Selective blockade of chain-walking as a novel strategy for the synthesis of functionalized and chemically modifiable polyethylene

Polymeric materials have become a permanent part of everyday life thanks to the possibility of precise adjustment of their properties for tailored applications. Polyolefins are polymeric materials of significant industrial importance, among the polyolefins, polyethylene (PE) should be highlighted thanks to its biological inertness, good thermal stability and ease of processability. Polyethylene consists of only carbon and hydrogen atoms, which makes it hydrophobic, therefore, PE exhibits poor compatibility to polar materials and inorganic compounds as a consequence of the lack of organic groups, which limits its wider application. The main factor determining properties of the polymeric material is the presence of functional groups in its structure. Considering the above, the introduction of organic groups into polyethylene chains will significantly influence the properties and make the functionalized PE a much more versatile material with a wider application potential. Unfortunately, classic copolymerization of ethylene with polar comonomers is usually ineffective, due to the high affinity of polar functional groups to metallic catalysts, leading to their deactivation. The catalysts that showed to be occasionally tolerant of the presence of polar functional groups are α-diimine Ni and Pd complexes. Moreover, the above-mentioned catalysts exhibit a characteristic feature, namely the promotion of *chain-walking* process, which opens the possibilities of the design and synthesis of various types of polyethylenes ranging from linear to hyperbranched ones. Unfortunately, chain-walking process resulting from the sequence of elementary reactions in the mechanism, makes the above-mentioned catalysts not suitable for the polymerization of ethylene with a wide range of functional monomers.

Considering to above, the goal of this project is to develop the innovative and versatile methodologies enabling the incorporation of organic functional groups into polyethylene chains, that are otherwise inaccessible to be introduced by conventional synthetic approaches. The goal of the project can be achieved by employing the carefully designed monomers that will be able to selectively block the chain-walking process on the desired position. Consequently, the side reactions responsible for the suppression of the polymerization process will no longer occur and functional groups will remain unaffected. Described in this project methods will afford investigation of the influence of incorporated functional moieties on properties of specially-designed copolymers.

The development of a versatile methodology enabling the incorporation of functional groups along the polyethylene backbone is one of the last “Holy Grails” in the field of polymer chemistry, in particular olefin polymerization.