

המעבדה לכימיה אורגנית ואי-אורגנית

סמינר

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בנושא:

Synthesis of New Chiral Ligands towards Enantioselective Cyclopolymerization of Dienes

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Cyclic polymers of olefin that contain cyclic repeating units on the main chain, have long been recognized as industrially valuable and easy-to-engineer thermoplastic materials with wide applications in the sectors of optical lenses/prisms, medical and food packaging, semiconductor, and liquid crystal display. Coordination cyclopolymerization methods are well-known to enable the cyclopolymerization of a broad range of (di)olefin monomers, controlling the region-, stereo-, and enantioselectivities of the resulting cyclic repeating units on the polymer backbone by utilizing well-defined metal/(chiral)ligand sites. A rare, but one successfully catalytic system allowing for chemo-, regio-, and stereoselective formation of cyclopolymers containing polar groups [e.g. ester, (sulfon)amide, ether, ketone moieties] is the κ^2 -diimine Pd catalysts that enable isospecific and trans-selective cyclopolymerization of highly functionalized κ^2 -dienes thanks to the intrinsically low oxophilicity of Pd.

Considering unique and tunable physical properties of cyclopolymers and excellent functional group compatibility of late metals (e.g. Pd, Ni, and Co), enantioselective cyclopolymerization of functionalized dienes by employing well-defined late metals and chiral ligands is envisaged highly promising. This methodology would provide a new family of optically active chiral cyclopolymers, at which the preinstalled polar functional groups are expected to readily be modified via simple organic reactions to afford post-modified new chiral cyclopolymers. Herein we wish to develop the chiral catalytic systems based on new chiral ligands and late metals - Pd, Ni, and Co to realize enantioselective cyclopolymerization of functionalized diene monomers. In this work, a variety of new chiral ligands designed for chiral catalysts towards enantioselective cyclopolymerization have been synthesized. Largely three types of chiral ligands were targeted. For the first type of ligand, one ketone moiety of acenaphthenequinone was substituted to an imine group to afford mono(imino)acenaphthenes (MIAN), while unfortunately MIAN was decomposed in the reaction with chiral (or racemic) alkylamines and the targeted chiral bis(imino)acenaphthenes (BIAN) was not obtained or formed in poor yields. As a second type of chiral ligand, a range of C₁-symmetric chiral bis(imino)pyridines (BIP) were synthesized, and these reacted with CoCl₂ to give the corresponding Co complexes. These complexes were tested as a catalyst for the polymerization reaction of 1,6-heptadiene in the presence of cocatalyst methylaluminumoxane (MAO) to reveal that unfortunately no polymer was observed. For the third type of ligand, 1,1'-Binaphthyl-2,2'-diamine (DABN) was utilized as the chiral amine source to synthesize a series of new chiral binaphthyl-diimino (BINA) ligands having different imino-backbones. The solid X-ray structures of some of new BINA ligands were unambiguously confirmed. Additionally, all ligands have been characterized by NMR spectroscopy and mass spectrometry. These ligands were applied for the complexation with Pd metal, while the complexation did not take place probably due to a weak coordinating power of the ligands..

