



Platinum nanoparticles onto pegylated poly(lactic acid) stereocomplex for highly selective hydrogenation of aromatic nitrocompounds to anilines

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ABSTRACT

A stereocomplexed poly(lactic acid)-polyethyleneglycol copolymer was synthesized and successfully used as recyclable support for Pt nanoparticles, generated by the metal vapor synthesis technique. The confinement of the Pt nanoparticles were determined by thermal analysis. Hydrogenation reactions of chlorinated aromatic nitro compounds, containing other reducible functional groups, to the corresponding anilines occurred with the latter supported Pt nanoparticles in MeOH under very mild reaction conditions (*i.e.* 30 °C, $p(\text{H}_2)=5.0$ bar). The covalently attached polyethyleneglycol polymer significantly increased the catalytic activity of the supported Pt nanoparticles compared to an analogous catalytic system which did not contain polyethyleneglycol but the same sized Pt nanoparticles.

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1. Introduction

Hydrogenation of nitroarenes to the corresponding anilines is a chemical transformation of remarkable interest, due to application of anilines as intermediates for the industrial production of polymers, agrochemicals, dyes and pharmaceuticals [1]. The hydrogenation of nitroarenes that contain also other reducible functional groups and halide atoms is especially challenging, since reduction of second functional group and dehalogenation reactions can occur [2]. In addition the hydrogenation of the nitro group itself can lead to various interesting intermediates such as hydroxylamines [3,4]. In order to make this hydrogenation reaction sustainable various supported metal nanoparticles (NPs) of Pd [5–7], Ni [8], Ru [9], Ag [10,11], Fe [12], Au [13,14] and Pt [15,16] were used. Pt NPs-mediated nitro compound hydrogenation reactions are generally chemoselective for the corresponding aniline, applying very mild reaction conditions (*i.e.* <40 °C, $p(\text{H}_2)=5.0$ bar, MeOH) [2]. The undesired dehalogenation reaction of aromatic

nitro compounds was decreased significantly by supporting Pt-NPs onto partially reduced $\gamma\text{-Fe}_2\text{O}_3$, decreasing the electron back-donation from d orbitals of Pt to the π^* anti-orbitals of the adsorbed molecules [17–19]. High chemoselectivity for the conversion of nitro arenes to anilines has been obtained with sol-gel encapsulated [20], porous polymeric framework confined [21–23], ionic polymer-[24] and ionic liquids-stabilized NPs [25,26]. Remarkable results have also been reported for polyethylene glycol (PEG)-stabilized Pt-NPs in methanol [27] and supercritical CO_2 [28]. PEG has unique applications in metal-mediated transformations as reaction medium, to stabilize heterogeneous catalysts and as phase transfer catalyst [2,29]. Recently we introduced stereocomplexed (sc) poly(lactic acid) (PLA) as a new biodegradable support for Pd-catalyzed selective hydrogenation reactions [30,31]. Herein we report the synthesis and application of a sc-PLA-PEG block copolymer [32] as new recyclable polymer support for chemoselective, Pt-NP-mediated hydrogenation reactions of aromatic Chloro-nitro compounds to the corresponding anilines in MeOH.

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2. Experimental

2.1. Materials

Tin octanoate ($\text{Sn}(\text{Oct})_2$), benzylalcohol, polyethyleneglycol monomethylether (PEG 5000, $M_n = 4870$ g/mol, polydispersity index (PDI) = 1.20) and *l*- and *d*-lactide were purchased from Aldrich. *l*- and *d*-lactide were sublimated before utilization and stored thereafter under nitrogen atmosphere at 4.0 °C. All operations involving the metal vapor synthesis (MVS) products were performed under a dry argon atmosphere. Mesitylene was purchased from Aldrich and purified by conventional methods, distilled and stored under argon. Ketjenblack EC-600JD (C) was purchased from Cabot Corp. USA, while solvents such as *n*-hexane, CH_2Cl_2 , CH_3OH , CDCl_3 , CD_3OD and HPLC-grade THF were purchased from Aldrich and used without further purification.

2.2. Instruments

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer, measuring at 400.13 and 100.62 MHz.

ATR-IR spectra were recorded on a Shimadzu model IR-Affinity apparatus, equipped with a Golden Gate single reflection diamond ATR accessory.

Gel-Permeation Chromatography (GPC) was carried out with a Waters Binary HPLC 1525 pump, a manual injector with a six way valve and a 200 μL loop, three in series connected Shodex KF-802, KF-803 and KF-804 columns (length: 300 mm each, inner diameter: 8.0 mm, 24500 theoretical plates, exclusion limit for polystyrene (PS) up to 400000 g mol^{-1} ; a refraction index (RI) detector (Optilab T-rEXTM, Wyatt Technology) and a UV detector (Waters model 2489). HPLC-grade THF with a water content of maximal 0.1 vol% was used as eluent at a constant flow of 1.0 mL min^{-1} , keeping the columns at 30.0 °C with a thermostat. The GPC system was calibrated using PS as standard. Samples were prepared by dissolving 5.0 mg of analyte in 1.0 mL of eluent. The obtained solution was filtered through a 0.2 μm PTFE filter and injected.

GC analyses were performed with a Shimadzu 2010 gas chromatograph equipped with a flame ionization detector and a 30.0 m (0.25 mm i.d., 0.25 μm film thickness) VF-WAXms capillary column.

GC-MS analyses were performed with a Shimadzu QP5000 apparatus, equipped with a 30 m (0.32 mm i.d., 0.50 μm film thickness) CP-WAX 52CB WCOT-fused silica column.

High resolution transmission electron microscopy (HRTEM) analyses of the supported Pt-NPs was carried out with a ZEISS LIBRA 200FE HRTEM instrument, equipped with a FEG source operating at 200.0 kV, in column second-generation omega filter for energy selective spectroscopy (EELS) and imaging (ESI), HAADF STEM facility, EDS probe for chemical analysis, integrated tomographic HW and SW. The samples were ultrasonically dissolved in a 1:1 solvent mixture of isopropanol/ CHCl_3 and a drop of the obtained solution was deposited on a holey-carbon film supported on a copper TEM grid of 300 mesh. Histograms of the particle size distribution were obtained by counting at least 500 particles. The mean particle diameter (d_m) was calculated by using the formula $d_m = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i .

Inductively coupled plasma-optical emission spectrometry (ICP-OES) was carried out with an iCAP 6200 Duo upgrade, Thermofisher instrument. A sample (0.5 mL) of Pt-solvated metal atoms (SMA) solution was heated over a heating plate in a porcelain crucible in the presence of aqua regia (2.0 mL) for six times followed by dissolving the solid residue in 0.5 M aqueous HCl.

Powder X-ray diffraction (PXRD) experiments were carried out at room temperature with a PANalytical X'PERT PRO pow-

der diffractometer, employing Cu K_α ($\lambda = 1.5418 \text{ \AA}$) radiation and a parabolic MPD-mirror.

Thermogravimetric (TG) analyses were carried out under nitrogen atmosphere using a Seiko, Parabiaco (Mi) Italy EXSTAR 7200 TG/DTA instrument. TG curves were collected on samples of 5–10.0 mg in the temperature range from 30.0–700.0 °C (N_2 flow = 200.0 mL/min) with a heating rate of 10.0 °C/min. The onset temperature of degradation (T_{onset}) is defined as the temperature that corresponds to the intercept of tangents to the curve before and after the degradation step. The maximum rate inflection temperature for the different degradation steps was extracted from derivative TG (DTG) curves.

Differential scanning calorimetry (DSC) analysis of all the samples was carried out under nitrogen atmosphere by using a Perkin-Elmer 4000 instrument. The instrument was calibrated with indium and lead as standards. The analysis was carried out in a temperature range depending on the thermal features of polymer blocks at 10.0 °C/min. As for example it was from –40.0 to 240.0 °C for the stereoblock-based samples. Crystallization and melting enthalpies were evaluated from the integrated areas of melting peaks recorded during second heating.

Environmental scanning electron microscopy (ESEM) images for L^1 and L^2 were acquired on a FEI ESEM Quanta 200 apparatus with a tungsten source using a gaseous secondary electron detector (GSED) with a 500.0 μm aperture. The images were collected with a magnification of 3000 \times a chamber pressure of 3.0 Torr and a working distance of 7.0 mm.

2.3. Synthesis

2.3.1. Synthesis of *l/d*-PLA-Bn

In a Schlenk tube, *l/d*-lactide (4.0 g, 28.0 mmol) was heated at 135.0 °C in the presence of $\text{Sn}(\text{Oct})_2$ (56.3 mg, 0.139 mmol) and benzylalcohol (BnOH) (43.3 mg, 0.40 mmol) for 3 h under a nitrogen atmosphere. Then the reaction mixture was allowed to cool to room temperature and the sublimed crystalline lactide fraction (ca. 1.0%) was removed mechanically from the Schlenk tube. The crude reaction product was dissolved in CHCl_3 (20.0 mL) and upon the slow addition of *n*-hexane (30.0 mL) to the latter solution the product precipitated as light pink powder. The solid was separated from solution by filtration, washed several times with *n*-hexane and dried by vacuum at room temperature for 12 h ^1H NMR data acquired of the product correspond to that reported in the literature [33].

Yield: *l*-PLA-Bn (3.8 g, 95%); *d*-PLA-Bn (3.5 g, 88%); M_n : *l*-PLA-Bn (10240 g/mol), PDI (1.31); *d*-PLA-Bn (9240 g/mol), PDI (1.33).

2.3.2. Synthesis of *l/d*-PLA-PEG

In a two necked round bottom flask *l/d*-lactide (3.0 g, 21.0 mmol) was solubilized in anhydrous toluene (30.0 mL) and refluxed for 24 h in the presence of $\text{Sn}(\text{Oct})_2$ (35.18 mg, 0.087 mmol) and PEG monomethyl ether (3.0 mg, 0.60 mmol). During the reaction the product precipitated as white solid, which was isolated and dissolved in CH_2Cl_2 (15.0 mL). Upon addition of *n*-hexane (30.0 mL) to the latter solution the product precipitated as off-white powder, which was separated from solution by filtration, washed with *n*-hexane (10.0 mL) and dried under vacuum for 12 h.

Yield: *l*-PLA-PEG (5.2 g, 87%); *d*-PLA-PEG (5.6 g, 93%). M_n : *l*-PLA-PEG (8980 g/mol), PDI (1.38); *d*-PLA-PEG (9163 g/mol), PDI (1.48).

^1H NMR of *l*-PLA-PEG (400.13 MHz, CDCl_3 , ppm) $\delta = 1.49$ (d, $^3J_{\text{HH}} = 7.2$ Hz, 3H, CH_3 (terminal)), 1.58 (d, $^3J_{\text{HH}} = 7.1$ Hz, 171H, CH_2), 3.39 (s, OCH₃), 3.47 (m, 2H, CH_2), 3.64 (s, 440H, CH_2), 4.38 (br. s, 1H, CH(terminal)), 5.15 (q, $^3J_{\text{HH}} = 7.1$ Hz, 57H, CH).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.62 MHz, CDCl_3 , ppm) $\delta = 16.63$ (s, CH_3), 20.51 (s, CH_3 (terminal)), 58.99 (s, OCH₃), 64.43 (s, OCH₂), 66.68 (s,

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