



Structure analysis of ethylene/1-octene copolymers synthesized from living coordination polymerization



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ABSTRACT

A series of ethylene/1-octene random and block copolymer samples were synthesized via a living coordination polymerization catalyzed by *bis*[*N*-(3-methylsilylidene)-2,3,4,5,6-pentafluoroanilino] titanium(IV) dichloride/dMAO. The chain microstructures of the copolymers were elucidated by analytic TREF and DSC thermal fractionation techniques in this work. It was found that the living random copolymers possessed narrower intra-chain composition distributions than those prepared from conventional metallocene catalysts. With the same short chain branching content, the melting temperature of living random copolymer was about 16 °C lower than metallocene-catalyzed random copolymer. The living block copolymers were also studied in comparison with the olefin multiblock copolymer (OBC) produced from chain shuttling polymerization. The interchain composition distribution of OBC was found broader than living block copolymers. However, the crystal thickness distribution of OBC was narrower. The diblock copolymer had a bimodal distribution in the crystal thickness and the step triblock copolymer showed a trimodal distribution, in contrast to OBC's single modal distribution.

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1. Introduction

Polyethylene is the most widely used commodity polymer. Depending on the short chain branching (SCB) distribution, its property varies from plastic to elastomer [1]. It is well known that the chain microstructure of polyolefin is determined by the catalyst [2]. Commercial ethylene/ α -olefin copolymers are mainly produced by Ziegler–Natta or metallocene catalysts. Most of them have a random chain microstructure. Copolymers by traditional Z–N catalysts (e.g. LLDPE) exhibit broad molecular weight and composition distributions [3]. Metallocene products (e.g.

m-LLDPE, POE) have much narrower SCB distribution than Z–N's [4], due to single-site nature of the former.

Recently, ethylene/1-octene multiblock copolymer (OBC) has been commercialized using a chain shuttling polymerization technique [5,6]. Chain shuttling polymerization employs two post-metallocene catalysts. One catalyst, good for ethylene/ α -olefin copolymerization produces soft amorphous segments. The other, poor in copolymerization, produces hard semi-crystalline segments. The hard and soft segments are alternatively connected through the function of an appropriate chain shuttling agent. Both soft and hard segments are random copolymers. The number and length of soft and hard segments are statistical. This type of multiblock chain structures gives the materials better elasticity at high temperature than random copolymers [7]. Nowadays, ethylene/ α -olefin copolymers become increasingly important in high-valued

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applications. For example, POE and OBC have become major materials for polyolefin-based thermoplastic elastomers [8].

Remarkable progress has been made in the areas of living coordination polymerization over the past decades [9,10]. As chain termination and transfer reactions are negligible, the chain microstructure of polyolefin could be precisely designed and controlled via living polymerization [11–14]. In living ethylene/ α -olefin copolymerization, the comonomer units are incorporated into chains in a living manner, polyethylenes with novel and complex architectures could thus be synthesized [15–17]. This level of richness and controllability in chain microstructure was not possible with traditional Z–N or metallocene catalysts. There is no doubt that living polymerization technique provides a powerful tool for tailor-making polyolefin materials. Structure analysis of the ethylene/ α -olefin copolymers thus becomes most desirable. It is of practical importance for designing new polyolefin materials, though challenging due to structural complexity.

The composition distribution of ethylene/ α -olefin copolymers can be characterized by two types of established methods. One is based on chromatographic separation of polymer chains with different crystallizabilities from a dilute solution, such as temperature rising elution fraction (TREF) technique, crystallization analysis fraction (CRYSTAF) technique [18,19] and the newly developed crystallization elution fraction (CEF) technique [20,21]. All these techniques could provide comparable results [18–21]. TREF is more time-consuming due to two fractionation steps, crystallization and elution. CRYSTAF was found to be more sensitive to crystallization kinetics and cocrystallization effects, although it takes only one crystallization step. CEF process is similar to TREF but time saving. It bears less cocrystallization effect comparing with CRYSTAF, because of the superior dynamic crystallization. All these techniques need toxic solvents and expensive instruments. As polymer chains are physically separated according to the comonomer incorporation, polymer interchain heterogeneity can be fully analyzed.

The other type of methods is based on DSC thermal fractionation, including step crystallization (SC) and successive self-nucleation and annealing (SSA) techniques [22]. In the DSC thermal fractionation, the polymer sample is fractionated from melt by a carefully designed temperature program. Polymer chains having different SCB densities form crystals or lamellas of different sizes. Subsequent heating of the fractionated sample gives a multimodal DSC melting curve, which can be correlated to its composition distribution. Because crystallization is sensitive to crystalline methylene sequence length (CMSL) and polymer chains are not physically separated, polymer intrachain sequence heterogeneity can also result in molecular segregation. The DSC thermal fractionation is reflective of both interchain and intrachain heterogeneities. In comparison, SSA has better resolution and takes shorter time than SC [23,24].

In general, the interchain and intrachain heterogeneities of olefin copolymers can be characterized by TREF/SC and/or TREF/SSA cross-fractionation. These methods are widely used in the characterization of commercial eth-

ylene/ α -olefin copolymer products [25–28]. However, it has not been applied to olefin copolymers produced from living coordination polymerization. The structural differences between the copolymers prepared by living and non-living polymerization are yet to be elucidated.

This work reports a study on the composition distribution of ethylene/1-octene random and block copolymers synthesized by living coordination polymerization. The interchain heterogeneities of all samples analyzed in this work were determined by the analytic TREF analysis. The SSA thermal fractionation technique was adopted for characterization of the intrachain heterogeneity. The intrachain heterogeneities of the living random and block copolymers were respectively compared to their commercial ethylene/1-octene random and block counterparts.

2. Materials and methods

In this work, the ethylene/1-octene copolymers were synthesized from *bis*[*N*-(3-methylsalicylidene)-2,3,4,5,6-pentafluoroanilinato] titanium(IV) dichloride/dMAO (fluorinated FI-Ti) [29], which is a famous living catalyst system. The synthesis procedures for the catalyst and the copolymers were described in our previous work [30]. In the synthesis of copolymers used in this work, the 1-octene conversion was controlled below 3% to avoid the copolymer composition drifting. The basic structure characteristics of the samples are listed in Table 1. LBC represents living block copolymer. In particular, LBC1 is a living diblock copolymer and LBC2 is a living step-triblock copolymer. The detailed specifications of LBC1 and LBC2 could be found in our previous work [31]. The commercial available products, Engage 8150 and Infuse 9000, are designated as MRC (metallocene-catalyzed random copolymer) and OBC (olefin multiblock copolymer), respectively. Engage 8150 is an ethylene/1-octene random copolymer produced by Dow Chemical's constrained geometry catalyst (CGC) technique. Infuse 9000 is an ethylene/1-octene multiblock copolymer with statistical block length distribution, produced by Dow Chemical's well-known chain shuttling polymerization technique [5,6].

High temperature gel permeation chromatography (PL-GPC 220 system) was used for the determination of molecular weights (M_n and M_w) and polydispersity index (PDI). The measurement was done at 150 °C, using 1,2,4-trichlorobenzene as solvent flowing at the rate of 1.0 ml/min. Universal calibration was performed on the monodisperse polystyrene (PS) standards. The Mark–Houwink constants of PS are $K = 5.91 \times 10^{-4}$ and $\alpha = 0.69$, and those of PE are $K = 1.21 \times 10^{-4}$ and $\alpha = 0.707$.

The comonomer incorporation was determined by the high temperature ^{13}C NMR spectra with deuterated *o*-dichlorobenzene (*o*-DCB) as solvent. Polymer solutions (10 wt%) were scanned at 125 °C using a Bruker AC 400 pulsed NMR spectrometer with a spectral width of 8000 Hz, pulse delay time of 8 s, acquisition time of 1.3 s and pulse angle of 90°. At least 5000 scans were required for a good signal to noise ratio. The ASTM D5017-96 method was employed for the carbon assignments and composition calculation [32].

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