CHAPTER 6

CONCLUSION

6.1 Chromium(III) Oxo-Trinuclear Carboxylate Complexes

Chromium based oxo-trinuclear carboxylate complexes have been used as Ziegler-Natta catalyst in olefins homo-polymerization and ethylene-propylene copolymerization. Chloro-substituted and non-substituted chromium(III) acetate complexes were synthesized by refluxing commercial chromium(III) nitrate salt with appropriate carboxylic acid[1,2].

Green chromium(III) monochloroacetate, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ with maximum percentage yield of 93.8% was obtained when the molar ratio of chromium salt and chloroacetic acid was 1:10. The solids are soluble in water, methanol, ethanol, isopropyl alcohol but are insoluble in chloroform and toluene. Complex with formula $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ was obtained by reacting chromium nitrate with dichloroacetic acid. The highest product yield was obtained at molar ratio 1:16 and refluxing period of fifteen hours. Fine green chromium(III) trichloroacetate solids, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$ formed during the reaction between chromium nitrate with trichloroacetate acid. When the reagents were allowed to reflux for ten hours at molar ratio of 1:6, optimum conversion, 90.8% was reached. Synthesis of chromium(III) acetate complex, $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$ was carried out by refluxing chromium(III) nitrate nonahydrate with glacier acetic acid. The highest yield, 92.4% complex was produced as the refluxing time between the two reagents was thirteen hours at molar ratio of 1:13. Reaction conditions for the optimum yield of each complex are summarized in Table 6.1.

Table 6.1: Refluxing time and reagents ratios for optimum yield

Complex	Ratio of chromium(III) nitrate to carboxylic acid	Refluxing time/hr	Yield/ g	Percentage yield / %
$[Cr_3O(CH_3CCOO)_6.3H_2O]NO_3.7H_2O$	1:13	13	5.77	92.4
$[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$	1:10	8	7.05	93.8
$[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$	1:16	15	8.30	95.0
$[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$	1:6	10	9.82	90.8

The synthesized chromium(III) complexes were characterized using Fourier Transform Infrared (FT-IR) spectroscopy and Thermal Gravimetric Analysis (TGA). Number of hydrated water molecules attached to each complexes can be determined from TGA thermograms thus the complex formulas can be deduced. The formulas were
Cr(III) acetate, $[Cr_3O(CH_3CCOO)_6.3H_2O]NO_3.7H_2O$;
Cr(III) monochloroacetate, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$;
Cr(III) dichloroacetate, $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ and
Cr(III) trichloroacetate, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$.

IR spectra[3-12] for chromium(III) catalysts produced by glacial acetic acid and different chloro-substituted carboxylic acid showed characteristic peaks of water molecules, carboxyl group, nitrate anion and C-Cl stretching mode.

Chromium content in the synthesized complexes were determined via titrimetric method where the complexes were titrated against sodium thiosulphate solution. The %Cr for $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ was found to be 17.3% while the %Cr for $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ was 14.6%. The percentage of chromium obtained agreed well with the calculated values. Similar observation was shown by $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$ and $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$ with chromium content 12.0% and 20.4% respectively.

6.2 Ethylene Polymerization

Polymerization of ethylene was carried out in a round-bottom flask connected to the gas line with constant volume setup of 2997 ml. The amount of polymer produced was calculated from the monomer pressure drop using ideal gas law. The kinetic data of ethylene polymerization was of the decay-type[13]. As the polymerization progresses, the catalytic activity decreased rapidly due to a decrease in number of active centers structural changes of the catalyst. Besides, increasing solution viscosity would also lead to a drop in polymerization rate.

6.2.1 Ethylene Polymerization at Various Al/Cr Molar Ratios

The polymerization activity is largely dependent on the molar ratio of cocatalyst to catalyst[14]. Maximum catalytic activity of 1768 gPE/gCr/hr/atm was attained at Al/Cr molar ratio 30.8 using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ catalyst system. Both increasing and lowering in Al/Cr ratio would lead to a decrease in acitivity[15-16].

Characteristic bands of polyethylene were shown in all FT-IR and ATR spectra. All PE samples were highly crystalline as the calculated FT-IR absorbance ratio for every samples were around 1.00. DSC thermograms for PE samples displayed well-defined endotherms and exotherms with melting temperatures and crystallization temperatures around 129-136°C and 118°C respectively.

6.2.2 Ethylene Polymerization at Various Temperatures

Polymerization reactions were carried out with temperature ranges from 18 to 40°C. The catalytic activity increases when the polymerization temperature increases from 18 to 29°C. The steady state of polymerization increased with increasing temperature. Further increase in the temperature caused the catalytic activity to drop. Maximum catalytic activity was obtained at temperature 29°C where 0.315g polymer was produced.

6.2.3 Ethylene Polymerization Using Different Chromium(III) Carboxylate Complexes

All four chromium complexes showed decay-type kinetic curves. Chromium(III) trichloroacetate complex, $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$ showed the highest activity with the maximum initial activity of 3116gPE/gCr/hr/atm and polymer yield 0.544g. The electron withdrawing power of chlorine atoms in the complexes affects the catalytic activity. $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$ complex having the highest electron withdrawing effect thus it was reduced most quickly by the cocatalyst.

6.3 Propylene Polymerization

Polymerization of propylene using $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$/ $AlEt_2Cl$ catalyst system was incapable to produced solid polypropylene product. Only yellowish oily product with bad smell was formed after the reaction. FT-IR spectra of product obtained from polymerization at Al/Cr molar ratio 59.7 and temperature 3°C showed some characteristic band absorptions of isotactic polypropylene. A broad endotherm with melting point 143°C was shown in the DSC thermogram of the product. This suggest the product formed was not 100% polypropylene.

6.4 Ethylene-Propylene Copolymerization

Copolymerization of ethylene and propylene was carried out using the same catalyst system and same constant volume setup as ethylene polymerization. Copolymer yield decreases with increasing propylene content used. Aging time between catalyst and cocatalyst plays an important role in the copolymerization reaction. Optimum activity was achieved if the mixture of catalyst and cocatalyst was allowed to 'age' for 30 minutes to 2 hours. Maximum yield of 0.09g E-P copolymer was obtained when catalyst aging time was 1 hour and the Al/Cr molar ratio used was 30.8. Decrease in activity was observed if the Al/Cr ratio used was lower than 30.8. Over-reduction of Cr^{3+} and competition between monomer and the cocatalyst for the same active sites of the catalyst[17] occured if the Al/Cr molar ratio exceeded 30.8 causing the catalytic activity to decrease.

IR spectra for ethylene-propylene copolymers showed characteristic bands of polyethylene and isotactic polypropylene. Band ratios of A_{720}/A_{1376} and A_{1376}/A_{1463} were used to analyze E-P copolymers. As propylene content in the copolymer sample increases, A_{720}/A_{1376} value decreases while A_{1376}/A_{1463} ratio increases. DSC results showed that the melting temperatures of E-P copolymers were lower than polyethylene homopolymer. More than one melting peak was observed in the thermograms of E-P copolymers with higher propylene content. This may be due to the presence of more than one crystallite which attributable to ethylene and propylene sequence.[18] Crystallinity of the sample decreases as propylene content increases. As the aging time between catalyst and cocatalyst increases, broader and clearer separation between two melting peaks was observed.

6.5 Suggestions for Future Work

Further study for the new development in Ziegler-Natta catalyst and polymerization should be carried out to increase the understanding of the present system. Suggestions for future work are listed below:

(a) Synthesis of mixed-metal catalyst could be investigated. Reflux process could be carried out between carboxylic acid and the mixture of chromium salt with other transition metal salt such as nikel and iron to produce a new catalyst system for olefin polymerization.

(b) Improvement of catalytic activities in the polymerization of propylene could be done by supporting the chromium(III) catalyst onto magnesium chloride.[19] Catalyst support could also be made on silica or alumina.[20-21]

(c) Investigation could be made to decide suitable conditions for the synthesis of oligomers. Influence of temperature, type of aluminium-alkyl compounds and pressure on the oligomers properties such as molecular weight distribution and melting temperatures could be studied.

References:

1. Ooi, C. P. ‘The Use of Trinuclear Chromium(III) Complexes as Ziegler-Natta Catalysts for the Polymerization of Ethylene’, University of Malaya, Kuala Lumpur, 1996

2. Vogel, A. I. ‘A Textbook Of Quantitative Inorganic Analysis’, 3th edn. Longman, London, 1971

3. Nakamoto, K. ‘Infrared and Raman Spectra of Inorganic and Coordination Compounds’, Wiley-Intersience Publication, 2nd Edition, 1986

4. Fujita, J. Nagakawa, K and Kobayashi, M., *J. Chem Soc*. 1956, **78**, 3963-3965

5. Gamo, I. *Bull. Chem. Soc. Jap*. 1960, **34(6)**, 764-766

6. Nagakawa, I. and Shimanouchi, T. *Spectrochim. Acta* 1963, **20**. 429-239

7. Gatehouse, B. M., Livingstone, S. E. and Nyholm, R. S. *J. Chem. Soc*. 1957, 4222-4225

8. Newman, R. and Halford, R. S. *The J. Chem. Phys*. 1950, **18(9)**. 1276-1294

9. Herzberg, ‘Infrared and Raman Spectra of Polyatomic Molecules’, Van Nostrand Pub., 1945

10. Randall, C. F., Fowler and Dangl, ‘Infrared Determination of Organic Structures’, Van Nostrand Pub., 1949

11. Johnson, M. K., Powell, D. B. and Cannon, R. D. *Spectrochim. Acta* 1981, **37A(11)**. 995-1000

12. Nakamoto, K., Carthy, P. G., Ruby, A. and Martell, E. *J. Am. Chem. Soc*. 1961, **83**, 1066

13. Keii, T. ‘Kinetics of Ziegler-Natta Polymerization’, Kodansha Ltd., Tokyo, 1972

14. Natta, G. and Pasquon, I., *Adv. Catal*. 1959, **11**, 1-65

15 McKenzie, I. D., Tait, P. J. and Burfield, D. R. *Polymer* 1972, **13**, 307

16. Gan, S. N., Chen, S. I., Ohnishi, R. and Soga, K. *Makromol. Chem. Rapid Commun*. 1984, **5**, 535

17. Bohm, L. L. *Polymer* 1978, **19**, 553

18. Gan, S. N. and Burfield, D. R. *Macromolecules*, 1985, **18**, 2684-2688

19. Soga, K., Chen, S. I., Doi, Y. and Shiono, T. *Macromolecules*, 1986, **19(12)**, 2983-2985

20. Tait, P. J. T. ‘Developments in Polymerization’, -2, Harward, R. N. (ed), Applied Science Publishers Ltd., England

21 Chien, J. W. C., Wu, J. C. and Kuo, C. J. *J. Polym. Chem. Ed*. 1982, **20**, 2019