Supporting information

ε-Caprolactone was purchased from Fluka and it was distilled under reduced pressure and stored under argon. D,L- lactide was purchased from PURAC biochem (Purasorb DL), recrystallized from toluene and stored under argon. $Ti(OiPr)_4$ and $Ti(OnBu)_4$ were purchased from Sigma Aldrich and used without further purification. Water content of the monomer at different temperatures was determined with a Metrohm 756 KF Coulometer.

In the case of ε-caprolactone polymerizations (runs 1-11), the monomer (4-48 ml) was transferred into a 50 ml beaker which was placed into a custom made aluminium heating block. The monomer was preheated 10 minutes at the polymerization temperature (70, 100 or 140 °C) followed by initiation of polymerization with appropriate amount of tin or titanium based catalyst. In the case of D,L- lactide, the monomer was first melted in a a 50 ml beaker and preheated 10 minutes at 140 °C. After the preheating the catalyst (470 μmol) was added.

Conversions of the monomers were determined by ^1H NMR (Varian Gemini 200 MHz spectrometer) using $CDCl_3$ as solvent. Molar mass and polydispersity of the polymers were determined by GPC equipped with a Waters column set styragel HR (1,2 and 4) and a Waters 2410 Refractive Index Detector. THF was used as an eluent with a flow rate of 0.80 ml/min at 35 °C. A conventional polystyrene calibration was used. Inherent viscosity values were measured with Lauda PVS instrumentation using $CHCl_3$ as solvent. The toxicity examinations were carried out at Nelson Laboratories, USA. The polymerization system for aseptic production of PCL was tested at University of Tampere.