

## Abstract

The main focus of the present work is on the synthesis of alternating ethene/propene copolymers with metallocene/MAO catalysts. One of the major problems of systems described in literature is the low molar mass of the produced polymers and the limited temperature stability of the catalysts, therefore one goal, beside reaching high alternating polymers, was to improve this disadvantages. In this work, the catalysts shown in figure 1 were synthesized, mainly for the first time.

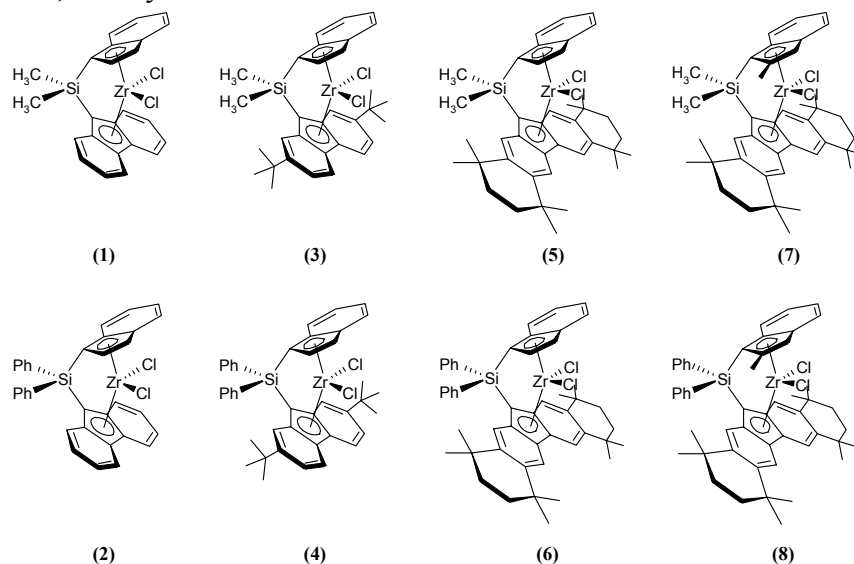


Fig. 1: Metallocenes used in this work.

The copolymerization properties of these catalysts at 30 °C were investigated as well as the effect of polymerization temperature and monomer concentration on the properties of the alternating copolymers.

The copolymerization behavior of the used catalysts is very similar, to gain an alternating 50:50 copolymer, 96 - 97 % propene in feed are necessary.

The activities of the catalysts decrease with growing sterical demand of the substituents at the ligand framework. At 30 °C, species (5), (6), (7) and (8) gain the lowest activities but at higher polymerization temperatures, these catalysts show a significant higher stability, resulting in increased activities. At 60 °C these species are much more active than (1), for this catalyst the lowest activity is found. In general, diphenylsilyl-bridges have a positive effect on the activity, with such catalysts higher values are reached than for the analog dimethylsilyl-bridged species.

The polymers with the highest amounts of alternating triads were observed when metallocene (3) is used. At 30 °C the value for this system is at about 78 %, 3 % above the reference catalyst (1). With increasing polymerization temperature the selectivity of the catalysts, and with it the alternating part of the copolymers, is going down.

Species (7) and (8) reach very high values for the alternating part even at 60 °C, with nearly 70 %, these metallocenes work with a much higher selectivity than the reference catalyst (1), which produces copolymers with an alternating part of only 63 %.

The substituents at the bridge have only a small influence on the percentage of the alternating triads, but with the diphenylsilyl-bridged complexes slightly lower values were observed. At lower temperatures the selectivity of catalysts (1), (2), (3) and (4) is increased as expected, higher values for the percentage of the alternating triads are reached. The other metallocenes have a different, unexpected behavior, because the alternating parts are, in part drastically, reduced. This behavior is only explainable with the very low activities of these catalysts at

low temperatures and the resulting increased importance of the backskips in these cases, which ends up in a disruption of the formation of alternating copolymers. The influence of the backskips was investigated in detail for a polymerization temperature of 30 °C by variation of the monomer concentration. With lowering the monomer concentration, the values for the alternating part were decreased. These results show the consequences of the backskips: The backskip is a reaction in competition to the insertion reaction, which is dependent on the monomer concentration. As the backskips are not dependent on the monomer concentration, an increase leads to a higher ratio of insertion reaction to backskip, and the higher this ratio, the higher is the amount of alternating triads.

The molar masses were increased by use of the substituted metallocenes, compared to the reference catalyst (1), clearly. With catalyst (8) the molar masses were increased by an order of magnitude up to more than 150,000 g/mol for the alternating copolymers. Generally an U-shaped distribution is observed for the molar mass in dependency of the propene incorporation.

The glass transition temperatures of the alternating copolymers are clearly underneath the values for statistical copolymers and are dependent on the percentage of the alternating triads. With catalysts (3) -65 °C were reached at a polymerization temperature of 0 °C.

By using metallocenes (5), (6), (7) and (8), extraordinary microstructures of ethene/propene copolymers and propene homopolymers were observed. The copolymers have a tendency towards isotactic structures, the propene homopolymers are slightly syndiotactic. The other catalysts yield polymers with the common microstructures: atactic ethene/propene copolymers and slightly isotactic propene homopolymers. The unexpected stereoselectivity of the catalysts with the cyclic substitution on the fluorene rings is probably due to this substitution, which makes the insertion of propene on both catalysts sides stereoselective.

The second part of this work deals with the propene polymerization with classical Ziegler-Natta-catalysts systems. Donoratom stabilized aluminum alkyls were used as cocatalysts and compared to the reference cocatalyst triethylaluminum (TEA). The decisive factor for the potential use of the stabilized cocatalysts in industrial processes is the activity these systems reach in comparison to TEA. For a number of compounds, very high activities were observed for the polymerization of propene, but overall only 85 % of the highest value reached by TEA. But it has to be pointed out, that two species reach the highest activities at very low ratios of cocatalyst to catalyst, at which TEA is almost completely inactive.

There are no adverse properties of the polymers when the stabilized compounds are used. The microstructure is not influenced by the type of cocatalyst, the tacticity of the polymers is only dependent on the ratio of cocatalyst to catalyst. The molar masses are significantly higher when the stabilized species are used: With TEA a maximum of 250,000 g/mol is observed, whereas some of the stabilized species reach more than 700,000 g/mol.

In the last part of this work the possibilities of the synthesis of microcrystalline waxes by oligomerization of ethene with propene and 1-butene were examined. The requested product properties were well defined with a molar mass lower 1,500 g/mol, a melting range from 90 to 60 °C and a crystallinity of about 50 %. It was possible to reach this goal by cooligomerization of ethene with 20 % of a mixture of propene and 1-butene in the feed at a temperature of 75 °C in the presence of 1 bar hydrogen with three different catalysts:  $[\text{Me}_2\text{C}(\text{Cp})_2]\text{ZrCl}_2$ ,  $[\text{Me}_2\text{Si}(\text{Cp})_2]\text{ZrCl}_2$  and  $[\text{Ph}_2\text{C}(\text{Cp})(\text{Ind})]\text{ZrCl}_2$ . The comonomer content of the obtained products was about 8 %.