POLYMERIZATION OF HIGHER ALPHA-OLEFINS WITH METALLOCENE CATALYSTS

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Introduction
The use of metallocene catalyst systems has revolutionized the polyolefin industry. Not only is it possible to synthesize polymers with desired properties, now the activities and molecular weights achieved compete well with those of the heterogeneous Ziegler-Natta catalysts presently used in industry. Since the discovery of these catalysts, a variety of polymers that could not be synthesized by heterogeneous catalyst systems are now available. The synthesis of polypropylene with metallocene catalysts has been studied extensively, and the structure-property-relationship is now well understood. Variations in the ligand structure of the catalyst result in prominent changes in polymer characteristics. However, all the knowledge gained to date is applicable more to the polymerization of propene than higher α-olefins.

Although polymers from higher α-olefins such as polybutene and poly(4-methyl-1-pentene) have found use in everyday life, not much effort has been made in studying these polymers, especially with metallocene catalyst systems. One of the reasons behind this might be the assumption that the knowledge gained from studying polypropylene synthesis can be applied to higher α-olefins. This paper reports on the synthesis of polypentene (PPen), poly(4-methyl-1-pentene) (P4MP) and poly(3-methyl-1-pentene) (P3MP) with various metallocene catalyst systems (Figure 1) under different conditions. The aim of this study was to understand the structure-property-relationship of metallocene catalysts relative to higher α-olefins. In addition, a relation between polymer characteristics and catalyst is highlighted.

Experimental
Materials. All operations were performed under argon using conventional Schlenk techniques. I and II were prepared according to reported methods. III and IV were donated by Saudi Basic Industries Corporation (Sabic). Methylaluminoxane (MAO) (10% in toluene) was purchased from WITCO and was used without purification. 4-Methyl-1-pentene (4M1P) was purchased from Fischer Scientific, 1-pentene from Aldrich and 3-methyl-1-pentene (3M1P) from GFS chemicals.

Polymerization procedure. The molar [Al]:[Zr] ratio for all runs was 5. All polymers were synthesized in a double wall glass reactor equipped with a cooling system. A thermostat bath was used to regulate the polymerization temperature, with a thermocouple inserted into the reactor. 300 mmol of monomer in 40 ml toluene was used. All the polymerization runs were carried out for 30 minutes. The reactions were quenched using 10% hydrochloric acid. The precipitated polymer was filtered then washed with ethanol and dried overnight at 80°C.

Results and Discussion
The type of monomer used also plays an integral role in determining the catalyst activity. The activity of a given catalyst depends on the monomer used as well as the polymerization conditions. Figure 2 shows the results obtained when I, II, III and IV were used at different temperatures to polymerize 1-pentene. It can be seen that the activity increases with increasing temperature. In addition, the activity varies depending on the type of catalyst used. The fact that III has the highest activity is rather surprising since the catalyst faired the poorest when used to polymerize propene. Even more intriguing is the very low activity when IV is used to polymerize higher α-olefins, especially at low polymerization temperatures. The lower activity was mainly due to the steric interaction between the monomer and growing chain with the bulky ligand framework. Although the differences in steric bulk between 1-propene and 1-pentene seem small, the discrepancy appears to have a huge effect during polymerization. The differences in steric hindrance of the growing chains are responsible for the apparent disparity.

Figure 1. C2-symmetric catalysts used in this study.

Figure 2. Activities of I, II, III and IV for 1-pentene polymerization.

Figure 3. Activities of I during the polymerization of 1-pentene, 4M1P and 3M1P.

Figure 4. Activities of I during the polymerization of 1-pentene, 4M1P and 3M1P at 10 and 70°C.
Not only is the presence of a substituent on the monomer important, but the position of that substituent should be taken into consideration as well. Figure 4 compares the activities of I when used to polymerize 1-pentene, 4M1P and 3M1P. It can be seen that the non-substituted 1-pentene results in higher activities, with 3M1P resulting in the lowest activities.

The type of catalyst used influences the molecular weight of the resultant polymer. As with activity, the molecular weight is also dependent on the polymerization temperature. Figure 5 and Figure 6 show the molecular weights of polypentene and P4MP synthesized with I, II, III and IV. The molecular weight decreases with increasing polymerization temperature, which is expected. For both monomers, II gave the highest molecular weight, which is more conspicuous at lower polymerization temperatures. The methyl substituent at the 2-position is responsible for the higher molecular weight, as was observed with polypropene. I, III and IV resulted in P4MP of almost equal molecular weights, which is rather strange considering the differences in the catalysts. IV resulted in polypentene with molecular weights higher than for the polymers synthesized with I and III. Evidently, the type of monomer used is paramount in determining the molecular weight of the polymer.

Compared with polypentene and P4MP, P3MP synthesized with I has the lowest molecular weight as can be seen from Figure 7. The difference in molecular weight of P4MP and P3MP highlights the impact of the position of the branch in the monomer. The proximity of the substituent to the reactive double bond regulates the polymer molecular weight to some extend. In addition, the molecular weight of P3MP seems to be more sensitive to polymerization temperature when compared to polypentene and P4MP.

The melting temperature of a polymer is a function of both the molecular weight and the tacticity. The activities of catalysts, polymer molecular weight as well as the melting behavior of polymers depend on the type of ligand framework in the catalysts, type of monomer as well as polymerization conditions.

**Conclusions**

The activities of catalysts, polymer molecular weight as well as the melting behavior of polymers depend on the type of ligand framework in the catalysts, type of monomer as well as polymerization conditions.

**Acknowledgements.** The authors are grateful to Dr. J. Severn and Sabic for some of the catalysts used in this study, as well as the Dutch Polymer Institute (DPI) for financial support.

**Reference**