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Supporting information

Synthesis of melt-processable PLA-based stereocomplexes through a sustainable melt-approach

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Experimental Section

Materials

L- and D-lactides (optical purity ≥ 99.5 %, free acid < 1 meq/kg, water content < 0.02 %) were supplied by Futerro S.A., Belgium, and used as received. Tin(II) 2-ethylhexanoate (Sn(Oct)2, ~ 95 %) and triphenylphosphine (PPh3, ≥ 98.5 %) were purchased from Sigma-Aldrich, used as received and diluted in dry toluene. 4,4'-diaminodiphenylmethane (MDA, Sigma-Aldrich, ≥ 97 %) was vacuum dried at 40°C and crushed prior to use. 4,4'-diisophenylmethane diisocyanate (MDI, Sigma-Aldrich, ≥ 98 %) was stored in inert atmosphere and crushed prior to use. Ultranox® 626 (U626, bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite, GE Specialty Chemicals) was selected as thermal stabilizer, used at preferred percentage of 0.3 wt.% and vacuum dried at 30 °C prior to use. Chloroform (Chem-Laboratory, 99.8%) and methanol (Chem-Laboratory, 99.8%) were analytical reagent (AR) grade and used as received.

Instruments and equipment

^{1}H NMR spectra were collected in CDCl3 solution on a Bruker AMX-300 apparatus. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q2000 apparatus from T.A. Instruments under nitrogen flow (Heat/cool/heat procedure: heating rate 10°C/min, cooling rate 20°C/min). First heating run was considered to erase thermal history of all samples. Glass transition temperatures (Tg), melting temperatures (Tm) and their corresponding enthalpies (Hm) were thereby acquired from the second heating run. To determine molecular weights of PLA, size exclusion chromatography (SEC) was performed in THF at 35°C using a Agilent liquid chromatograph equipped with a Agilent G322A degasser, an isocratic HPLC pump G1310A (flow rate = 1 mL/min), a Agilent autosampler G1329A (loop volume = 100 µL, solution conc. = 1 mg/mL), a Agilent-DRI refractive index detector G1362A and three columns: a PL gel 10 µm guard column and two PL gel Mixed-D 5µm columns (linear columns for separation of MWPS ranging from 600 to 106 g/mol). Polystyrene standards were used for calibration. The Mark-Houwink parameters used were as follows:

K = 0.4055 and a = 1.048 within $[\eta]_{PS}=\kappa\times[\eta]_{PLA}$[a]

Synthesis by multi-step process

a α,ω-dihydroxyl polylactide by Ring-Opening Polymerization

PL(D)LA macrodiols with a targeted number average molecular weight of 10,000 g/mol were synthesized by ring-opening polymerization (ROP) of L(D)-LA in bulk. The reaction was performed in a 2 L double-walled glass reactor equipped with an argon inlet and mechanical stirrer. For the synthesis, 1750 g L(D)-LA (12.15 mol, MM=144 g/mol, 70 eq.), 34.42 g MDA (0.1736 mol, MM=198.26 g/mol,1 eq.) and 5.25 g U626 (0.3 wt %) were charged in the reactor and stirred at 160 °C under argon until the complete melting of monomer. Then, 5 ml of Sn(Oct)2/PPh3 (1:1 molar ratio, 0.54 mol/L) solution in dry toluene were added via a syringe for an initial [LA]0/[Sn(Oct)2]0 molar ratio of 4,500. The polymerization was performed under gentle stirring (50 rpm) under inert atmosphere for 10 min at 180 °C. The viscous reaction medium was then transferred to a rectangular stainless steel and let cool down to room temperature (r.t.). In order to determine the monomer conversion, the polymer was dissolved in chloroform and precipitated in 7 fold (v/v) excess of cold methanol (non-solvent of PLA and good solvent of the LA monomer). The white precipitate was recovered by filtering and drying to constant weight at 40 °C under reduced pressure overnight. Yield ~ 98 %.

For SEC characterizations, the polymer was dissolved in chloroform and washed once with 0.1 M hydrochloric acid solution, then twice with demineralized water for the catalyst extraction, and precipitated in 7 fold (v/v) excess of cold heptane. The white precipitate was recovered by filtering and drying to constant weight at 40 °C under reduced pressure overnight.

^{1}H NMR (300 MHz, CDCl3, r.t.,δ): 1.50-1.70 (d, 3H, –OCH(CH3)C(O)– from lactide repeating unit), 3.9 (s, 2H, –PhCH2Ph– from inserted MDA), 4.35 (q, 1H, HOCH(CH3)C(O)– from lactide repeating unit), 5.16 (q, 1H, –OCH(CH3)C(O)– from lactide repeating unit), 5.33 (q, 1H, –OCH(CH3)C(O)NH– from last lactide repeating unit), 7.1 and 7.6 (d, Ar H from inserted MDA), and 7.92 (s, 1H,–C(O)NHPh– from inserted MDA).

Chain extension and stereocomplexation

L and D enantiomers were introduced into two separate twin-screw corotating extruders, Leistriz TZSE18-HP with a screw

diameter of 18 and a L/D ratio of 50 or 40 (see Supporting Information). Within the extruder with the L/D of 40, all the following components were reduced in powder and introduced by a weight feeder: 500 g PDLA (0.05 mol, Mn SEC = 9,800 g/mol), 25.5 g MDI (0.1 mol, MM= 250.26 g/mol, [NCO]/[OHPLA+NH2]=1.2), 6.7 g MDA (0.03 mol, MM=198.26 g/mol, PLA/MDA= 60/40 mol%) and 1.5 g U626 (0.3 wt%). The temperature profile was 140/160/200/230/230/235/235/235 from the feed throat to the connection with the other extruder. Within the extruder with the L/D of 50, all the following components were reduced in powder and introduced by a weight feeder: 500 g PLLA (0.05 mol, Mn SEC = 9,300 g/mol), 26.9 g MDI (0.11 mol, MM= 250.26 g/mol, [NCO]/[OHPLA+NH2]=1.2), 7.1 g MDA (0.04 mol, MM=198.26 g/mol, PLA/MDA= 60/40 mol%) and 1.5 g U626 (0.3 wt%). The temperature profile was 140/170/170/200/230/230/230/230/230/230 from the feed throat to the die. The feed rate of both extruders was set at 300 g/h and the screws speed varied from 75 to 150 rpm. Accordingly, the melt temperature measured at the die was successively 237, 242 and 247 °C.

b. Synthesis in continuous process: ROP, chain extension, stereocomplexation

In the continuous process, pre-polymerization of L- and D-lactide was performed in a reactor (90% conversion) prior to introduction in Leistritz L/D 50 for the L-lactide pre-polymer and Leistritz L/D 40 for the D-lactide pre-polymer without any more addition of catalytic solution. The extruder was connected in T-shape in zone 5 of the Leistritz L/D 50. The temperature profile was 50/80/200/210/220/230/235/235 from the feed throat for the Leistritz L/D 40. For the temperature profile was 50/80/150/195/240/235/235/235/235/230 from the feed throat to the die. The feed rate of both extruders was set at 800 g/h and the screws speed was 100 rpm. Measured temperature at the die was 242 °C.

According to the feed rate of L-LA and D-LA in the two extruders, a ratio of MDI/MDA is introduced with a gravimetric vibratory feeder via an open port in the Leistritz L/D 50, which corresponds also to the T-shape junction with the Leistritz L/D 40.