Supporting Information

Topological Behavior Mimicking Ethylene – Hexene Copolymers Using Branched Lactones and Macrolactones

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Experimental Details

Materials. ω-Pentadecalactone (PDL), ε-decalactone (εDL), ε-caprolactone (εCL) and benzyl alcohol (BnOH) (Sigma-Aldrich) were dried over CaH₂ and distilled prior to use. 1,5,7-Triaazabiclyclo[4.4.0]dec-5-ene (TBD), 3,5-di-tert-butyl-2-hydroxybenzaldehyde, N,N-dimethyl-1,2-ethanediamine, diethyl zinc (Sigma-Aldrich) were used without further purification. Dry ethanol (Biosolve) was used as received. Toluene (Sigma-Aldrich) was dried using an engineering drying column. Catalyst 1 was prepared following literature procedures.¹

Typical procedure for PDL homopolymerization. In the glovebox, a glass crimp cap vial was charged with PDL and an equimolar amount of catalyst 1 and benzyl alcohol and the vial was capped. The reaction mixture was removed from the glovebox and stirred for a given time at 100 °C. At the end of the polymerization an aliquot of crude polymer was withdrawn and dissolved in CDCl₃ in order to determine the conversion by ¹H NMR spectroscopy. The rest of the reaction mixture was quenched with acidic methanol and the precipitated polymer was filtered, washed with methanol several times and dried under vacuum for 18 h before characterization.

Typical copolymerization procedure for synthesizing poly(eCL-co-PDL) random copolymers. In a glove box, PDL, εCL, catalyst 1 and an equimolar amount (to catalyst) of BnOH were added to a glass crimp cap vial. The vial was capped, removed from the glove box and heated at 100 °C for the given time (1 to 18 h). An aliquot of crude polymer was removed to determine the monomer conversion. The copolymer was then precipitated in acidified methanol, washed with methanol several times and dried under vacuum for 18 h before characterization.

Typical copolymerization procedure for synthesizing PeCL-block-PPDL copolymers. In the glovebox, a glass crimp cap vial was charged with PDL and an equimolar amount of catalyst 1 and benzyl alcohol after which the vial was capped and placed in oil bath at 100 °C for a predetermined reaction time. At the end of the reaction period, the vial was transferred back into the glovebox and an aliquot was taken for analysis. Subsequently, a calculated amount of εCL was added, the vial was resealed and then placed for an additional predetermined time in an oil bath at 100 °C. At the end of the reaction, again an aliquot was removed and dissolved in CDCl₃ for ¹H NMR and MALDI-ToF-MS analysis. The rest of the reaction mixture was quenched with acidic methanol and the precipitated polymer was filtered, washed with methanol several times and dried under vacuum for 18 h before characterization.

Typical copolymerization procedure for synthesizing PeDL-block-PPDL copolymers. A glass crimp cap vial was charged with PDL, εDL and an equimolar amount of catalyst 1 and benzyl alcohol. All manipulations were carried out in the glovebox. Then, the mixture was removed from the glovebox and stirred in an oil bath at 100 °C. The progress of the reaction was followed...
by $^1$H NMR spectroscopy of aliquots taken at set time intervals. The synthesized copolymer was cooled to room temperature and quenched using acidified methanol, isolated and dried in vacuum at room temperature for 18 h before characterization.

**Characterization**

**Size exclusion chromatography (SEC).** The experiments were performed at 160 °C on a Polymer Laboratories PLXT-20 Rapid GPC Polymer Analysis System (refractive index detector and viscosity detector) with 3 PLgel Olexis (300 × 7.5 mm, Polymer Laboratories) columns in series. 1,2,4-Trichlorobenzene was used as eluent at a flow rate of 1 mL·min⁻¹. The molecular weights were calculated with respect to polyethylene standards (Polymer Laboratories). A Polymer Laboratories PL XT-220 robotic sample handling system was used as autosampler.

**Recycling preparative GPC.** The low molecular weight cyclic material present in the as-synthesized PeDL-block-PPDL sample was removed using recycling preparative GPC (Japan Analytical Industry JAIGEL-2H+2.5H, eluent: chloroform) with a flow rate of 3.0 mL·min⁻¹.

**MALDI-ToF-MS.** Analysis was performed on a Voyager DE-STR from Applied Biosystems equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer samples were dissolved in CHCl₃ at a concentration of 1 mg·mL⁻¹. The cationization agent used was potassium trifluoroacetate (Fluka, > 99%) dissolved in THF at a concentration of 5 mg·mL⁻¹. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg·mL⁻¹. Solutions of matrix, salt, and polymer were mixed in a volume ratio of 4:1:4. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflection mode. All MALDI-ToF-MS spectra were recorded from the crude products.

**DSC analysis.** Melting temperatures ($T_m$) were measured by differential scanning calorimetry (DSC) using a DSC Q100 from TA Instruments. The measurements were carried out at a heating and cooling rate of 10 °C·min⁻¹ from -60 °C to 150 °C. The transitions were deduced from the second heating and cooling curves.

**Liquid-State NMR.** $^1$H NMR and $^{13}$C NMR spectra were recorded at room temperature using a Varian Mercury Vx spectrometer operating at frequencies of 400 MHz and 100.62 MHz for $^1$H and $^{13}$C NMR, respectively. For $^1$H NMR experiments, the spectral width was 6402.0 Hz, acquisition time 1.998 s and the number of recorded scans equal to 64. $^{13}$C NMR spectra were recorded with a spectral width of 24154.6 Hz, an acquisition time of 1.300 s and minimum of 256 scans.

**Solid-State NMR.** Solid-state $^{13}$C($^1$H) Cross-Polarization/Magic-Angle Spinning (CP/MAS) NMR and $^{13}$C($^1$H) Insensitive Nuclei Enhanced by Polarization Transfer (INEPT) experiments were carried out on a Bruker AVANCE-III 500 spectrometer employing a double-resonance H-X probe for rotors with 2.5 mm outside diameter. These experiments utilized a MAS frequency of 25.0 kHz, a 2.5 μs π/2 pulse for $^1$H and $^{13}$C, a CP contact time of 2.0 ms and TPPM decoupling during acquisition. The CP conditions were pre-optimized using L-alanine. The $^{13}$C($^1$H) INEPT spectra were recorded using the refocused-INEPT sequence with a J-evolution period of either 1/3 $J_{CH}$ or 1/6 $J_{CH}$ assuming a $^{1}J_{CH}$ of 150 Hz, i.e. for a J-evolution time of 1/3 $J_{CH}$ the signals from CH and CH$_3$.
groups are positive, while those of CH$_2$ are negative.$^{2,3}$ The 2D $^1$H-$^1$H double quantum-single quantum (DQ-SQ) correlation experiments and DQ build-up experiments were carried out on a Bruker AVANCE-III 700 spectrometer using a 2.5 mm solid-state MAS double-resonance probe. These experiments employed a spinning frequency of 25.0 kHz. DQ excitation and reconversion was performed using the broadband back-to-back (BaBa) sequence.$^4$ Signals for the DQ build-up were normalized compensating site dependent spin relaxation behavior.$^5$ Chemical shifts for $^1$H and $^{13}$C are reported relative to TMS using solid adamantane as an external.$^6$

**X-ray Diffraction.** Analysis of the crystalline structure of the polyesters was performed on as-synthesized samples using wide-angle X-ray scattering measurements by means of a computer-controlled goniometer coupled to a sealed-tube source of CuK$_\alpha$ radiation (Philips), operating at 50 kV and 30 mA. The CuK$_\alpha$ line was filtered using electronic filtering and the usual thin Ni filter. The data were collected at room temperature. The 1D profiles were subsequently background-corrected and normalized. Since reflections from the different crystallographic phases frequently overlap with each other, it was necessary to separate them by deconvolution. Analysis of diffraction profiles of the examined samples and peak deconvolution were performed using WAXSFit software designed by M. Rabiej at the University of Bielsko-Biała (AHT), Poland.$^7$ The software allows to approximate the shape of the peaks with a linear combination of Gauss and Lorentz or Gauss and Cauchy functions and adjusts their settings and magnitudes to the experimental curve with a “genetic” minimizing algorithm.

**Supplementary Figures**

![DSC curves of PPDL, PeCL-block-PPDL and PeDL-block-PPDL representing the second heating run.](image)

**Figure S1.** DSC curves of PPDL, PeCL-block-PPDL and PeDL-block-PPDL representing the second heating run.
**Figure S2.** Liquid-state $^{13}$C NMR spectrum of PeDL-\textit{block}-PPDL (a), poly(eDL-co-eCL) (b) and poly(eCL-co-PDL) (c). The spectra show the C$^1$ and C$^{22}$ of PDL- and eDL-derived nuclei next to the ester groups of the block copolymer as well as the C$^{16}$, C$^{22}$ and C$^1$ of eCL, eDL and PDL nuclei next to the ester groups of the random copolymers. The assignment follows that of Figure 1.

**Figure S2a.** Liquid-state $^{13}$C NMR spectrum of PeCL-\textit{block}-PPDL after randomization experiment using 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) as a transesterification catalyst. The spectrum shows that the blocky structure of the copolymer is preserved. The spectrum of PeCL-\textit{block}-PPDL is compared with the spectra of poly(eCL-co-PDL) where random distribution of PDL and eCL units in the polymer chain is indicated: see PDL-CL, CL-PDL linkages.
**Figure S3.** Left side: section of $^1$H NMR spectra in the range 3.8-5.3 ppm recorded after 5h (a), 14h (b), 24h (c) of eDL and PDL copolymerization. On the right side the spectrum recorded at the reaction time $t=0$ is shown while in the table integration of the signals visible in the spectra are presented.

<table>
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<th>Signal [ppm]</th>
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<th>Spectrum c</th>
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**Figure S4.** Structures of transition states (TS1) for non-branched eCL and branched eDL, and PDL with corresponding TS1 Gibbs free energies with respect to the coordinated complex energies (C1).
**Figure S5.** Section of MALDI-ToF-MS spectrum of PeDL-block-PPDL copolymer synthesized via catalytic ROP of eDL and PDL. The spectrum was recorded with sodium trifluoroacetate as an ionization salt.

**Figure S6.** Section of MALDI-ToF-MS spectrum of PPDL synthesized via catalytic ROP of $\omega$-pentadecalactone. The spectrum was recorded with sodium trifluoroacetate as an ionization salt.
Figure S7. Liquid-state $^{13}$C NMR spectra of random poly(eDL-co-PDL) copolymer. The spectra show the $C_1$ and $C_{22}$ resonances of PDL and eDL repeating units as well as the resonances of the linkages between PDL-eDL and eDL-PDL. The presence of pronounced signals corresponding to PDL-eDL at 64.45 ppm and eDL-PDL at 73.75 ppm clearly indicates randomization of the block copolymer. The assignment follows that of Figure 1.

Figure S8. X-ray powder diffraction profiles of the PDL-based polyesters. 1: PPDL, 2: PeCL-block-PPDL, 3: PeDL-block-PPDL.

Table S1. X-ray diffraction spacings of the homo- and copolyesters.

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<td>001 110 200</td>
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</table>

*1 = PPDL, 2 = PeCL-block-PPDL, 3 = PeCL-block-PPDL
**Figure S9.** 2D $^{13}$C($^1$H) DEPT-45 NMR correlation spectrum of poly(eDL-b-PDL) before recycling preparative GPC recorded at 11.75 T using a spinning frequency of 5.0 kHz. The assignment follows that of Figure 1.

**Figure S10.** $^1$H NMR spectra of PeDL-block-PPDL before (bottom) and after (top) recycling preparative GPC. Both spectra were recorded on Bruker AVANCE-III 850 spectrometer operating at 20.0 T (850.15 MHz for $^1$H).
**Figure S11.** Section of MALDI-ToF-MS spectrum of PeDL-block-PPDL copolymer synthesized via catalytic ROP of eDL and PDL after separation of low molecular weight cyclic material by recycling preparative GPC – the spectrum is silent indicating the absence of cyclic PPDL and that PeDL-block-PPDL is of relatively high molecular weight.

**Figure S12.** 2D $^{1}$H-$^{1}$H DQ-SQ correlation spectra and relaxation-normalized $^{1}$H-$^{1}$H DQ build-up curves for PeDL-block-PPDL (a) before and (b) after GPC purification

**References**