We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter 1

Palladium-Based Catalysts-Supported onto End-Functionalized Poly(lactide) for C–C Double and Triple Bond Hydrogenation Reactions

Marco Frediani, Werner Oberhauser, Luca Rosi,
Elisa Passaglia and Mattia Bartoli

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/65447

Abstract

Poly(lactide) (PLA), which is the polymer that will be discussed in this chapter, was functionalized with nitrogen containing aromatic groups by means ring opening polymerization (ROP) reactions. The obtained macroligands were successfully employed to coordinate Pd(II), which chemoselectively hydrogenated αβ–unsaturated carbonyl compounds to give the saturated counterparts as main product. The catalyst could be easily recycled upon a simple filtration process.

End-functionalized isotactic PLA chains were used to generate stereocomplexes, featured by a higher thermal and hydrolytic resistance. The chemical nature of the nitrogen ligand introduced at the chain end of PLA was exploited to stabilize Pd-nanoparticles (Pd-NP_s) by interactions of the aromatic or nitrogen functionality with the NP_s– surface. The polymer-anchored Pd-NP_s were generated by a classical approach which comprised the coordination of Pd(II) by the functional group followed by reduction with hydrogen or by the metal vapor synthesis technique. The polymer-supported Pd-NP_s were successfully applied to catalyze the selective hydrogenation of alkynes to the corresponding alkene and cinnamylalcohol to the corresponding saturated aldehyde. In this book chapter the synthesis and structure-performance relationship of the new hydrogenation catalysts will be discussed.

Keywords: poly(lactide), palladium, nanoparticles, alkynes, hydrogenation

INTECH
open science | open minds

© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. CC BY

1. Introduction

In the realm of hydrogenation reactions, the selective hydrogenation of unsaturated carbon-carbon bonds is very attractive [1]. Asymmetric and partial hydrogenation reactions are pivotal for the access of important compounds employed as pharmaceuticals, food additives, pesticides, flavors, and fragrances [2]. In this respect, α,β-unsaturated carbonyl compounds present an interesting group of chemicals whose enantio- [3], chemo [4], and regio-selectivities [5] are highly challenging. For instance, Lindlar's [6] and Lindlar types' catalysts [7] are widely used to chemoselectively hydrogenate alkynes to the corresponding alkene. In parallel, a variety of different selective hydrogenation methods have been developed [8]. In particular, bimetallic catalysts [9], noble metal-based catalysts supported onto carbon-based materials [10] or inorganic matrixes [11], in combination with supercritical solvents [12] and "*flow*" reactors [13], have been studied. Also for the partial alkyne hydrogenation, a great deal of catalytic systems were proposed based on the use of noble metals and different approaches like reactions conducted in gas [14] and liquid phase [15], combined with ultrasound techniques [16] and biphasic catalytic systems [17].

The interest on polymer-based catalysts applied for hydroformylation reactions [18], hydrotreatment [19], and strong acid/base [20, 21] catalyzed reactions is steadily increasing. Since functional polymer-based catalytic systems generally exhibit notable advantages over traditional catalysts such as the tunable solubility and improved catalytic selectivity [22], the biodegradable polyester, poly(lactide) (PLA) was used as a polymer matrix [23], which is rather straightforwardly end-capped as reported by Helle et al. [24]. The possibility to produce carboxylic end-capped PLA chains functionalized with nitrogen containing moieties, called macroligands by Giachi et al. [25], allowed the synthesis of well-defined macrocomplexes containing metal cations, such as Pd(II). The latter Pd-based macrocomplexes were efficiently used to catalyze hydrogenation reactions conducted in the homogeneous phase followed by an easy separation step, as reported by Giachi et al. [26] and Bartoli et al. [27]. Isotactic end-functionalized PLA with opposite tacticity can be combined to form a supramolecular structure named stereocomplex [28]. Functionalized PLA stereocomplexes show high resistance against hydrolysis and thermal degradation and in addition, a poor solubility in all organic solvents. This latter property was exploited by Petrucci et al. [29] and Oberhauser et al. [30] for catalytic purposes to easily separate PLA-stereocomplex-based catalysts from catalytic solution.

In the following sections, synthesis, characterization, and catalytic application of homogeneous and heterogeneous Pd-catalysts supported on end-functionalized PLA were reported.

2. Pd-Nps supported onto PLA stereocomplexes: synthesis and characterization

The synthesis of PLA can be achieved by different synthetic pathways such as polycondensation of lactic acid [31] or through ring opening polymerization (ROP) of lactide (i.e., the cyclic

http://dx.doi.org/10.5772/65447

dimer of lactic acid) [32]. ROP is the adopted synthetic methodology, which allows a carboxylic-end functionalization along with a strict control of the resulting molar mass. The ROP can be either performed by cationic, anionic, or carbene-type mechanism or by a coordination insertion mechanism [33], which shows an advancement over the former mechanisms regarding the efficiency of the polymer chain growth and racemization of the stereogenic center of the lactic acid units. In addition, functionalized PLA at the carboxylic chain-end are straightforwardly obtained by using a suitable initiator molecule for the polymerization. ROP can be performed in solution or in the bulk of the monomer except for some glycolides that decompose at the melting temperature [34]. Typically, PLA is polymerized in bulk due to the low melting temperature of the corresponding cyclic monomers. The mechanism of ROP, through a coordination-insertion mechanism, is mainly based on organic salts of Sn(II). In particular, $Sn(Oct)_2$ (Oct = octanoate) is one of the most employed catalysts for PLA synthesis due to its relatively low cost, solubility in the monomer, which is important for bulk reactions, high catalytic activity (yields over 90%) and a low racemization tendency of the starting glycolide. The mechanism regarding the $Sn(Oct)_2$-catalyzed ROP is shown in **Figure 1**.

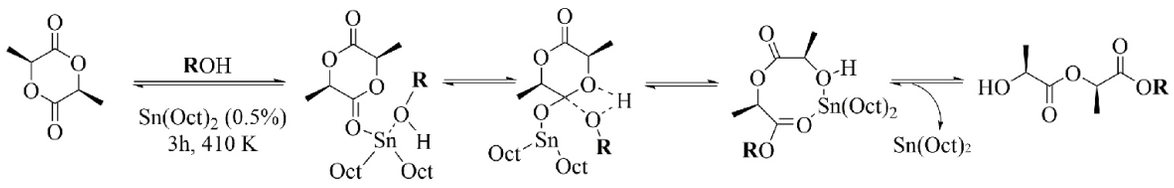
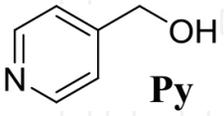
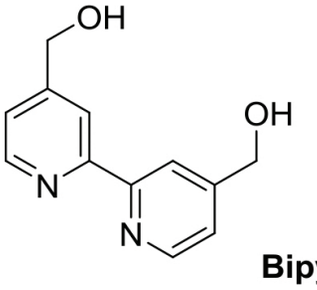
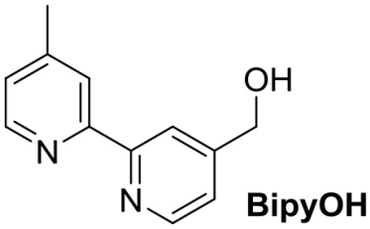
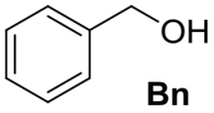


Figure 1. $Sn(Oct)_2$-catalyzed ROP of lactide in the presence of a hydroxylic initiator molecule (ROH).

As shown in **Figure 1**, the ROP of lactide starts with a simultaneous coordination of lactide and the initiator molecule to the metal center of the catalyst. This *cis*-coordination of the two reagents is a prerequisite for the nucleophilic attack of the coordinated hydroxyl oxygen atom on the lactide carboxylic carbon atom. Afterwards, the metal center inserts into the six-membered ring giving an eight member metallacycle. The obtained end-functionalized linear form of the lactide acts as a new initiator in the following polymerization cycle. The ROH, where R contains the new functional group, is incorporated at the carboxylic acid PLA chain end. The presence of water traces in the lactide melt notably influences the final molecular weight due to the competition role of water as an initiator molecule leading to a carboxylic acid end group which coordinates as carboxylate to the metal center. Nitrogen containing initiators, such as pyridine and 2-2′-bipyridine derivatives, were used in order to obtain carboxylic end-functionalized PLA chains. Synthesis conditions and obtained molar masses are compiled in **Table 1**.

The end-functionalized PLA-based macroligands were mainly analyzed by gel-permeation–chromatography (GPC) equipped with UV-Vis and refraction index (RI) detectors and by ^1H NMR spectroscopy. The UV-Vis detector confirmed the presence of the corresponding chromophore in the polymer chain. The ^1H NMR spectra of the macroligands show, apart the typical multiplets stemming from the polymer chain (i.e., doublet for CH_3 and quartet for CH of the repeating lactide unit), signals that are typically in the range of aromatic hydrogen atoms.

The ratio of the ^{1}H NMR integrals of these aromatic hydrogen atoms with that of the methyl group assigned to the terminal lactic acid gives the average number molar weight (M_n) of the polymer obtained, which is in good agreement with the experimental results of GPC analyses, in those cases where the polydispersity of the obtained material is low.

Initiator	Polymer chain	ID	MW (g/mol)
 **Py**	**Py**-P(L)LA-OH	**L**[1]	5000
	Py-P(D)LA-OH	**L**[2]	5000
 **BipyOH$_2$**	**BipyOH$_2$**-P(L)LA-OH	**L**[3]	10,000
	Bipy$_2$-P(D)LA-OH	**L**[4]	10,000
	Bipy-(PLA-P(L)LA-OH)$_2$	**L**[5]	10,000
	Bipy-(PLA-P(D)LA-OH)$_2$	**L**[6]	10,000
 **BipyOH**	**BipyOH**-P(L)LA-OH	**L**[7]	10,000
	BipyOH -P(D)LA-OH	**L**[8]	10,000
 **Bn**	**Bn**-P(L)LA-OH	**L**[9]	10,000
	Bn-P(D)LA-OH	**L**[10]	10,000
H$_2$O	HOOC-P(L)LA-OH	**L**[11]	10,000
	HOOC-P(D)LA-OH	**L**[12]	10,000

[a]Theoretical of the molar mass.

[b]Bulk synthesis, 410 K, 3 h.

[c]R-PLA (i.e., atactic PLA) bulk synthesis, 410 K, 3 h, R-PLA-P(L or D)LA toluene reflux, 24 h.

[d]Toluene reflux, 24 h.

Table 1. Overview of the synthesized macroligands.

The obtained PLA-based macroligands were used to provide the corresponding stereocomplexes upon mixing equimolar CH_2Cl_2 solutions of functionalized PLA of opposite stereochemistry, followed by evaporation of the solvent. Differential Scanning Calorimetry (DSC) analyses conducted on the obtained material showed clearly the absence of the melting peak of characteristic PLA (ca. 435 K); new endothermic transition at higher values, typically around 495 K, attributable to the melting of PLA-stereocomplex was observed. The melting enthalpy

http://dx.doi.org/10.5772/65447

changed in the same sense from around 38.0 (PLA) to 61.0 J/g (PLA-stereocomplex). These data support the formation of a supramolecular structure more thermally stable. Importantly, the type of end-group does not influence the powder X-ray diffraction (PXRD) pattern of functionalized PLA-stereocomplexes, while PLA and the corresponding stereocomplex are featured by a completely different PXRD pattern as shown in **Figure 2**.

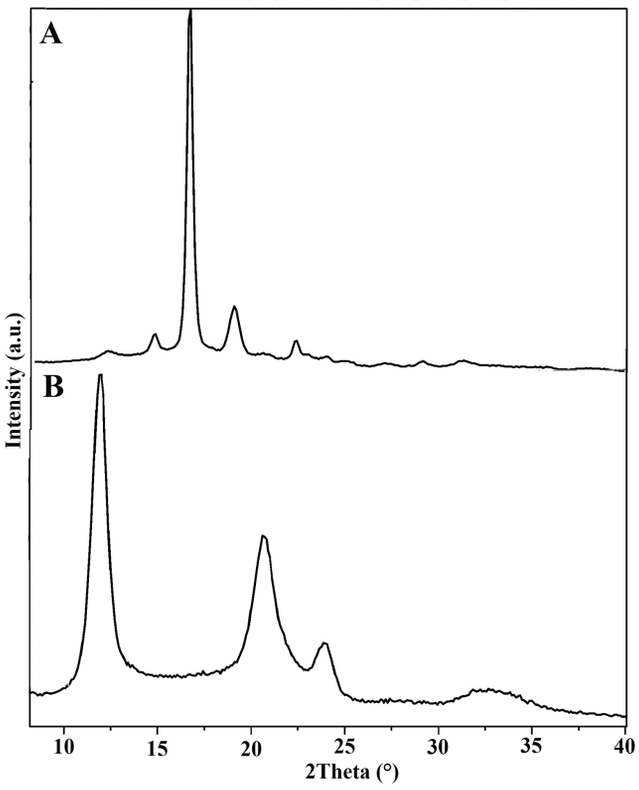


Figure 2. PXRD patterns of isotactic PLA (A) and of the corresponding stereocomplex (B).

The 2,2′-bipyridine or pyridine end-group of the macroligands easily react with $Pd(OAc)_2$ (OAc = acetate) in a 1:1 and 2:1 molar ratio, respectively, giving the expected *cis*-coordination of the nitrogen atoms to Pd(II) in case of 2,2′-bipyridine or *trans*-coordination in case of pyridine. $Pd(OAc)_2$ is a highly suitable Pd(II) precursor since it is soluble in noncoordinating solvents, for instance CH_2Cl_2, which is the solvent of choice for suspending PLA-stereocomplexes. In addition, coordinated $Pd(OAc)_2$ is easily reduced in the presence of hydrogen, giving the acetic acid as a removable side product from reaction medium.

The coordination of either the end-functionalized macroligands or stereocomplexes to Pd(II) was proved by ^1H NMR spectroscopy conducted in CD_2Cl_2. The use of $CDCl_3$ to characterize Pd-acetate macrocomplexes was avoided due to the easy protonation of acetate by trace amounts of acidity present in $CDCl_3$. The occurred coordination of the macroligands to Pd(II) was proved by ^1H NMR, UV-Vis spectroscopy and by comparison of this latter spectroscopic data with that obtained from an analogous model compound (i.e., molecular species without the polymer part), which is exemplified in **Figure 3**.

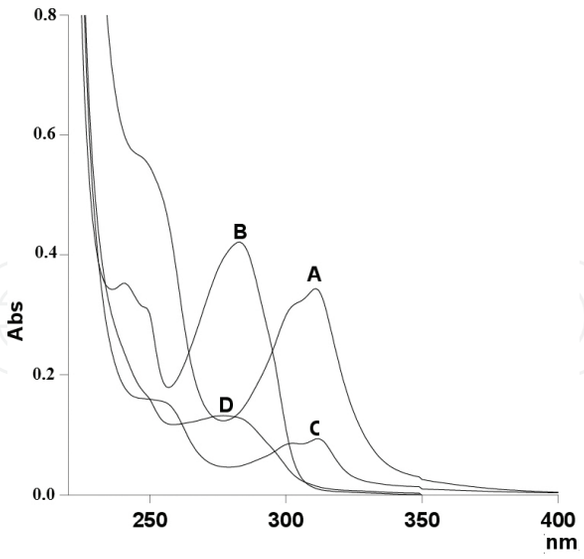


Figure 3. UV-Vis spectra of (A) $Pd(OAc)_2$**(**BipyOH**)**, (B) BipyOH, (C) $Pd(OAc)_2$ $\mathbf{L}^7$, and (D) $\mathbf{L}^7$.

For the synthesis of well-defined Pd-nanoparticles (Pd-NPs), the size and shape of which strongly influence their catalytic activity and chemoselectivity [35], different synthetic approaches were applied:

- Synthesis of Pd-NPs by coordination of $Pd(OAc)_2$ to the functional groups of PLA-stereocomplexes, followed by metal reduction in the presence of hydrogen pressure (p = 1.5 MPa) at 305 K.
- Synthesis of Pd-NPs by the MVS technique [36], which has the great advantages over the former synthesis approach that the final metal content can be adjusted upon choosing the desired metal concentration of the solvated metal particles, the size of which are defined by the type of solvent chosen, which acts as a ligand.

Transmission electron microscopic (TEM) analyses carried out on Pd-NPs supported onto PLA-stereocomplexes clearly confirmed the influence of the synthetic procedure on the size of NPs and their distribution and the effect of the nitrogen-containing functional groups on the dispersion of Pd-NPs on the polymer-based support as shown in **Figure 4**.

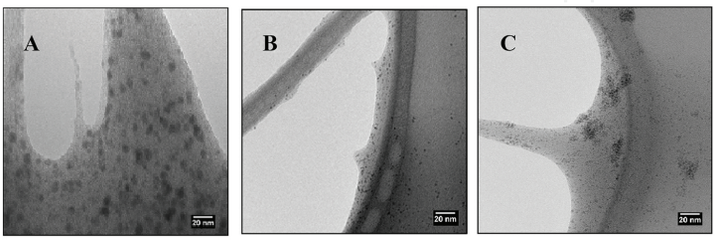


Figure 4. Comparison of TEM analysis of Pd@$\mathbf{L}^{7/8}$ obtained through MSV technique (A), average diameter of 2.0 nm, reduction of Pd precursors (B), average diameter of 3.8 nm, and Pd@$\mathbf{L}^{11/12}$ obtained through MSV technique (C), which showed a strong aggregation.

http://dx.doi.org/10.5772/65447

The thermal gravimetric analysis (TGA) of $\mathbf{L}^{11/12}$ and Pd@$\mathbf{L}^{11/12}$ showed that the presence of Pd-Np strongly affected the thermal stability of stereocomplex structures [30] as shown in **Figure 5**.

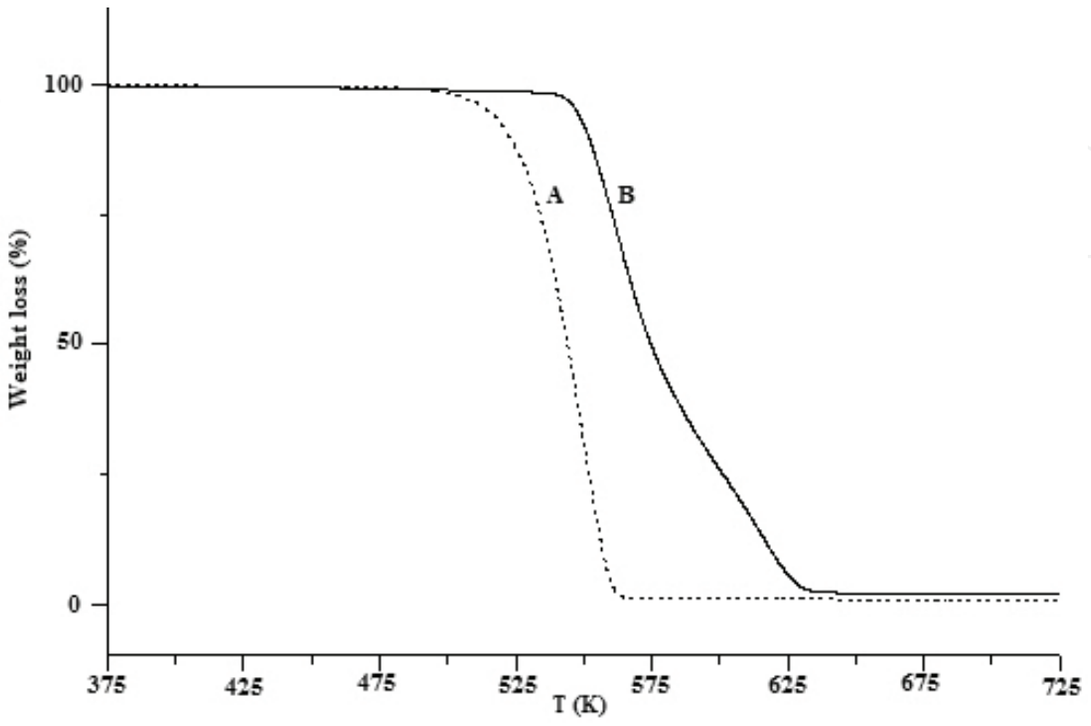


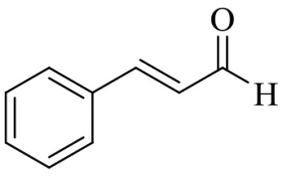
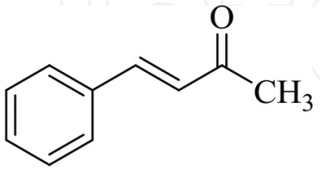
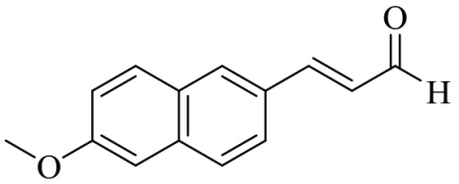
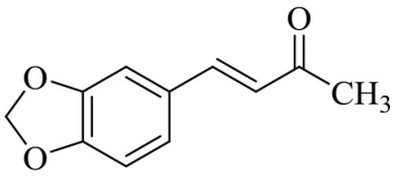
Figure 5. Comparison of TGA of $\mathbf{L}^{11/12}$ (A) and Pd@$\mathbf{L}^{11/12}$ (B).

The decomposition process of $\mathbf{L}^{11/12}$ started at 552 K instead of Pd@$\mathbf{L}^{11/12}$ that did not show a meaningful loss of weight up to 575 K. So, not only PLA-stereocomplexes prevent the aggregation of Pd-NPs but the latter increase the thermal stability of the stereocomplex structure.

3. Hydrogenation of C–C double and triple bonds

The chemoselective hydrogenation of selected α,β-unsaturated carbonyl compounds was carried out in toluene in the presence of the homogeneous precatalyst *trans*-$Pd(OAc)_2(\mathbf{L}^1)_2$ at 303 K. In all cases the corresponding saturated carbonyl compound was observed in a range of chemoselectivity between 46 and 100%, as shown in **Table 2** [27].

The obtained chemoselectivity was found to be strongly structure dependent and with the employed catalyst in some cases even higher chemoselectivities compared to other palladium-based catalysts were obtained [35]. The low chemoselectivity of substrate (IV) is due to the formation of the corresponding saturated alcohol, which is mainly explained by steric effects exerted by the α-methyl group of compound IV. Importantly, in all hydrogenation reactions carried out with the selected substrates (**Table 2**), the corresponding allyl alcohol was not formed.

Substrate	Conversion (%)	Selectivity (%)
 **(I)**	96	94
 **(II)**	>99	>99
 **(III)**	24	100
 **(IV)**	13	46

Reaction conditions adopted: catalyst (5×10^{-2} mmol Pd), cinnamaldehyde = 10.5 mmol; toluene = 10 mL; $p(H_2)$ = 0.1 MPa; and T = 305 K.

[a]After 24 h.

[b]After 2 h.

[c]After 2 h at 0.2 MPa.

Table 2. Catalytic performances of *trans*-$Pd(OAc)_2(\mathbf{L}^1)_2$.

The main advantage of the catalytic system used is the complete solubility in the reaction medium (toluene) and the easy separation of the catalyst as solid upon addition of either MeOH or *n*-hexane to the catalytic solution, exploiting the fact that PLA is not soluble in both solvents. The occurrence of the catalytic reaction in the homogeneous phase mediated by a polymer anchored molecular Pd-based catalyst and not by Pd-NPs, was tested by performing catalytic reactions in the presence of Hg(0), which poisons heterogenous catalyst (colloidal and nanoparticle-based catalysts). As a result, the catalytic activity remained unchanged. The stability of the Pd-catalyst as Pd(II) in the presence of hydrogen was proved by X-ray photo-electron spectroscopy (XPS) of Pd3d, showing no occurred reduction of Pd(II) to Pd (0).

Pd-NPs synthesized by the MVS-technique and stabilized by differently end-functionalized PLA-stereocomplexes (i.e., $\mathbf{L^{1/2}}$, $\mathbf{L^{7/8}}$, $\mathbf{L^{9/10}}$, and $\mathbf{L^{11/12}}$) with pyridine, BipyOH, Bn, and OH-end groups, respectively (**Table 1**) were tested in the chemoselective C═C double bond cinnamaldehyde in Tetrahydrofuran (THF) [30]. As a result, the following order of decreasing catalytic activity as well as chemoselectivity was found: $\mathbf{L^{7/8} > L^{1/2} > L^{9/10} > L^{11/12}}$ (**Table 3**), which is in line with the decreasing Pd-NPs' dispersion on the polymer surface.

Catalyst	Conversion (%)	TOF (h^{-1})	Selectivity (%)
$Pd@L^{1/2}$	54	485	88
$Pd@L^{1/2}$	30	269	68
$Pd@L^{7/8}$	74	664	97
$Pd@L^{7/8}$	72	646	96
$Pd@L^{7/8}$	88	n.d	90
$Pd@L^{9/10}$	30	n.a.	65
$Pd@L^{11/12}$	14	n.a.	60

Catalytic conditions: Pd (1.2×10^{-3} mmol), cinnamaldehyde (141.2 μmol), THF (10.0 mL), $p(H_2)$ = 1 MPa, t = 2 h, and T = 335K.

[a]Turn-over frequency (TOF) referred to substrate accessible Pd-NPs' sites.

[b]Chemoselective for 3-phenylpropanal.

[c]Fourth recycling experiment.

[d]Solventless catalytic reaction (Pd = 1.4×10^{-2} mmol, cinnamaldehyde = 24.0 mmol, and t = 6 h).

Table 3. Catalytic performances of different $Pd@L^{x|y}$ in the selective hydrogenation of cinnamaldehyde.

$Pd@\mathbf{L^{7/8}}$ gave a 95% chemoselectivity at 100% conversion which is notably higher compared to other heterogeneous polymer based catalysts. The role of the polymer-anchored 2,2′-bipyridine functionality in $\mathbf{L^{7/8}}$ is that of an efficient small Pd-NP size (i.e., 2 nm) stabilizer, which leads to the high chemoselectivity found for 3-phenylpropanale, due to the efficient C═C double bond coordination to small Pd-NPs [30]. High chemoselectivity for $Pd@\mathbf{L^{7/8}}$ was also found under solventless catalytic conditions (90% chemoselectivity for 3-phenylpropanal at 88% substrate conversion) conducted with a catalyst to a substrate ratio of 1:1714.

Pd-Nps generated by a stepwise synthesis which comprised the coordination of $Pd(OAc)_2$ to end-functionalized $\mathbf{L^{3/4}}$ and $\mathbf{L^{5/6}}$ followed by a successive reduction with hydrogen in either THF or CH_2Cl_2 [29]. As a result, CH_2Cl_2 reveled the solvent of choice, since the PLA-stereocomplex is much better suspended compared to THF and as a consequence, the size of the obtained Pd-Nps in CH_2Cl_2 were of 3.11 nm in either cases. $Pd@\mathbf{L^{3/4}}$ and $Pd@\mathbf{L^{5/6}}$ were employed to partially hydrogenate phenylacetylene and diphenylacetylene employing THF as the reaction medium. From a comparison of the catalytic data, shown in **Table 4**, emerges that $Pd@\mathbf{L^{5/6}}$, which is build up by the crystalline PLA-stereocomplex unit and amorphous (i.e., syndiotactic PLA) part, where the functional groups are located.

Catalyst	Substrate	Time (h)	Conversion (%)	TOF (h^{-1})	Chemoselectivity (%)	Regioselective (%)
Pd@**L**$^{3/4}$	Phenylacetylene	1	14	2340	88	n.a.
		2	28	2340	89	n.a.
Pd@**L**$^{5/6}$		1	44	6560	95	n.a.
		2	62	4623	95	n.a.
Pd@ **L**$^{3/4}$	Diphenylacetylene	1	28	9195	90	91.
		2	39	6404	92	92
Pd@ **L**$^{5/6}$		1	76	11335	90	94
		2	100	n.a.	85	95

Catalytic conditions: Pd (8.34×10^{-4} mmol), alkyne (4.0 mmol), THF (10.0 mL), and p = 0.3 MPa.

[a]TOF referred to substrate accessible Pd sites.

[b]Chemoselectivity referred to the corresponding alkene.

[c]T = 298 K.

[d]T = 333 K.

Table 4. Catalytic performances of different Pd@L$^{x|y}$ in the partial hydrogenation alkynes.

Hence the higher catalytic activity and chemoselectivity of Pd@**L**$^{5/6}$ compared to Pd@**L**$^{3/4}$ were explained in terms of a much easier access of Pd-Nps situated in an amorphous polymer phase. In addition, the easier access of the substrate to the Pd-NPs in Pd@**L**$^{5/6}$ removes more efficiently styrene (i.e., partial hydrogenation product of phenylacetylene) thus avoiding the styrene coordination to the Pd-Nps and hence the hydrogenation to ethylbenzene [37]. The partial hydrogenation of diphenylacetylene to *cis*-stilbene occurred at 333K. A comparison of the performance of Pd@**L**$^{5/6}$ with other heterogeneous Pd catalysts, such as Pd-Nps supported onto carbon without additional organic modifiers led to much lower chemoselectivities (i.e., styrene <80% and *cis*-stilbene 85%) [38]. The heterogeneous PLA-stereocomplex-based Pd catalysts were easily recovered from the catalytic solution simple by centrifugation of the catalytic THF solution followed by decantation of the solution in air atmosphere. ICP-OES analysis of the THF solution confirmed a very low level of Pd leaching (i.e., >0.5 ppm). HRTEM images acquired of the different recovered heterogeneous catalyst, showed that Pd@**L**$^{7/8}$ is the most promising support for Pd-NPs, avoiding Pd-Nps' stabilization property of **L**$^{7/8}$ is due to interactions between the Pd-Nps' surface and the bipyridine functionality of **L**$^{7/8}$ as shown by IR-spectroscopy [35].

4. Conclusions

PLA based biopolymers have found to be easily functionalized at the carboxylic acid end. The introduced functional group which is located at the chain end of the polymer chain can be

exploited to coordinate metal ions, which are successively reduced to form metal nanoparticles, the growth and stabilization of which is controlled by the nature of the introduced functional group. The stereocomplexation of these latter macroligands leads to a polymer-based support which is featured by a much more thermal and hydrolytic stability compared to PLA, due to many hydrogen bond-based interactions between PLA-chains of opposite stereochemistry. In addition, the stereocomplex is insoluble in most organic solvents, so that recycling of the support is easily done upon a simple filtration process. We found that the end-functionalized of the stereocomplex with 2,2′-bipyridine (**L**$^{7/8}$) leads to an ideal support for Nps' surface. The stabilization of small Pd-Nps (2.0 nm) generated by the MSV technique, with **L**$^{7/8}$ in the course of the catalytic hydrogenation of α,β-unsaturated carbonyl compounds brings about the notable catalytic activity and chemoselectivity found for the corresponding saturated carbonyl compounds.

Author details

Marco Frediani[1*], Werner Oberhauser[2], Luca Rosi[1], Elisa Passaglia[3] and Mattia Bartoli[1]

*Address all correspondence to: marco.frediani@unifi.it

1 Department of Chemistry "Ugo Schiff," University of Florence, Sesto Fiorentino, Italy

2 Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), Sesto Fiorentino, Italy

3 Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), UOS Pisa, Area della Ricerca, Pisa, Italy

References

[1] De Vries, J. Elsevier, editors. The Handbook of Homogeneous Hydrogenation. 1st ed. Weinheim, Germany: WILEY-VCH Verlag GmbH & Co. KGaA; 2013. 1568 p.

[2] Blaser, HU. Heterogeneous catalysis for fine chemicals production. *Catal Today* 2000, 60(3), 161–165.

[3] Teichert J, den Hartog T, Hanstein M, Smit C, ter Horst B, Hernandez-Olmos V, Feringa B, Adriaan Minnaard. Organocatalytic reduction of carbon-carbon double bonds in racemization-sensitive compounds. *ACS Catalysis* 2011, 1(4), 309–315.

[4] Li X, Li L, Tang Y, Zhong L, Cun L, Zhu J, Liao J, Deng J. Chemoselective conjugate reduction of α,β-unsaturated ketones catalyzed by rhodium amido complexes in aqueous media. *J. Org. Chem*. 2010, 75(9), 2981–2988.

[5] Mahoney W, Stryker J. Hydride-mediated homogeneous catalysis. Catalytic reduction of α,β-unsaturated ketones using [(Ph_3P)CuH]6 and H_2. *J. Am. Chem. Soc*. 1989, 11(24), 8818–8823.

[6] Lindlar H. A new catalyst for selective hydrogenation. *Helv. Chim. Acta* 1952, 35(2), 446–450.

[7] Cramer D, Allinger N. Macro rings. XIII. Synthesis and properties of 1,7-cyclododecadiyne and related compounds. *J. Am. Chem. Soc*. 1956, 78(11), 2518–2524.

[8] Busca G. Chapter 9 - Metal Catalysts for Hydrogenations and Dehydrogenations. In: Heterogeneous Catalytic Materials. 2nd ed. Amsterdam: Elsevier; 2014. pp. 297–343.

[9] Prakash MG, Mahalakshmy R, Krishnamurthy KR, Viswanathan B. Studies on Ni–M (M = Cu, Ag, Au) bimetallic catalysts for selective hydrogenation of cinnamaldehyde. *Catal. Today* 2016, 263, 105–111.

[10] Matsubara EY, Rosolen JM, Donate PM, Gunnella R. Palladium decoration of hybrid carbon nanotubes/charcoal composite and its catalytic behavior in the hydrogenation of trans-cinnamaldehyde. *J. Mol. Catal. A: Chem*. 2015, 410, 34–40.

[11] Wu Q, Zhanga C, Zhanga B, Lia X, Yinga Z, Liua T, Lina W, Yua Y, Chenga H. Highly selective Pt/ordered mesoporous TiO_2–SiO_2 catalysts for hydrogenation of cinnamaldehyde: The promoting role of Ti^{2+}. *J. Colloid Interface Sci*. 2016, 463, 75–82.

[12] Piquerasa M, Puccia V, Vegab DA, Volpe MA. Selective hydrogenation of cinnamaldehyde in supercritical CO_2 over Me–CeO2 (Me = Cu, Pt, Au): Insight of the role of Me–Ce interaction. *Appl. Catal. B*. 2016, 185, 265–271.

[13] Müller A, Ludwig M, Arlit M, Lange R. Evaluation of reactor concepts for the continuous production of fine chemicals using the selective hydrogenation of cinnamaldehyde over palladium catalysts. *Catal. Today* 2015, 241, 214–220.

[14] McCuea AJ, Guerrero-Ruizb A, Rodríguez-Ramosc I, Andersona JA. Palladium sulphide—A highly selective catalyst for the gas phase hydrogenation of alkynes to alkenes. *J. Catal*. 2016, 340, 10–16.

[15] Sasaki T, Bhanage BM. Silica supported palladium phosphine as a robust and recyclable catalyst for semi-hydrogenation of alkynes using syngas. *J. Mol. Catal. A: Chem*. 2016, 414, 78–86.

[16] Wu Z, Cravotto G, Gaudino EC, Giacomino A, Medlock J. Ultrasonically improved semi-hydrogenation of alkynes to (Z-)alkenes over novel lead-free Pd/Boehmite catalysts. *Ultrason. Sonochem.* 2016, 16, 30161–30164.

[17] Ogweno AO, Ojwach SO, Akerman MP. Cationic pyridyl(benzoazole) ruthenium(II) complexes: Efficient and recyclable catalysts in biphasic hydrogenation of alkenes and alkynes. *Appl. Catal. A*. 2014, 486, 250–258.

[18] Kontkanen M, Vlasova L, Suvanto S, Haukka M. Microencapsulated rhodium/cross-linked PVP catalysts in the hydroformylation of 1-hexene. *Appl. Catal. A.* 2011, 401(1–2), 141–146.

[19] Klimov OV, Nadeina KA, Dik PP, Koryakina GI, Pereyma VY, Kazakov MO, Budukva SV, Gerasimov E, Prosvirin IP, Kochubey DI, Noskov AS. CoNiMo/Al_2O_3 catalysts for deep hydrotreatment of vacuum gasoil. *Catal. Today* 2016, 271, 56–63

[20] Reddya MV, Reddyb GCS, Jeong YT. Polystyrene-supported p-toluenesulfonic acid (PS/PTSA): As a highly active and reusable heterogeneous bronsted acid catalyst for the synthesis of novel 1H-indol-3-yl-4H-chromene-3-carbonitriles under neat conditions. *Tetrahedron Lett.* 2016, 57(11), 1289–1292.

[21] Shan R, Chena G, Yana B, Shia J, Liu C. Porous CaO-based catalyst derived from PSS-induced mineralization for biodiesel production enhancement. *Energ. Convers. Manage*. 2015, 106, 405–413.

[22] Leadbeater NE. Chapter 12.14—Polymer-supported Organometallic Catalysts. In: Reference Module in Chemistry, Molecular Sciences and Chemical Engineering. 2nd ed. Oxford: Elsevier; 2007. pp. 663–753.

[23] Meng X, Shi G, Wu C, Chen W, Xin Z, Shi Y, Sheng Y. Chain extension and oxidation stabilization of Triphenyl Phosphite (TPP) in PLA. *Polym. Degrad. Stab.* 2016, 124, 112–118.

[24] Heller M, Schubert US. Optically active supramolecular poly(L-lactide)s end-capped with terpyridine. *Macromol. Rapid Commun*. 2001, 22 (16), 1358–1363.

[25] Giachi G, Oberhauser W, Frediani M, Passaglia E. Pd(II)-pyridine macrocomplexes based on poly(lactide). *J. Polym. Sci., Part A: Polym. Chem*. 2011, 49(21), 4708–4713.

[26] Giachi G, Oberhauser W, Frediani M, Passaglia E. Aerobic alcohol oxidation catalyzed by polyester-based Pd(II) macrocomplexes. *J. Polym. Sci., Part A: Polym. Chem*. 2012, 50 (13), 2725–2731.

[27] Bartoli M, Rosi L, Petrucci G, Armelao L, Oberhauser W, Frediani M, Piccolo O, Rathod VD, Paganelli S. An easily recoverable and recyclable homogeneous polyester-based Pd catalytic system for the hydrogenation of α,β-unsaturated carbonyl compounds. *Catal. Comm.* 2015, 65, 228–233.

[28] Tsuji H. Poly(lactide) stereocomplexes: Formation, structure, properties, degradation, and applications. *Macromol. Biosci.* 2005, 5(7), 569–597.

[29] Petrucci G, Oberhauser W, Bartoli M, Giachi G, Frediani M, Passaglia E, Capozzoli L, Rosi L. Pd-nanoparticles supported onto functionalized poly(lactic acid)-based stereocomplexes for partial alkyne hydrogenation. *Appl. Catal. A.* 2014, 469,132–138.

[30] Oberhauser W, Evangelisti C, Jumde RP, Petrucci G, Bartoli M, Frediani M, Mannini M, Capozzoli L, Passaglia E, Rosi L. Palladium-nanoparticles on end-functionalized

poly(lactic acid)-based stereocomplexes for the chemoselective cinnamaldehyde hydrogenation: Effect of the end-group. *J. Catal.* 2015, 330, 187–196.

[31] Turner SR, Liu Y. 5.14 - Chemistry and Technology of Step-Growth Polyesters- Matyjaszewski, Krzysztof. In: Möller, Martin, editors. Polymer Science: A Comprehensive Reference. 1st ed. Amsterdam: Elsevier; 2012. pp. 311–331.

[32] Duda A. 4.11 - ROP of Cyclic Esters. Mechanisms of Ionic and Coordination Processes. In: Möller, Martin, editors. Polymer Science: A Comprehensive Reference. 1st ed. Amsterdam: Elsevier; 2012. pp. 213–246.

[33] Löfgren A, Albertsson A, Dubois P, Jérôme R. Recent advances in ring-opening polymerization of lactones and related compounds. *Macromol. Sci. Rev. Macromol. Chem. Phys*. 1995, 35(3), 379–418.

[34] Liu T, Simmons TL, Bohnsack DA, Mackay ME, Smith III MR, Baker GL. Synthesis of polymandelide: A degradable polylactide derivative with polystyrene-like properties. *Macromolecules.* 2007, 40(17), 6040–6047.

[35] Evangelisti C, Panziera N, D'Alessio A, Bertinetti L, Botavina M, Vitulli G. New monodispersed palladium nanoparticles stabilized by poly-(N-vinyl-2-pyrrolidone): Preparation, structural study and catalytic properties. *J. Catal.* 2010, 212(12), 246–252.

[36] Dyson PJ. Arene hydrogenation by homogeneous catalysts: Fact or fiction? *J. Chem. Soc. Dalton Trans*. 2003, 15, 2964–2974.

[37] Domínguez S, Berenguer-Murcia A, Pradhan BK, Linares-Solano A, Cazorla-Amorós D. Semihydrogenation of phenylacetylene catalyzed by palladium nanoparticles supported on carbon materials. *J. Phys. Chem. C* 2008, 112(10), 3027–3834. DOI: 10.1021/jp710693u

[38] Starodubtseva EV, Vinogradova MG, Turova OV, Bumagin NA, Rakov EG, Sokolov VI. Palladium(0) supported on carbon nanotubes as an efficient catalyst of the C triple bond; length of m dash C bond hydrogenation. *Catal. Comm.* 2009, 10(10), 1441–1442.