9th International Seminar on Polymer Science and Technology

Iran Polymer and Petrochemical Institute, Tehran, Iran
17-21 October 2009

Ethylene Polymerization Using of Fluorinated FI Zr-based Catalyst

R. Sandaroos, G. H. Zohuri[*], S. Damavandi
Department of Chemistry, Ferdowsi University of Mashhad, P.O. Box 91775 Mashhad, Iran.

Abstract

A fluorinated FI Zr-based catalyst of Bis[N-(3,5-dicumylsalicylidene)-2',6'-Flouroanilinato]zirconium(IV) dichloride was prepared and used for polymerization of ethylene. It was shown that ortho-F substituted phenyl ring on the N electronically plays a key point in the suppression of chain transfer reactions especially ß-hydride transfer leading to increase the molecular weight and moderation of the catalyst activity as well. Methylaluminoxane (MAO) and triisobuthylaluminum (TIBA) were used as a cocatalyst and a scavenger respectively. Involvement of ortho-F not only increased the activity, but reduced the [Al]/[Zr] molar ratio in comparison with the similar non fluorinated FI catalysts. The catalyst showed the maximum activity at about [Al]:[Zr]=32000:1 molar ratio and further addition didn't affect the activity of the catalyst. The highest activity of the prepared catalyst was obtained at 40 °C. At the monomer pressure of 3 bars was obtained polyethylene with the viscosity average molecular weight ($\overline{MV}$) of 1.3×10^6 indicating the dramatic effect of ortho-F substitution on the polymerization mechanism.

Keywords: fluorinated FI catalyst, catalytic polymerization, Zr-based catalyst, olefin polymerization.

Introduction

FI catalysts have been found to produce various new polymers such as low molecular weight, ethylene-propylene copolymer and ultra high molecular weight PE[1]. In this contribution, we studied syntheses and ethylene polymerization behavior of FI catalyst having fluorine containing ligand. We found that ligand comprising fluor atom effectively impresses the polymerization behavior and the ($\overline{MV}$) of the obtained polymer as well.

Experimental

Zirconium tetrachloride, phenol and aniline derivatives and 4-toluenesulfonic acid (Merck, Germany), n-Butyllithium and MAO (Sigma Aldrich Chemicals) were used as received. Ligand preparation, catalyst preparation and ethylene polymerization procedure were carried out under dried N_2.

Result and discussion

Polymerization of ethylene using the prepared catalysts (Figure 1) was studied in the different

[Al]/[Zr] molar ratio. The optimum activity was obtained at [Al]:[Ti]=32000:1 molar ratio. The relatively low ratio of [Al]:[Ti] obtained for the catalyst with reasonable activity comparing to this type of FI catalysts could be an advantage of the catalyst. It is important to point out that using the [Al]/[Zr] molar ratio more than this value didn't cause a further enhancement in the activity of the catalysts indicating low chain transfer specially ß-hydride transfer which is responsible to produce low molecular weight polymer (Figure 2). The behavior could be due to the electronically interaction between $H_ß$ and ortho F atom substituted phenyl ring on the N. At the monomer pressure of 3 bars the catalyst could produce polyethylene with the ($\overline{MV}$) of 1.3×10^6 which is high value in comparison of the similar FI catalysts indicating the dramatic effect of ortho-F substitution on the polymerization mechanism. It was proposed that attractive interaction, which is expected to effectively curtail ß-H transfer to the central metal and incoming monomer, is responsible for the unprecedented behavior [2,3]. However, for ethylene coordination, the transition state of the ß-H transfer is probably disfavored. This fact was proved with the moderation of activity of the catalyst. The highest activity of the catalyst was 3.2×10^5 g PE/mmol Zr. h at the temperature of 35 °C and monomer pressure of 2 bars.

The highest activity of the catalyst was obtained at about 35 °C. The catalytic activity was increased with increasing the temperature from 20 °C to 35 °C following to a decrease at higher temperature. An increase in the propagation rate coefficient and also an irreversible deactivation of the catalytic active

---

[*] E-mail: zohuri@um.ac.ir

sites at high temperature can explain the increase and decrease in activity respectively[4]. Meanwhile solubility of the monomer gas in the polymerization solvent decreased with increasing temperature Activity was slightly increased with the increasing of the monomer pressure (Figure 3).

Conclusion

A FI catalyst comprised of fluorinated bis(phenoxy-imine)Zr complex was prepared and used for ethylene polymerization. Ortho-F substituted phenyl ring on the N electronically plays a key point in the suppression of chain transfer reactions especially ß-hydride transfer leading to increase the molecular weight and moderation of the catalyst activity too. The highest activity of the catalyst and the $\overline{MV}$ of the obtained polymer were 3.2×10^5 g PE/mmol Zr. h and 1.3×10^6 respectively. Crystallinity and melting point of the obtained polymer were between 60-65 % and 125-130 $^{\circ}$C. The highest activity of the catalyst was obtained at about 35 $^{\circ}$C.

References

1- Fujita, T.; Tohi, Y.; Matsui, S.; Saito, J.; Makio, H.; Tsutsui, T. *EP-0874005 Mitsui Chemicals Inc*, 1998.
2- Mitani, M.; Mohri, J.; Yoshida, Nakano, Fujita, T. *J Am Chem Soc;* **124**, 3327, 2002.
3- Tian, J.; Hustad, P. D.; Coates, G. W. *J Am Chem Soc*, **123**, 5134, 2001.
4- Busico, V.; Talarico, G.; Cipullo, R.; *Macromol Symp*, **226**, 1, 2005.

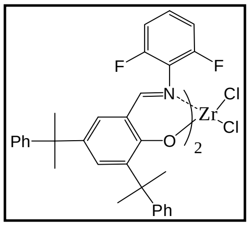

Figure 1. Structure of the catalyst

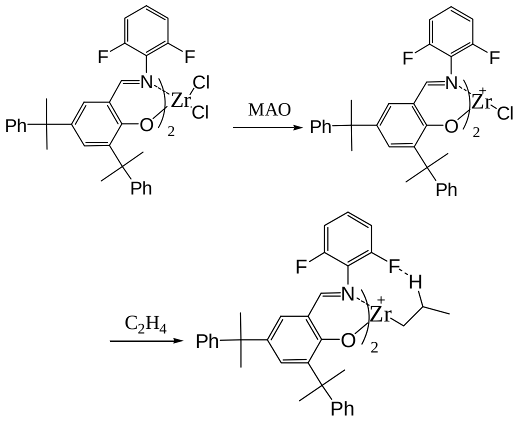

Figure 2. The electronically interaction between H_{β} and ortho F atom substituted phenyl ring

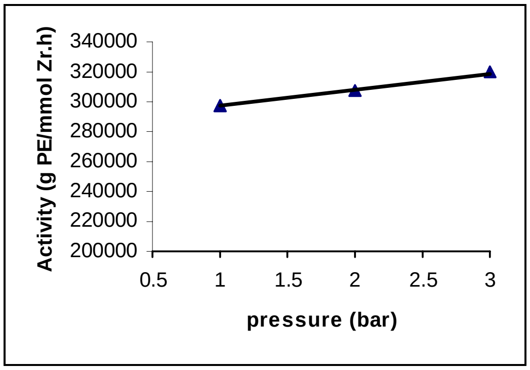

Figure 3. Effect of monomer pressure on the average rate of polymerization.