Supporting information for:

Organocatalyzed ring opening polymerization of regio-isomeric lactones: reactivity and thermodynamics considerations

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List of supplementary information materials:

Experimental part

Figure S6. Formation of macrocyclic structure for the P_4-*t*Bu catalyzed ROP of TMCL with a) GPC traces, b) MALDI-ToF-MS spectrum, and c) details of the MALDI-ToF-MS spectrum with distribution initiated by benzyl alcohol and macrocyclic structures.

Figure S7. Kinetics for the polymerization of TMCL with organophosphorus catalysts at 80 °C, except for bis(pentafluorophenyl) phosphinic acid performed at room temperature a) $\ln([M]_0/[M])$ vs. time (bottom); benzyl alcohol initiator efficiency as determined by GC vs. time (bottom) and b) $M_{n,GPC}$ vs. % conversion (bottom); $Đ$ vs. % conversion (top).

Figure S8. MALDI-ToF analysis for DPP catalyzed ROP of TMCL (Table 1, entry **6**) with a) full MALDI-ToF-MS spectrum, and b) details of the MALDI-ToF-MS spectrum with distribution initiated by benzyl alcohol (• in blue), by water (▪ in red), macrocyclic structures (Δ in black) and some unknown distributions.

Figure S9. Polymerization profiles of TMCL-I and TMCL-II catalyzed by a) DPP (23 °C, $[TMCL]_0$ = 5.29 M), b) P_4-*t*Bu phosphazene (-20 °C, 4 M), and b) TBD (30 °C, 5.29 M).

Figure S10. Amount of TMCL-I in monomer mixture at equilibrium as a function of monomer conversion at equilibrium.

Figure S11. Determination of the thermodynamic parameters of TMCL with a) monomer conversion at equilibrium as a function of the temperature, and b) van 't Hoff analysis.

Table S2. Calculated thermodynamic values for the ring opening of TMCL-I and TMCL-II with methanol in the gas phase (corresponding to Figure 5).

List of atomic coordinates:

TMCL-I (S) with the conformation C
TMCL-I (S) with the conformation B
TMCL-I (S) with the conformation C'
TMCL-I (S) with the conformation B'
TMCL-II (R) with the conformation C
TMCL-II (R) with the conformation B
TMCL-II (R) with the conformation C'
TMCL-II (R) with the conformation B'
Extended methyl ester product from the ring opening of TMCL-I (S) with methanol
Extended methyl ester product from the ring opening of TMCL-II (R) with methanol

References

EXPERIMENTAL SECTION

Chemicals. Anhydrous tetrahydrofuran (THF) was purified using a MBraun SPS-compact solvent purification system. Benzyl alcohol (BnOH; 99%, Alfa Aesar) was distilled over CaH_2 prior to use. *p*-Toluene sulfonic acid (*p*-TSA; <99%, Acros Organic), bis(4-nitrophenyl)phosphate (99%, Sigma-Aldrich), dimethyl phosphate (Aldrich^{CPR}), diphenyl phosphate (DPP) (> 99%, TCI), methyl phosphonic acid (98%, Sigma-Aldrich), phenyl phosphonic acid (98%, Sigma Aldrich), pinacolyl methyl-phosphonate (97%, Sigma-Aldrich), ethyl methyl phosphonate (98%, Sigma Aldrich), *t*-butylphosphonic acid (98%, Sigma Aldrich), diphenyl phosphinic acid (> 98%, Sigma-Aldrich), and dimethyl phosphinic acid (97%, Sigma-Aldrich) were freeze-dried prior to use. Bis(pentafluorophenyl)-phosphinic acid was synthesized from tris-pentafluorophenylphosphine (97%, Sigma Aldrich) following a procedure reported in the literature,[1] and freeze-dried prior to use. 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi(phosphazene) (P_4-*t*-Bu solution at 0.8 M in hexanes, Sigma-Aldrich) was vacuum dried prior to use. Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$; 95%, Sigma-Aldrich), titanium(IV) butoxide (Ti(*n*-BuO_4)); 97%, Sigma-Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; 98%, Sigma-Aldrich), 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene) (P_2-Et phosphazene, > 98 %, Sigma), hexadecane (<99.5%, TCI), $CDCl_3$ (99.8%, Cambridge Isotope Laboratories) and 1,1,2,2-tetrachloroethane-d_2 (99.6%, Cambridge Isotope Laboratories) were used as received.

^{1}H and ^{13}C NMR. NMR spectra were recorded on a Bruker Avance apparatus at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR at ambient probe temperature in $CDCl_3$ or in $C_2D_2Cl_4$. ^{1}H NMR experiments were recorded with 32 scans and ^{13}C NMR experiments were recorded with 1024 scans. Chemical shifts are reported in ppm.

GC-FID. Gas chromatography with flame ion detection (**GC-FID**) measurements were performed on a Shimadzu GC-2010 equipped with a Supelco SPB-1 capillary column (30 m × 0.25 mm × 0.25 µm film thickness) or a SH-RXI-1ms column (30 m × 0.25 mm × 0.25 µm film thickness). The temperature program was as follows: an initial temperature of 80 °C was maintained for 3 min, then increased to 140 °C with a heating rate of 10 °C/min. This temperature was maintained for 1 min, and further increased to 300 °C with a heating rate of 20 °C/min and was maintained at 300 °C for 5 min.

GPC analysis. Gel permeation chromatography (GPC-THF) was performed at 30 °C using a Waters GPC equipped with a Waters 2414 refractive index detector. THF was used as eluent at a flow rate of 1 mL/min. Three linear columns were used (Styragel HR1, Styragel HR4 and Styragel HR5). Molecular masses are given relative to polystyrene standards.

DSC. Differential scanning calorimetry (**DSC**) spectra were recorded on a Netzsch Polyma 2014 DSC. DSC data of the purified polymers was measured with heating/cooling rates of 50 °C/min under a nitrogen flow of 20 mL/min. DSC heating and cooling cycles were performed from -70 °C to 100 °C in duplicates. The glass transition values reported correspond to the second heating cycle.

MALDI-ToF-MS. Matrix-assisted laser desorption/ionization time-of-flight mass spectra were recorded on a Bruker UltrafleXtreme spectrometer with a 355 nm Nd:Yag laser (2 kHz repetition pulse/Smartbeam-II™) and a grounded steel plate. *Trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (Sigma-Aldrich, >98%) was used as matrix (20 mg/mL in THF), potassium trifluoroacetate (Sigma Aldrich, 98%) was used a cationization agent (10 mg/mL in THF). The polymers were dissolved in chloroform (10 mg/mL). Solutions of matrix, salt and polymer were mixed in volumetric ratios of 200:10:30, respectively. All mass spectra were collected in the reflector mode. Poly(ethylene glycol) standards with M_n equal to 5 000, 10 000 and 15 000 g/mol were used for calibration. Data was processed using the FlexAnalysis (Bruker Daltonics) software package.

Synthesis of the mixture of β,δ,δ-trimethyl-ε-caprolactone (TMCL-I) and β,β,δ-trimethyl-ε-caprolactone (TMCL-II) monomer (TMCL). The monomer mixture was synthesized by Baeyer-Villiger oxidation of 3,3,5-timethylcyclohexanone following a modified version of a procedure reported in the literature.[2] 3,3,5-Trimethylcyclohexanone (33.6 g, 0.24 mol, 1 eq) was dissolved in dichloromethane (1.2 L) and 3-chloroperoxybenzoic acid (107.6 g, 0.48 mol, 2 eq) was added in portions within 30 minutes at room temperature. The mixture was left stirring until full conversion was reached (2 days) and the precipitate was removed by filtration. The filtrate was washed with basic aqueous solution at 7 % NaOH (2 × 250 mL) and then with brine (2 × 250 mL). The solvent was removed by evaporation and the lactone was purified and dried by vacuum distillation over CaH_2 (1.10^{-3} mbar, 95-105 °C). TMCL was obtained as a colorless liquid (66 g, 77 % yield). The ^{1}H-NMR and ^{13}C-NMR were similar to what was reported in the literature.[2]

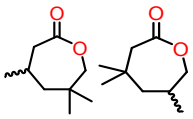
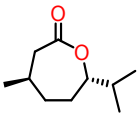
Typical ROP of TMCL. In a vacuum-dried flask, BnOH (20 µL, 0.2 mmol, 1 eq) was added to a mixture of TMCL (1 mL, 5.29 mmol, 30 eq) and hexadecane as internal standard (typically 5 mol % relative to the amount of TMCL). The mixture was left to reach the desired reaction temperature. Polymerizations at room temperature were performed in a water bath. Polymerizations at higher temperature were performed in an oil bath. Polymerizations at -20 and -50°C were performed in a double wall flask and cooled down with a Julabo FP89-HL ultra-low refrigerated-heating circulator. The polymerization was started by adding the catalyst (0.2 mmol, 1 eq) to the reaction mixture via a funnel at the desired temperature under nitrogen atmosphere. Conversion and initiator efficiency were determined by GC-FID. Samples were prepared by dissolving an aliquot of the reaction mixture in chloroform containing either triethylamine for polymerization performed with organoacids or acetic

anhydride for polymerizations performed with organobases and metal-based catalysts, in order to neutralize the catalysts and quench the polymerization. When P_4-*t*Bu phosphazene was employed as catalyst, a mixture consisting of TMCL, BnOH and hexadecane was thermostated at the desired reaction temperature and then added to the dried catalyst to start the polymerization.

Determination of the thermodynamic parameters of TMCL. The polymerization reactions were performed from 25 °C to 170 °C using DPP as catalyst (BnOH 1eq, TMCL 30 eq, DPP 1 eq, hexadecane 5 mol %) as described in the previous paragraph. The reaction was left to react until the equilibrium monomer conversion was reached as monitored by GC-FID.

DFT calculations. Geometry optimization and frequency calculations were performed using a density functional theory (DFT) method with diffusion functions on heavy atoms and polarization functions on hydrogen using the B3-LYP/6-31G (d,p) basis set with the Gaussian 09 and GaussView 05 software package.[3] The substrates and products were optimized to the minimum structure with 0 negative frequency.

Table S1. Thermodynamic properties of TMCL at bulk concentration and at 1 M (extrapolated) as compared to other monomers.

Monomer	$[M]_0$ (mol L^{-1})[a]	State[b]	ΔH_p (kJ mol^{-1})	ΔS_p (J $mol^{-1}K^{-1}$)	T_c (°C)	Ref
 **TMCL**	5.29	l/a	- 9.1	- 15.8	302	This work
	1[b]	s/s	- 9.1	- 29.7	34	This work
 **Menthide**	1[b]	s/s	- 16.8 ± 1.6	- 27.4 ± 4.6	334	[4]
 **ε-caprolactone**	8.7	l/c	- 28.8	- 35.9	530	[5]
	1[b]	s/s	- 28.8	- 53.9	261	[5]
 **δ-valerolactone**	10	l/c	- 12.2	- 9.5	1018	[6]
	1[b]	s/s	- 12.2	- 28.6	153	[6]

[a] The values at 1 M were extrapolated from the values in bulk using the change of entropy as a function of the temperature. [b] State of the monomer/polymer: l liquid monomer, s solid monomer, an amorphous polymer, c semi-crystalline polymer, and s polymer and monomer in solution.

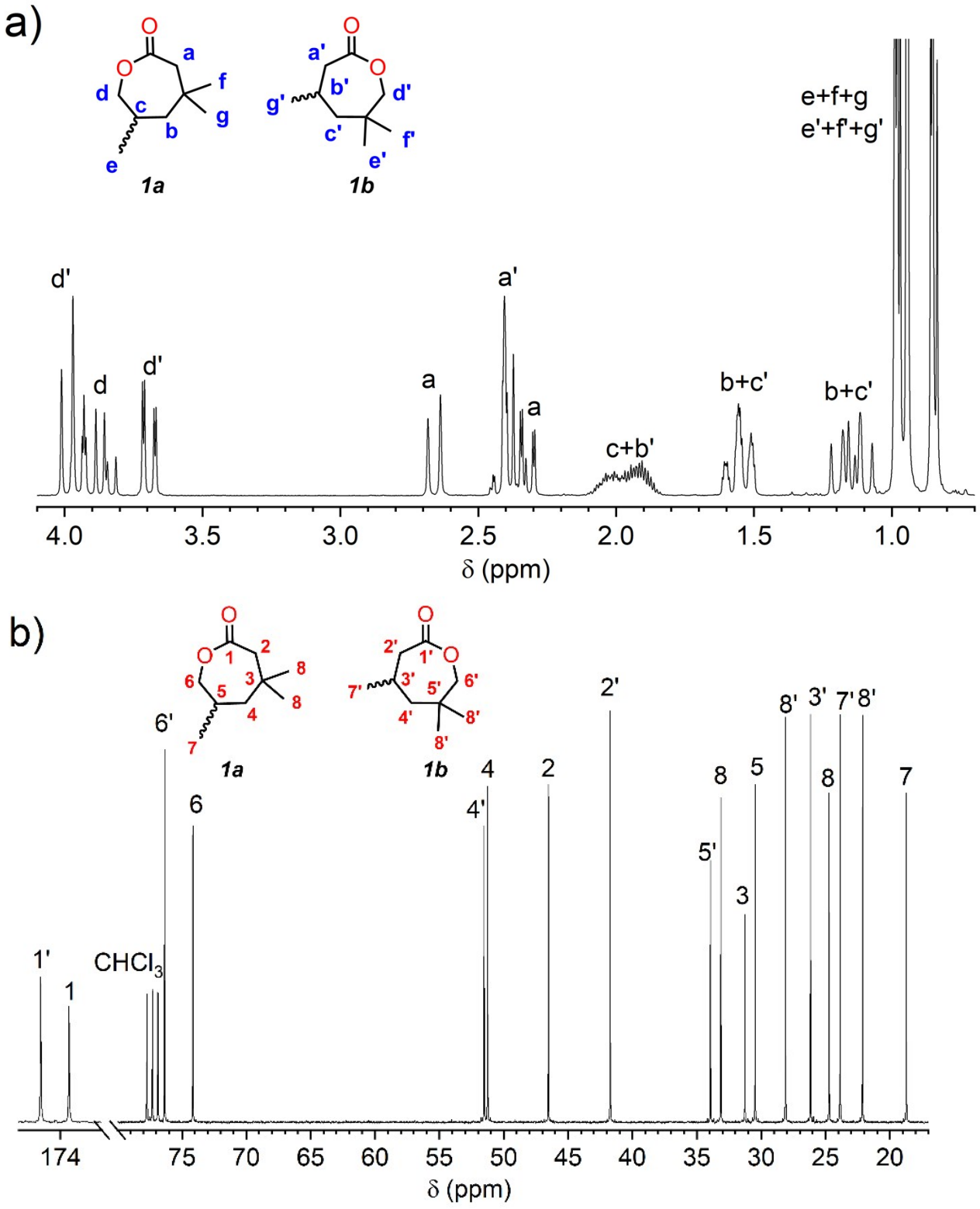


Figure S1. NMR spectra of TMCL in $CDCl_3$ with a) ^{1}H NMR and b) ^{13}C NMR.

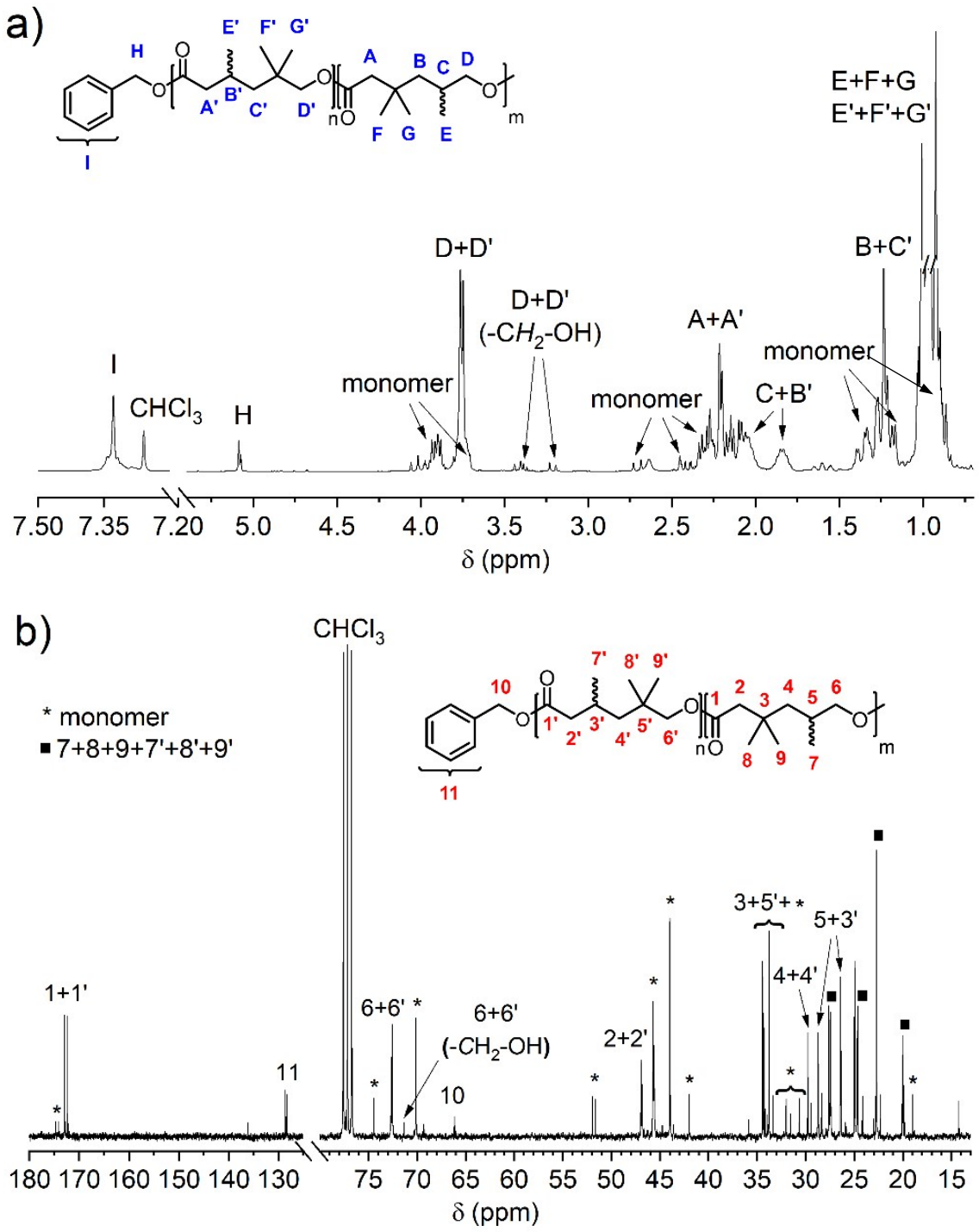


Figure S2. NMR spectra of poly(TMCL) in $CDCl_3$ with a) ^{1}H NMR and b) ^{13}C NMR.

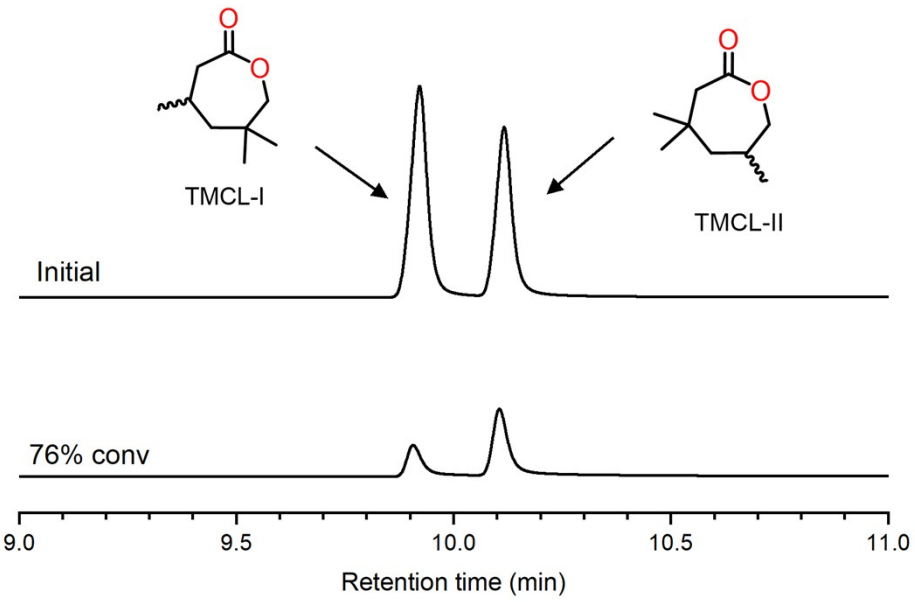


Figure S3. GC-FID trace of the mixture of TMCL-I and TMCL-II lactones during polymerization with the composition at the start of the polymerization (above), and during the polymerization (below).

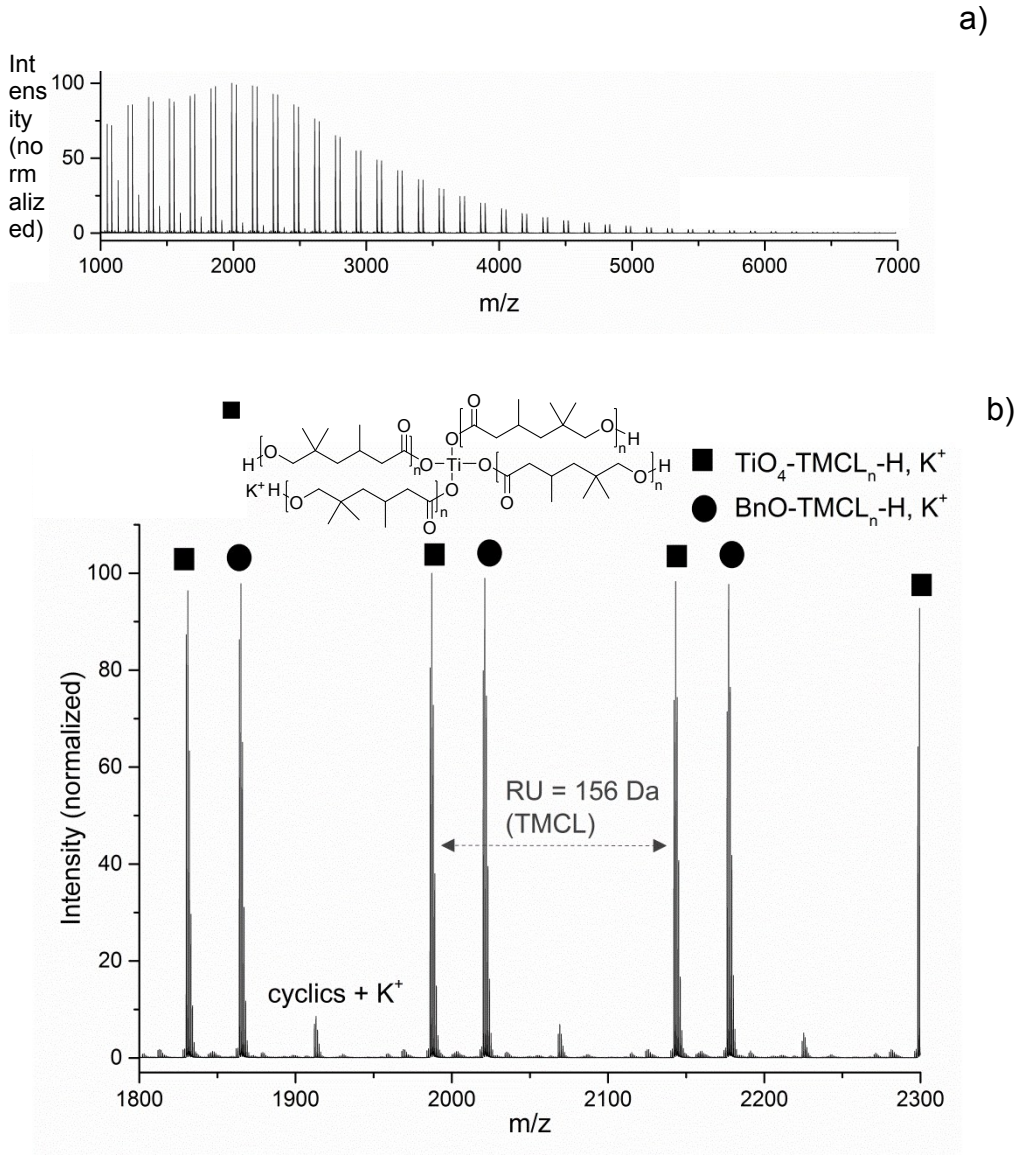


Figure S4. MALDI-ToF analysis for the Ti(*n*-OBu)$_4$ catalyzed ROP of TMCL (Table 1, entry **11**) after 30 min reaction a) full spectrum, and b) zoom in with a distribution initiated by benzyl alcohol (•) and Ti(*n*-OBu)$_4$ (▪).

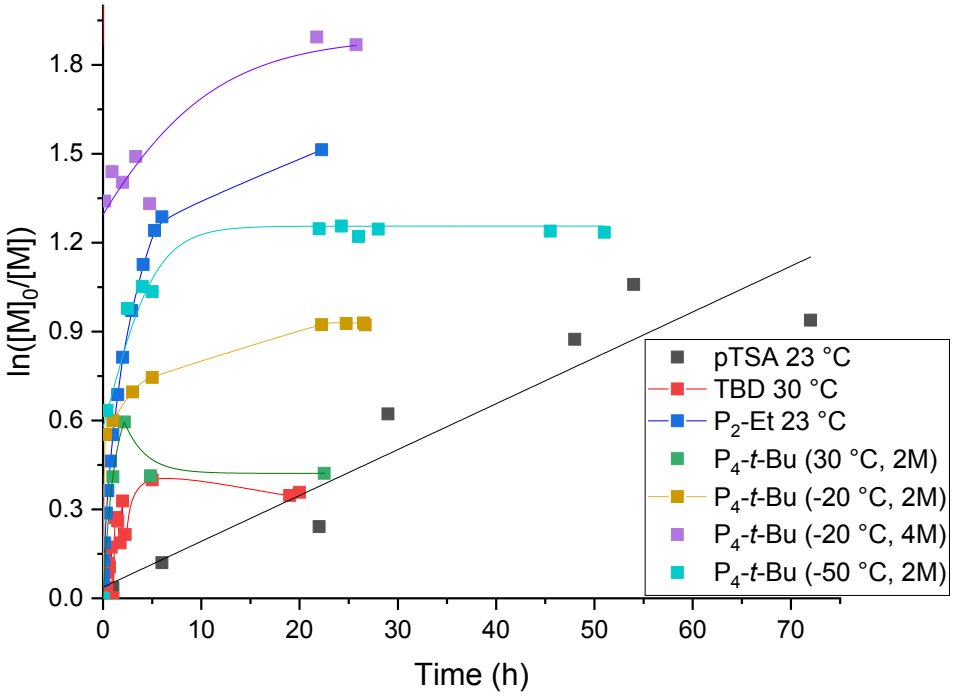


Figure S5. Effect of organic catalysts on the polymerization kinetics of TMCL (Table 1, entries **1-3** and **5-8**).

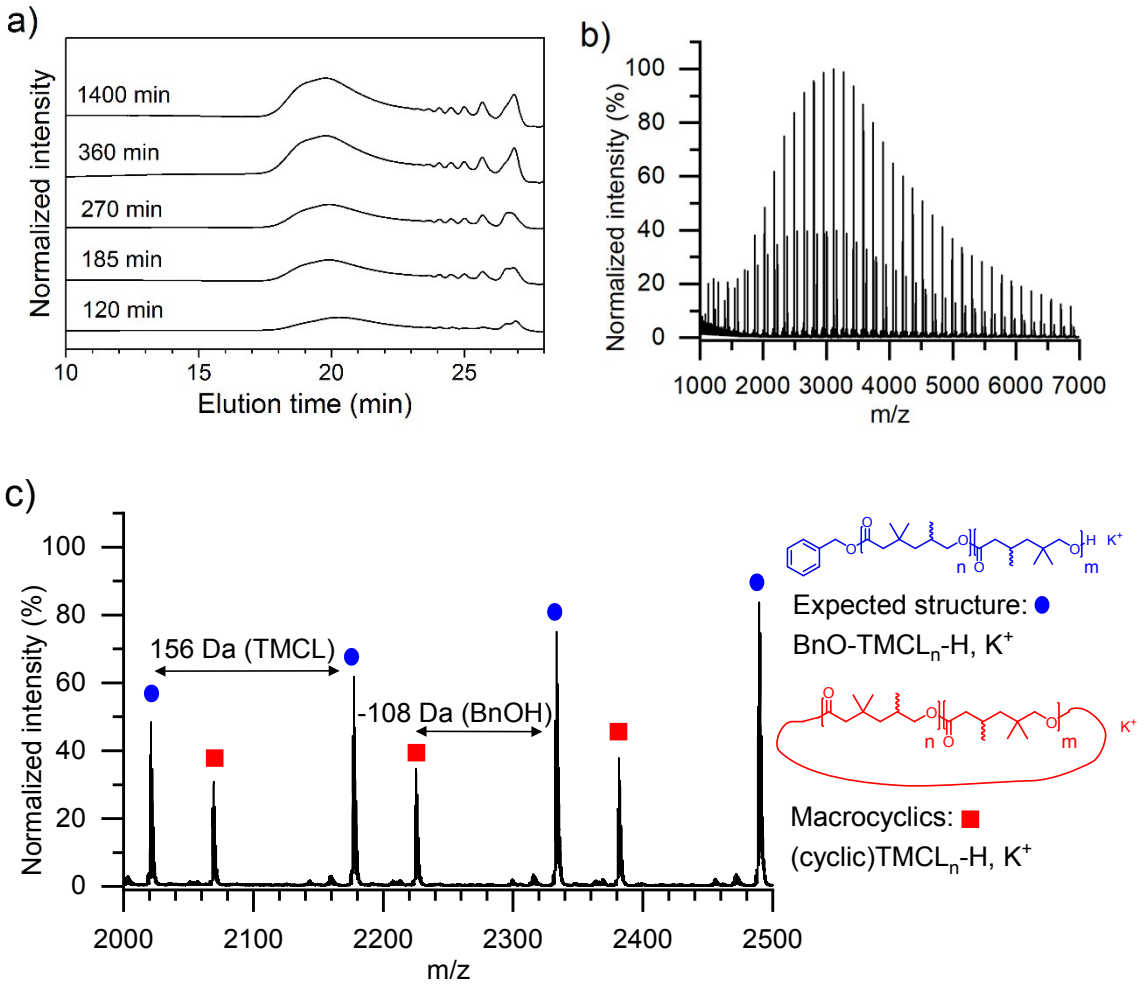


Figure S6. Formation of macrocyclic structure for the P_4-*t*Bu catalyzed ROP of TMCL (Table 1, entry **4**) with a) GPC traces, b) MALDI-ToF-MS spectrum, and c) details of the MALDI-ToF-MS spectrum with distribution initiated by benzyl alcohol (in blue) and macrocyclic structures (in red).

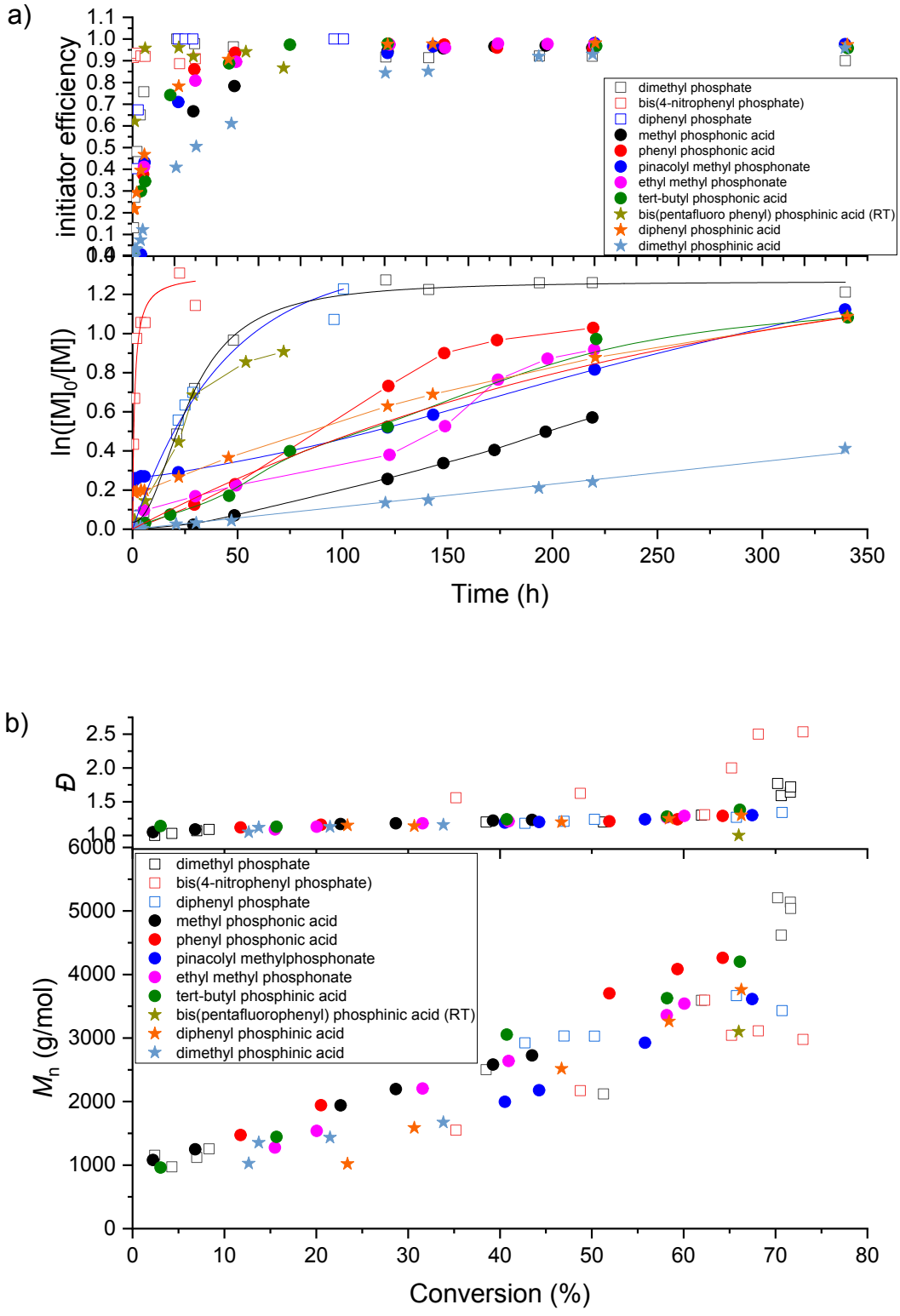


Figure S7. Kinetics for the polymerization of TMCL with organophosphorus catalysts at 80 °C, except for bis(pentafluorophenyl) phosphinic acid performed at room temperature a) $\ln([M]_0/[M])$ vs. time (bottom); benzyl alcohol initiator efficiency as determined by GC vs. time (bottom) and b) $M_{n,GPC}$ vs. % conversion (bottom); $Đ$ vs. % conversion (top).

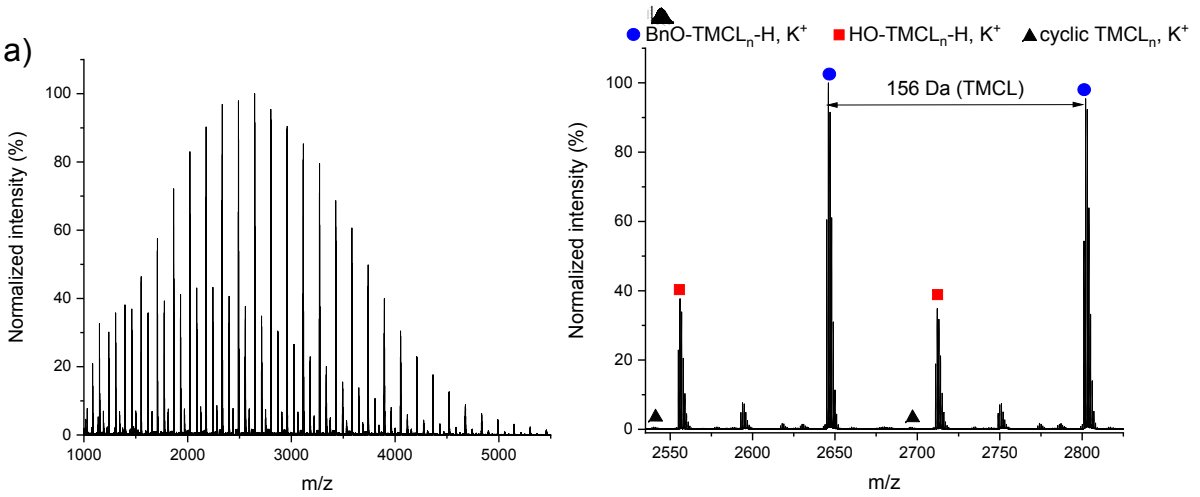


Figure S8. MALDI-ToF analysis for DPP catalyzed ROP of TMCL (Table 1, entry **6**) with a) full MALDI-ToF-MS spectrum, and b) details of the MALDI-ToF-MS spectrum with distribution initiated by benzyl alcohol (• in blue), by water (▪ in red), macrocyclic structures (Δ in black) and some unknown distributions.

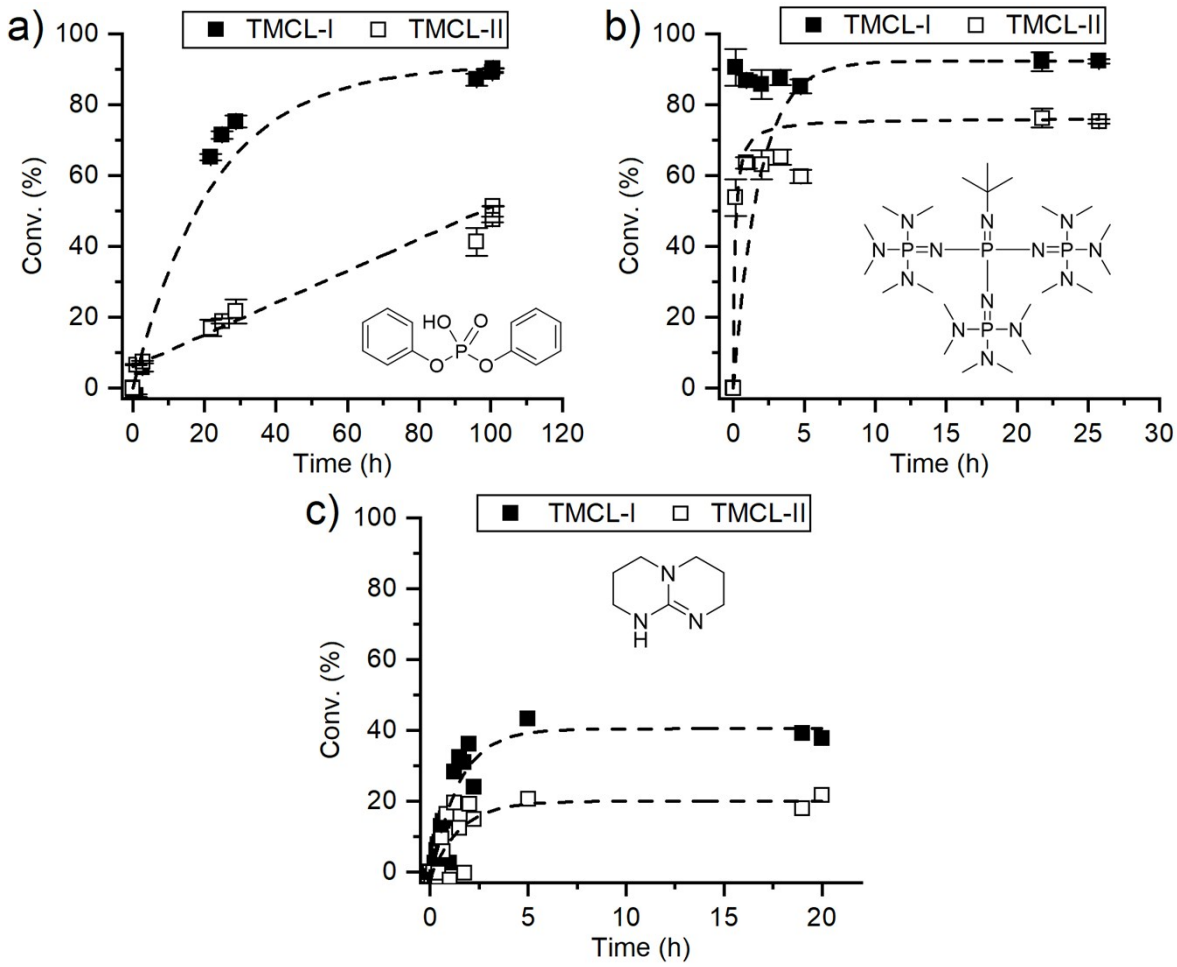


Figure S9. Polymerization profiles of TMCL catalyzed by a) **P3** (DPP) (23 °C, $[TMCL]_0$ = 5.29 M; Table 2, entry **6**), b) P_4-*t*Bu phosphazene (- 20 °C, $[TMCL]_0$ = 4 M in THF; Table 1, entry **8**), and c) TBD (30 °C, $[TMCL]_0$ = 5.29 M; Table 1, entry **2**).

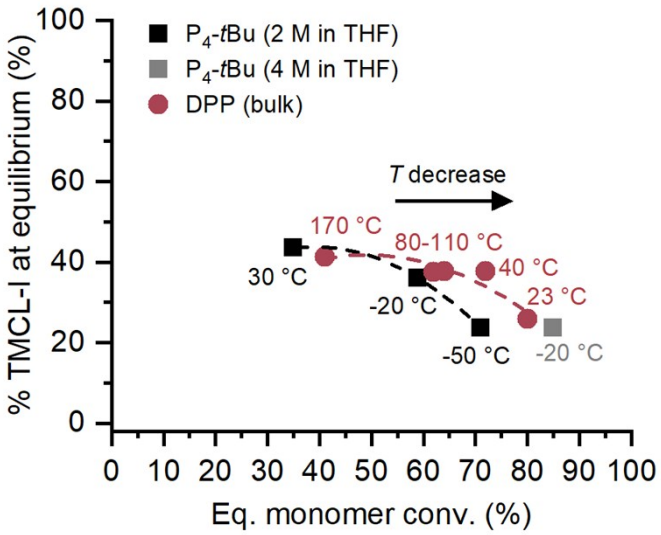


Figure S10. Amount of TMCL-I in remaining monomer mixture at equilibrium as a function of monomer conversion at equilibrium and temperature (Table 1, entries **5-7** and **8** for P_4-*t*Bu, conversions are shown in Figure S11a for DPP).

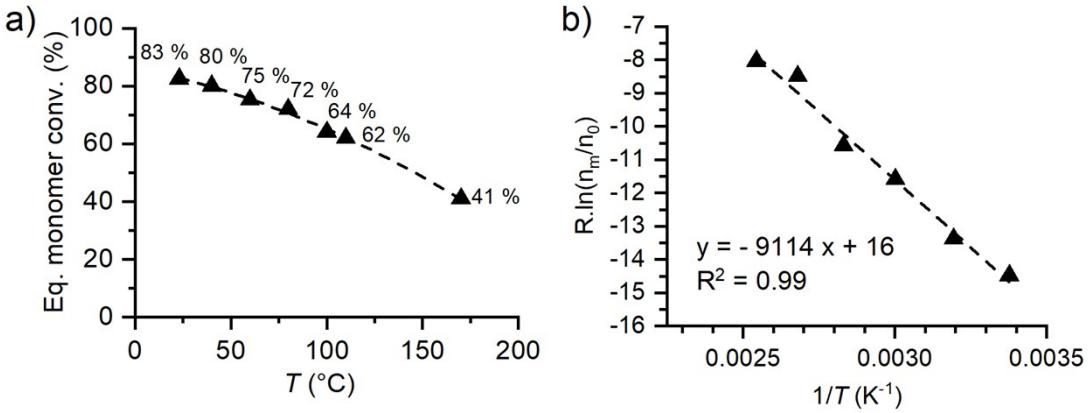


Figure S11. Determination of the thermodynamic parameters of TMCL with a) monomer conversion at equilibrium as a function of the temperature (in bulk), b) van 't Hoff analysis with ΔH_p determined from the slope and ΔS_p determined from the intersection with the y-axis (in bulk). Reaction conditions: benzyl alcohol/monomer/DPP 1/30/1. Conversion determined by GC-FID using hexadecane as internal standard.

Table S2. Calculated thermodynamic values for the ring opening of TMCL-I and TMCL-II with methanol in the gas phase (corresponding to Figure 5).

	TMCL I				TMCL-II			
T (K)	$\Delta G_{reaction}$ (kJ/mol)	$\Delta H_{reaction}$ (kJ/mol)	$\Delta S_{reaction}$ (kJ/mol/K)	$T.\Delta S_{reaction}$ (kJ/mol)	$\Delta G_{reaction}$ (kJ/mol)	$\Delta H_{reaction}$ (kJ/mol)	$\Delta S_{reaction}$ (kJ/mol/K)	$T.\Delta S_{reaction}$ (kJ/mol)
-50	5.83386	-22.44803	-126.91023	-28.30098	9.56207	-17.39394	-120.9566	-26.97332
25	15.20427	-21.31118	-122.53921	-36.51668	18.38375	-16.27285	-116.31344	-34.66141
100	24.22024	-20.13496	-118.9888	-44.38282	27.06365	-15.11238	-113.14403	-42.20272
150	30.11449	-19.33156	-116.97914	-49.48218	32.57195	-14.32735	-110.94597	-46.93015

List of atomic coordinates:

TMCL-I

Conformation C

Symbol	X	Y	Z
C	-0.6817750	1.2872280	-0.1148260
C	-1.4795910	-0.0312850	0.0327940
C	-0.8339500	-1.1724160	-0.7789020
C	0.8101940	1.2827390	0.2628520
C	1.6348610	0.2685820	-0.5682120
H	-0.7596690	1.6180950	-1.1617190
H	-0.5873890	-0.8329380	-1.7933630
H	0.9136440	1.0114820	1.3219880
H	2.6985420	0.5043780	-0.4986700
H	-1.1876390	2.0576420	0.4817670
H	-1.5438350	-1.9986580	-0.8726240
H	1.3517310	0.3450180	-1.6266770
C	1.5186460	-1.1671310	-0.0859700
O	2.4447300	-1.7741760	0.3976750
O	0.3112320	-1.7887880	-0.1677370
C	-1.6215850	-0.4437270	1.5093580
H	-2.1255550	0.3454610	2.0775670
H	-2.2183030	-1.3575310	1.6020880
H	-0.6552140	-0.6386400	1.9799280
C	-2.8828160	0.1998410	-0.5662740
H	-3.5192870	-0.6822690	-0.4385270
H	-3.3775970	1.0427900	-0.0730590
H	-2.8312380	0.4276740	-1.6374290
C	1.3959130	2.6924020	0.0881940
H	2.4410040	2.7298180	0.4110620
H	1.3581180	3.0069410	-0.9616580
H	0.8356080	3.4270570	0.6757440

TMCL-I

Conformation B

Symbol	X	Y	Z
C	0.7901820	1.3446800	0.2850380
H	0.3708460	1.8782840	1.1472650
C	1.6065950	0.1259940	0.8358160
H	1.3592100	-0.0528000	1.8880420
H	2.6763880	0.3375890	0.7972930
C	-0.8956060	-1.0965110	0.7758590
H	-0.5717200	-0.7406080	1.7596180
H	-1.6424030	-1.8780850	0.9411240
C	-1.4964160	0.0549300	-0.0541000
C	-0.3680440	0.9367640	-0.6489700
H	0.0616670	0.4186650	-1.5164660
H	-0.8291990	1.8485790	-1.0486280
O	0.1877480	-1.7588680	0.1045290
C	1.4216470	-1.1757290	0.0677830
O	2.3017910	-1.7194300	-0.5548870
C	-2.4149280	0.8756170	0.8698970
H	-2.9352150	1.6546390	0.3030650
H	-3.1782380	0.2397630	1.3330380
H	-1.8566940	1.3637180	1.6759940
C	-2.3205610	-0.5292170	-1.2176490
H	-3.1940170	-1.0767460	-0.8461230
H	-2.6811330	0.2657080	-1.8794000
H	-1.7154970	-1.2190390	-1.8139090
C	1.7287010	2.3142650	-0.4501930
H	1.1834700	3.1890610	-0.8198540
H	2.5265360	2.6697480	0.2098830
H	2.2002740	1.8231530	-1.3089670

TMCL-I

Conformation C'

Symbol	X	Y	Z
C	0.8665870	1.1841480	-0.6093170
C	1.4738560	-0.0920780	0.0354300
C	0.7330990	-1.3613770	-0.4270590
C	-0.6526030	1.4648400	-0.5354890
C	-1.5124440	0.2916740	-1.0683040
H	1.1254920	1.1495090	-1.6770580
H	1.3182790	-2.2438840	-0.1543800
H	-1.1071470	-0.0596410	-2.0254670
H	1.3970800	2.0558620	-0.2038950
H	0.6181310	-1.3662370	-1.5184540
H	-2.5331660	0.6337810	-1.2507660
C	-1.6467540	-0.8685670	-0.0959900
O	-2.6875430	-1.1593480	0.4444140
O	-0.5354120	-1.5934570	0.2084660
C	2.9237290	-0.2153310	-0.4836260
H	3.4979060	0.6835380	-0.2365480
H	3.4348440	-1.0719300	-0.0314330
H	2.9549130	-0.3385480	-1.5724290
C	1.5107420	-0.0343360	1.5746510
H	2.0668470	-0.8892970	1.9752970
H	2.0133660	0.8781670	1.9120640
H	0.5148730	-0.0611890	2.0182380
C	-1.1628980	1.9709280	0.8232820
H	-1.1548970	1.1973810	1.5949580
H	-0.5523260	2.8072880	1.1787930
H	-2.1957770	2.3231680	0.7347040
H	-0.8146620	2.2850610	-1.2481200

TMCL-I

Conformation B'

Symbol	X	Y	Z
C	-0.5557810	0.4929450	1.0391630
C	-1.3480380	-0.4037380	0.0458150
C	-0.4094590	-0.9915620	-1.0260550
C	0.5390780	1.4673860	0.5334520
C	1.6256430	0.7979560	-0.3621030
H	-0.0662650	-0.1785350	1.7548710
H	-0.1836980	-0.2516600	-1.8006980
H	1.0566920	1.7814500	1.4489490
H	2.5951300	1.2684780	-0.1896960
H	-1.2794080	1.0689510	1.6298610
H	-0.8865550	-1.8430980	-1.5195310
H	1.3823410	0.9506070	-1.4200860
C	1.8209640	-0.6879660	-0.1069650
O	2.8108180	-1.1619880	0.3960410
O	0.8067590	-1.5251770	-0.4760400
C	-1.9693790	-1.5605480	0.8558040
H	-2.5705710	-1.1773200	1.6873720
H	-2.6229280	-2.1742510	0.2256340
H	-1.1903390	-2.2083290	1.2688350
C	-2.4747490	0.3615550	-0.6741640
H	-3.0232380	-0.3014600	-1.3534170
H	-3.1943850	0.7568470	0.0502170
H	-2.0988800	1.2021110	-1.2632930
C	0.0174710	2.7488150	-0.1329910
H	0.8387410	3.4528940	-0.3062100
H	-0.4488770	2.5512960	-1.1035510
H	-0.7228770	3.2502820	0.4990110

TMCL-II

Conformation C

Symbol	X	Y	Z
C	-0.8242360	1.2212540	-0.1280900
C	-1.6696130	0.0147220	0.3184140
C	-1.3309010	-1.2693510	-0.4479520
C	0.7160890	1.1177510	-0.0218510
C	1.2570120	-0.1031960	-0.8219840
H	-1.0797830	1.4381320	-1.1763860
H	-1.2450970	-1.0732470	-1.5253150
H	2.3338500	0.0061400	-0.9683780
H	-1.1450780	2.1002150	0.4464370
H	-2.1262960	-2.0063420	-0.3118330
H	0.7924610	-0.1205040	-1.8163310
C	1.0924400	-1.4517800	-0.1400550
O	2.0285070	-2.0938740	0.2748280
O	-0.1605100	-1.9514060	0.0336210
C	1.3157470	2.3879180	-0.6587180
H	2.4072270	2.3933640	-0.5708210
H	1.0630690	2.4591400	-1.7226720
H	0.9354300	3.2881570	-0.1637200
C	1.1706240	1.0404800	1.4491240
H	2.2611040	0.9713620	1.5168020
H	0.8547540	1.9371260	1.9935350
H	0.7584110	0.1710640	1.9693740
C	-3.1644800	0.3322180	0.1470860
H	-3.7920750	-0.4793670	0.5290560
H	-3.4334280	1.2461740	0.6853520
H	-3.4195130	0.4856510	-0.9085550
H	-1.4851100	-0.1949140	1.3800220

TMCL-II

Conformation B

Symbol	X	Y	Z
C	-1.1693730	-0.7089840	0.0159610
C	-1.1707830	0.6871540	0.7280220
H	-0.8795420	0.5743750	1.7771190
H	-2.1778870	1.1084170	0.7197980
C	1.5875450	0.4189620	0.9375160
H	1.0876700	0.3506630	1.9085300
H	2.6336020	0.6704250	1.1301000
C	1.4840070	-0.9083920	0.1587000
C	0.1884040	-1.0047880	-0.6731890
H	0.2911430	-0.3244370	-1.5283270
H	0.1362720	-2.0127500	-1.1030970
O	1.0783760	1.5455100	0.2010440
C	-0.2698330	1.7089410	0.0551000
O	-0.6747250	2.6347120	-0.6069780
C	2.7019600	-1.1018710	-0.7587660
H	3.6312780	-1.1443090	-0.1810020
H	2.6230680	-2.0299410	-1.3341260
H	2.7840900	-0.2715560	-1.4684490
C	-2.2498410	-0.6879830	-1.0840590
H	-2.2385180	-1.6173430	-1.6641110
H	-3.2486830	-0.5759340	-0.6488860
H	-2.0896770	0.1465560	-1.7743630
H	1.4903570	-1.7104810	0.9095300
C	-1.5119170	-1.7977970	1.0485620
H	-2.4704650	-1.5871390	1.5355270
H	-1.5914200	-2.7793880	0.5682450
H	-0.7515170	-1.8703820	1.8339010

TMCL-II

Conformation C'

Symbol	X	Y	Z
C	0.4613080	-1.4719870	-0.4709170
C	-1.0795150	-1.4605170	-0.3291910
C	-1.7335540	-0.2436660	-0.9923050
C	1.3092950	-0.2484450	-0.0304560
C	0.7871290	1.0655170	-0.6814570
H	0.6753810	-1.6334530	-1.5369390
H	-2.8095650	-0.4087900	-1.0910870
H	0.6440050	0.9061150	-1.7578900
H	0.8483810	-2.3593950	0.0467600
H	-1.3289910	-0.0798490	-1.9987030
H	1.5379070	1.8502700	-0.5658040
C	-0.4759550	1.6370740	-0.0579220
O	-0.4818900	2.6543470	0.5945840
O	-1.6494320	0.9669000	-0.2194180
C	-1.6202530	-1.6861930	1.0921910
H	-2.6965880	-1.8876050	1.0622070
H	-1.1326680	-2.5464480	1.5613080
H	-1.4735010	-0.8174930	1.7362290
C	1.3830570	-0.0922120	1.5018970
H	0.4156110	0.1367170	1.9530420
H	1.7600910	-1.0115230	1.9628030
H	2.0641130	0.7220260	1.7708760
C	2.7420590	-0.4820680	-0.5564180
H	3.4097200	0.3301720	-0.2504580
H	3.1529170	-1.4185200	-0.1631520
H	2.7629480	-0.5418680	-1.6504940
H	-1.4206030	-2.3153530	-0.9325600

TMCL-II

Conformation B'

Symbol	X	Y	Z
C	-0.6253820	0.5128480	1.0088370
C	-1.5878910	-0.6207350	0.5725890
C	-0.9178910	-1.6834220	-0.3164120
C	0.3027850	1.2246480	-0.0181510
C	1.0386100	0.1995750	-0.9405160
H	0.0274030	0.0840470	1.7783410
H	-0.9638680	-1.3960800	-1.3727870
H	1.9640820	0.6402970	-1.3172440
H	-1.2167470	1.2810630	1.5231720
H	-1.4397210	-2.6390710	-0.2218410
H	0.4156630	-0.0357780	-1.8090630
C	1.4305800	-1.0773920	-0.2169540
O	2.5558190	-1.3279470	0.1448550
O	0.4382130	-1.9732130	0.0595940
C	-2.8998340	-0.1600790	-0.0819520
H	-3.5754460	-1.0090250	-0.2369460
H	-3.4202640	0.5623100	0.5543290
H	-2.7378570	0.3097400	-1.0569150
C	-0.4597380	2.2286550	-0.9023750
H	0.2299350	2.7506440	-1.5751930
H	-1.2184230	1.7432530	-1.5224150
H	-0.9608270	2.9852080	-0.2885240
C	1.3676920	1.9914540	0.7952240
H	1.9988960	2.5973890	0.1364980
H	0.8965570	2.6632600	1.5211320
H	2.0189790	1.3013800	1.3405790
H	-1.8642140	-1.1226700	1.5095540

Geometries of extended methyl esters:

Methyl ester from TMCL-I

Symbol	X	Y	Z
C	1.5271000	-0.5862220	-0.4897840
C	0.3173860	0.2515630	-0.0332070
H	1.3743150	-1.6462530	-0.2436550
H	1.6558590	-0.5486270	-1.5776650
C	-0.9750620	-0.4699040	-0.4784740
H	-0.9955350	-0.5131960	-1.5774390
H	-0.8769010	-1.5129850	-0.1426290
C	-3.3337120	-1.1430880	-0.1847980
H	-3.3057070	-1.4553020	-1.2422020
H	-2.9918010	-1.9980420	0.4212860
C	2.8328010	-0.1837720	0.1681010
O	2.9454960	0.4386330	1.2028970
C	5.1801740	-0.3639630	0.0353330
H	5.2684700	-0.8122710	1.0280900
H	5.9082130	-0.8010460	-0.6477850
H	5.3353870	0.7141580	0.1228260
O	3.8921950	-0.6453610	-0.5371260
C	-2.3308900	0.3991570	1.5161010
H	-1.9225480	-0.4242750	2.1141190
H	-1.7183080	1.2854210	1.7061910
H	-3.3435220	0.6027100	1.8731680
O	-4.6494700	-0.7531600	0.1940660
H	-5.2365890	-1.5053250	0.0517770
C	-2.3598350	0.0389400	0.0188820
C	-2.8830660	1.2327870	-0.8064330
H	-2.2895910	2.1353750	-0.6477910
H	-2.8646300	1.0046780	-1.8787850
H	-3.9169800	1.4525910	-0.5299150
H	0.3499720	0.2740230	1.0617600
C	0.4548940	1.6954870	-0.5401530
H	0.3454810	1.7450150	-1.6304310
H	-0.2950060	2.3549460	-0.0986730
H	1.4349040	2.1016020	-0.2743480

Methyl ester from TMCL-II

Symbol	X	Y	Z
C	1.2743080	-0.6817590	-0.0078170
C	0.0895810	0.3215560	0.0542820
H	1.1665920	-1.4277530	0.7922730
H	1.2397350	-1.2508210	-0.9438340
C	-1.1780760	-0.5367090	-0.2531490
H	-1.1601800	-0.8012190	-1.3211740
H	-1.0598540	-1.4863190	0.2886670
C	-2.5834650	-0.0038320	0.1022230
C	-3.5932850	-1.1445520	-0.0870340
H	-3.6545560	-1.4073150	-1.1569330
H	-3.2433120	-2.0402580	0.4510500
C	2.6814080	-0.1267420	0.1265210
O	3.0156450	0.9356310	0.6084800
C	4.9574790	-0.6440640	-0.2246860
H	5.2208970	-0.4859710	0.8240960
H	5.5301330	-1.4719880	-0.6422430
H	5.1558650	0.2768830	-0.7783450
O	3.5773920	-1.0245500	-0.3509470
C	0.3084200	1.4166770	-1.0105520
H	1.2365310	1.9595970	-0.8167320
H	0.3691320	0.9791570	-2.0144020
H	-0.5060890	2.1427490	-1.0160480
C	0.0034470	0.9496180	1.4586840
H	-0.1950760	0.1863050	2.2209840
H	0.9403370	1.4492780	1.7108000
H	-0.8021730	1.6881090	1.5119200
O	-4.8589910	-0.7209270	0.4099850
H	-5.5085640	-1.4008080	0.1933000
C	-3.0418670	1.2325840	-0.6848980
H	-2.5026000	2.1347200	-0.3867070
H	-2.8929070	1.0917390	-1.7625540
H	-4.1060650	1.4062080	-0.5078860
H	-2.6079090	0.2398100	1.1721630

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