

Supplementary Information

Chemical recycling to monomer: thermodynamic and kinetic control of the ring-closing depolymerization of aliphatic polyesters and polycarbonates

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Experimental

Materials

All chemicals were used as received, unless otherwise is described. Trimethylene carbonate (TMC) was synthesised from diethyl carbonate (> 99%, anhydrous, Sigma-Aldrich) and 1,3-propane diol (99% Fisher Scientific), with sodium hydride (NaH, 60% dispersion in mineral oil, Sigma-Aldrich) as catalyst. δ -Valerolactone (δ VL, 99%, Apollo Scientific) was dried and distilled over calcium hydride (CaH_2 , > 90%, Sigma-Aldrich) prior to use. L-lactide (LA, Beohringer-Ingelheim) was purified via recrystallization in toluene (Fischer Scientific, >99.8%) followed by drying under vacuum prior to use. Benzyl alcohol (BnOH, 99.8%, anhydrous, stored over 3 Å molecular sieves) was used as initiator for all ring-opening polymerization (ROP) reactions. The ROP and ring-closing depolymerization (RcDP) reactions were catalysed by either 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98% Sigma-Aldrich), tin(II) 2-ethylhexanoate (SnOct_2 , > 92.5%, Sigma-Aldrich, stored over 3 Å molecular sieves) or diphenyl phosphate (DPP, Sigma-Aldrich, 99%). Reactions catalysed by TBD were quenched with acetic acid (100%, Merck), and reactions catalysed by DPP were quenched with triethylamine (Sigma-Aldrich, >99.5%). Toluene (PhMe, 99.8%, anhydrous, Sigma-Aldrich), 1,4-dioxane (DX, 99.8%, anhydrous, Sigma-Aldrich), γ -valerolactone (GVL, 99%, ReagentPlus, Sigma-Aldrich, stored over 3 Å molecular sieves), *N,N*-dimethylformamide (DMF, 99.8%, anhydrous, Sigma-Aldrich), propylene carbonate (PrC, 99.7%, anhydrous, Sigma-Aldrich), dimethyl sulfoxide (DMSO, VWR Chemicals, anhydrous), chlorobenzene (PhCl, Fluka Chemika, >98%, stored over 3 Å molecular sieves) and dichloromethane (CH_2Cl_2 , > 99.8%, anhydrous, Sigma-Aldrich) were used as solvents for ROP and RcDP.

Synthetic procedures

Monomer synthesis

The synthesis of TMC is described elsewhere.¹

ROP and RcDP reactions

All preparations for ROP and RcDP were done inside a glove box (N_2 atmosphere).

The polymerization thermodynamic parameters (ΔH_p and ΔS_p) of δ VL and TMC in the different solvents were determined through equilibrium ROP at three or four different temperatures per solvent. As a general procedure, δ VL (0.10 g, 1.0 mmol, 1.0 equiv.), BnOH (20 μL of 0.5 M stock solution in GVL, 0.01 mmol, 0.01 equiv.) and GVL (1.9 mL) were added to a head space vial. The vial was sealed with a septum crimp cap and was, thereafter, transferred out of the glove box. The ROP was carried out at 60 °C under stirring in a preheated sand bath, and the reaction was initiated by addition of TBD (0.1 mL of 0.2 M stock solution in GVL stored under N_2 atmosphere, 0.02 mmol, 0.02 equiv.). The reaction was monitored by ^1H NMR of aliquots withdrawn at regular time intervals quenched by addition of acetic acid (2.5 equiv. to TBD).

PTMC was synthesized by ROP of TMC. TMC (1.02 g, 10 mmol, 500 equiv.), BnOH (0.002 g, 0.02 mmol, 1 equiv.), TBD (0.003 g, 0.02 mmol, 1 equiv.) and CH_2Cl_2 (5 mL) was added to a head space vial. The vial was sealed, and the reaction was carried out at room temperature (22 °C) under stirring. The reaction was quenched after 1 h by addition of acetic acid (2.5 equiv. to TBD). The polymer was precipitated in cold methanol and, thereafter, dried under vacuum at RT.

P δ VL was synthesized by ROP of δ DL. δ VL (1.00 g, 10 mmol, 500 equiv.), BnOH (0.002 g, 0.02 mmol, 1 equiv.) and SnOct_2 (0.008 g, 0.02 mmol, 1 equiv.) were added to head space vial. The vial was sealed with a septum crimp cap before it was transferred out of the glove box. The reaction was carried out at 110 °C under

stirring in a preheated sand bath. The reaction was quenched by cooling after in total 6 h. The polymer was dissolved in chloroform, followed by precipitation in cold methanol. The polymer was dried under vacuum at RT.

PLA was synthesized by ROP of LA. LA (20.0 g, 139 mmol, 100 equiv.), BnOH (0.150 g, 1.39 mmol, 1 equiv.) and SnOct₂ (0.563 g, 1.39 mmol, 1 equiv.) was added to a round bottom flask. The flask was sealed with a glass stopper before it was transferred out of the glove box. The reaction was carried out at 100 °C under stirring in a preheated oil bath. The reaction was quenched by cooling after 1 h. The polymer was dissolved in chloroform, followed by precipitation in cold methanol. The polymer was dried under vacuum at RT.

The R_cDP of PδVL, PTMC and PLA was carried out in GVL ($[M]_{0,\delta VL} = [M]_{0,PTMC} = [M]_{0,PLA} = 0.5$ M) at 80-140 °C with either SnOct₂ or DPP as catalyst ([cat] = 0.05 M). As an example of a general procedure, PδVL (0.100 g, 1.00 mmol), PTMC (0.102 g, 1.00 mmol) and PLA (0.144 g, 1.00 mmol) were added to a space cap vial equipped with a magnetic stirrer. SnOct₂ (0.041 g, 0.10 mmol) and GVL (2 mL) were added and the vial was sealed. The vial was transferred out of the glove box, and the reaction was carried out at 140 °C in a preheated sand bath. The reaction was monitored by ¹H NMR of aliquots withdrawn at regular time intervals.

Characterization

Nuclear magnetic resonance (NMR)

A Bruker Advance III HD (400 MHz) spectrometer was used for the recording of all ¹H NMR. The experiments were performed at RT with CDCl₃ as solvent. The signal from residual CHCl₃ (7.26 ppm) was used as internal reference.

Size exclusion chromatography (SEC)

A Malvern GPCMAX instrument was used for molecular weight analysis. The instrument was equipped with a PLgel 5 μm guard column (7.5 x 50 mm) followed by two PLgel 5 μm MIXED-D (300 x 7.5 mm) columns. The analysis was performed at 35 °C in CHCl₃, using narrow dispersity polystyrene standards with molecular weights ranging from 1.20 to 400 kg mol⁻¹.

Polymerization thermodynamics

Table S1. Data for determination of polymerization thermodynamic parameters of δVL . All polymerizations were performed at $[M]_0 = 0.5 M$, with 2 mol% TBD as catalyst and monomer:initiator ratio $[M]:[I] = 100:1$.

Solvent	Temperature (°C)	Equilibrium conversion (%)
DMF	22	35
DMF	30	26
DMF	40	15
GVL	22	31
GVL	40	21
GVL	60	9
DMSO	22	22
DMSO	30	16
DMSO	40	8
DX	22	79
DX	40	69
DX	70	46
DX	80	38
PhMe	40	82
PhMe	60	73
PhMe	70	67
PhMe	80	64

Table S2. Data for determination of polymerization thermodynamic parameters of TMC. All polymerizations were performed at $[M]_0 = 0.5 M$, with 2 mol% TBD as catalyst and monomer:initiator ratio $[M]:[I] = 100:1$.

Solvent	Temperature (°C)	Equilibrium conversion (%)
DMF	60	69
DMF	70	63
DMF	80	61
DMF	90	49
DMSO	60	69
DMSO	70	63
DMSO	80	61
DMSO	90	49
DX	60	97
DX	70	96
DX	80	95
DX	90	93
PhCl	70	96
PhCl	90	94
PhCl	110	92
PhCl	130	90

Solubility parameters

The Hildebrand solubility parameters of the solvents used in this study were calculated from the heat of vaporization ΔH_{vap} ,²

$$\delta = \sqrt{\frac{\Delta H_{\text{vap}} - RT}{V_m}} \quad (\text{S1})$$

where R is the gas constant, T is the temperature and V_m denotes the molar volume. The used values for ΔH_{vap} and the resulting δ are presented in **Table S1**.

Table S3. Heat of vaporization (ΔH_{vap}) and Hildebrand solubility parameters (δ) of solvents.

	DMF	GVL	PrC	DMSO	DX	PhMe	PhCl	THF
ΔH_{vap} (kJ·mol ⁻¹)	46.9	54.8	55.2	52.9	38.6	38.0	41.20	32.5
δ (MPa ^{1/2})	24.0	23.4	24.8	26.6	20.5	18.2	19.5	19.2

Relationship between solubility parameters and T_c

A relationship between the Hildebrand solubility parameters of monomer, solvent and polymer was derived in our previous study (see Supporting Information to reference):³

$$T_c = A(\delta_m - \delta_s)^2 + B(\delta_s - \delta_p)^2 + C \quad (\text{S2})$$

The expression can be expanded and rearranged accordingly:

$$T_c = A\delta_m^2 + A\delta_s^2 - 2A\delta_m\delta_s + B\delta_s^2 + B\delta_p^2 - 2B\delta_s\delta_p + C \quad (\text{S3})$$

$$T_c = (A + B)\delta_s^2 + (-2A\delta_m - 2B\delta_p)\delta_s + A\delta_m^2 + B\delta_p^2 + C \quad (\text{S4})$$

Considering one specific monomer-polymer system, both δ_m and δ_p will be constant. (S4) can therefore be rewritten accordingly (where $a = A + B$; $b = -2A\delta_m - 2B\delta_p$; $c = A\delta_m^2 + B\delta_p^2 + C$):

$$T_c = a\delta_s^2 + b\delta_s + c \quad (\text{S5})$$

References

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3. L. Cederholm, J. Wohlert, P. Olsén, M. Hakkarainen, K. Odellius, *Angew. Chem., Int. Ed.*, 2022, **61**, e202204531.