAO) was purchased from Akzo as 8.2 wt% solution in toluene. The monomers, ethylene, propylene, norbornene (bicyclo[2,2,1]hept-2-ene), 1-hexene and 1-octene, were purchased commercially and purified over molecular sieves, CuO and Al_2O_3.

2.2. Polymerization

2.2.1. Copolymerization of ethylene/norbornene or propylene/norbornene

All manipulations were performed in an inert atmosphere using standard Schlenk techniques in conjunction with a VAC dry-box. The copolymerization was carried out using a 500 mL jacketed stainless steel reactor, equipped with a mechanical stirrer. Norbornene was dissolved in toluene to obtain 150 mL solution with the desired mol%. The solution was passed through a purification column and injected into the reactor. After the reactor temperature was stabilized at 70 °C, the MAO toluene solution (Al/Zr = 2000, 6.0 mL, 12.0 mmol, 8.2 wt% in toluene) was injected into the reactor and the reaction mixture was stirred for 15 min. The catalyst (**1**) in toluene (6×10^{-6} mol/L) was added to the reactor and polymerization began as gaseous ethylene or propylene was added to the reactor at a constant pressure. The polymerization time was measured from the moment stirring began. After polymerization occurred, the reactor was vented and the reaction mixture was added into ca. 2 L of acetone. The precipitated white polymer was filtered, washed with acetone several times and dried in a vacuum oven at 80 °C.

2.2.2. Copolymerization of 1-hexene or 1-octene AO/norbornene

All polymerization runs were performed with a 250 mL Schlenk flask immersed in an oil thermostat at 70 °C since the AO is a liquid. With vigorous stirring with a magnetic stirrer, the norbornene and appropriate amount of 1-hexene or 1-octene was dissolved in toluene to obtain 150 mL of a desired mol% solution and then the MAO toluene solution (Al/Zr = 2000, 5.0 mL, 10.0 mmol, 8.2 wt% in toluene) was added to the flask. After ca. 30 min of mixing, polymerization was initiated by addition of the catalyst **1** in toluene (5×10^{-6} mol/L). After polymerization occurred, the reaction mixture was quantitatively transferred into 2 L of acetone. The precipitated white polymer was filtered, washed with smaller quantities of acetone several times and finally dried in a vacuum oven at high temperature.

2.3. Characterization of copolymers

The glass transition temperatures (T_g) were measured with a TA DSC 2010 instrument. The sample was first heated to 300 °C, then cooled to 30 °C at a rate of 20 °C/min, and reheated to 250 °C at a rate of 20 °C/min. The data used in this work was taken from the second heating. The average molecular weights (M_w) and the molecular weight distributions were determined by a Waters/Wyatt GPC-MALLS system at

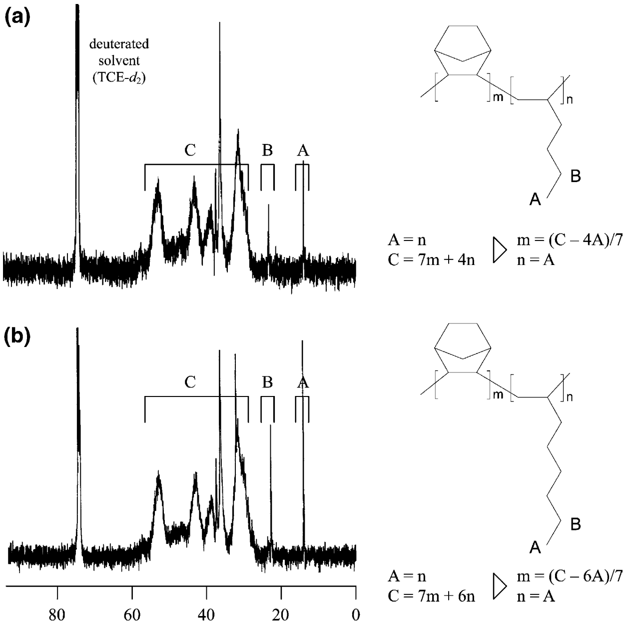

Fig. 1. Representative ^{13}C NMR spectra of (a) 1-hexene/norbornene copolymer (entry 7) and (b) 1-octene/norbornene copolymer (entry 10). Calculation of each monomer incorporation ratio, *m* and *n*, from the peak integration is presented to the right. TCE = 1,1,2,2-tetrachloroethane.