Summary

The performance of supported metallocene/MAO-catalysts in the syndiospecific polymerization of propene, in the homo- and copolymerization of ethene and propene, and in the polymerization of 1,3-butadiene is the object of this thesis. Emphasis of this investigation is to determinate on which scale the polymer properties are influenced by the immobilization of the catalyst on an inorganic solid.

In the first part of this thesis C_S-symmetric catalysts of the type $[(RPh)_2C(Cp)(2,7\text{-}^{tert}Bu_2Flu)]ZrCl_2$ are investigated in the syndiospecific polymerization of propene under four sets of conditions: in toluene solution, bulk, toluene slurry, and gas phase. Generally, highly syndiotactic polypropene (*rrrr* > 99 %) with high molar masses ($M_\eta > 10^6$ g·mol^{-1}) and high melting temperatures (T_m up to 153 °C) are produced. The highest activities are obtained in the solution process (11 000 $kg_{PP}/(mol_{Zr}\cdot h\cdot mol_{propene}/l)$), since physical and kinetic limitations such as diffusion and sorption occur, when the heterogeneous systems are applied. The determination of the activation energy in dependence on the polymerization process illustrate this. Comparisons between relevant polymer properties show that the polymerization performance is only slightly influenced by the support. The dependence of the molar mass of the produced polymers on the polymerization process is depicted in figure 2.1. In the homogeneous solution and in the heterogeneous slurry process polymers with similar molar masses are obtained. The microstructure and melting temperatures are affected in the same way by the monomer concentration as the molar mass of the polymers.

Furthermore, the morphology of the obtained polypropenes is investigated. Polymerization in liquid propene results in a high bulk density, whereas applying the supported metallocene in a gas phase process a good replication of the original catalyst morphology is observed.

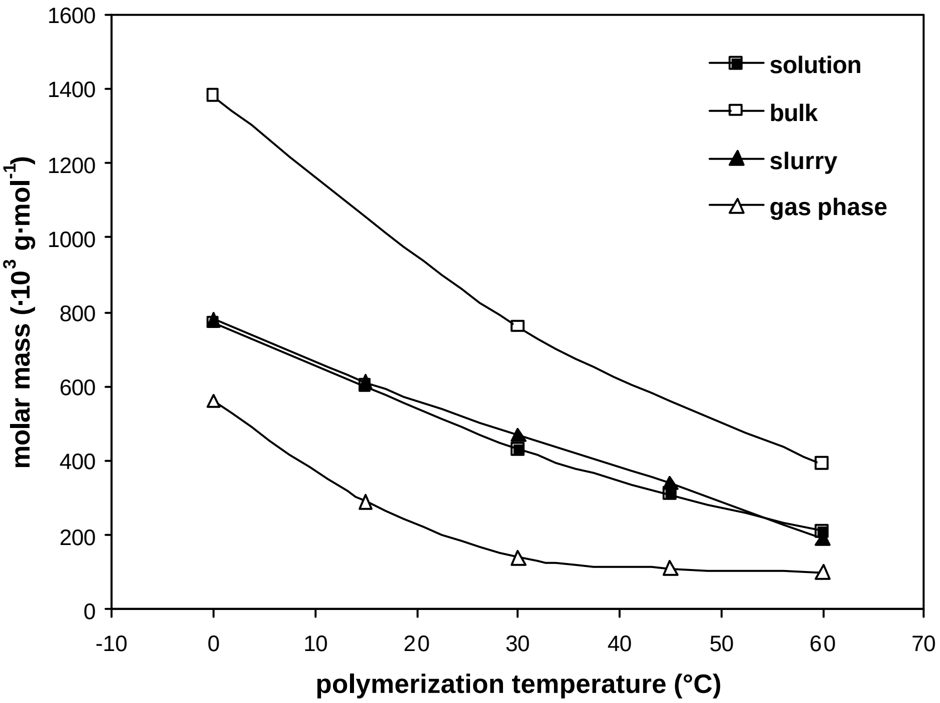

Fig. 2.1: *Polymerization of propene with [(4-MePh)$_2$C(Cp)(2,7-^{tert}Bu$_2$Flu)]ZrCl$_2$. Dependence of molar masses (M_h) on polymerization temperature and process.*

The second part of this thesis encloses the copolymerization of ethene and propene under different processes. Again the highest activities are obtained with the homogeneous catalyst (94 700 $kg_{Pol}/(mol_{Zr}\cdot h\cdot mol_{Mon}/l)$ at 8 mol% propene in the polymer), whereas the activity decreases by a factor of 2 when the metallocene is supported (slurry polymerization). In gas phase polymerizations the observed activities are about 20 times lower than in solution. In all polymerization processes a comonomer effect is observed. The molar masses of the produced polymers are mainly influenced by the monomer concentration and not by the support. Technical relevant EPM elastomers with molar masses higher than 100 000 $g\cdot mol^{-1}$ can be produced in all processes.

Considering the local monomer concentration at the active sites, the corrected incorporation behavior of the supported catalyst in gas phase polymerizations is compared to those of the solution and slurry processes (fig. 2.2). In gas phase polymerizations the incorporation of propene is enhanced. Any influence of the support can be excluded by comparing the solution and slurry process.

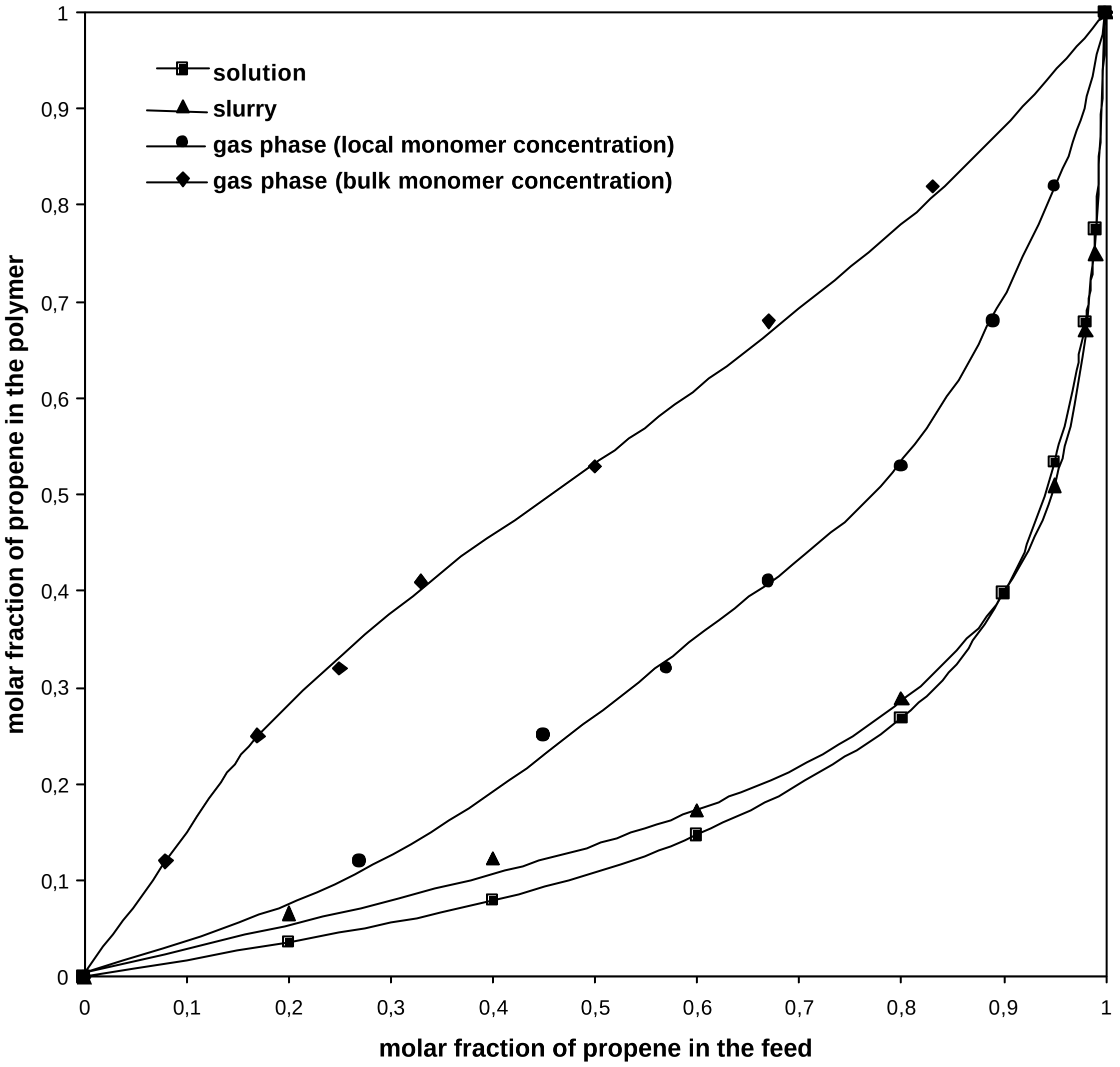

Fig. 2.2: *Dependence of the incorporation rate of propene on the polymerization process in the copolymerisation of ethene and propene at 30 °C.*

The intramolecular distribution of the comonomers can be modelled by a second order Markovian statistic in case of solution and slurry polymerizations. The reactivity ratios are in the same range under both conditions. In contrast to this, the triad distribution of the polymers produced in gas phase polymerizations can not be described by a first order Markovian model nor a second order Markovian model. Due to mass transport limitations the comonomers are distributed less alternatingly but rather statistically in gas phase process.

Moreover, gas phase polymerizations of ethene with the pentalenyl bridged *ansa*-metallocene [$Me_3Pen(Flu)]ZrCl_2$ are investigated in this thesis. Because of the bridge the catalyst system is remarkable thermostable and a deactivation of the metallocene on the support can be suppressed even at a polymerization temperature of 90 °C. Compared to the non-supported catalyst, the application of the heterogeneized system in a gas phase process leads to a decrease of the activities by factor 80. Furthermore, the molar masses of the polyethenes produced in gas phase only slightly decrease with increasing polymerization temperature. Due to a degree of branching of 20 – 30 per 1 000 C the obtained melting temperatures are 10 °C lower than those of linear polyethene.

In order to obtain more detailed information about supported metallocene/MAO catalysts, two catalysts are supported onto flat silicon wafers by spincoating impregnation. These model catalysts are characterized by SEM and EDX showing a film of the metallocene catalyst dispersed inside the methylaluminoxane matrix as well as regions of a localized increased concentration of the catalyst. Applying these model catalysts in a gas phase polymerization reactor results in rather homogeneous films of polyethene and polypropene, respectively. In addition crater-like and spherical polymer structures can be observed probably formed by inhomogeneous catalyst distribution. In comparison with other olefin polymerization catalysts metallocenes are supposed to be neither truly anchored on the surface nor weakly physisorbed on the support.

The last part of the thesis examines the polymerization of 1,3-butadiene with halfsandwich-titanium compounds such as $Cp'TiCl_3$. The effect of immobilization of the catalyst in slurry polymerizations is evaluated. A triisobutylaluminum concentration of 10 $mmol \cdot l^{-1}$ has turned out to be optimal. The microstructure and glass transition temperatures of the obtained polymers are not affected by the polymerization process, whereas the molar masses are 1.5 – 4 times lower when the supported catalyst is applied. The influence of the process on the activity can hardly be estimated since the activation conditions and therefore the kinetics are different in solution and slurry processes. Basically the activities are in the same order of magnitude. Polymerizing in hexane as solvent usually leads to lower activities.

Furthermore, the control of the molar mass in the homogeneous polymerization with 1,2,4-$Me_3CpTiCl_3$ is investigated. Using 1,5-cyclooctadiene as chain transfer agent results in a decrease of the obtained molar masses from 4 000 to 1 900 $kg \cdot mol^{-1}$ (125 $mmol \cdot l^{-1}$ cyclooctadiene). However, also the polymerization activity is decreased. Compared to 1,5-cyclooctadiene, hydrogen is an excellent suitable chain transfer agent in the polymerization of 1,3-butadiene as shown in figure 2.3. Even a small partial pressure of 0.05 bar hydrogen is sufficient for decreasing the molar mass of the polymers to 10 % of the initial value.

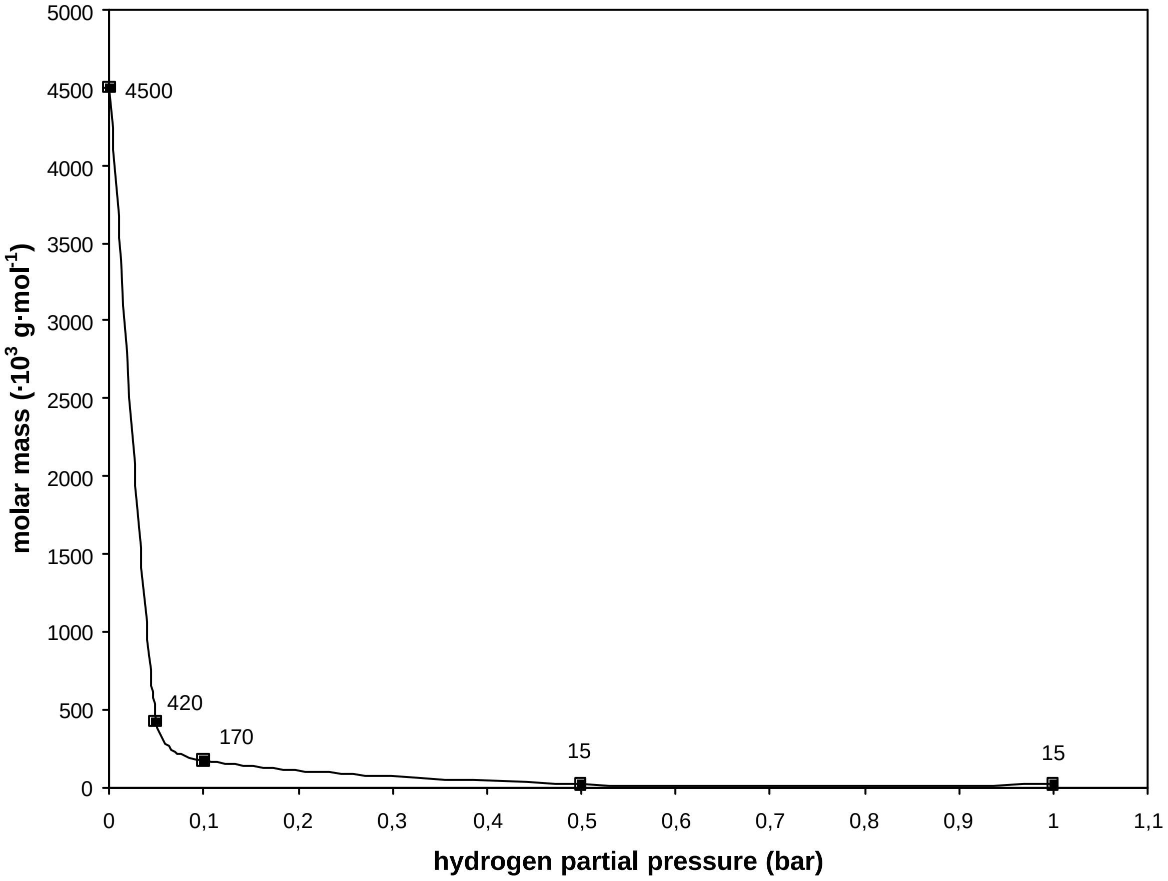

Fig. 2.3: *Polymerization of 1,3-butadiene with 1,2,4-$Me_3CpTiCl_3$ at 30 °C. Dependence of molar masses (M_h) on hydrogen partial pressure.*

Probably due to formation of a greater number of active sites, an increased activity is obtained at small hydrogen amounts. A long lasting "*quasi-living*" initial period is observed in polymerizations without hydrogen. The concentration of active sites is 2 % corresponding to the starting catalyst amount. In addition the turnover frequency of monomer insertion and chain transfer are estimated at 83 s^{-1} and $5 \cdot 10^{-4}$ s^{-1}, respectively.

By an external preactivation of 1,2,4-Me_3CpTiF_3 with MAO a greater number of active sites is generated, whereby the activity increases up to 12 000 $kg_{BR}/(mol_{Ti} \cdot h)$. Further rises of polymerization activities are possible by extension of the preactivation time.