Electronic Supporting Information for

Ring-opening polymerization of bile acid macrocycles by *Candida antarctica* lipase B

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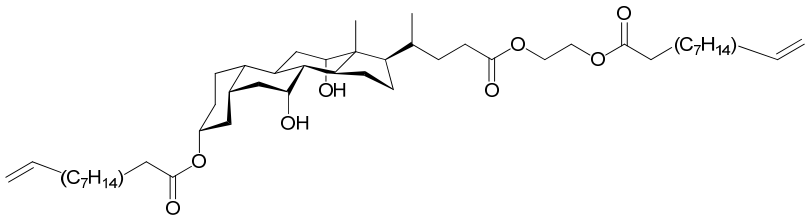
1. Materials and Methods

Cholic acid, ω-undecylenoyl chloride, triethylamine, Grubbs' 1st generation catalyst, ethyl vinyl ether, and *Candida antarctica* lipase B (CALB) immobilized on acrylic resin were purchased from Aldrich, and solvents were purchased from VWR. Diene **P1** (precursor for monomer) was synthesized according to an earlier procedure.[1] Anhydrous and oxygen-free toluene was obtained by passage through solvent purification columns (Glass Contour, Irvine, CA).



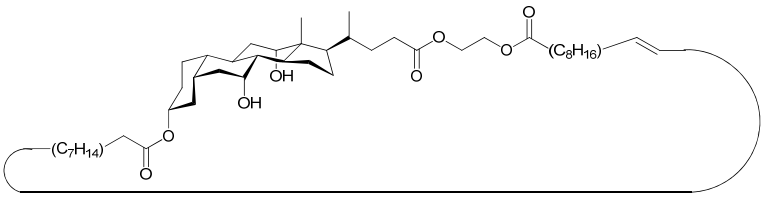
Scheme S1. Structure of the precursor **P1** of monomer **1**

^{1}H NMR spectra were recorded by Bruker AV400 spectrometer operating at 400.13 MHz for proton. FT-IR spectra were recorded on TA Instruments Nicolet 6700 spectrometer equipped with attenuated total reflectance (ATR) accessory. Size exclusion chromatography (SEC) was performed in THF on a Waters system equipped with a 717 plus autosampler, a 1525 Binary HPLC pump, a 2410 refractive index detector, and three Phenomenex columns in series, calibrated with polystyrene standards. Thermogravimetric analyses (TGA) were performed on a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments) under N_2 atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on a TA Q1000 differential scanning calorimeter (TA Instruments) with a heating rate of 10.0 °C·min^{-1}.

Preparation of polymer films was carried out by evaporating concentrated polymer solution in THF (100 mg/mL) in a PTFE mold under atmospheric pressure for 24 h, and then under reduced pressure for another 24 h. Smaller rectangular samples (4.0 x 20 mm) were cut from the films and used for mechanical tests (dimensions of the films were measured with an electronic digital caliper with a precision of 0.01 mm). Dynamic mechanical analyses (DMA) were carried out on DMA 2980 dynamic mechanical analyzer from TA instruments. For controlled force (stress-strain) experiments, a preload force of 0.01 N and a force ramp of 0.1 $N \cdot min^{-1}$ to 18 N were used. Dynamic experiments were performed at 1 Hz, where a preload force of 0.01 N was applied to the sample subjected to the heating rate of 1 $°C \cdot min^{-1}$, and the oscillation amplitude was 10 µm.

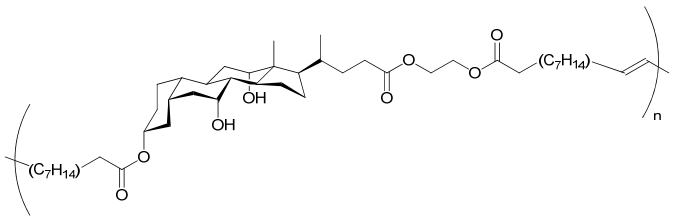
2. Syntheses

2.1. Synthesis of macrocyclic monomer 1



Compound **P1** (3.0 g, 3.89 mmol) was dissolved in freshly distilled and degassed dichloromethane (1.5 L) in a flame-dried three-neck flask (2 L) and heated up to reflux under argon. A solution of 1st generation Grubbs' catalyst (81.2 mg, 0.099 mmol) in 10 mL of freshly distilled and degassed dichloromethane was added by using a syringe, and the mixture was stirred under argon for 5 h. The solution was brought to room temperature and the catalyst was quenched by adding ethyl vinyl ether (2 mL, excess). After 1 h of mixing, dimethyl sulfoxide (0.4 mL) was added to help the Ru removal. After stirring overnight, the solution was concentrated and purified with column chromatography (silica gel, 70/30 hexane/ethyl acetate) to obtain white solid (monomer **1**, 2.4 g, 79%). The ^{1}H NMR assignments of **1** are given in the Notes and References section of the manuscript.

2.2. Polymerizations



Prior to the reaction, resin-immobilized CALB was dried under vacuum at room temperature for 24 h in the presence of P_2O_5. In a typical procedure, monomer **1** (151.5 mg, 0.2 mmol) was dissolved in purified and degassed toluene (0.5 mL) in a flame-dried flask (10 mL). Dried enzyme-containing beads (for example, 7.8 mg, 5 % of the weight of the monomer) were added to the solution, and the flask was sealed with a septum and heated to 80 °C. Stirring was continued for a predetermined reaction time and small aliquots of purified and degassed toluene (0.05 mL) were added to reduce the viscosity of the mixture after 24 h, 48 h and 72 h, when necessary (for 48-h and 96-h reactions). After the reaction, a small quantity of chloroform (10 mL) was added to the reaction mixture to ease the filtration. The solution was filtered to remove the immobilized enzyme and concentrated. The polymer was precipitated in ethanol, dried overnight in vacuum, and purified by reprecipitation. The final product was dried in vacuum at room temperature, yielding white solid. The ^{1}H NMR assignments of the polymer are given in the Notes and References section of the manuscript.

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[1] J. E. Gautrot, and X.X. Zhu, *Macromolecules* 2009, **42**, 7324-7331.