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Ethylene Polymerization Using FI Zr-Based Catalyst

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Abstract

A FI Zr-based catalyst of Bis[N-(3,5-dicumylsalicylidene)-2`,4`,6`-trimethylanilinato]zirconium(IV) dichloride was prepared and used for polymerization of ethylene. Triisobuthylaluminum (TIBA) and methylaluminoxane (MAO) were used as scavenger and cocatalyst respectively. Activity of the catalyst was increased with increasing concentration of MAO and monomer pressure to a maximum value of 6.5×10^5 g PE/mmol Zr. h. The optimum activity of the catalyst was obtained at reaction temperature of 45 °C. The rate/time profile of the polymerization decayed with a short acceleration period. Crystallinity and melting point of the obtained polymer were between 55-65 % and 125-135 °C respectively. The behaviour indicate of semicrystaline polyethylene obtained using the catalyst system. Viscosity average molecular weigh ($\overline{MV}$) of obtained polyethylene was about 6.2×10^5.

Keywords: FI catalyst, Zr-based catalyst, slurry polymerization, olefin polymerization, polyethylene.

Introduction

Recently, new classes of metal complex have been studied as precursors for a new generation of olefin polymerization [1,2]. Specially ethylene polymerization catalysts have been developed from phenoxy-imine and diimine ligands [3]. In the present work we prepared a FI Zr-based catalyst which displays a high ethylene polymerization activity at ambient temperature and atmosphere pressure. Polymerization activity at different conditions was investigated. Some specification of the obtained polymer was investigated.

Experimental

Zirconium tetrachloride, phenol and aniline derivatives and 4-toluenesulfonic acid (Merck, Germany), n-Butyllithium and MAO (Sigma Aldrich Chemicals) were used as received. All of the solvents were distilled and purified before use.

Result and Discussion

Polymerization of ethylene using the prepared FI catalyst (Figure 1) was studied in the different [Al]/[Zr] molar ratio. As expected, the activity of the catalyst increased with the addition of the [Al]/[Zr] molar ratio and no optimum activity was observed in the range studied. The more hindered catalysts structure as a result of using bulkier large substitutions may effectively separate the cationic active species from the anionic cocatalyst species following to increase the unsaturation degree of the active species [4,5] easier coordination of ethylene to the active center, more possibility of insertion reaction to take place than the chain transfer reactions and ultimately causes the activity of the catalyst to increase. The influence of polymerization temperature on activity was investigated at the temperature between 25 and 65 °C, while the [Al]/[Zr] molar ratio were kept constant at [Al]/[Zr]=65000:1. Polymerization activity showed maximum value at the temperature of 45 °C with a sensible shortfall at higher temperature (Figure 2). The decrease in the polymerization activity could be due to the β-hydride elimination reactions that take place at high temperature. Increasing of the monomer pressure of 1 to 5 bars increased activity of the catalyst. The maximum activity of the catalyst was observed after 15 min of the polymerization for the reaction carried out at 45 °C. At the monomer pressure of 2 bars the prepared FI catalyst could produce polyethylene with the ($\overline{MV}$) value of 6.2×10^5. Bulky cumyl group in the ortho position of the phenoxy oxygen promotes chain propagation. Crystallinity and melting point of the obtained polymers were between 55-60 % and 125-135 °C respectively usng DCC method.

Conclusion

The study has demonstrated that the performance of the FI Zr-based catalysts is strongly influenced by the substitution of the catalyst also by the polymerization parameters. The prepared catalyst showed higher activity for polymerization of

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ethylene. The highest activity obtained at 45 °C. The activity was increased with increasing the MAO concentration. Steric bulk cumyl substitution in the ortho position of the phenoxy oxygen is strongly capable to enhance the activity of the catalyst.

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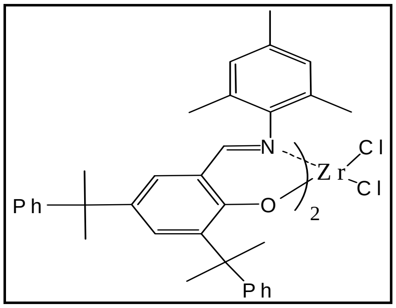

Figure 1. Structure of catalyst.

Figure 2. Effect of polymerization temperature on the average rate of polymerization.