Supporting Information

Poly(L-lactide-co-ε-caprolactone)-matrix composites produced in one step by *in situ* polymerization in TP-RTM

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Experiment details

1. Materials and storage

L-lactide (L-LA) monomer (assay > 99.5 % and water content < 0.02 %) provided by Purac Biochem (Netherlands) was stored into a glove-box to avoid moisture and used as received. ε-caprolactone (ε-CL) monomer (assay = 99% and water content < 0.02 %) and tin (II) 2-ethylhexanoate ($Sn(Oct)_2$) (assay = 97.6 %) were both obtained from AlfaAesar (USA) and used without further purification. Fiber glass fabrics, HexForce® E GLASS FABRIC 01113 1250 TF970 (390 g/m^2) supplied by Hexcel (USA) were dried at 100°C for 24 h prior use.

2. TP-RTM equipment

A single component TP-RTM machine (CIJECT III) and the mold were supplied by DIATEX (France). The mold with dimensions of 120x 120x 5 mm was used under press and pre-prepared with a release agent Zyvax® supplied by ChemTrend (France) in order to facilitate the demolding step.

3. Samples preparation

The plate-shaped composites were prepared by *in-situ* (co-)polymerization of the monomer(s) with the use of TP-RTM machine. Ten layers of pre-dried glass fabric were placed into the mold for each experiment. The monomers L-LA, ε-CL and the catalyst $Sn(Oct)_2$ were put into the TP-RTM tank under dynamic vacuum (-0.5 bar), pre-heated at 150°C during 30 minutes to enable the melting of L-LA. The reactive system was then injected through PTFE tubes (4x 6 mm) into the mold with pre-disposed glass fabric using a nitrogen flow. Once the mold was completely filled, the PTFE tubes were clamped with a steel clamp. The mold was kept under pressure during 5 h at 185°C to enable the (co-)polymerization reaction. After 5 h, the plates were cooled to room temperature and the plates demolded.

1.1.4. ^{1}H NMR experiments

The ^{1}H NMR spectra of the copolymers were recorded in a Bruker Avance at 300 MHz at 300K using 5 mm O.D sample tubes. The samples (5 – 15 mg) were dissolved in 0.5 mL of deuterated chloroform ($CDCl_3$) supplied by Sigma Aldrich (assay > 99.8 %). Experimental conditions were as follows: 32 scans, 4 s delay time, 5.24 s acquisition time and spectral width 6250 Hz. The conversion of the reaction was determined by the integration of PLLA and PCL signals and their respective residual monomers. In the ^{1}H NMR spectra, the quadruplet splitting peak centered at 5.16 ppm comes from methine group (– CH) of PLLA and the quadruplet splitting peak centered at 5.03 ppm corresponds to methine group of L-LA.[1] The triplet splitting peak at 4.06 ppm comes from the methylene group (– CH_2) of PCL and the triplet splitting peak at 4.23 corresponds to methylene group of ε-CL.[2] The integration peaks in the ^{1}H NMR spectra were also used to determine the microstructural magnitude of the copolymers.[3] The chemical shifts of CL – CL, LA – CL and LA – LA dyads are summarized below :

Dyad	Group	Multiplicity	Chemical shift (δ)
CL – CL	ε methylene	Triplet	4.06
LA – CL		Heptet	4.11
LA – LA	methine	Quadruplet	5.16

5. Size Exclusion Chromatography

The number–average molar masses and dispersities of the polylactides matrices synthesized by RTM process were determined by size exclusion chromatography in $CHCl_3$ at 22 °C with a triple detection system, equipped with a multiangle light scattering detector (Wyatt TREOS), and a refractive index detector (schimadzu RID 10A). The SEC system was equipped with three PL gel MIXED C (300 x 7,5 mm polystyrène/divinylbenzène) columns from Aligent. The MALS method was used to determine the absolute molar masses of the PLA. The dn/dc used

for PLA in chloroform is 0.023. Samples were prepared by dissolving the product (2-5 mg) in 1 mL of $CHCl_3$. The solutions were put under stirring for one night, and then filtered with 0.45 µm filters. See chromatograms of runs 1-6 of table 1 in the article as figures S1 to S6.

6. Thermogravimetric analysis

The thermal stability of the PLLA and PLCL matrices was investigated by thermogravimetric analysis, using a TGA instrument (TA Instruments). All analysis was conducted under nitrogen atmosphere from 20 °C to 800 °C at a heating rate 10 °C min^{-1}.

7. Thermal properties

The thermal properties of PLLA and PCL matrices in the absence of fibers were determined on a differential scanning calorimetry (DSC) (TA Instruments). At the first scan, samples of 5 – 10 mg were cooled at - 80 °C and heated to 200 °C at 10 °C.min^{-1}. The enthalpy of fusion (ΔH_f), the melting temperature (T_m), and the enthalpy of crystallization (ΔH_c) were obtained from the first scan. The second scan was made from -80 °C to 200°C at 10 °C.min^{-1} (cooling and heating rate) to determine glass transition temperature (T_g). The degree of crystallinity (X_c) was calculated using Equation 1.

$$X_c = \frac{100\ (\Delta H_f - \Delta H_c)}{\Delta H_f^0 . w} \quad \text{Equation 1}$$

where $\Delta H_f^0 = 93$ J is the enthalpy of fusion of 100 % crystalline PLLA and *w* is the lactide mass fraction in the copolymer.[1]

1. E. W. Fischer , Hans J. Sterzel, G. Wegner. Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Kolloid-Zeitschrift und Zeitschrift für Polym.* **1973**, *251*, 980–990.

8. Impact properties

Impact test specimens were obtained from the plaques by means of water assisted cutting. Rectangular specimens, of 80 mm length, 15 mm width and 5 mm thick were tested for each composition on the basis of the ISO 179-1 standard. Un-notched Charpy tests are carried out following using a 50 J hammer on a CEAST 9050 Charpy impact tester (instron). The average values of notched Charpy impact energy are obtained from each group of six specimens.

Table S1. Copolymerization experiments of L-LA / ε-CL with $Sn(Oct)_2$ in bulk at small scale.[a]

Run	[L-LA] / [ε-CL]	t (h)	Conversion PLLA / PCL (%)	M_n ($g.mol^{-1}$)	*Đ*
1	30 / 70	2	94 / 73	41400	1.83
2	30 / 70	5	99 / 85	40620	1.90
3	40 / 60	2	75 / 60	44830	1.74
4	40 / 60	5	99 / 88	48120	1.71

[a] Experimental conditions: T=150°C, $Sn(Oct)_2$ as catalyst, m(L-LA + ε-CL) = 1 g, [L-LA + ε-CL] / [Sn] = 2000. [b] Determined by ^1H NMR in $CDCl_3$. [c] M_n measured by SEC in THF at 22°C with RI detector, M_n corrected with Mark-Houwink coefficient for PLLA of 0.58.

Chromatograms (SEC in chloroform, 22°C, absolute M_n)

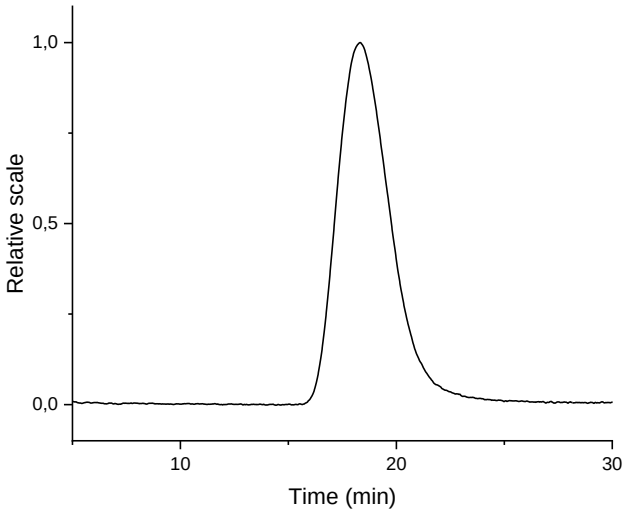

Figure S1. Poly(L-Lactide), M_n = 87980 g.mol^{-1}, $Đ$ = 1.37 (Table 1, run 1)

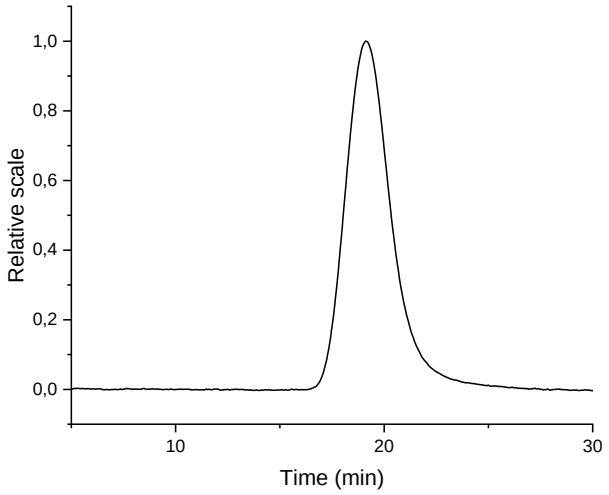

Figure S2. Poly(L-Lactide-co-ε-caprolactone), 10 wt % ε-CL, M_n = 71100 g.mol^{-1}, $Đ$ = 1.27 (Table 1, run 2)

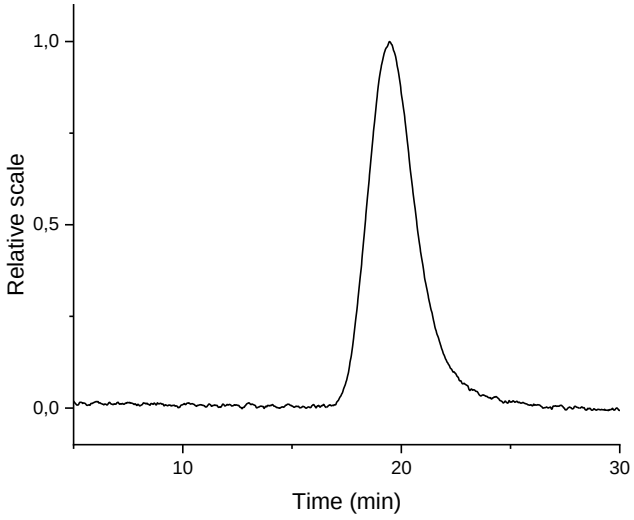

Figure S3. Poly(L-Lactide-co-ε-caprolactone), 20 wt% ε-CL, M_n = 43200 g.mol^{-1}, $Đ$ = 1.42

(Table 1, run 3)

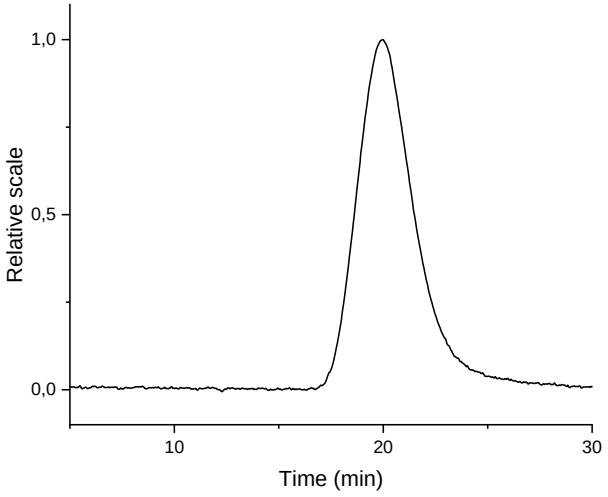

Figure S4. Poly(L-Lactide-co-ε-caprolactone), 20 wt% ε-CL, M_n = 52200 g.mol^{-1}, $Đ$ = 1.32

(Table 1, run 5)

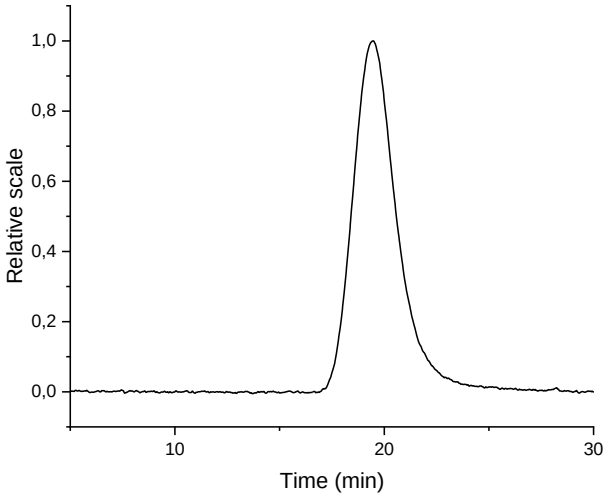

Figure S5. Poly(L-Lactide-co-ε-caprolactone), 30 wt% ε-CL, M_n = 53230 g.mol^{-1}, $Đ$ = 1.34 (Table 1, run 6)