Precision Polymerization with Sterically Congested Metallocenes - The Search for the Perfect i-PP Helix

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Previous investigations have led us to asymmetric hafnocenes, which afforded polypropylenes of ultra-high molecular weight showing excellent elastic material properties. These products were formed according to a specific back-skip polymerization mechanism. In a new approach, we recently designed C2-symmetric hafnocenes, bearing the metal center in a sterically extremely congested ligand environment. These structures also afford ultra-high molecular weight PPs, however of an almost perfect, isotactic microstructure (pi-PP). Especially designed NMR experiments give mmmm-pentad concentrations up to 99.9% and melting transition higher than 180°C after annealing of the samples. The present contribution discusses synthetic and mechanistic aspects of the hafnocene catalysts and gives insight into the fascinating properties of the new PP materials.