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Thermal and morphological properties of polyethylene reactor alloys using ZN/BLTM catalytic system

Mostafa Khoshsefat,[1] Gholam Hossein Zohuri,[2] Saeid Ahmadjo, *[1] Mohammad Mahdi Mortazavi[1]

1. Department of Catalyst, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran

2. Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, P.O. Box: 91775, Mashhad, Iran.

Abstract

To study on the effect of counterpart catalyst on the final produced polyethylene properties, the polymerizations were carried out under similar condition for catalyst mixing and each catalyst, solely. In this system, each catalyst can be active and produce blend of two or more kind of polymers altogether. A mixture of Ziegler-Natta (ZN) and a binuclear late transition metal (BLTM) catalyst was employed in presence of methylaluminoxane (MAO) and triethylaluminium (TEA) as cocatalyst and impurity scavenger, respectively. A moderate activity observed for ZN/BLTM catalytic system due to counterpart catalyst effect in comparison to ZN and BLTM single catalyst system. SEM Images showed a partially spherical morphology for synthesized polyethylene alloys while there is no distinct shape for obtained polyethylene using each catalyst, separately. The observed morphologies were achieved without prepolymerization. Moreover, DSC thermograms illustrated two distinct melting peaks which can be attributed to each catalyst. Besides, the melting points shifted to lower temperature which can devoted to flux role. Crystallinity degree of polyethylene alloys were 45.8 %while crystallinity for synthesized polyethylene in presence of ZN and BLTM were 53.7% and 24. 1%, respectively.

Keywords: Catalytic polymerization –Binary catalytic system -Polyethylene –counterpart effect- Reactor alloys.

Introduction

One of the main strategies used for the development of polyolefin catalyst, which is still being studied in the lab scale is the use of combination of different types of catalysts during polymerization. Catalyst alloys, hybrid catalysts, and multi-catalyst systems are the common expressions used in this respect [1-2]. 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. Along the route making new types of polyolefins different strategies have been used for making polymeric reactor alloys. We may categorize the strategies as operational strategies and catalytic strategies. In the operational strategies, the reactors and reaction conditions play the main roles while in the catalytic strategies the catalyst and its structure plays the main role. Employing a series of reactors, such tandem or cascade reactor systems, is one of the operational route in which each reactor runs under different polymerization reaction conditions, generating the desired bimodal polymers with different MWs and microstructures [1,3,4].

In this work, the polymerizations were carried out under similar condition for catalyst mixing and each catalyst, solely. Thermal and morphological properties of PE along with the catalytic features were comprised.

Experimental

The experiments were carried out under similar condition for catalyst mixing and each catalyst, solely. In this system, each catalyst can be active and produce blend of two or more kind of polymers altogether. A mixture of Ziegler-Natta (ZN) and a binuclear late transition metal (BLTM) catalyst was employed in presence of methylaluminoxane (MAO)

* Correspondence to: S. Ahmadjo (E-mail: S.ahmadjo@ippi.ac.ir)

and triethylaluminium (TEA) as cocatalyst and impurity scavenger, respectively.

Results and Discussion

A moderate activity observed for ZN/BLTM catalytic system in comparison to ZN and BLTM single catalyst system. SEM Images showed a partially spherical morphology for synthesized polyethylene alloys while there is no distinct shape for obtained polyethylene using each catalyst, separately. The observed morphologies were achieved without prepolymerization. Moreover, DSC thermograms illustrated two distinct melting peaks which can be attributed to each catalyst (scheme A). Besides, the melting points shifted to lower temperature. Crystallinity degree of polyethylene alloys were 45.8% while crystallinity for synthesized polyethylene in presence of ZN and BLTM were 53.7% and 24.1%, respectively. Chain-walking mechanism allowing the growing center to migrate along the polymer chain which is more pronounced in polymers produced by LTM catalysts. Based on aforementioned reasons, less crystallinity due to variable degrees of chain branching and the broadening transition to a sequence of melting followed by recrystallization steps of less ordered domains [5].

Conclusion

Using a binary catalytic system including a Ziegler-Natta (ZN) and a binuclear late transition metal (BLTM) in ethylene polymerization led to produce polyethylene reactor alloys. A moderate activity observed for ZN/BLTM catalytic system due to counterpart catalyst effect. Besides, the melting points shifted to lower temperature which can devoted to flux role. Enhancement of Morphology of PE without using prepoymerization was a counterpart effect of employing catalytic system.

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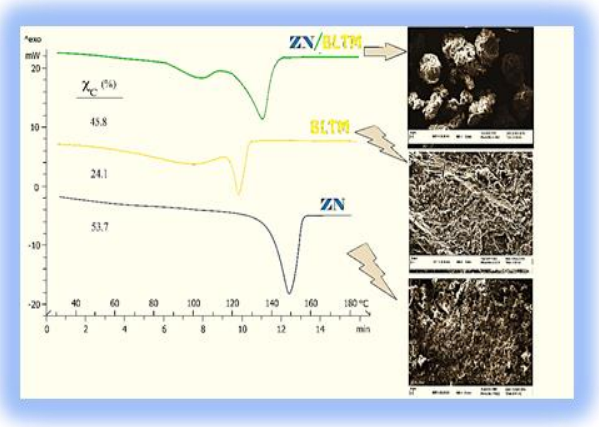

Scheme A. DSC thermograms and SEM Images (500X) of PE synthesized catalytic systems