

# **Chapter VI**

## **GENERAL CONCLUSION**

## 6.1 Contributions to research

The development of new catalysts, able to polymerize monomers with high activity, is the key factor in the polymer industry. In this research, two trinuclear oxo-centered carboxylate complexes, of formula  $[\text{Cr}_3\text{O}(\text{F}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$  and  $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCO}_2)_6 \cdot 2\text{H}_2\text{O}]\text{Cl}_3\text{CCO}_2 \cdot 3\text{H}_2\text{O}$ , have been synthesized by refluxing commercial  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  with  $\text{F}_3\text{CCO}_2\text{H}$  and  $\text{Cl}_3\text{CCO}_2\text{H}$  respectively. Both complexes are stable at ambient temperature. In addition, they are simple to prepare, handle and can be stored for a long period of time. Furthermore, they easily dissolve in polar solvents, but are partially soluble or insoluble in non polar solvents. The complexes were characterized by elemental analysis, titration, Phenom SEM, FTIR, TGA, magnetic measurements and single-crystal X-ray structure determination. In addition, conventional chemical analysis data all agreed well with proposed stoichiometries.

Another topic of interest was the use of these complexes, in combination with  $\text{AlEt}_2\text{Cl}$ , as potential catalysts for ethylene polymerization. An appropriate route was devised to investigate these catalytic systems and measure their polymerization rate. The effects of various monomer pressures on both catalytic activity and the end polymer properties were investigated. It was observed in all cases that the polymerization rate was of the decaying type. In addition, the initial polymerization rate was first order and dependent of the monomer pressure. The rate of the polymerization increases with increase in ethylene pressure.

The maximum activity for  $[\text{Cr}_3\text{O}(\text{F}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O} / \text{AlEt}_2\text{Cl}$  catalytic system was 13.9 kg-PE/g-Cr/hr/atm, obtained at Al / Cr molar ratio of 45 and initial monomer pressure of 1320 kPa. In comparison, the maximum activity, with  $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCO}_2)_6 \cdot 2\text{H}_2\text{O}]\text{Cl}_3\text{CCO}_2 \cdot 3\text{H}_2\text{O} / \text{AlEt}_2\text{Cl}$  catalytic system was 36.71 kg-PE/g-

Cr/hr/atm, obtained at Al / Cr molar ratio of 45 at 795 kPa. As can be seen, the chromium complex  $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCO}_2)_6 \cdot 2\text{H}_2\text{O}]\text{Cl}_3\text{CCO}_2 \cdot 3\text{H}_2\text{O}$  is more reactive than  $[\text{Cr}_3\text{O}(\text{F}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ . This may be due to the fact that the structure of  $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCO}_2)_6 \cdot 2\text{H}_2\text{O}]\text{Cl}_3\text{CCO}_2 \cdot 3\text{H}_2\text{O}$  (complex 1) has seven substitute acetate groups connected to the three chromium atoms while  $[\text{Cr}_3\text{O}(\text{F}_3\text{CCOO})_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$  (complex 2) has only six. Thus the molecular weight ( $M_w$ ) of complex 1 is higher than the  $M_w$  of complex 2. This means that, when the same amount of complex ( $\sim 0.08$  g) is used for the reaction, complex 2 has bigger amount of Cr. The activity is obtained in terms of kg-PE/g-Cr/hr/atm. Therefore, the polymerization with lower amount of chromium will give higher activity.

The polymer produced is white in color. Irregular, clumpy PE particles were obtained with complex 1 while flat and homogenous shapes were synthesized when complex 2 was used. They were all characterized by FTIR, TGA, DSC, hardness, density, DMA and NMR techniques. The PE samples, produced using both complexes, had high melting, density and crystallinity characteristics, which were all found to depend on the degree of crystallinity.

## 6.2 Research limitations

The experimental design used to investigate the effect of monomer pressure on the polymerization of ethylene using the two chromium carboxylate complexes was matched to the facilities available in the department. It was very important to have reliable measurements of the amount of PE product. It was necessary to determine the best polymerization conditions, with error estimate by varying the amount of liquid nitrogen used to cool the reactor and the time used to fill the reactor with ethylene gas.

The reaction was only successful when the monomer was in gas phase. In some cases (not reported in this thesis), bigger amounts (~ 20 g) were obtained at low pressure (500 kPa). This is due to the fact that ethylene had been condensed for a longer time, thus the vapor-liquid phase equilibrium influences the polymerization. The lack of a mass flow meter and/or vapor-liquid phase program forced not to consider those samples.

### **6.3 Suggestions for future work**

The followings are some suggestions which may extend the understanding of these chromium(III) catalytic systems.

#### **6.3.1 Gel permeability chromatography (GPC)**

GPC analysis study would help further investigate the microstructure of the polymer. In addition, it will be helpful in confirming if the polyethylenes produced using complex 2 are UHMWPE or HDPE.

#### **6.3.2 In situ kinetics studies**

In situ experiments can be carried out to study stepwise polymerization rates, This will probably help probe the active sites of the catalysts.

#### **6.3.3 Copolymerization**

Propylene or higher 1-alkenes can be carried out with polyethylene produced using both complexes. This could produced less crystalline and elastometric polymers with many industrial applications.