
Abstract

In this thesis catalytic active zinc complexes stabilised by neutral N-donor functionalised ligands were synthesised and investigated towards their application in the solvent-free polymerisation of lactide.

Most of the introduced single-site metal catalysts for the ring-opening polymerisation of cyclic esters contain anionic ligand systems. They provide high catalytic activity but also cause the high sensitivity of these catalysts. To develop application oriented catalyst systems combining high activity with high robustness, neutral ligand systems are used in this approach. They cover bisguanidines, guanidine-amine-hybrids, imidazoline based guanidines as well as aliphatic, aromatic and cyclic amines. For a systematic investigation, the modular assembled guanidine and guanidine-amine hybrid ligands are well suited. Their flexible synthesis protocol allows the easy variation of the individual moieties and thus permits the elucidation of influencing variables of the complex properties.

By reacting the ligands with various zinc components, a library of zinc complexes was generated. Its variety (67 complexes prepared of 29 varying ligands and 9 different zinc salts) allows the systematic evaluation of the catalytic properties of its single components as well as the elucidation of crucial influencing parameters. Based on this analysis it could be demonstrated that all utilised ligand classes are suitable for the synthesis of active initiator systems. The impact of the anionic component of the zinc salt on the molecular structure and on the polymerisation behaviour of the corresponding zinc complexes was determined and in the case of guanidine-pyridine hybrid ligands a structure-reactivity relationship was developed.

The most auspicious initiators were guanidine-pyridine zinc triflate complexes which combine excellent catalytic activity with high robustness towards air, moisture and small impurities in the monomer as well as thermal stability. They do not need co-catalysts like alkoxides or alcohols to give PLAs with high molecular masses under industrially attractive conditions via a coordination-insertion mechanism.

The herein described introduction of three neutral ligand classes into the field of single-site metal catalyst systems for the ring-opening polymerisation shall enable the development of improved initiators and contribute to a deeper understanding of the metal catalysed polymerisation process.