

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In ethylene copolymerization by half-titanocenes containing imidazolin-2-iminato ligand, $\text{Cp}'\text{TiCl}_2[1,3\text{-R}_2(\text{CHN})_2\text{C}=\text{N}]$ [$\text{Cp}' = \text{Cp}$ (**1**), $t\text{-BuC}_5\text{H}_4$ (**2**); $\text{R} = t\text{-Bu}$ (**a**), $2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ (**b**)], (**1a**) exhibited remarkable catalytic activity for ethylene/1-hexene copolymerization in the presence of MAO cocatalyst, affording poly(ethylene-co-1-hexene)s with ultrahigh molecular weights as well as with uniform molecular weight distributions ($M_n = 1.07\text{-}1.31 \times 10^6$, $M_w/M_n = 1.43\text{-}1.82$). Although the activity was higher than that observed for the imidazolidin-2-iminato analogue, $\text{CpTiCl}_2[1,3\text{-}t\text{Bu}_2(\text{CH}_2\text{N})_2\text{C}=\text{N}]$ (**1c**), the 1-hexene contents in the copolymers obtained with **1a** were lower than those obtained with **1c** as well as with the Cp-ketimide analogue under the same conditions. The r_E values in the ethylene/1-hexene copolymerization by **1a, b, 2a** were 9.56-9.62 (**1a**), 11.8 (**1b**), 17.4 (**2a**), respectively, and these values were much larger than those by **1c** (4.95), **Cp-Ket** (4.5), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu}_2)]\text{TiCl}_2$ (3.42), and $\text{Cp}^*\text{TiCl}_2(\text{O-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (2.70), but were similar to those by the ordinary *ansa* zirconocenes (8.2-18.9).

The complex **1a** also exhibited remarkable catalytic activity with better NBE incorporation, affording high molecular weight copolymers with uniform molecular weight distributions, whereas the *tert*- BuC_5H_4 analogue (**2a**) showed low activity and the resultant polymer prepared by the Cp-2,6-diisopropylphenyl analogue (**1b**) possessed broad molecular weight distribution. The microstructure analysis of the poly(ethylene-co-NBE)s prepared by **1a** suggests the formation of random copolymers including two and three NBE repeating units.

In the study of terpolymerization of ethylene, 1-hexene and styrene by using aryloxo-modified half-titanocenes, $\text{Cp}'\text{TiCl}_2(\text{O-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}' = \text{Cp}^*$ (**1**), $t\text{-BuC}_5\text{H}_4$ (**2**)], in the presence of MAO, the resultant polymer possessed relatively high molecular weights with uniform molecular weight distributions. The Cp^* analogue (**1**) exhibited higher catalytic activities than $t\text{-BuC}_5\text{H}_4$ analogue (**2**). However, **2** provided higher α -olefin and styrene contents in the resultant

terpolymers. The use of borate cocatalyst in place of MAO was also effective in the terpolymerization. Although the lower catalytic activities were observed, no atactic polystyrene was produced in this system. The microstructure analysis and DSC thermograms strongly suggested that the resultant polymers are terpolymers (amorphous materials) with uniform composition. The terpolymerization with *p*-methylstyrene (*p*-MS) in place of styrene was also attained in the presence of borate cocatalyst, and *p*-MS was incorporated in an efficient manner affording the high molecular weight polymers with uniform molecular weight distributions.

Efficient, precise introduction of a reactive functionality into poly(ethylene-*co*-styrene)s and poly(ethylene-*co*-1-hexene)s was achieved by using 3,3'-divinylbiphenyl (DVBP) as a termonomer in the ethylene copolymerizations with styrene or 1-hexene by aryloxo-modified half-titanocenes – MAO systems. The method adopted here should be promising, because no probable side reactions (ex. cross-linking and/or cyclization observed in the copolymerization with vinylcyclohexene, etc.) were accompanied under these conditions, and the termonomer (DVBP) could be incorporated in an efficient manner.

5.2 Recommendations

The recommendations for future work are as follows:

1. To explore the efficient copolymerization of ethylene with norbornene macromonomer, which is considered as bulky monomer for olefin polymerization.
2. To investigate the appropriate conditions for post polymerization of poly(ethylene-*co*-styrene-*co*-3,3'-divinylbiphenyl)