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Synthesis of PE reactor alloys using Ziegler-Natta/ Late Transition Metal hybrid catalyst: Study of vinyl content and molecular weight

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Abstract

Various polyethylene (PE) reactor alloys are synthesized through heterogeneous ethylene polymerization with a new type of Ziegler-Natta (ZN)/Late Transition Metal (LTM) hybrid catalyst in the presence of Methyl Aluminoxane (MAO) as the sole cocatalyst. The effects of various parameters including weight ratio of the catalysts (ZN/LTM =25, 50, 100) and polymerization temperature (T_P=30, 30-60, 60°C) are investigated on vinyl content and molecular weights of obtained polymers. As the share of LTM increased in the hybrid catalyst the vinyl contents of PE increased.

Keywords : Hybrid catalyst, vinyl content, Late Transition Metal catalyst, Ziegler-Natta catalyst, Reactor Alloy, Polyethylene

Introduction

Since the pioneering researches of Karl Ziegler and Giulio Natta on the polymerization of simple olefins in the early 1950's, there has been an intense interest in the application of various catalysts in olefin polymerization [1]. In this way using mixtures of catalysts became one of interesting areas of olefin polymerization due to the characteristics of obtained polymers. Catalyst alloys, hybrid catalysts and multi-catalyst systems are the common expressions used in this respect [2-4]. In these systems each of the catalysts produces polymers with different properties and therefore the final polymer is a blend of two or more kinds of polymers. In this paper a novel combination of ZN/LTM hybrid catalyst is utilized in ethylene polymerization and the properties of produced polymers including molecular weight and vinyl contents are studied.

Experimntal

Material

Methylaluminoxane (MAO; 10 wt% solution in toluene) and Triethylaluminum (TEA) were purchased from Aldrich chemical company. Toluene was provided by Bandar Imam Petrochemical Company (BIPC, Iran) and was refluxed and distilled over sodium before use and kept over 4A/13X activated molecular sieves. The fourth generation ZN catalyst and ethylene were obtained from Jam Petrochemical Company (Iran). Aniline derivatives were supplied by Merck Chemicals. The gases were purified as explained elsewhere [5].

Preparation of hybrid catalyst

The hybrid catalysts were prepared as follows: TEA was added to ZN catalyst along with mechanical stirring. The mixture was washed and finally the solid powder was dried. Then Specific amounts of LTM catalyst were added to the suspension of pretreated ZN catalyst stirring with a magnet bar. Eventually the reaction mixture was fully filtered, washed.

Characterization

The intrinsic viscosities were determined in decahydronaphthalene at 135 ± 0.1°C using Ubbelohde viscometer. For calculation of M_v, the Mark–Houwink– Sakurada equation was used. The requisite constants α and K for polyethylene were

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achieved from elsewhere (α= 0.7 and K= 0.062 mL/g). FTIR analyses of the samples were recorded using FTIR Bruker 55 instrument to determine the vinyl content of polyethylene samples.

Results and Discussion

Ethylene polymerization

According to Figure **1**, it is observed that as the share of LTM in the hybrid catalyst increases, molecular weight of synthesized PE decreases steadily. Also as polymerization temperature increases, the molecular weight of polymer samples decreases [6]. The maximum molecular weight was achieved at polymerization temperatures about 30ºC. Unsaturated polymer chain ends, caused by β -hydrogen elimination transfer reaction is more pronounced in LTM catalysts. Therefore it is depicted in Figure **2**, as the share of LTM in the hybrid catalyst increases, the vinyl content of polymers increases.

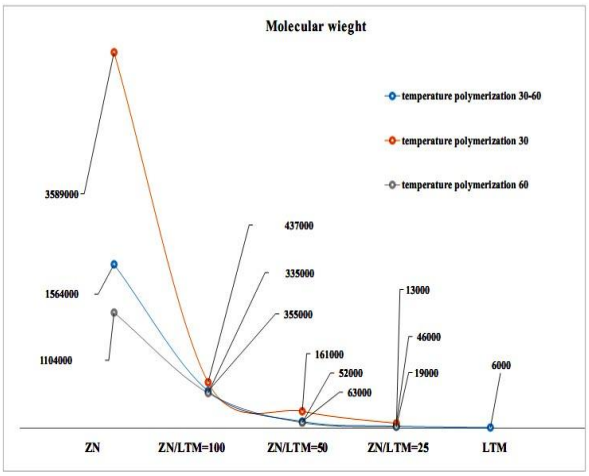

Figure 1. Effect of various ZN/LTM ratio and polymerization temperature on molecular weights of reactor alloy PEs

Conclusion

A new combination of Ziegler-Natta / Late transition metal hybrid catalyst was used in ethylene polymerization and properties of final products were investigated. Increasing LTM share on hybrid catalyst led to lower molecular weight and increased vinyl content of obtained polymers. Maximum molecular weight of hybrid catalyst was observed at low polymerization temperatures (T_p= 30 ºC). The molecular weight can also be controlled by changing other parameters like polymerization temperatures.

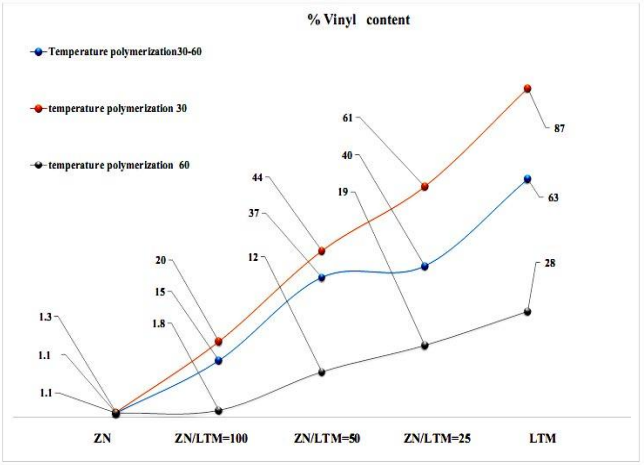

Figure 2. Effect of various ZN/LTM ratio and polymerization temperature on vinyl content of PE reactor alloys.

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