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The interrelationships between microstructure and melting, crystallization and thermal degradation behaviors of fractionated ethylene/1-butene copolymer

Abbas Kebritchi · Mehdi Nekoomanesh · Fereidoon Mohammadi · Hossein Ali Khonakdar

Abstract The interrelationships between microstructure and melting, crystallization and thermal degradation behaviors of a commercial Ziegler–Natta (Z–N)-based ethylene/1-butene copolymer were investigated. The copolymer was fractionated based on short chain branch (SCB) content by preparative temperature-rising elution fractionation (P-TREF) method. A broad multipeak chemical composition distribution was obtained for both molecular weight distribution and short chain branch distribution. A difference of about 48 °C in melting temperature (T_m) has been observed for fractions with 50 branches of different SCB contents. A logarithmic relationship was obtained between the methylene sequence length calculated based on proton-1 nuclear magnetic resonance results and the P-TREF elution temperature (ET). A relationship between the SCB content and the inverse of lamellae thickness (L_c) was established. Two linear functionalities were found for T_m versus ET and crystallization temperature (T_c) versus the SCB content. To the best of our knowledge, as a first effort, surprisingly a linear relationship between the temperature at the maximum rate of degradation (T_{max}) and the SCB content was acquired, which showed less sensitivity to the SCB content than T_m. Also, it was found that the degradation initiation temperature ($T_{5\%}$) and activation energy (E_a) are increased by the decreasing SCB content. Moreover, it was demonstrated that Hosoda equation is not applicable for different ethylene/α-olefin copolymers based on different catalyst types with dissimilar fractionations and experimental conditions.

Introduction

Linear low-density polyethylenes (LLDPEs), produced by the copolymerization of ethylene and α-olefins with either Ziegler–Natta (Z–N) or metallocene catalysts, are major commodity polymers used worldwide [1–3]. 1-Butene, 1-hexene, and 1-octene are frequently used in ethylene polymerization to control LLDPE density by varying the amounts of comonomer incorporated [4, 5]. This maintains polymer chain linearity in an overall configurational sense but leads to short chain branches (SCBs) randomly spaced along the polymer backbone [6]. LLDPEs of similar density might exhibit significant differences in branching parameters due to differences in the kinds of catalyst, reactor processing technology and polymerization conditions [7].

The SCB content, the SCB length, and the SCB distribution (SCBD) are the key structural parameters that determine the performance and applications of linear PEs [8]. The SCB content by affecting rheological parameters [9, 10], activation energy (E_a) [11], glass transition temperature [12], and both α and β relaxation peaks [13] determines the crystallite morphologies of PE [14] as well as phase behaviors of PE blends [15]. The length of SCB affects tensile [16], impact [17], and tear properties at high strain rates [16], due to interlamellar tie molecules with the increasing SCB length [17]. Finally, SCBD controls the

A. Kebritchi · M. Nekoomanesh (✉) · F. Mohammadi
Iran Polymer and Petrochemical Institute, 14965-115 Tehran, Iran
e-mail: m.nekoomanesh@ippi.ac.ir

H. A. Khonakdar
Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany

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