POLYOLEFINS – DEAD OR STILL BOOMING?

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The success story of polyolefins (PO) basically started with the discovery of high-pressure ethylene polymerization at ICI in the UK in 1933. This accidental discovery [1] initiated the focused development and production of low-density polyethylene (LDPE). The commercial breakthrough started with the development of catalyst systems, which enabled the polymerization of olefins at mild process conditions but good control of the molecular architecture. For polyethylene (PE) this remarkable landmark was set by the discovery of Karl Ziegler, that a combination of transition metal halides (e.g. $TiCl_4$) with aluminum alkyls (e.g. triethylaluminum) affords linear high molar mass PE at moderate pressures and temperatures. The combination of transition metal compounds with an aluminum alkyl is now known as a Ziegler–Natta (ZN) catalyst, acknowledging the important contribution of Giulio Natta in preparing and characterizing polypropylene (PP) and other α-olefin based polymers. Ziegler and Natta were awarded the Nobel Prize in Chemistry in 1964 for their breakthrough developments.

From the 1960ies onwards consumption growth rates have been high, with the PO materials becoming widely used for fibers, films, pipes, bottles and injection moldings. New applications for the PO's were constantly being found making them the most used plastics family.

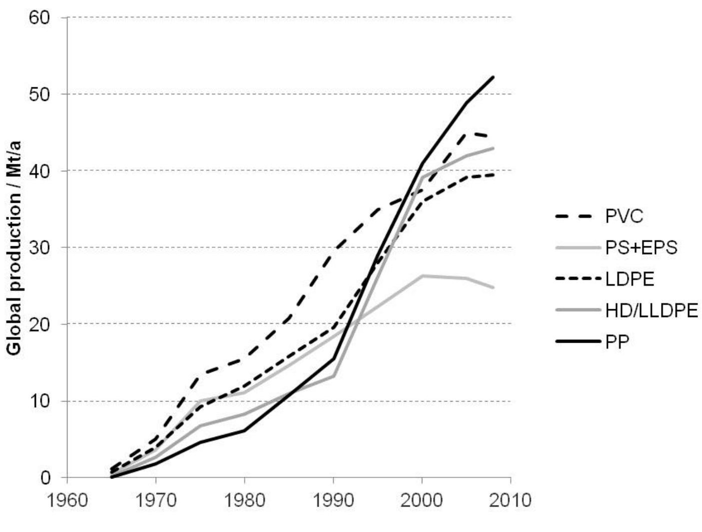

Figure 1: Production volume development of standard thermoplastics [2]

This success story is based on the ability to tailor the material properties of PO's in a wide range and by the excellent price performance relationship for this class of polymers. The raw materials, ethylene and propylene, are large volume industrial chemicals available at reasonable costs. The industrial processes are mature and working at low costs. The development routes rest on the availability of optimized catalyst/co-catalyst systems, the on going tuning of the polymerization technology and a sound knowledge of physical and chemical processes on all scales. Understanding structure-property relationships along the whole value chain is essential as well. In PE, especially bimodal materials with their ample possibilities to fine tune product properties will further expand the existing product windows. An important factor with respect to the usability of polypropylene (PP) was the development of impact modified products, long time referred to as "block copolymers". These materials combine a crystalline PP matrix with embedded rubbery particles. Especially for the development of this class of PP materials improved catalysts and multi-reactor polymerization units were necessary.

Next to the ZN catalysts also metallocenes can be used for the polymerization of olefins. Already Natta had discovered the usability of metallocenes for the homogenous polymerization of olefins. But only the discovery of Sinn and Kaminsky in 1975 that methylaluminoxane (MAO) substantially accelerates the polymerization reaction as co-catalyst triggered research and development in the field of metallocene catalysis of polyolefins [3]. However, the commercial implementation of metallocenes and other single-site catalysts has been significantly slower than expected due to the continuous improvement and cheaper price of traditional ZN systems. On the other hand single-site based catalysts allow for exact tuning of the polymer chain microstructure by catalyst ligand design as shown in Figure 2.

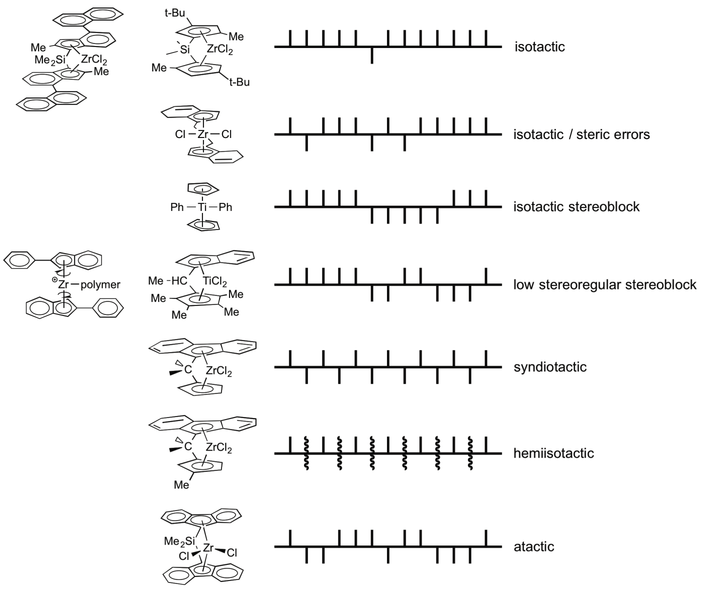

Figure 2: Correlations between metallocene structures and PP architecture [4]

However, after some decades of success, polymers have been going through a hard time recently. For the first time since the oil crisis of the early 1970ies, global production decreased in 2008 as a result of the economic crisis. At the same time, public perception of "plastics" deteriorated, with critical views on issues like the release of endocrine disruptors, littering and waste. Polyolefins have several advantages here over other polymers, through the absence of halogens, plasticizers and other critical chemicals, and because of their advantageous results of the respective life-cycle analysis (LCA). In contrast to a complete LCA, other measures like carbon footprint (essentially a specific CO_2 emission number per weight unit or application) or water footprint can only cover some aspects of the situation. The chemical structure and inherent properties of PO's also make them well suited to recycling operations [5]. There is no fear about complications with plasticizers or chlorine-rich species. Other factors to be considered in reprocessing as well as ageing are a loss of oxidation stability, discoloration, contamination and odor development. Recycling PO in the production stream is rather easy compared to the situation after its service life, as in recycling of post-consumer plastic.

While future achievements will depend upon the availability of new catalyst generations giving better control over molar mass distribution and comonomer incorporation (metallocene catalysts, new donors, innovative substrate systems), developments in process technology (super condensed mode, new reactor constructions) will support this advance. Together, this should allow PO's to enter new performance regions for example in the area of elastomers and self-reinforced materials.

Parallel to actual polymer development progress can be expected within the next years particularly through the application of special modification processes after polymerization. Promising areas of research are the ones of micro- or nanofillers already established in the polyamide area. Highest levels of stiffness are presently reached by the use of long-glass fibers, presently focusing on automotive applications and substituting metal elements there [6]. Self-reinforcement through organic fibers with high compatibility and/or special conversion processes has recently regained interest. Here, next to the aspects of sustainability and weight reduction, waste management and recycling are also gaining importance.

REFERENCES

[1] Roberts R.M., in: *Serendipity Accidental discoveries in Science*, Wiley Science Edition, New York (1989).
[2] Gahleitner M., Paulik C., Neissl W., Kunstst. Int., *100*, 18 (2010).
[3] Chum P.S., Swogger K.W., Prog. Polym. Sci., *33*, 797 (2008).
[4] Mühlhaupt R., Macromol. Chem. Phys., *204*, 289 (2003).
[5] Xanthos M., Science, *337*, 700 (2012).
[6] Senthil Kumar K., Ghosh A.K., Bhatnagar N., Polym. Compos., *28*, 259 (2007).