

Modifications of Ziegler-Natta catalysts for improved comonomer incorporation

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Ziegler-Natta catalysts are commonly used for the production of polyethylene and its various types like linear low-density polyethylene (LLDPE). This polymer is made by the copolymerization of ethylene with higher α -olefines, like 1-butene or 1-hexene. Using Ziegler-Natta catalysts usually leads to a random incorporation of the comonomers, with a higher comonomer content in the low-molecular weight fractions. This results in a faster degradation of the polymer. Therefore, a homogenous incorporation profile is preferred. In the presented work attempts were made to achieve a favourable copolymerization behaviour by optimizing the catalyst synthesis.

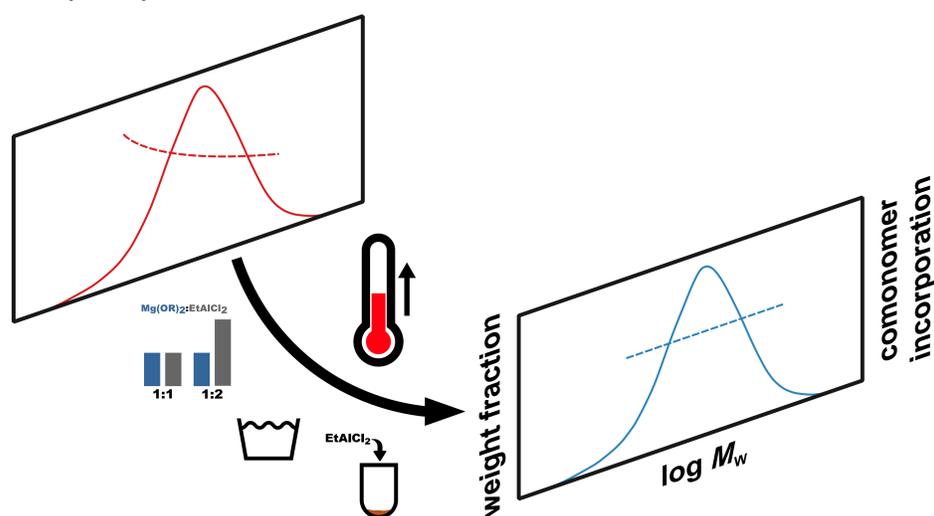


Figure 1: Several factors of the catalyst synthesis (temperature, ratio of educts, number of washing steps, additional EtAlCl_2) were varied with the intention to change the properties of the obtained polymer.

Experimental

The carrier material of the synthesized catalysts was prepared by adding 2-ethylhexanol to a solution of butyloctylmagnesium (BOMAG). Further reaction with ethylaluminumdichloride (EtAlCl_2) gave a MgCl_2 slurry. The addition of TiCl_4 yielded the catalyst. Varying several factors of the synthesis resulted in catalysts with different properties.

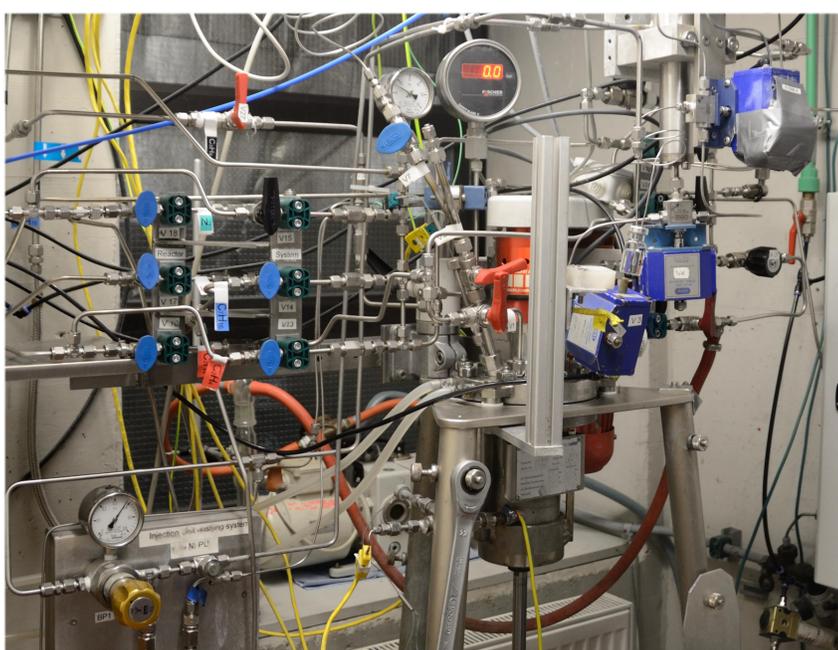


Figure 2: The polymerization experiments were carried out in a 0.5 L reactor system.

These catalysts were tested in slurry-phase polymerizations with 1-butene as the comonomer.

Results

The results show that the temperature during the addition of TiCl_4 has a particularly strong effect. With increasing temperature the polymerization activity rises. The exception is the catalyst prepared at 40 °C which shows the highest activity. Analyzing the obtained polymers with size exclusion chromatography gave information on the comonomer distribution. Interestingly, the catalyst prepared at 40 °C exhibits a homogenous incorporation profile.

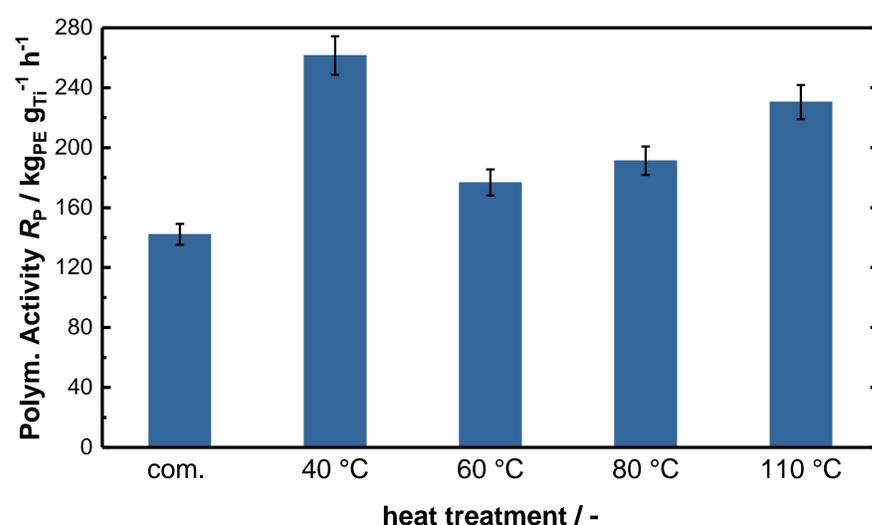


Figure 3: Polymerization activity for a commercial catalyst (com.) and the catalysts prepared at different temperatures.

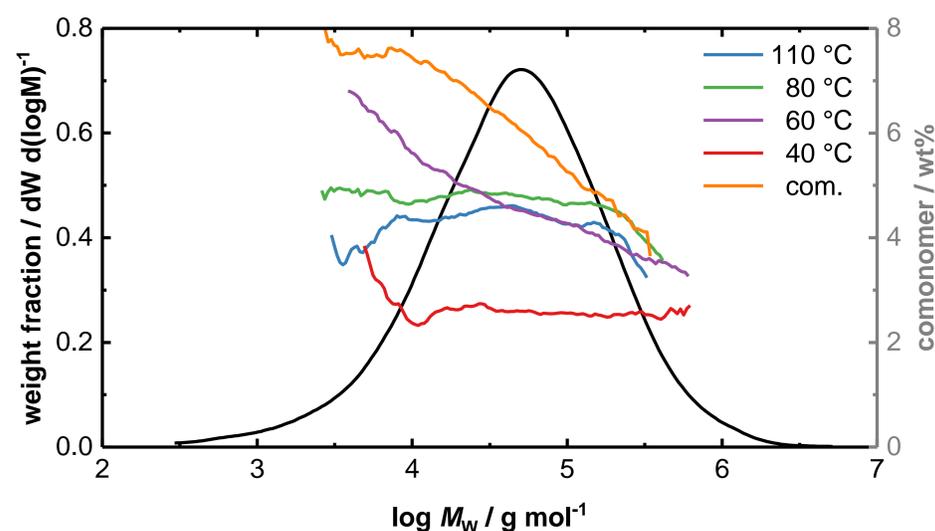


Figure 4: Distribution of 1-butene for the polymers obtained with different catalysts.

Conclusion

Several Ziegler-Natta catalysts were prepared in this work by varying different synthesis factors. The heat treatment had the biggest impact on polymerization activity and comonomer incorporation. By varying the temperature it was possible to obtain a catalyst exhibiting a homogenous incorporation of 1-butene. A property that is usually only known from metallocene catalysts.

Additional information

Aigner P., Averina E., Garoff T., Paulik C., *Macromol. React. Eng.* 2017, DOI: 10.1002/mren.201700009