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Pyridine and bipyridine end-functionalized polylactide: synthesis and catalytic applications

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The search for new recyclable hydrogenation catalysts stimulated the synthesis of a great deal of heterogeneous metal-supported catalysts. In this context, mainly metallo-supramolecular polymers and block copolymers found a wide range of applications as catalyst support due to the unique possibility to tune the chemical and physical properties of the polymer backbone combined with its low cost, good performance and recyclability under real catalytic conditions(2, 3). In addition, the solubility of functionalized polymers in certain solvents, while they are insoluble in others was successfully employed to recycle the catalytic metal centers anchored to these polymers(4). Poly(lactic acid) (PLA) was functionalized with nitrogen containing aromatic groups such as pyridine and asymmetric 2,2'-bipyridine at the carboxylic acid-end of the polymer chain by means of tin octanoate-catalysed ring opening polymerization(5). The obtained macroligands have been successfully employed to coordinate Pd(II), which chemoselectively hydrogenated α,β -unsaturated carbonyl compounds to give the saturated counterpart as major product (Figure 1)(6) The catalyst was easily recycled upon a simple filtration process. End-functionalized isotactic PLA chains with opposite stereochemistry were used to generate, through a known supramolecular self-assembling process, functionalized stereocomplexes, featured by a higher thermal and hydrolytic resistance compared to isotactic PLA(7). The chemical nature of the nitrogen ligand introduced at the chain end of PLA was exploited to stabilize Pd-nanoparticles (NPs) by interactions of the aromatic or nitrogen functionality with the NPs' surface. The polymer-anchored Pd-NPs were generated by: (i) a classical approach which comprised the coordination of Pd(II) to the nitrogen donor atoms of the functional group prior to reduction with hydrogen; (ii) the interaction of solvent-stabilized Pd-clusters, obtained by the metal vapor synthesis(8), with the functionalized PLA-stereocomplexes. The polymer-supported Pd-NPs were successfully applied to catalyze the selective hydrogenation of selected alkynes to the corresponding alkene (Figure 2a)(9) and cinnamyl alcohol to the corresponding saturated aldehyde (Figure 2b)(10). A key finding with functionalized PLA-stabilized Pd-NPs was that the end-group controls the Pd-NPs' size and distribution, exerting hence a pronounced effect on the observed chemoselectivity of the catalytic reactions.

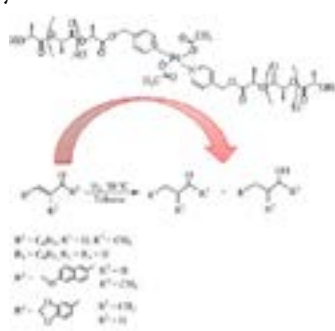
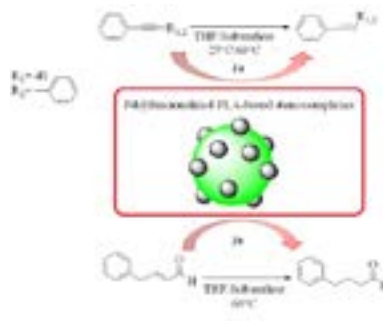
Figure 1: Selective hydrogenation of α,β -unsaturated carbonyl compounds.

Figure 2: Selective hydrogenations catalyzed by functionalized PLA-based stereocomplexes

Biography

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