



Comparative Study of Ethylene Polymerization Using FI-Zr Based Catalysts

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Abstract

The slurry polymerization of ethylene was carried out using two Phenoxy Imine (FI) catalysts of Bis-[N-(3-ter-butyl)-5-methyl-salicylidene)anilinato]zirconium(IV) dichloride (catalyst (a)) and Bis-[N-(5-methyl-allylidene)anilinato]zirconium(IV) dichloride (catalyst (b)). It was shown that the catalyst structure has significant effect on the catalyst behavior. The catalyst (a) contains ter-butyl substitute on the ortho position to the phenoxy oxygen showed higher activity. Thermal stability of the catalyst (a) and viscosity average molecular weight (\bar{M}_V) of the polymer obtained using catalyst (a) were more than the catalyst (b).

Keywords: catalytic polymerization, FI catalyst, Zr-based catalyst, polyethylene.

Introduction

The FI catalysts display a very high ethylene polymerization activity using methylaluminoxane (MAO) as a cocatalyst even at ambient temperature. Substitution position has strong and critical effect on activity of the catalyst, for example the substitution adjacent to the phenoxy oxygen atom of the catalyst has substantial effect on the the catalyst activity[1-4]. In the present work, two Zr-based FI catalysts were prepared. One of the catalysts contained a tert-butyl and a methyl groups substituted on ortho and para position to the phenoxy group respectively. The other prepared catalyst was without the tert-butyl substitution. Polymerization of ethylene was carried out using the catalysts at various

Results and Discussion

Slurry polymerization of ethylene was carried out using the prepared catalysts (Figure 1) at different conditions and was found that The olymerization activity (R_p) was continuously increased with increasing the [Al]:[Zr] molar ratio in the range studied. In contrast to the catalyst (a), the catalyst (b) showed completely different behavior with increasing MAO concentration. As shown in Figure 2 the catalyst (b) was more affected with the MAO concentration. The behavior could be due to less bulky substitution groups of the ligand of the catalyst (b) which makes it susceptible to the chain transfer reaction easier than the propagation reaction in

comparison with the catalyst (a). The sterically large substitution may effectively separate the cationic active species from the anionic cocatalyst nature species. The ion separation cause increase the unsaturation degree of the active species[3,7] and coordination of ethylene to the active center following to insertion reaction more possible to take place than the chain transfer reactions. The polymerization of ethylene was carried out at temperature between 25 and 75 °C. The highest activity of the catalyst (a) was obtained at about 45 °C. However, the highest productivity of the catalyst (b) occurred at 25 °C, in the range studied. An increase in the propagation rate coefficient with increasing temperature and also an irreversible deactivation of the catalytic active sites at high temperature has been reported[1,7,8]. The decrease in the polymerization activity could be due to the β -hydride elimination reactions that take place at high temperature[8]. It was revealed that the catalyst (b) had lower thermal stability comparing to the catalyst (a) which contain bulky group in the ortho position of the phenoxy oxygen. In this work it was found that the presence of sterically bulky group could affect on thermal stability of the catalyst. The R_p /time profile was a decay type with a short acceleration period for both of the catalysts. The profile for the catalyst (a) is more stable which indicate longer life time of its catalyst activity. The bulky substituent on ortho position to the phenoxy oxygen of the catalyst (a) provides a steric protection to the phenoxy-oxygen

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against electrophilic attack by the cocatalyst which may survive its activity even for longer time[7]. The effect of the monomer pressure between 1 and 5 bars on the catalysts behavior was studied. The polymerization activity was increased with increasing the monomer pressure with a similar trend for both of the catalysts. The same behavior has been reported.

Conclusion

The following results were obtained using the homogeneous FI catalysts:

- 1- At the temperature above 75 °C, the catalyst (a) produced some polyethylene, whereas the catalyst (b) at temperature higher than 60 °C only produced a trace amount of oligomer.
- 2- Incorporation of tert-butyl substitution on ortho to the phenoxy-oxygen in catalyst (a) caused its thermal stability and also moderate kinetic behavior.
- 3- It seems that the large substitution on ortho position to the phenoxy-oxygen not only increased the activity of the catalyst, but also increased the crystallinity and the \bar{M}_V of the resulting polymer. The \bar{M}_V increased with increasing the monomer pressure.

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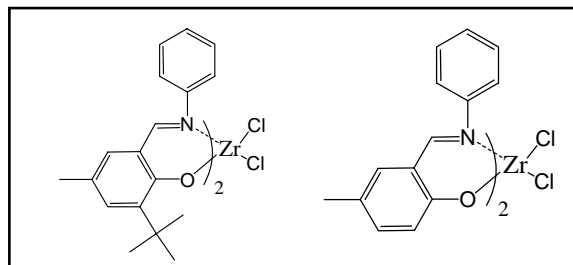


Figure 1. Structure of the prepared catalysts. Cat (a, left), Cat (b, right).

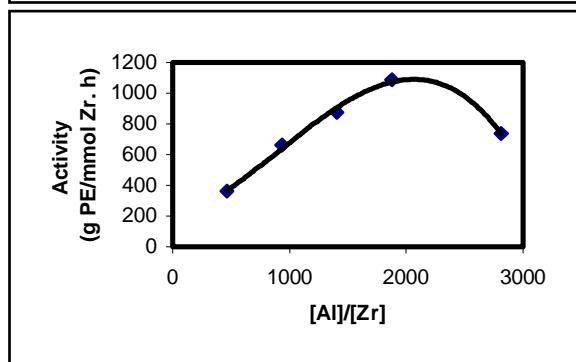
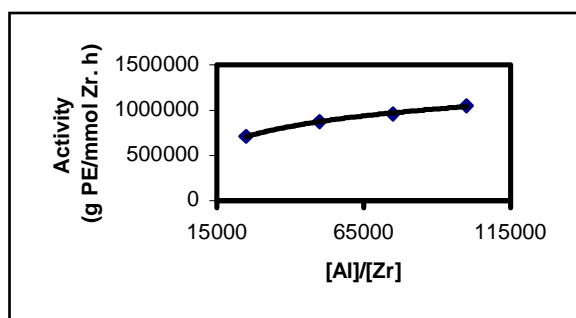


Fig 2. Effect of MAO concentration on the average rate of polymerization using FI catalysts (a, up) and (b, down).



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