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Microstructural study of synthesized polyethylenes by homogeneous and heterogeneous nickel α-diimine catalysts

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Abstract In this work, ethylene polymerization was investigated by using homogeneous and heterogenouse nickel α-diimine catalysts [1,4-bis(2,6-diisopropylphenyl) acenaphthene diimine nickel(II) dibromide]. Methyl aluminoxane (MAO) and triethyl aluminum (TEA) were used as cocatalysts in homogenous and heterogeneous polymerizations, respectively. The heterogeneous catalyst showed lower activity than its homogeneous equivalent. The influence of polymerization temperature and heterogenization conditions was studied on the microstructure properties of the prepared polymers. Increasing polymerization temperature (T_P) up to 50 °C decreased the activity of both homogenous (LN) and heterogeneous (LNS) nickel α-diimine catalysts. The highest activities were 1286 and 982 kg PE (mol Ni bar h)$^{-1}$ obtained at $T_P = 30$ °C for LN and LNS catalysts, respectively. The polymer samples obtained by supported catalyst (LNS) showed lower unsaturation contents. Moreover, DSC analysis did not show any melting peaks for polymers obtained by LN catalyst due to their amorphous structure, which was confirmed by XRD analysis. The microstructure of the prepared polymers was completed by successive self-nucleation annealing (SSA) and was investigated by ^{13}C NMR studies. The SSA thermogram of samples made by LNS catalyst exhibited several crystal types with different lamella thicknesses. The branches in polyethylene samples produced by homogenous catalyst were higher and showed more diversity. The total methyl branch percentages for both LN and LNS catalysts were 13.1 and 3.4%, respectively.

Keywords Ethylene polymerization · Nickel α-diimine catalyst · Branching · Heterogenization · ^{13}CNMR

Introduction

Polyethylenes containing long and short branches have attracted great attention in the recent decades [1]. The existence of long branches in the polyethylene backbone improves its microstructural properties, e.g., polymer processability, toughness, impact resistance, and tensile strength [2]. Usually, Ziegler–Natta or metallocene catalysts incorporate short branches into polymers by ethylene copolymerization with α-olefin comonomers such as 1-butene, 1-hexene, and 1-octene [3, 4]. Other methods for creating branched polyethylene are based on using late-transition metal catalysts such as those reported by Svejda et al. [5], Paulovicova et al. [6], and Younkin et al. [7]. These types of catalysts have the ability to produce polymers with different microstructures in a wide range from relative linear polymers to hyper-branched or dendritic without using α-olefin co-monomers [8–10]. Special polymers can also be prepared by varying metal center and ligand type on the coordination sphere of late-transition metal catalysts [10, 11]. Late-transition metal catalysts possessing α-diimine ligands can enhance or hinder chain transfer reactions using different substitute in aryl rings. Besides, various substitutions in the *ortho*-position of the aryl ring of the catalyst may also induce the production of polyethylene with low or high degree of branching [12–14]. Heterogenization of these

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