“Like Recycles Like”: Selective Ring-Closing Depolymerization of Poly(L-Lactic Acid) to L-Lactide

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Supporting Information

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Experimental section

Materials

L-Lactide (LLA, Boehringer-Ingelheim), purified through recrystallization in toluene (Fischer Scientific, > 99.8%), was used to synthesize poly(L-lactic acid) (PLLA), and all polymerizations were performed with benzyl alcohol (BnOH, Sigma–Aldrich, anhydrous, 99.8%, stored over molecular sieves) as the initiator. Tin(II) 2-ethylhexanoate (Sn(Oct)2, Sigma–Aldrich, 92.5-100%, stored over molecular sieves), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Sigma–Aldrich, > 99.0%) and 1,5,7-triazabicyclodec-5-ene (TBD, Sigma–Aldrich, 98%) were used as catalysts for polymerization and/or depolymerization reactions. N,N-Dimethylformamide (DMF, Sigma–Aldrich, anhydrous, 99.8%), γ-valerolactone (GVL, Sigma–Aldrich, ReagentPlus, 99%, stored over molecular sieves), dimethyl sulfoxide (DMSO, VWR Chemicals, anhydrous), acetone (VWR Chemicals, technical grade, > 99%, stored over molecular sieves), toluene (PhMe, Sigma–Aldrich, anhydrous, 99.8%), chloroform (CHCl3, Fisher Scientific, analytical reagent grade, > 99.8%, stored over molecular sieves), 1,4-dioxane (DX, Sigma–Aldrich, anhydrous, 99.8%) and chlorobenzene (PhCl, Fluka Chemika, > 98%, stored over molecular sieves) were used as solvents in the depolymerization experiments. For the end capping experiment, a cetyl chloride (Acros Organics, >99%), triethylamine (Sigma Aldrich, >99.5%) and dichloromethane (CH2Cl2, Sigma–Aldrich, anhydrous, >99.8%) were used without further purification. Chloroform (CHCl3, Fisher Scientific, analytical reagent grade, > 99.8%), heptane (VWR Chemicals, 99.8%) and methanol (VWR Chemicals, technical grade, > 98.5%) were used for purification of synthesized PLLA through precipitation. For all NMR analyses, deuterated chloroform (CDCl3, VWR Chemicals, 99.8%) was used as the solvent, and CHCl3 was used as the internal reference. Poly(lactic acid) (PLA) Ingeo™ Biopolymer 4043D (NatureWorks, DLA content: 3-5%) was included as commercial grade PLA. The PLA arrived as granules, which were grinded to finer particles during cooling by liquid nitrogen (Supporting Fig. 2) prior to depolymerization. Pieces of postconsumer plastic of PLA, polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET) and polycarbonate (PC) (Supporting Fig. 10) and pellets of polyamide 6.6 (PA6.6, Sigma Aldrich) represented a mixed plastic waste stream.

Polymerization of LLA

Synthesis of PLLA

PLLA was synthesized in bulk by varying the ratio of initiator (BnOH) to monomer (LLA) to target different molecular weights (Supporting Table 1.1). As an example of the general procedure, LLA (20.0 g, 0.139 mol) was added to a round-bottom flask together with BnOH (0.150 g, 0.00139 mol) and Sn(Oct)2 (0.563 g, 0.00139 mol) as catalysts. ROP was carried out under a N2 atmosphere at 100 °C for 1 h, after which the reaction was quenched by cooling. The polymer was dissolved in CHCl3 and precipitated in a mixture of cold heptane and methanol (10 mol% methanol). The precipitation was repeated four times to remove Sn(Oct)2 and unreacted monomers. The purified polymer was dried in a fume hood overnight and thereafter under vacuum (4 days at room temperature and 2 days at 60 °C). The polymer was stored in a glove box under a N2 atmosphere.

End capping of PLLA

PLLA (Mn,SEC = 14.1 kDa, D = 1.13; Supporting Table 1.1) (1.0 g, 0.42 mmol -OH end groups) was added to a 25 mL round bottom flask equipped with a magnetic stirrer together with CH2Cl2 (10 mL) and triethylamine (290 μL, 2.1 mmol). Acetyl chloride (75 μL, 1.1 mmol) was added dropwise under stirring. The flask was kept under a N2 atmosphere, and the reaction was let to proceed for 1 h at RT (Supporting Figure 6). The solution was washed with HClaq (10 mL, 0.5 M) followed by water (10 mL) and brine (3x10 mL). CH2Cl2 was removed on the rotary evaporator followed by drying under vacuum for 2 days.
Calculation of polymerization thermodynamic parameters

To calculate the thermodynamic parameters ($\Delta H_p$ and $\Delta S_p$) of LLA polymerization in different solvents (DMF, GVL, DMSO and PhCl), polymerization was carried out in solution ($[M]_0 = 0.5$ M LLA) at four different temperatures per solvent. As a general procedure, LLA (0.144 g, 1.00 mmol) was added to a 10 mL flask equipped with a magnetic stirrer together with BnOH (0.1 mL of 1 mM DMF stock solution, 0.01 mmol) and 1.7 mL of DMF (Supporting Table 3). The preparation of the reaction vessel was performed inside a glove box under a N$_2$ atmosphere. The vial was sealed with an aluminum/Teflon crimp cap with a rubber septum before being transferred out of the glove box into the open laboratory. The vial was immersed in a preheated oil bath, and the reaction was started by adding DBU (0.2 mL of 0.5 M DMF stock solution, 0.1 mmol) through the septum with a syringe. Aliquots of 0.1 mL were removed through the septum at regular time intervals, quenched by cooling in 0.6 mL of CDCl$_3$, and analyzed by $^1$H NMR spectroscopy. The reaction was allowed to proceed until an equilibrium monomer concentration was established. This process was repeated at four different temperatures, and the equilibrium monomer concentration $[M]_\text{eq}$ was recorded. Thus, $\Delta H_p$ and $\Delta S_p$ were determined via linear regression of $R^*\ln([M]_\text{eq}/[M]_0)$ as a function of $1/T$ (Supporting Note 2).

Depolymerization of PLA

Six different polymers with varying molecular weights were utilized for depolymerization experiments. Four polymers were synthesized as described above, while the fifth was commercial grade PLA (PLA Ingeo™ Biopolymer 4043D, NatureWorks) (Supporting Fig. 1). The fifth polymer was end capped as described above. All polymers were used as crushed powders (Supporting Fig. 2).

The solvent, polymer concentration, catalyst, catalyst concentration and temperature were varied to explore the effect on the depolymerization and side reactions. In general, PLLA (0.072 g or 0.144 g; 0.5 or 1.0 mmol) was added to a 10 mL flask equipped with a magnetic stirrer together with catalyst (1-10 mol %; Sn(Oct)$_2$, DBU or TBD) and 2.0 mL of solvent (DMF, GVL, DMSO, PhCl, DX, acetone, CHCl$_3$ or PhMe), resulting in a concentration of 0.5 M (based on the LLA repeating unit). The preparation was performed inside a glove box under a N$_2$ atmosphere. The vial was sealed with an aluminum/Teflon crimp cap with a rubber septum before being transferred out of the glove box. The vial was quickly heated with a heating gun to obtain a homogenous solution directly before it was immersed in a thermostatic oil bath (65 °C, 140 °C 160 °C or 180 °C). Aliquots of 0.1 mL were removed through the septum at regular time intervals, quenched by cooling in 0.6 mL of CDCl$_3$, and analysed by $^1$H NMR spectroscopy without further purification.

For depolymerization in a mixed plastic waste stream, pieces of postconsumer plastic composed of PE, PP, PET and PC (Supporting Fig. 10) and pellets of PA6.6 were used. The experiments were performed with both PLLA ($M_n = 14,000$ g mol$^{-1}$, $D = 1.13$) and with pieces cut from a PLA cup (Supporting Figure 10). The mixed plastics were added to DMF (0.5 PLLA/PLA based on the LL/LA repeating unit). After depolymerization the insoluble plastic pieces were separated from the solution by filtration. The pieces were photographed before and after the reaction (Figure 3c, Supporting Figure 10).

Repolymerization of LA

Direct repolymerization

PLLA ($M_{n,SEC} = 14.1$ kDa, $D = 1.13$; Supporting Table 1.1) was depolymerized in DMF (0.5 M based on the LLA repeating unit) at 140 °C (details described above). 10 mol% TBD was added directly to the reaction mixture. The polymerization was performed at RT, and aliquots were withdrawn at regular time intervals, quenched by acetic acid, and analyzed by $^1$H NMR spectroscopy without further purification.

Isolation and repolymerization of LA

PLA (3.60 g, 25.0 mmol; Ingeo™ Biopolymer 4043D, NatureWorks, $M_n = 110$ kDa, $D = 2.02$; Supporting Figure 1) was depolymerized in DMF (50 mL) with Sn(Oct)$_2$ (1.01g, 2.50 mmol) at 140 °C. The sample was
concentrated from 0.5 M to 3 M LLA by distillation of DMF at 25 °C under dynamic vacuum (0.2-0.3 mbar) for 10 h. Thereafter, 50 mL of n-heptane was added and distilled off at 25 °C. This was repeated four times until a thick viscous slurry was obtained. LA was recrystallized from the slurry in toluene, and the crystals were dried under vacuum overnight. ROP of recycled LA was performed as described above (details in Supporting Table 1.5). The crude polymer was analysed by ¹H NMR and SEC without further purification (Supporting Figure 1).

**Characterization**

*Nuclear magnetic resonance (NMR) spectroscopy*

¹H NMR spectra were recorded on a Bruker Avance III HD (400 MHz) spectrometer. All experiments were performed at RT with CDCl₃ as the solvent and with CHCl₃ as the internal reference.

*Size exclusion chromatography (SEC)*

Molecular weight analysis via SEC was performed on a Malvern GPCMAX instrument equipped with an autosampler, a PLgel 5 μm guard column (7.5 x 50 mm) and two PLgel 5 μm MIXED-D (300 x 7.5 mm) columns. The polymer sample (4-5 mg mL⁻¹) was dissolved in chloroform containing 2% v/v toluene, which also was used as eluent. The flow rate was 0.5 mL min⁻¹, and the temperature was kept at 35 °C. Narrow disperse polystyrene standards with molecular weights in the range of 1,200-400,000 g mol⁻¹ were used for calibration.

*Molecular dynamics (MD) simulations*

All MD simulations were performed using GROMACS¹¹ version 2020.2 using a stochastic integration algorithm² with a basic time step of 2 fs. Nonbonded interactions were cut off at 1.2 nm and shifted to ensure zero potential at the boundary. Electrostatic interactions were treated with PME³,⁴ using a real-space cutoff of 1.2 nm. Pressure was maintained at 1 atm using a Parrinello-Rahman barostat⁵ and a compressibility of 5·10⁻⁵ bar⁻¹, while temperature was controlled by the integration algorithm. All covalent bonds were constrained to their equilibrium value using P-LINCS.⁶ All simulations employed a replica exchange protocol⁷ using eight temperatures ranging from 323 K to 363 K in steps of 8 K. Exchange between neighboring replicas was attempted every 1000 steps.

The simulations were run on cyclic L-lactide and PLLA oligomers of DP 5 or 6 in different solvents using a fully periodic computational box in the shape of a truncated octahedron with an approximate nearest-image distance of 3.5 nm. The liquid molecules included in the simulations were DMSO, DMF, DX, and PhCl. All compounds were modeled using the general CHARMM force field (CGenFF) version 2.4.0.⁸⁻¹⁰ The liquid densities showed good agreement with the experimental values (Supporting Fig. 11).

Solvation free energies were calculated using Computational Alchemy¹¹ in which solute-solvent interactions were linearly decoupled using a single coupling parameter. The decoupling was performed in 20 discrete steps, where the first ten were used to decouple electrostatic interactions, followed by van der Waals interactions in the remaining steps. Thus, the fully decoupled state corresponds to the gas phase of the solute and the pure liquid state of the solvent. For each value of the coupling parameter, a 2 ns equilibrium simulation was performed during which the derivative of the total potential with respect to the coupling parameter was sampled. This quantity can finally be connected to the free energy difference between the start and end states, ΔGₛ, using Bennett’s acceptance ratio.¹²
Synthesis and characterization of PLA

Supporting Tab. 1. Synthesis of PLLA. Synthesis details and molecular weight analysis.

|   | LLA (g) (mmol) | BnOH (g) (mmol) | Sn(Oct)2 (g) (mmol) | Temp. (°C) | Time (h) | Conv. (%) | Mn,theo^a (kDa) | M_n,NMR^b (kDa) | M_n,SEC^c (kDa) | D^d |
|---|---------------|-----------------|---------------------|------------|----------|-----------|----------------|----------------|----------------|-----|
| 1 | 20.0          | 0.150           | 0.563               | 100        | 1        | 79        | 11.4           | 14.8           | 14.1           | 1.13|
|   | 139           | 1.39            | 1.39                |            |          |           |                |                |                |     |
| 2 | 50.0          | 0.077           | 0.281               | 110        | 15       | 99        | 68.5           | 13.7           | 7.5            | 1.73|
|   | 347           | 0.71            | 0.69                |            |          |           |                |                |                |     |
| 3 | 1.44          | 0.055           | 0.040               | 100        | 1        | 99        | 2.80           | 5.35           | 5.70           | 1.14|
|   | 10.0          | 0.51            | 0.010               |            |          |           |                |                |                |     |
| 4 | 1.44          | 0.108           | 0.041 g             | 100        | 1        | 99        | 1.43           | 2.94           | 2.31           | 1.21|
|   | 10.0          | 1.00            | 0.010               |            |          |           |                |                |                |     |
| 5^d| 0.290         | 0.002           | 0.008               | 100        | 1        | 94        | 13.6           | 15.4           | 17.2           | 1.07|
|   | 2.01          | 0.02            | 0.02                |            |          |           |                |                |                |     |

^a Determined from LLA and BnOH feed and conversion

^b Determined by end-group analysis of ^1^H NMR spectra

^c Determined by CHCl3SEC analysis

^d Repolymerization of recycled LLA

Supporting Fig. 1. Molecular weight data. SEC molecular weight data of commercial grade PLA (Ingeo™ Biopolymer 4043D, NatureWorks) (orange; M_n = 110 kDa, D = 2.02), PLLA synthesised in the lab (green, M_n = 14 kDa, D = 1.13; grey, M_n = 7.5 kDa, D = 1.73; blue, M_n = 5.7 kDa, D = 1.14; yellow, M_n = 2.3 kDa, D = 1.21) and PLA synthesized from recycled LA (purple, M_n = 17 kDa, D = 10.7).
Supporting Fig. 2. PLLA and PLA used for depolymerization. All images show 10 mg of polymer.

Depolymerization of PLLA

Supporting Fig. 3. DMF stability at 140 °C in the presence of Sn(Oct)₂. Due to concerns regarding potential safety hazards linked to the use of DMF in chemical reactions,[13] the stability of DMF under the set reaction conditions was assessed. The figure shows the ¹H NMR spectrum of DMF after 1 h and 3 h at 140 °C in the presence of Sn(Oct)₂ (0.05 M). No changes could be observed in the spectra within this time range.
Supporting Fig. 4. 1H NMR peak assignment. Spectra recorded of sample taken of PLLA (M_n = 14,000, D = 1.13) depolymerization in DMF (0.5 M) at 140 °C after 5 h. Due to the presence of DMF in the solution, the chemical shifts are altered as compared to those found in pure CDCl_3.

Supporting Note 1. Calculation of relative amounts of LLA, DLA meso-LLA and PLLA.

The fraction of meso-LA (b) in the crude lactide mixture was calculated from the integrals of the CH_3 peaks for meso-LA and LLA/DLA:

\[ b = \frac{\int \text{CH}_3(\text{meso-LA})}{\int \text{CH}_3(\text{meso-LA}) + \int \text{CH}_3(\text{LLA/DLA})} \]  

(SE1)

Based on the probability law, the LLA (L) and DLA (D) content in the crude lactide can be calculated from b accordingly:

\[ L = \frac{(1+\sqrt{1-2b})^2}{4} \]  

(SE2)

\[ D = \frac{(1-\sqrt{1-2b})^2}{4} \]  

(SE3)

The total conversion to monomer was calculated from the CH peaks for LLA/DLA and meso-LA/PLLA:

\[ \text{Conversion} = C = \frac{\int \text{CH(LLL/DDL)}}{\int \text{CH(LLL/DDL)} + \int \text{CH(meso-LA/PLLA)}} \]  

(SE4)

Thus, the relative amounts of LLA, DLA, meso-LA, and PLLA presented in Supporting Tab. 1 was calculated accordingly:

\[ \text{LLA \%} = L \times C \times 100 \% \]  

(SE5)

\[ \text{DLA \%} = D \times C \times 100 \% \]  

(SE6)

\[ \text{meso-LA} = b \times C \times 100 \% \]  

(SE7)

\[ \text{PLLA \%} = (1 - C) \times 100 \% \]  

(SE8)
Supporting Tab. 2. Depolymerization kinetics. Depolymerization kinetics and the relative amounts of LLA, DLA, meso-LA, PLA and acrylic acid in DMF, DMSO and GVL. Following parameters were varied: i) PLA and PLLA concentrations; ii) molecular weight; iii) catalyst type iv) catalyst concentration; v) temperature. The DLA content was estimated according to a method based on the law of probability reported elsewhere.[14]

| Reaction | Time (min) | LLA (%) | DLA (%) | meso-LA (%) | PLA (%) | Acrylic acid (%) | Total conv. (%) |
|----------|------------|---------|---------|-------------|---------|-----------------|----------------|
| 1        | 10         | 30.7    | <0.0    | <0.0        | 69.3    | N.D             | 30.7           |
|          | 30         | 70.1    | <0.0    | 0.3         | 29.6    | N.D             | 70.4           |
|          | 60         | 96.1    | <0.0    | 0.7         | 3.9     | N.D             | 95.5           |
|          | 120        | 98.4    | <0.0    | 1.7         | 1.6     | N.D             | 96.8           |
|          | 180        | 93.6    | <0.0    | 2.1         | 1.4     | N.D             | 91.5           |
|          | 240        | 94.4    | <0.0    | 2.8         | 5.6     | N.D             | 91.5           |
|          | 300        | 98.8    | <0.0    | 3.5         | 1.2     | N.D             | 95.2           |
| 2        | 5          | 33.3    | <0.0    | <0.0        | 66.7    | N.D             | 33.3           |
|          | 10         | 64.5    | <0.0    | <0.0        | 35.5    | N.D             | 64.5           |
|          | 30         | 89.2    | <0.0    | 0.3         | 10.8    | N.D             | 89.2           |
|          | 60         | 87.0    | <0.0    | 0.7         | 13.0    | N.D             | 87.0           |
|          | 120        | 92.4    | <0.0    | 1.5         | 7.6     | N.D             | 92.4           |
|          | 180        | 89.3    | <0.0    | 2.2         | 10.7    | N.D             | 89.3           |
| 3        | 2          | 14.8    | <0.0    | <0.0        | 85.2    | N.D             | 14.8           |
|          | 5          | 41.3    | <0.0    | <0.0        | 58.7    | N.D             | 41.3           |
|          | 10         | 69.2    | <0.0    | 0.1         | 30.8    | N.D             | 69.2           |
|          | 30         | 84.5    | <0.0    | 0.4         | 15.5    | N.D             | 84.5           |
|          | 60         | 87.6    | <0.0    | 0.6         | 12.4    | N.D             | 87.6           |
|          | 120        | 84.3    | <0.0    | 1.1         | 15.7    | N.D             | 84.3           |
|          | 180        | 81.7    | <0.0    | 1.7         | 18.3    | N.D             | 81.7           |
| 4        | 10         | 17.9    | <0.0    | 0.4         | 82.1    | N.D             | 17.9           |
|          | 30         | 52.6    | <0.0    | 0.2         | 47.2    | N.D             | 52.8           |
|          | 60         | 78.5    | <0.0    | 0.4         | 21.1    | N.D             | 78.9           |
|          | 120        | 97.2    | <0.0    | 0.9         | 1.9     | N.D             | 98.1           |
|          | 180        | 93.4    | <0.0    | 1.4         | 5.2     | N.D             | 94.8           |
|          | 300        | 92.4    | <0.0    | 2.0         | 5.6     | N.D             | 94.4           |
|          | 420        | 96.0    | <0.0    | 3.0         | 1.0     | N.D             | 99.0           |
| 5        | 10         | 9.8     | <0.0    | <0.0        | 90.2    | N.D             | 9.8            |
|          | 30         | 28.6    | <0.0    | <0.0        | 71.4    | N.D             | 28.6           |
|          | 60         | 58.8    | <0.0    | 0.2         | 41.2    | N.D             | 58.8           |
|          | 120        | 88.9    | <0.0    | 0.7         | 10.4    | N.D             | 89.6           |
|          | 180        | 88.9    | <0.0    | 0.8         | 10.3    | N.D             | 89.7           |
|          | 300        | 95.8    | <0.0    | 1.6         | 2.5     | N.D             | 97.5           |
|          | 420        | 95.8    | <0.0    | 2.2         | 2.0     | N.D             | 98.0           |
| Reaction | Time (min) | LLA (%) | DLA (%) | meso-LA (%) | PLA (%) | Acrylic acid (%) | Total conv. (%) |
|----------|------------|---------|---------|-------------|---------|-----------------|-----------------|
| 6        | 10         | 23.6*   | -       | 1.4         | 75.0    | N.D             | 25.0            |
|          | 30         | 71.9*   | -       | 5.1         | 23.0    | N.D             | 77.0            |
|          | 60         | 89.8*   | -       | 6.1         | 4.2     | N.D             | 95.8            |
|          | 120        | 94.6*   | -       | 7.5         | < 0.0   | N.D             | > 99.9          |
|          | 240        | 93.7*   | -       | 8.9         | < 0.0   | N.D             | > 99.9          |
| 7        | 10         | 19.5    | < 0.0   | < 0.0       | 80.5    | N.D             | 19.5            |
|          | 30         | 57.7    | < 0.0   | < 0.0       | 42.3    | N.D             | 57.7            |
|          | 60         | 79.6    | < 0.0   | 0.3         | 20.0    | N.D             | 80.0            |
|          | 120        | 90.8    | < 0.0   | 1.1         | 8.1     | N.D             | 91.9            |
|          | 180        | 90.6    | < 0.0   | 1.6         | 7.7     | N.D             | 92.3            |
|          | 240        | 93.9    | < 0.0   | 1.9         | 4.3     | N.D             | 95.7            |
|          | 300        | 95.7    | < 0.0   | 2.6         | 1.7     | N.D             | 98.3            |
|          | 360        | 91.9    | < 0.0   | 2.3         | 5.7     | N.D             | 94.3            |
| 8        | 10         | 16.4    | < 0.0   | 0.1         | 83.5    | < 0.0           | 16.5            |
|          | 30         | 46.1    | < 0.0   | 0.8         | 53.0    | < 0.0           | 47.0            |
|          | 60         | 73.2    | < 0.0   | 3.0         | 23.7    | 0.1             | 76.3            |
|          | 120        | 85.7    | 0.1     | 5.7         | 8.3     | 0.1             | 91.7            |
|          | 180        | 88.4    | 0.2     | 7.9         | 3.2     | 0.3             | 96.8            |
|          | 240        | 86.0    | 0.3     | 9.2         | 4.2     | 0.3             | 95.8            |
|          | 300        | 83.4    | 0.5     | 13.2        | 2.5     | 0.3             | 97.5            |
| 9        | 10         | 23.3    | < 0.0   | 0.3         | 76.4    | N.D             | 23.6            |
|          | 30         | 55.3    | < 0.0   | 0.2         | 44.5    | N.D             | 55.5            |
|          | 60         | 76.5    | < 0.0   | 0.6         | 22.9    | N.D             | 77.1            |
|          | 120        | 89.6    | < 0.0   | 1.1         | 9.3     | N.D             | 90.7            |
|          | 180        | 91.1    | < 0.0   | 1.3         | 7.5     | N.D             | 92.5            |
|          | 240        | 91.0    | < 0.0   | 2.0         | 7.0     | N.D             | 93.0            |
| 10       | 1          | 61.6    | 0.9     | 15.0        | 22.4    | N.D             | 77.6            |
|          | 4          | 62.3    | 1.3     | 17.7        | 18.7    | N.D             | 81.3            |
|          | 6          | 63.5    | 1.1     | 16.7        | 18.7    | N.D             | 81.3            |
|          | 8          | 63.4    | 1.1     | 16.7        | 18.8    | N.D             | 81.2            |
|          | 10         | 62.6    | 1.1     | 16.7        | 19.6    | N.D             | 80.4            |
|          | 15         | 62.2    | 1.1     | 16.2        | 20.6    | N.D             | 79.4            |
| 11       | 1          | 52.0    | 1.0     | 14.4        | 32.6    | N.D             | 67.4            |
|          | 4          | 54.2    | 1.0     | 14.6        | 30.2    | N.D             | 69.8            |
|          | 6          | 53.9    | 1.0     | 14.9        | 30.2    | N.D             | 69.8            |
|          | 8          | 55.6    | 1.2     | 16.3        | 26.8    | N.D             | 73.2            |
|          | 10         | 54.8    | 1.2     | 16.0        | 28.0    | N.D             | 72.0            |
|          | 15         | 55.1    | 1.0     | 15.0        | 28.8    | N.D             | 71.2            |
| Reaction | Time (min) | LLA (%) | DLA (%) | meso-LA (%) | PLA (%) | Acrylic acid (%) | Total conv. (%) |
|----------|------------|---------|---------|-------------|---------|-----------------|----------------|
| 12       | 1          | 2.7     | < 0.0   | 0.2         | 97.1    | N.D             | 2.9            |
|          | 2          | 2.8     | < 0.0   | 0.3         | 69.9    | N.D             | 3.1            |
|          | 4          | 2.8     | < 0.0   | 0.4         | 96.8    | N.D             | 3.2            |
|          | 6          | 2.9     | < 0.0   | 0.2         | 96.9    | N.D             | 3.1            |
|          | 8          | 3.2     | < 0.0   | 0.3         | 96.4    | N.D             | 3.6            |
|          | 10         | 3.4     | < 0.0   | 0.4         | 96.2    | N.D             | 3.8            |
|          | 15         | 3.8     | < 0.0   | 0.5         | 95.6    | N.D             | 4.4            |
|          | 120        | 9.1     | 0.1     | 1.8         | 89.0    | N.D             | 11.0           |
|          | 180        | 11.7    | 0.1     | 2.5         | 85.7    | N.D             | 14.3           |
| 13       | 10         | 51.2    | 0.9     | 13.5        | 34.4    | N.D             | 65.6           |
|          | 30         | 54.7    | 1.0     | 14.8        | 29.6    | N.D             | 70.4           |
|          | 60         | 55.0    | 1.0     | 14.5        | 29.5    | N.D             | 70.5           |
|          | 120        | 49.3    | 0.9     | 13.5        | 36.3    | N.D             | 63.7           |
| 14       | 10         | 37.8    | 2.1     | 18.0        | 42.1    | N.D             | 57.9           |
|          | 30         | 44.6    | 1.6     | 16.9        | 36.9    | N.D             | 63.1           |
|          | 60         | 49.1    | 1.9     | 19.3        | 29.7    | N.D             | 70.3           |
|          | 120        | 43.5    | 0.9     | 12.4        | 43.2    | N.D             | 56.8           |
| 15       | 10         | 10.2    | < 0.0   | 0.2         | 89.5    | < 0.0           | 10.5           |
|          | 30         | 30.8    | < 0.0   | 0.4         | 68.8    | < 0.0           | 31.2           |
|          | 60         | 52.9    | < 0.0   | 1.0         | 46.1    | < 0.0           | 53.9           |
|          | 120        | 76.3    | < 0.0   | 3.3         | 20.2    | 0.1             | 79.8           |
|          | 180        | 80.9    | 0.1     | 5.4         | 13.4    | 0.2             | 86.6           |
| 16       | 10         | 15.1    | < 0.0   | 0.1         | 84.8    | < 0.0           | 15.2           |
|          | 30         | 58.7    | < 0.0   | 1.8         | 39.4    | 0.1             | 60.6           |
|          | 60         | 79.7    | 0.1     | 5.2         | 14.6    | 0.4             | 85.4           |
|          | 120        | 77.2    | 0.2     | 7.7         | 13.6    | 1.3             | 86.4           |
| 17       | 1          | 0.6     | < 0.0   | < 0.0       | 99.4    | < 0.0           | 0.6            |
|          | 10         | 25.5    | < 0.0   | 0.3         | 74.2    | 0.3             | 25.8           |
|          | 30         | 74.6    | 0.1     | 4.2         | 20.7    | 4.2             | 79.3           |
|          | 60         | 81.0    | 0.2     | 7.3         | 10.5    | 7.3             | 89.5           |
|          | 120        | 62.1    | 0.1     | 5.9         | 27.4    | 5.9             | 72.6           |
|          | 240        | 76.1    | 0.2     | 7.4         | 15.1    | 7.4             | 84.9           |
| Reaction | Time (min) | LLA (%) | DLA (%) | meso-LA (%) | PLA (%) | Acrylic acid (%) | Total conv. (%) |
|----------|------------|---------|---------|-------------|---------|-----------------|----------------|
| 18       | 10         | 30.1    | < 0.0   | 0.5         | 69.4    | < 0.0           | 30.6           |
|          | 30         | 74.9    | < 0.0   | 3.5         | 20.8    | 0.8             | 79.2           |
|          | 60         | 69.9    | 0.1     | 5.2         | 22.5    | 2.3             | 77.5           |
|          | 120        | 44.3    | 1.5     | 1.5         | 42.2    | 11.9            | 57.8           |
| 19       | 60         | 89.1    | < 0.0   | 0.9         | 10.0    | N.D.            | 90.0           |
|          | 90         | 92.0    | < 0.0   | 1.2         | 6.7     | N.D.            | 93.3           |

*Reaction 6: represents the total amount of LLA+DLA. The DLA content could not be calculated since the polymer contains 3-5 % DLA from the beginning, and equation (SE3) is only valid for depolymerization of pure PLLA.\[14\]

**Supporting Fig. 5. Decrease in molecular weight in relation to polymer conversion.** Data from PLLA ($M_n = 14,000$ g mol$^{-1}$, $D = 1.13$) depolymerization in DMF (0.5 M) at 140 °C with 10 mol% Sn(Oct)$_2$. The molecular weight was determined by end-group analysis of $^1$H NMR spectra.
Supporting Fig. 6. End capping and subsequent depolymerization. a) $^1$H NMR before end capping. PLLA ($M_n = 14,000 \text{ g mol}^{-1}; D = 1.13$) with -OH end group functionality (PLLA-OH). b) $^1$H NMR after end capping. PLLA with -OC(=O)Me end group functionality (PLLA-OC(=O)Me). c) Depolymerization rate in relation to end group functionality. Data from reaction performed in DMF (0.5 M calculated on LLA repeating unit) at 140 °C with 10 mol% Sn(Oct)$_2$. The lower depolymerization rate of PLLA-OC(=O)Me supports that the depolymerization takes place through an “unzipping” mechanism from the OH functional chain end.

Supporting Fig. 7. Direct repolymerization. Depolymerization of PLLA (14,000 g mol$^{-1}$) in DMF (0.5 M calculated on the PLLA repeating unit) at 140 °C, followed by direct repolymerization of crude LLA in DMF by addition of 10 mol% TBD. The polymerization was performed at RT for 24 h. The equilibrium conversion to polymer was 83%, which can be compared to the theoretical equilibrium conversion to polymer at 20 °C (82% at 0.5 M concentration in DMF; calculated from thermodynamic data in Supporting Tab. 3). Hence, the formed LLA is active for ROP and exhibits the same equilibrium behavior as is expected for neat LLA. However, $^1$H NMR end group analysis suggests a new molecular weight of around 3,000 g mol$^{-1}$. 
Supporting Fig. 8. Isolation of recycled LA. 
a) Setup for distillation of DMF. b) DMF recovered after distillation (84% yield). c) Recycled and isolated LA (38% yield). d) $^1H$ NMR of recovered DMF (99.9% purity). e) $^1H$ NMR of recycled and isolated LA (meso-LA content: 3%).
Supporting Fig. 9. Catalytic activity of solvents. To investigate the catalytic activity of the solvents, PLLA ($M_n = 14,000\text{ g mol}^{-1}; \ PDI = 1.13$) dissolved in DMF and DMSO (0.5 M) were heated at 140 °C for at least 2 h. $^1$H NMR revealed no ring-closing depolymerization during this period of time, indicating that the solvents have no catalytic activity toward ring-closing depolymerization at this temperature.

Supporting Fig. 10. PLA recycling in the presence of mixed plastic waste. a) Images of the six post consumer plastics used in the experiment. The PE flask used to contain mustard, the PP boxes cookies and PET bottle hand sanitizer. b) Images of plastic pieces before and after depolymerization.
Polymerization thermodynamics

Supporting Tab. 3. Data for determination of polymerization thermodynamic parameters. All polymerizations were performed at \([M]_0 = 0.5 \text{ M}\), with 10 mol\% DBU as catalyst and monomer:initiator feed ratio \([M]:[I] = 100:1\).

| Solvent | Temperature (°C) | Equilibrium conversion (%) |
|---------|------------------|---------------------------|
| DMF     | 65               | 56.4                      |
| DMF     | 75               | 46.9                      |
| DMF     | 85               | 37.3                      |
| DMF     | 95               | 29.3                      |
| GVL     | 55               | 74.4                      |
| GVL     | 65               | 69.7                      |
| GVL     | 75               | 62.8                      |
| GVL     | 95               | 47.9                      |
| DMSO    | 65               | 39.0                      |
| DMSO    | 75               | 33.1                      |
| DMSO    | 85               | 26.8                      |
| DMSO    | 95               | 21.0                      |
| DX      | 55               | 87.2                      |
| DX      | 65               | 85.3                      |
| DX      | 75               | 82.9                      |
| DX      | 85               | 79.6                      |
| PhCl    | 35               | 98.3                      |
| PhCl    | 65               | 96.7                      |
| PhCl    | 95               | 93.3                      |
| PhCl    | 125              | 89.3                      |

Supporting Note 2. Calculation of polymerization thermodynamic parameters. The Dainton-Ivin\cite{15} equation defines the relationship between polymerization temperature \(T\), \(\Delta H_p\), \(\Delta S_p\), and the monomer equilibrium concentration \([M]_{eq}\), were \(R\) is the gas constant:

\[
T = \frac{\Delta H_p}{\Delta S_p + R \ln[M]_{eq}} \tag{SE9}
\]

Under the assumption that the volume does not change upon polymerization, the relationship can be expressed in terms equilibrium molar fraction \([M]_{eq}/[M]_0\) rather than \([M]_{eq}\):

\[
T = \frac{\Delta H_p}{\Delta S_p + R \ln([M]_{eq}/[M]_0)} \tag{SE10}
\]

The temperature at which \([M]_{eq} = [M]_0\) is defined as the ceiling temperature \(T_c\):

\[
T_c = \frac{\Delta H_p}{\Delta S_p} \tag{SE11}
\]

Further, equation SE10 can be rearranged to:

\[
R \ln([M]_{eq}/[M]_0) = \frac{1}{T} \Delta H_p - \Delta S_p \tag{SE12}
\]
In this form, the Dainton-Ivin equation can be used to calculate $\Delta H_p$ and $\Delta S_p$ via linear regression of $R \ln ([M]_{eq}/[M]_0)$ as a function of $1/T$. The equation can also be rearranged to express the equilibrium molar fraction as a function of $T$ when $\Delta H_p$ and $\Delta S_p$ are known:

$$[M]_{eq}/[M]_0 = e^{\frac{\Delta H_p - \Delta S_p}{RT}}$$  \hspace{1cm} (SE13)

**Supporting Note 3. Polymerization thermodynamics for short linear chains.** Equation SE9 is based on Flory’s assumption that the reactivity of the propagating end becomes independent of molecular weight after a certain macromolecular chain length. Disregarding this assumption, the degree of polymerization $D_P_n$ should be considered. Thus, SE9 can be rewritten accordingly:\(^{[16]}\)

$$T = \frac{\frac{\Delta H_p}{\Delta S_p + R \ln \left(\frac{D_P_n - 1}{D_P_n} [M]_{eq}\right)}$$  \hspace{1cm} (SE14)

Further, the equation can be rearranged to:

$$[M]_{eq} = \frac{D_P_n}{D_P_n - 1} e^{\frac{\Delta H_p - \Delta S_p}{RT}}$$  \hspace{1cm} (SE15)

For long linear chains, the term $(D_P_n - 1)/D_P_n$ will be approaching 1 and can, therefore, be neglected (Flory’s assumption). However, for shorter oligomeric chains (approx. $D_P_n \leq 20$) the effect of $D_P_n$ on the thermodynamic equilibrium between polymer and monomer is noteworthy, and the $[M]_{eq}$ will decrease with decreasing $D_P_n$. This explains the observed decline in conversion of polymer to monomer with decreased feed molecular weight (Supporting Tab. 1.1-1.3).

**Supporting Tab. 4. Relationship between depolymerization behaviour and polymerization thermodynamics.**

All depolymerizations were performed at 65 °C with $[M]_0 = 0.5 \text{ M}$ and 10 mol% DBU as catalyst. The predicted values were calculated from $\Delta H_p$ and $\Delta S_p$ in each solvent according to equation SE13. The experimental values were determined from the $^1H$ NMR $CH$ peaks for LLA/DLA and meso-LA/PLA:

$$[M]_{eq}/[M]_0 = \frac{\int CH(LLLADLA)\text{ peaks for LLA/DLA and meso-LA/PLA}}{\int CH(LLLADLA) + \int CH(\text{meso-LA/PLA})}$$  \hspace{1cm} (SE16).

| Solvent | Experimental $[M]_{eq}/[M]_0$ (%) | Predicted $[M]_{eq}/[M]_0$ (%) |
|---------|-------------------------------|---------------------------------|
| DMF     | 43.5                          | 44.0                            |
| GVL     | 27.0                          | 30.2                            |
| DMSO    | 54.1                          | 60.9                            |
| DX      | 17.3                          | 15.0                            |
| PhCl    | 3.30                          | 3.50                            |
Relationship between solubility parameters and $T_c$

Supporting Note 4. Variation in $T_c$ with different solvents. The ceiling temperature $T_c$ is determined according to equation SE11. We are interested in how $T_c$ varies in solvent A compared to solvent B:

$$\Delta T_c = T_c^A - T_c^B = \frac{\Delta H_p^A}{\Delta S_p^A} - \frac{\Delta H_p^B}{\Delta S_p^B}$$  \hspace{1cm} (SE17)

We can write the free energy of polymerization $\Delta G_p$ hence also $\Delta H_p$ and $\Delta S_p$, as a sum of several contributions – the actual chemical reaction, an ideal part (changes in entropy of mixing), and the direct effects from the solvent (interactions and entropic effects due to restructuring around the monomer/polymer):

$$\Delta G_p = \Delta G_{\text{react}} + \Delta G_{\text{ideal}} + \Delta G_{\text{solv}}$$  \hspace{1cm} (SE18)

$$\Delta T_c = \frac{\Delta H_{\text{react}}^B + \Delta H_{\text{ideal}}^B + \Delta H_{\text{solv}}^B}{\Delta S_{\text{react}}^B + \Delta S_{\text{ideal}}^B + \Delta S_{\text{solv}}^B} - \frac{\Delta H_{\text{react}}^A + \Delta H_{\text{ideal}}^A + \Delta H_{\text{solv}}^A}{\Delta S_{\text{react}}^A + \Delta S_{\text{ideal}}^A + \Delta S_{\text{solv}}^A}$$  \hspace{1cm} (SE19)

All contribution from the chemical reaction and the ideal contribution are solvent independent. Then how about the solvent contribution? The change in free energy of solvation upon polymerization, $\Delta G_{\text{solv}}$, can be written as the difference between the solvation energy of the polymer and the solvation energy of the monomer:

$$\Delta G_{\text{solv}} = \Delta G_{\text{solv}}^P - \Delta G_{\text{solv}}^m$$  \hspace{1cm} (SE20)

The solvation energies of LLA and PLLA were calculated from molecular dynamics (MD) simulations as a function of temperature. Since, $\Delta S_{\text{solv}}$ of both LLA and PLLA are solvent independent (Fig. 7a-b. in article), equation SE19 can be rewritten accordingly, which leads to $T_c$ being proportional to $\Delta G_{\text{solv}}$:

$$\Delta T_c = \frac{\Delta H_{\text{solv}}^B - \Delta H_{\text{solv}}^A}{\Delta S_p} = \frac{\Delta C_{\text{solv}}^B - \Delta C_{\text{solv}}^A}{\Delta S_p} \rightarrow T_c \propto \Delta G_{\text{solv}}$$  \hspace{1cm} (SE21)

This is supported by the experimentally determined $T_c$ that has a linear relationship $\Delta G_{\text{solv}}$ (Fig. 5c. in main article). Thus, MD simulations can be used to predict differences in $T_c$ between different solvents. However, a tool that is simpler than MD simulations would be useful for screening and to predict which solvents might be suitable to promote ring-closing depolymerization.

According to the Ivin-Léonards theory,[17] $\Delta G_p$ can be written as a function of the Flory-Huggins interaction parameter of monomer-solvent, solvent-polymer and monomer-polymer ($\chi_{ms}$, $\chi_{sp}$ and $\chi_{mp}$, $\varphi_m$, $\varphi_p$ and $\varphi_s$ denotes volume fractions of monomer, polymer and solvent; $V_m$ and $V_i$ denotes molar volumes of monomer and solvent):

$$\Delta G_p = RT \left( \ln \varphi_m + 1 + \left( \chi_{ms} - \chi_{sp}(V_m/V_s) \right) \varphi_s + \chi_{mp}(\varphi_p - \varphi_m) \right)$$  \hspace{1cm} (SE22)

Since $\chi_{mp}$ is solvent independent, the solvent effect on the monomer-polymer equilibrium can be summarized in the term:

$$\beta = \chi_{ms} - \chi_{sp}(V_m/V_s)$$  \hspace{1cm} (SE23)

The difference in $\Delta G_p$ between solvent A and B, at a constant $\varphi_m$ can be written accordingly:

$$\Delta G_p^B - \Delta G_p^A = RT(\beta^B - \beta^A)\varphi_s$$  \hspace{1cm} (SE24)

Combining equation SE24 with SE21, it becomes clear that $T_c$ is proportional to $\beta$: 

S17
\[ \Delta T_c = \frac{(\beta_B - \beta_A) \phi_c}{\Delta S_p} \rightarrow T_c \propto \beta \]  
(SE25)

While \( \chi_{ms} \) and \( \chi_{sp} \) have to be determined for each solvent experimentally, the Hildebrand solubility parameters \( \delta_m, \delta_p \) and \( \delta_s \) can easily be obtained from tables or physical data found in literature. In contrast to the Flory-Huggins interaction parameter, which contains both an enthalpic and an entropic contribution, the Hildebrand solubility parameter only counts for the enthalpic contribution. However, MD simulations showed that the differences in solvation entropy between different solvents were neglectable (Fig. 5 a-b. in main article), why the difference in \( T_c \) can be assumed to be an entropic effect alone. Hence, it is likely that the Hildebrand solubility parameter can be used for the purpose of screening and to predict which solvents should be the suitable to promote ring-closing depolymerization:

\[ \chi_{ms} \propto (\delta_m - \delta_s)^2 \text{ and } \chi_{sp} \propto (\delta_s - \delta_p)^2 \rightarrow T_c \propto (\delta_m - \delta_s)^2 \text{ and } (\delta_s - \delta_p)^2 \]  
(SE26)

Supporting Tab. 5. Hansen’s solubility parameters. Physical data and Hansen’s solubility parameters \( \delta \) calculated according to equation SE27. The temperature \( T = 298 \, K \) was used for all calculations, and \( R \) denotes the gas constant:

\[ \delta = \sqrt{\frac{H_{\text{vap}} - RT}{M / \rho}} \]  
(SE27)

| Substance | \( \Delta H_{\text{vap}} \) (kJ·mol\(^{-1}\)) | \( \rho \) (g·mL\(^{-1}\)) | \( M \) (g·mol\(^{-1}\)) | \( \delta \) (MPa\(^{1/2}\)) |
|----------|------------------|-----------------|-----------------|-----------------|
| DMF      | 46.9\(^{[18]}\)  | 0.94\(^{[19]}\) | 73.1            | 24.0            |
| GLV      | 54.8\(^{[18]}\)  | 1.05\(^{[20]}\) | 100.1           | 23.4            |
| DMSO     | 52.9\(^{[18]}\)  | 1.10\(^{[19]}\) | 78.1            | 26.6            |
| DX       | 38.6\(^{[18]}\)  | 1.03\(^{[19]}\) | 88.1            | 20.5            |
| PhCl     | 41.2\(^{[18]}\)  | 1.11\(^{[21]}\) | 112.6           | 19.5            |
| LLA      | 69.3\(^{[22]}\)  | 1.2             | 144.1           | 23.6            |
| PLA      | -                | -               | -               | 20.2\(^{[23]}\) |

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**Supporting Tab. 6. Relationship between solubility parameters and \( T_c \).** Multiple linear regression input and summary of results. The ceiling temperatures \( T_c \) were calculated according to equation SE11, based on values of \( \Delta H_p \) and \( \Delta S_p \) determined via equation SE12. \((\delta_m-\delta_s)^2\) and \((\delta_s-\delta_p)^2\) were calculated from values in Supporting Tab. 5, where the subscripts denote monomer (m), polymer (p) and solvent (s). The multiple linear regression was performed using the data analysis regression function in Microsoft Excel, at a confidence level of 95%.

### INPUT

| Solvent | \( T_c \) (K) | \((\delta_m-\delta_s)^2\) | \((\delta_s-\delta_p)^2\) |
|---------|---------------|---------------------------|---------------------------|
| DMF     | 390.8         | 0.138                     | 14.1                      |
| GVL     | 410.3         | 0.0263                    | 10.4                      |
| DMSO    | 398.9         | 9.03                      | 40.9                      |
| DX      | 550.2         | 9.31                      | 0.113                     |
| PhCl    | 615.3         | 16.4                      | 0.434                     |

### RESULTS

\( R^2 = 0.998 \)

| Coefficient | \( \text{Coefficient} \) | \( \text{P-value} \) |
|-------------|--------------------------|----------------------|
| Intercept   | 444                      | 0.00015              |
| \( x_1 \)   | 10.8                     | 0.00196              |
| \( x_2 \)   | -3.53                    | 0.00318              |

Molecular modelling

**Supporting Fig. 11. Liquid densities as a function of temperature.** Experimental data from Pacak\(^{[24]} \) (DMSO and DMF); Campbell\(^{[25]} \) (DMSO); Brummer\(^{[26]} \) (DMF); Nikam and Kharat\(^{[27]} \) (DMF and Chlorobenzene); Papanastasiou et al.\(^{[28]} \) (DX)
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