

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 CONCLUSIONS

The discovery of homogeneous metallocene based Ziegler-Natta catalysts in the 1980s has opened up new possibilities to explore the mechanism of Ziegler-Natta catalysis. Metallocene catalysts for polyolefins are now in the early stages of commercialization. The homogeneous zirconocene system is sometimes referred to as a single-site catalyst. A true single-site catalyst should produce polymer having a sharp, and narrow molecular weight distribution ( $M_w/M_n$ ). Another relevant point is the fact that the catalytic activity of homogeneous metallocene in combination with methylaluminoxane (MAO) catalyst system in ethylene polymerization is much higher (normally 50 or 70 times) than that of the heterogeneous Ziegler-Natta catalysts system. Better understanding about the conditions that provides the optimum catalytic activity is required. The results of the present investigation, namely, ethylene polymerization by bis(cyclopentadienyl)zirconium dichloride [ $Cp_2ZrCl_2$ ] in combination with methylaluminoxane (MAO) catalyst system, are summarized as follows:

1. The suitable conditions that give the good results in the studied  $Cp_2ZrCl_2/MAO$  catalyst system in toluene are the conditions of Al/Zr mole ratio of 6000, ethylene partial pressure at 70 psi., and polymerization temperature of 348 K.

2. The studied of water releasing rate of hydrated salt by TGA showed that the suitability of hydrated salt for preparing methylaluminoxane can be arranged in the following order:  $Al_2(SO_4)_3 \cdot 18H_2O > Al_2(SO_4)_3 \cdot 16H_2O > CuSO_4 \cdot 5H_2O > Na_2S_2O_3 \cdot 5H_2O > AlCl_3 \cdot 6H_2O$ . This study found that  $Al_2(SO_4)_3 \cdot 18H_2O$  had water releasing rate suitable for supply the water for reaction with trimethylaluminum to methylaluminoxane.

3. From conclusion no. 2, the preferred hydrated salt for preparation methylaluminoxane are the aluminum sulfate, especially aluminum octahydrate [ $Al_2(SO_4)_3 \cdot 18H_2O$ ] because of the extreme reactivity of trimethylaluminum with water. The

mole ratio of water to aluminum for this investigation are 1 to 1, the reaction is conducted at temperature ranging from about 273 K to about 303 K and the time for preparing methylaluminoxane can range from about 50–80 hours, more preferably 60–75 hours. This condition are suitable for preparing methylaluminoxane by reaction of trimethylaluminum with hydrated salt.

4. Properties of polyethylene produced are affected by catalytic activity and type of hydrated salt for preparing methylaluminoxane. The results indicate that the melting temperature ( $T_m$ ) of polyethylene products decreased with an increase in the catalytic activity, and MAO (in case of used  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  to supply the water) is acting as better chain transfer agent when compared to MAO (in case of used  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  to supply the water).

## 6.2 RECOMMENDATIONS

The recommendations for further research may be given as follows:

1. Synthesize new bridged zirconocenes which make isotactic polypropylene when used in polymerizations of propylene with methylaluminoxane as cocatalyst and study steric effects of catalyst on properties of polypropylene.

2. Study supported metallocene catalyst on olefins polymerization such as the effect of compositional and specific surface of supported on catalytic activity and properties of polyolefin.

3. Use B-compound such as  $\text{B}(\text{C}_6\text{F}_5)_3$  to replace methylaluminoxane as cocatalyst. Study this cocatalyst in catalytic activity, properties of polymer products and kinetic reaction.

4. Develop equipment for studied kinetic modeling of polymerization reactions such as FT-IR,  $^{13}\text{C}$ -NMR, etc. and used this information data to increase the catalytic activity.