Supporting Information

Triacetic acid lactone conversion to methylene-δ-caprolactone: a renewable monomer for bio-based circular polymer synthesis

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Table S1. Surface area and CO chemisorption of Pt-based catalysts.

Entry	Catalysts	BET (m^2/g)	Site density (μmol/g)	Dispersion	Particle size (nm)
1	1 wt% Pt/TiO_2	51.6	10.2	20%	4.6
2	1 wt% Pt/CeO_2	163.6	55.2	107%	0.8
3	1 wt% Pt/ZrO_2	108.8	34.6	67.5%	1.37
4	1 wt% Pt/γ-Al_2O_3	214.3	36.6	71.4%	1.30
5	1 wt% Pt/SiO_2	128.5	34.3	66.9%	1.38

Table S2. Surface area, metal loading, and CO_2 uptake of silica-supported base catalysts.

Entry	Catalysts	Surface area (m^2/g)	Metal loading (μmol/g)	CO_2 uptake (μmol/g)	CO_2 uptake from stepwise TPD (μmol/g)			
					50-150 °C	150-250 °C	250-350 °C	350-450 °C
1	SiO_2	263	-	-	-	-	-	-
2	5 wt% CaO/SiO_2	165	1250	345	176	88	50	28
3	5 wt% BaO/SiO_2	182	364	259	135	61	38	24
4	5 wt% Cs_2O/SiO_2	170	376	303	154	64	46	39
5	15 wt% Cs_2O/SiO_2	84	1129	600	352	130	71	47

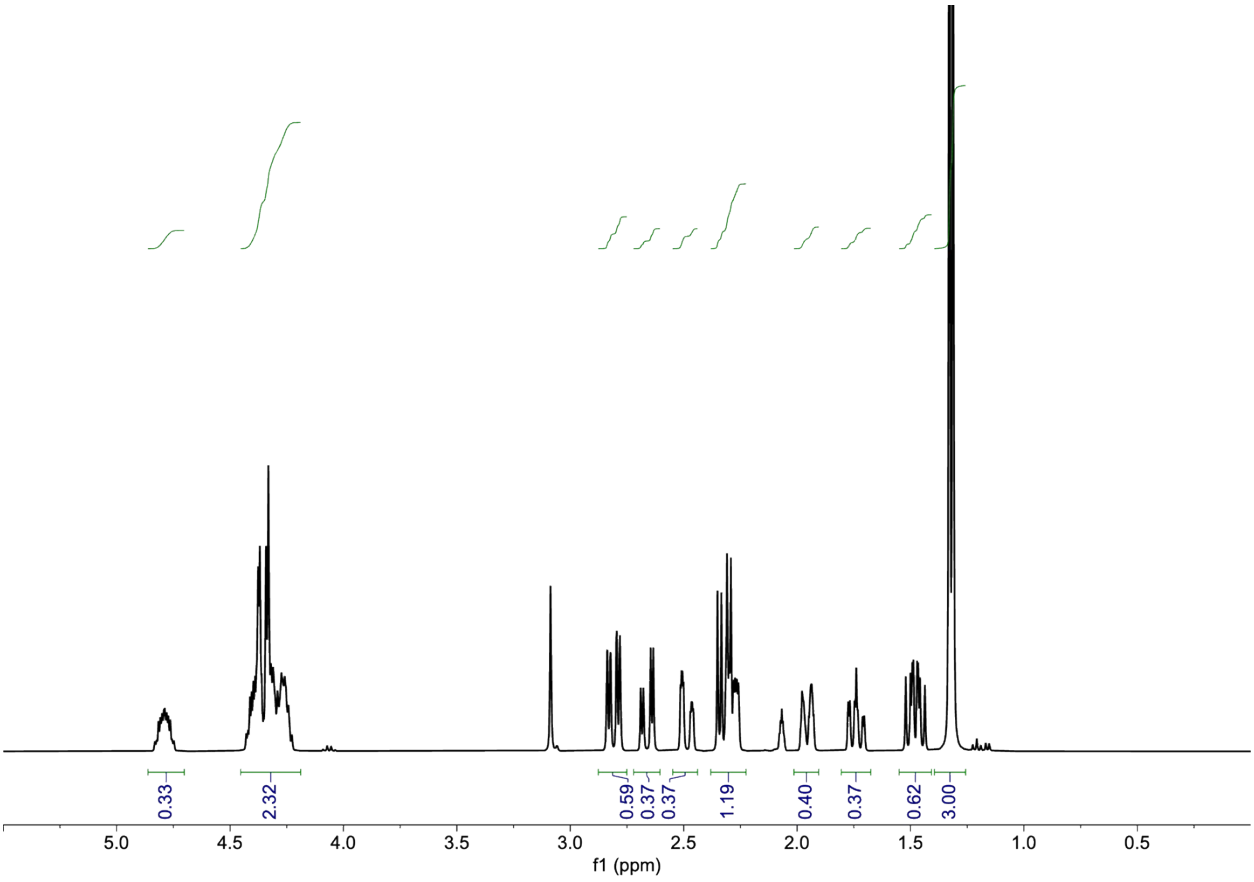

Fig. S1 ^{1}H NMR isolated 4-hydroxy-6-methyltetrahydro-2-pyrone (HMTHP) from TAL hydrogenation reaction.

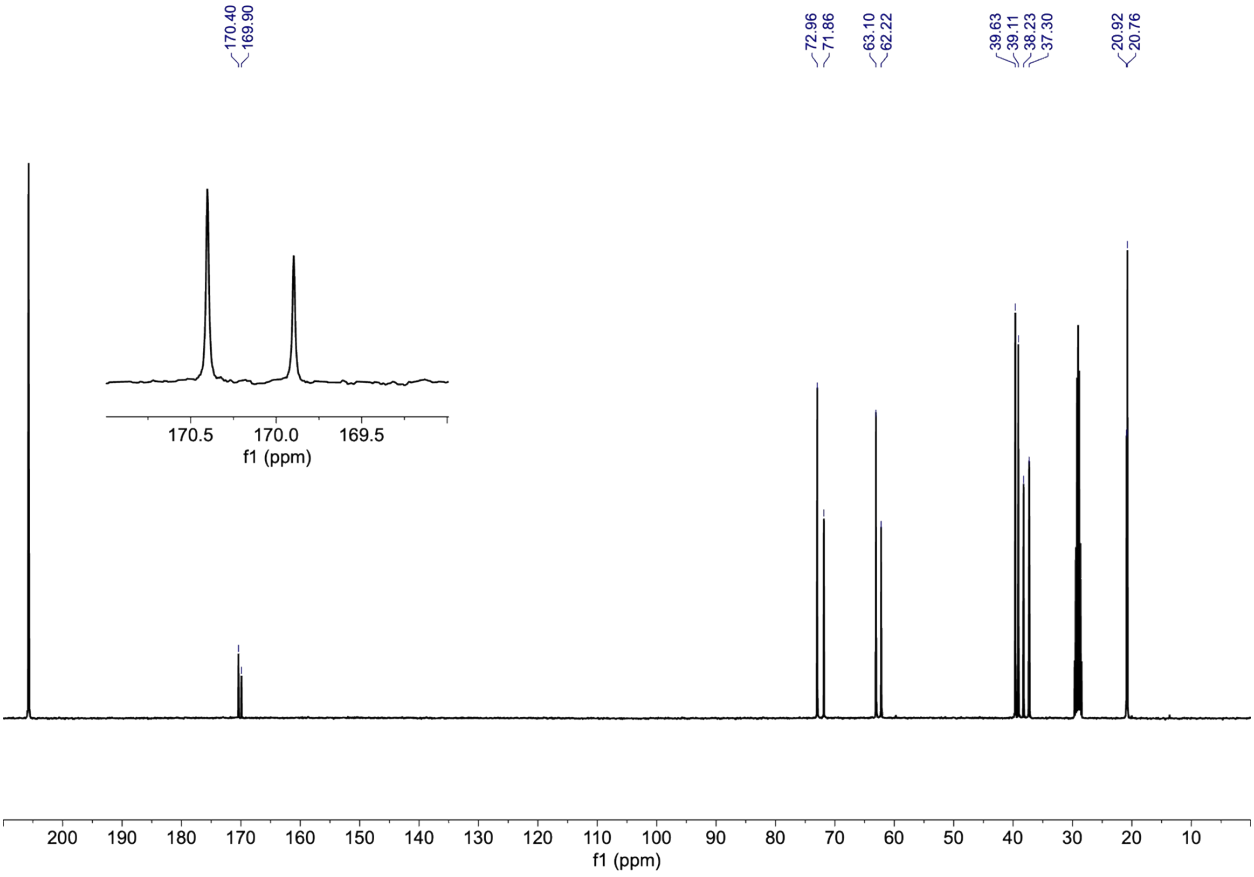

Fig. S2 ^{13}C NMR isolated 4-hydroxy-6-methyltetrahydro-2-pyrone (HMTHP) from TAL hydrogenation reaction.

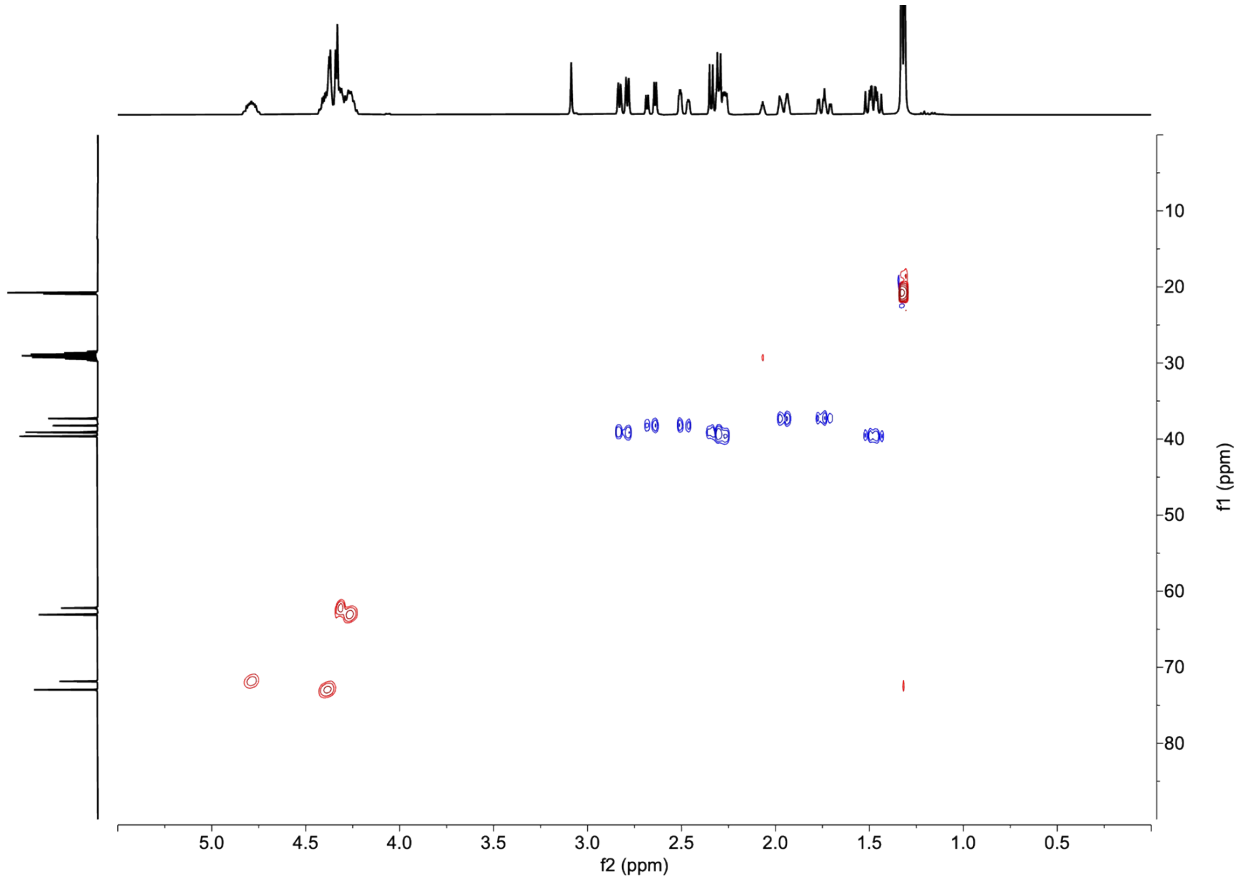

Fig. S3 HSQC spectra (acetone-d6) of isolated 4-hydroxy-6-methyltetrahydro-2-pyrone (HMTHP) from TAL hydrogenation reaction. NMR spectra of HMTHP from TAL hydrogenation are shown in Fig. S1. Two isomeric sets are present, as indicated by paired ^{13}C resonances (e.g., carbonyl signals at 169.9 and 170.4 ppm). HSQC NMR deconvolution assigns these to the diastereomeric pairs RR/SS and RS/SR. Integration of the ^{1}H NMR signals indicates a composition of ~33% RR/SS (δ 4.78, m, 1H) and ~67% RS/SR (δ 1.48, m, 1H). The diastereomeric pairs then were converted into indistinguishable R/S dCL during the dehydration reaction after removal of the R or S hydroxyl group.

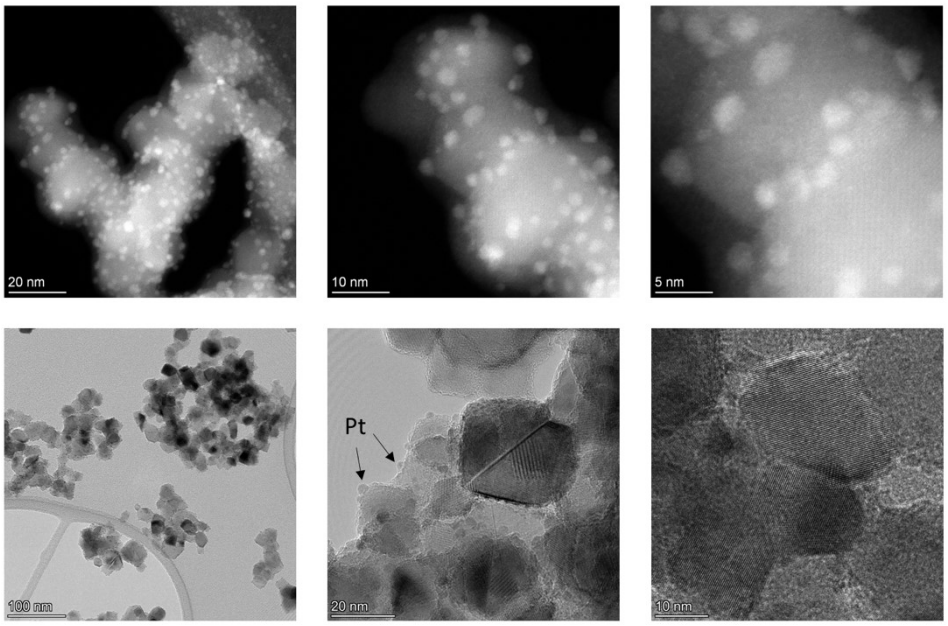

Fig. S4 HAADF-STEM images of fresh 1 wt% Pt/TiO_2 catalyst.

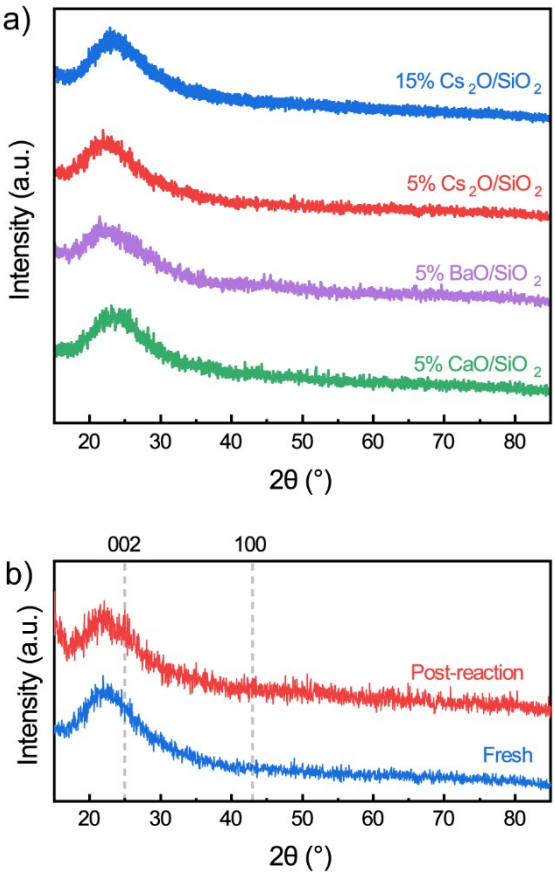

Fig. S5 a) XRD patterns of supported metal oxide catalysts. The only observable feature is a broad band near 22° that is attributed to amorphous SiO_2 support. **b)** XRD patterns of 5wt% Cs_2O/SiO_2 catalyst before and after reaction. Referenced lines represent planes from graphite.

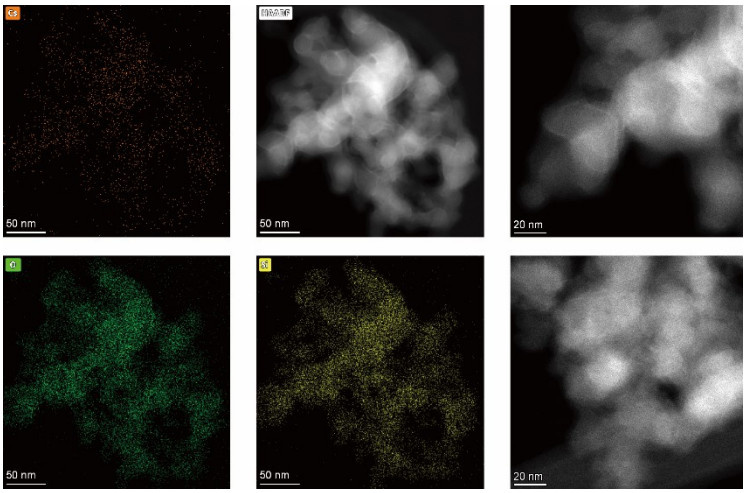

Fig. S6 STEM-EDS images of fresh 5wt% Cs_2O/SiO_2 catalyst.

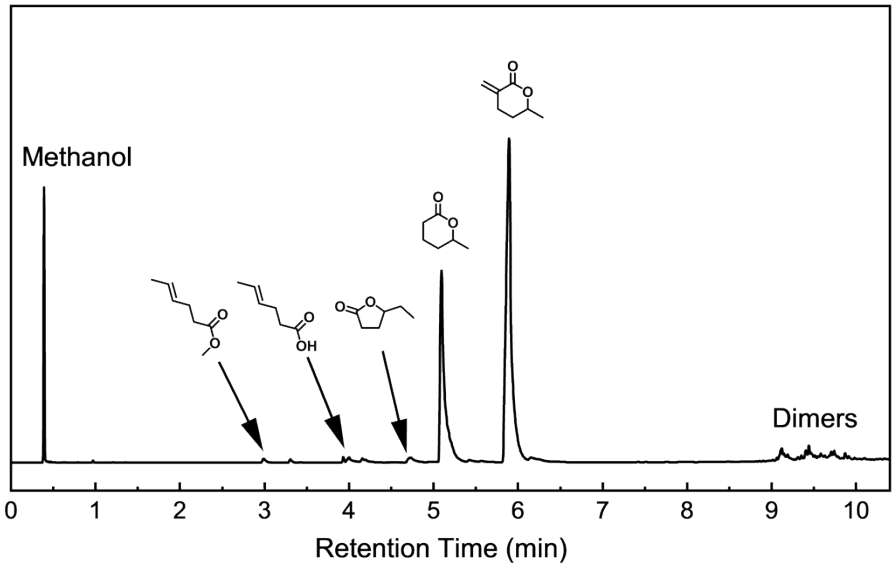

Fig. S7 Typical GC chromatogram from online gas phase analysis showing the compounds and their retention times.

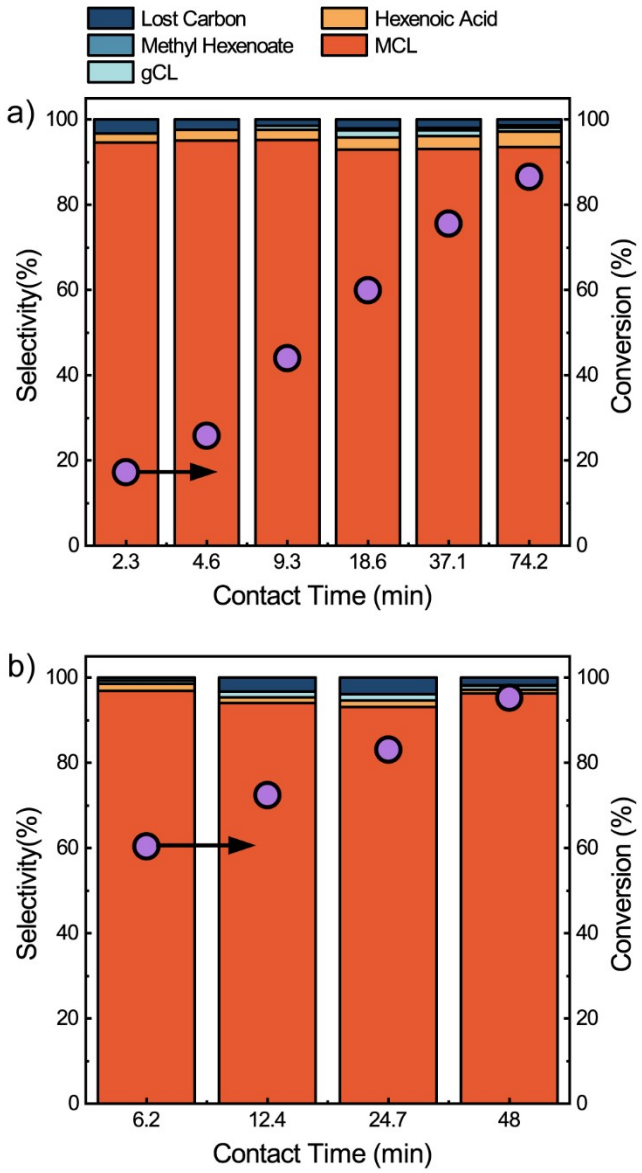

Fig. S8 Product distribution (bar chart) and dCL conversion (scatter) during the aldol condensation reaction of dCL and formalin over **a)** 5 wt% and **b)** 15 wt% Cs_2O/SiO_2. Condition: 0.4 mol% dCL, 1.2 mol% formaldehyde, 220 ˚C, 1 bar, N_2 balanced.

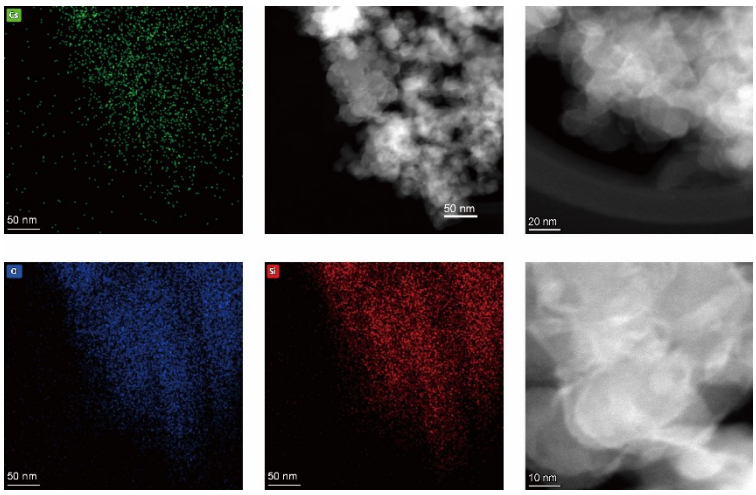

Fig. S9 STEM-EDS images of fresh 15wt% Cs_2O/SiO_2 catalyst.

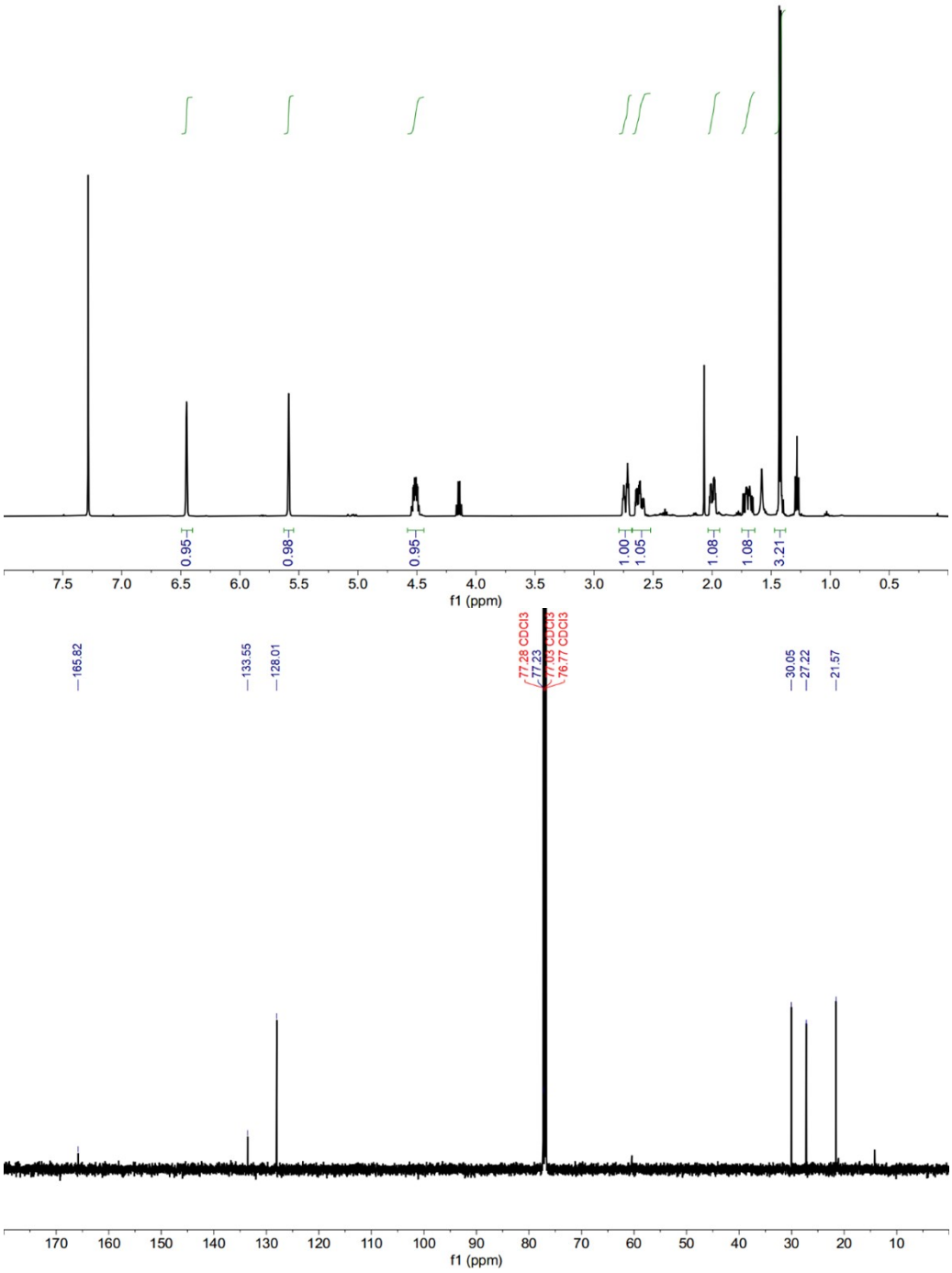

Fig. S10 ^{1}H NMR and ^{13}C NMR spectra ($CDCl_3$) of MCL obtained from gas phase aldol condensation reaction via condensing in a bubbler under room temperature.

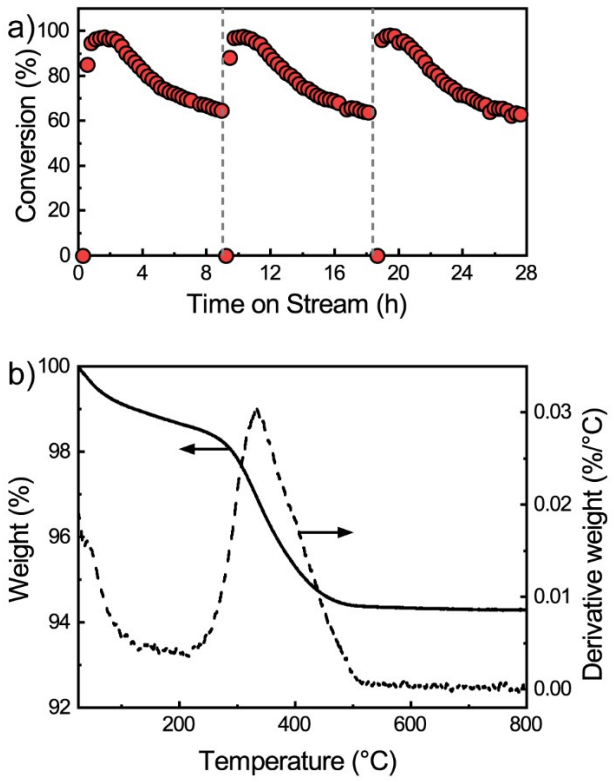

Fig. S11 a) dCL conversion as a function of time on stream over 15wt% Cs_2O/SiO_2. Condition: 220 °C, contact time = 6 min, 0.4 mol% dCL, 1 bar, N_2 balanced. Dashed lines represent regenerations in 50 mL/min of air for 4 h. **b)** TGA of post-reaction 15wt% Cs_2O/SiO_2 catalyst after ~50 h on stream. Condition: 45 mL min^{-1} air, 5 mL min^{-1} N_2, 1 °C min^{-1} ramp rate.

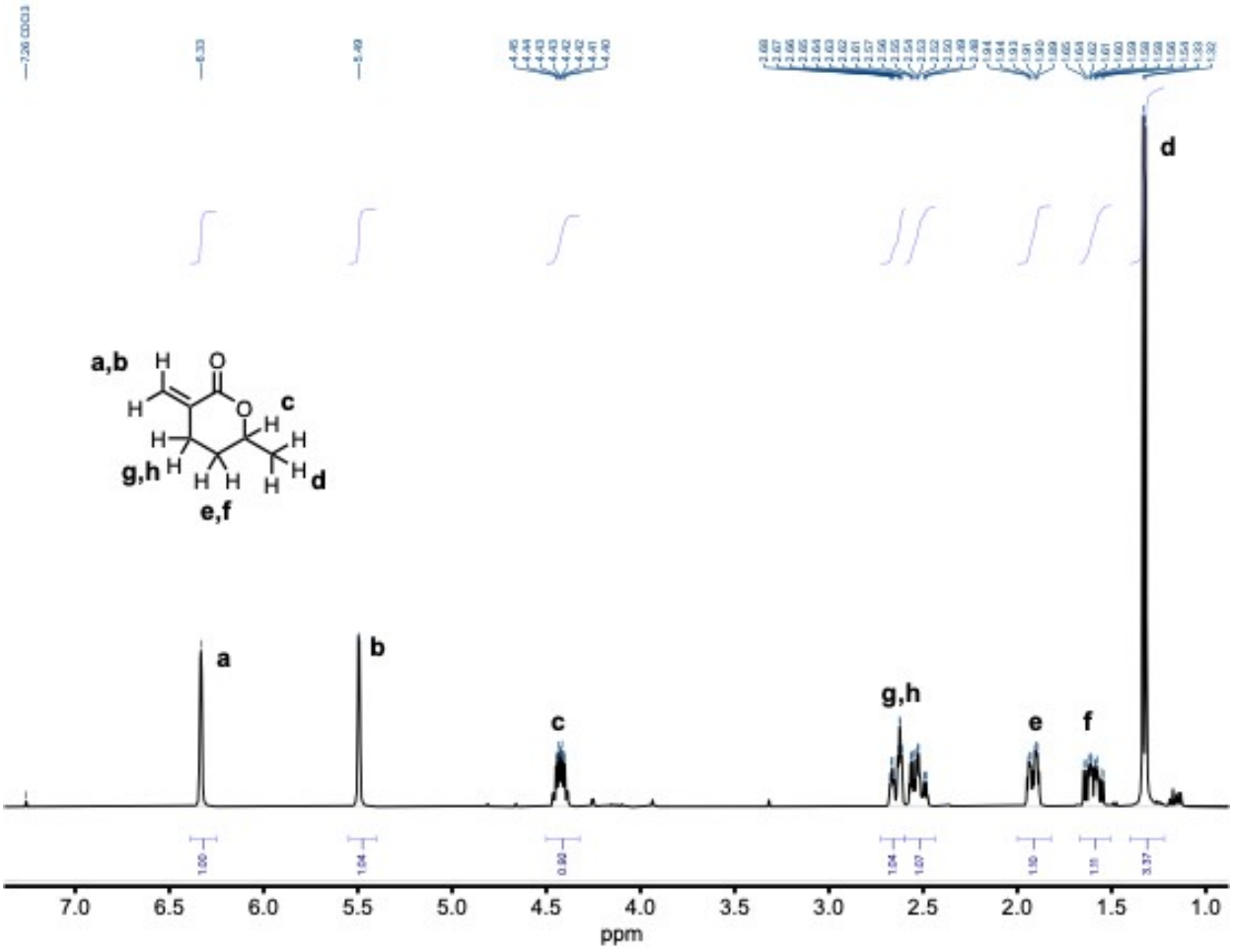

Fig. S12 ^{1}H NMR spectrum ($CDCl_3$, 23 °C) of MCL obtained from the herein reported continuous synthetic method before polymerization.

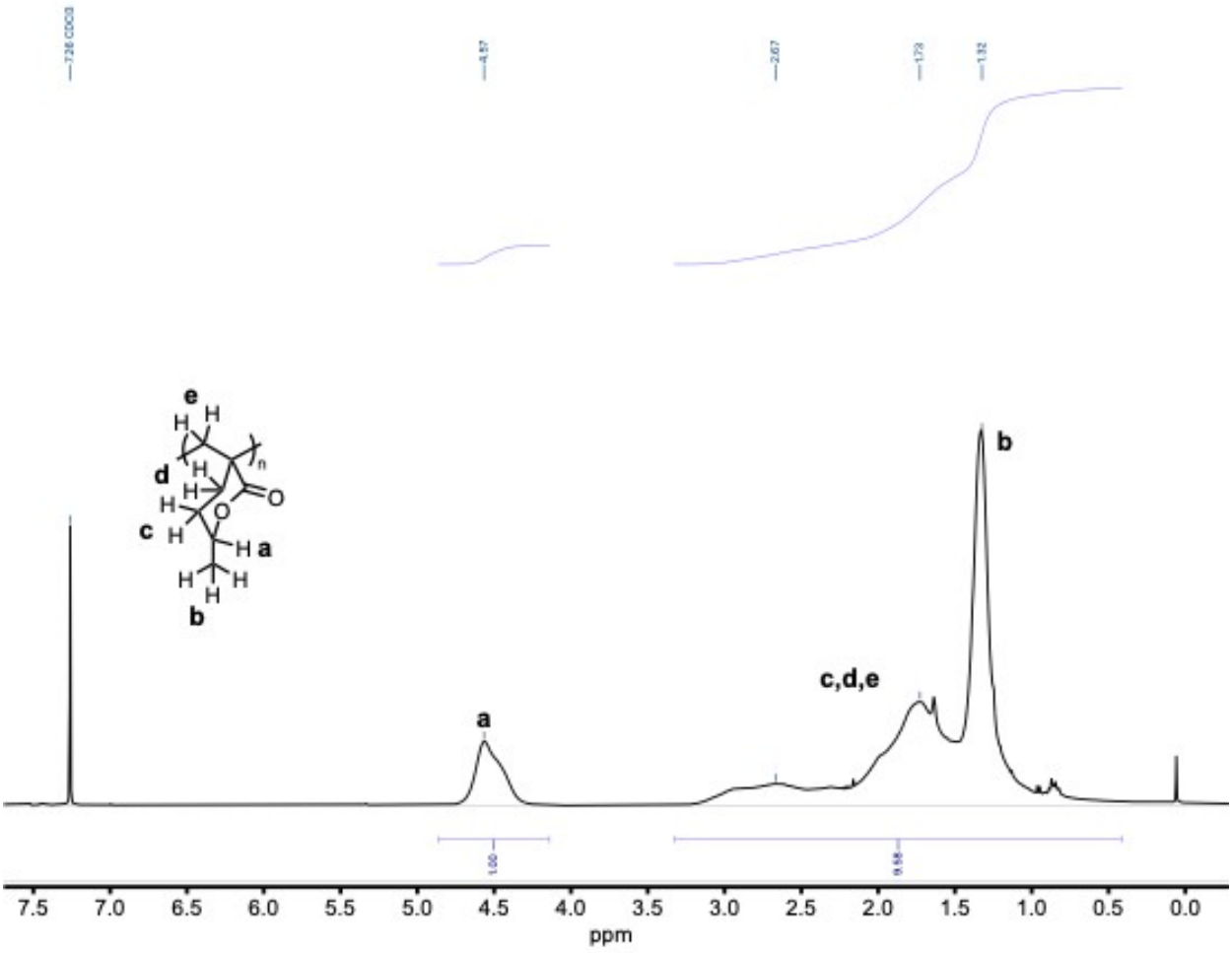

Fig. S13 ^{1}H NMR spectrum ($CDCl_3$, 23 °C) of purified PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 62.5 kDa, $Đ$ = 1.86). Peak around 1.56 ppm corresponds with water and 0.87 ppm corresponds with grease.

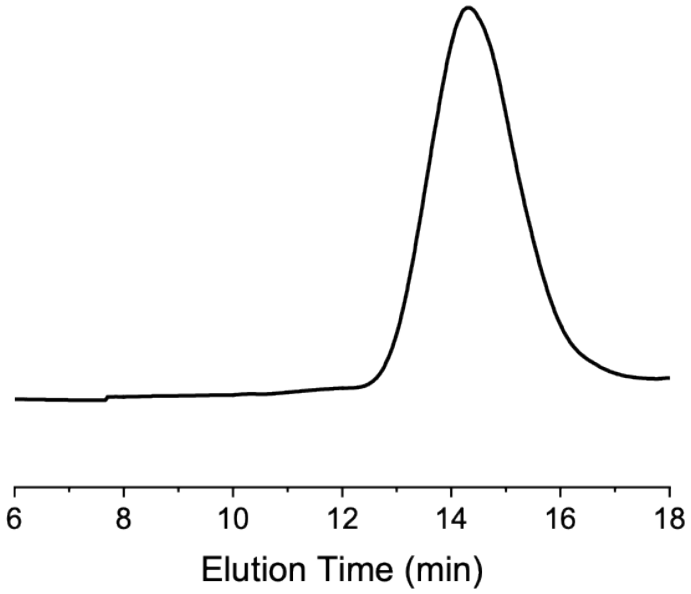

Fig. S14 SEC trace of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1. (M_n = 62.5 kDa, $Đ$ = 1.86).

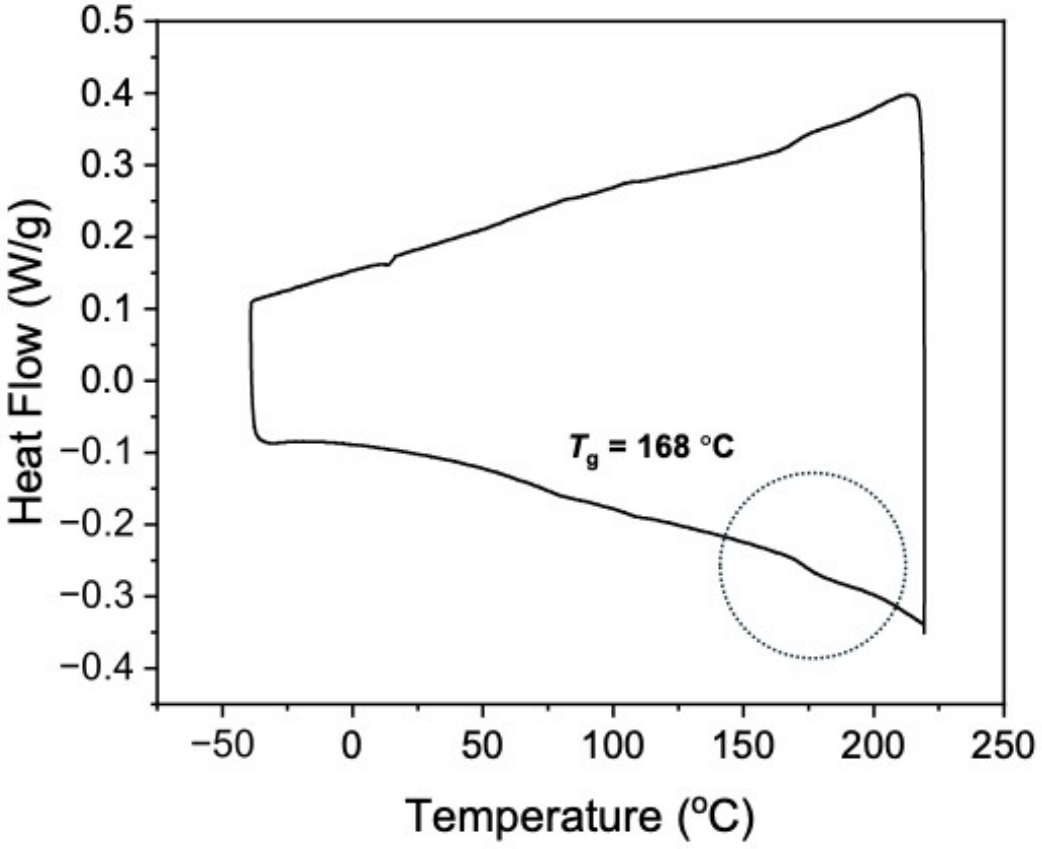

Fig. S15 DSC curve of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 62.5 kDa, $Đ$ = 1.86).

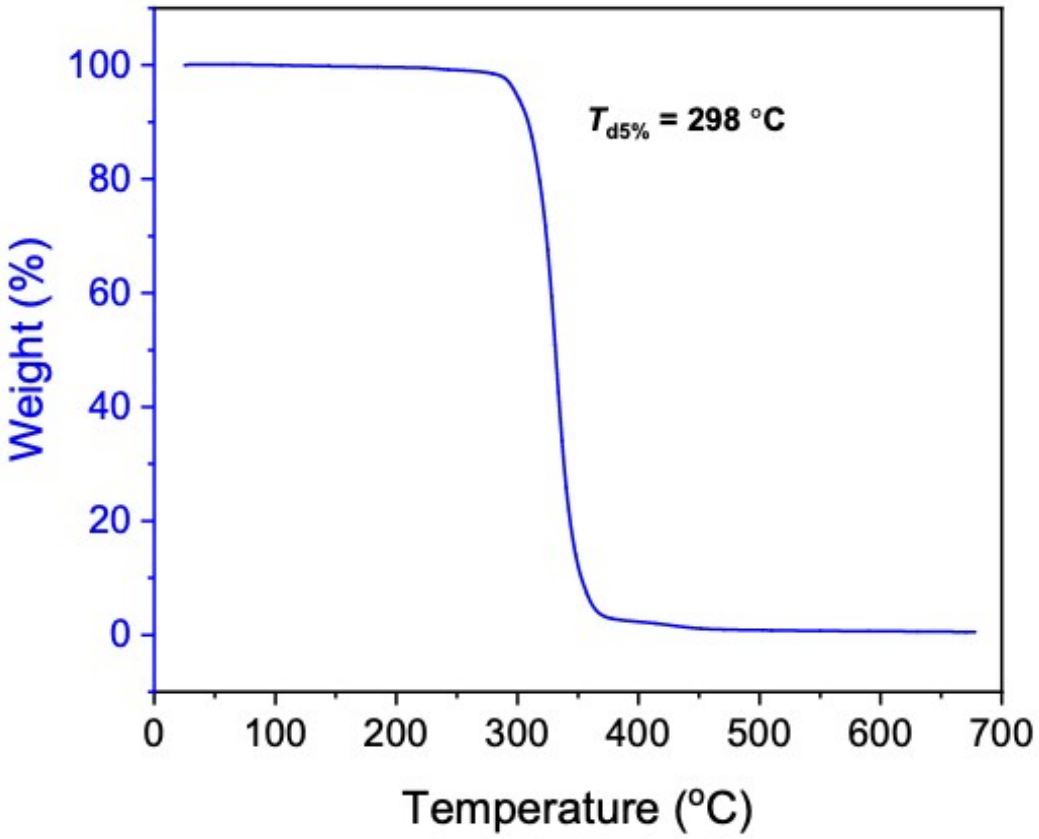

Fig. S16 TGA curve of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 62.5 kDa, $Đ$ = 1.86).

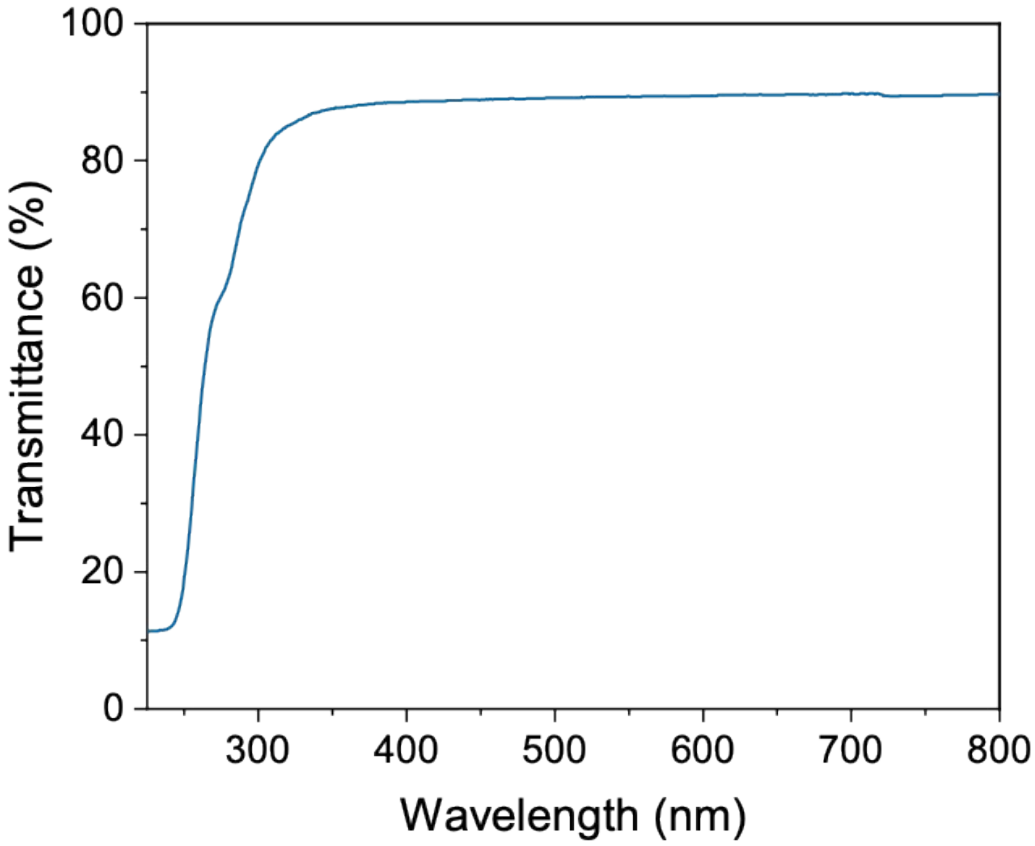

Fig. S17 Optical transparency of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 62.5 kDa, $Đ$ = 1.86). Visible light region starts at 400 nm.

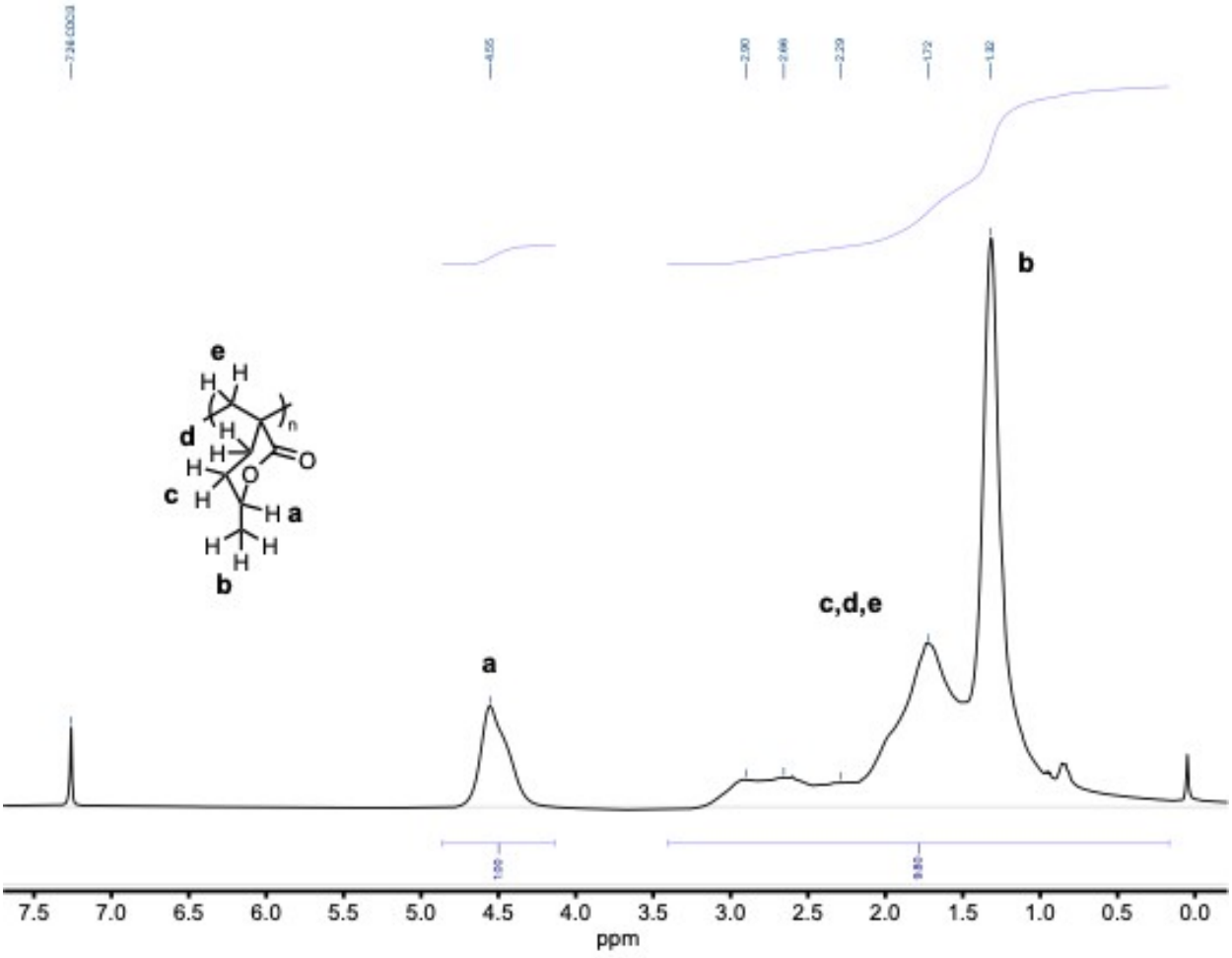

Fig. S18 ^{1}H NMR spectrum ($CDCl_3$, 23 °C) of purified PMCL produced from a ratio of [MCL]:[[La(OBn)$_3$]$_x$] = 1000:1 (M_n = 470 kDa, $Đ$ = 1.46). Peak around 0.86 ppm corresponds with grease.

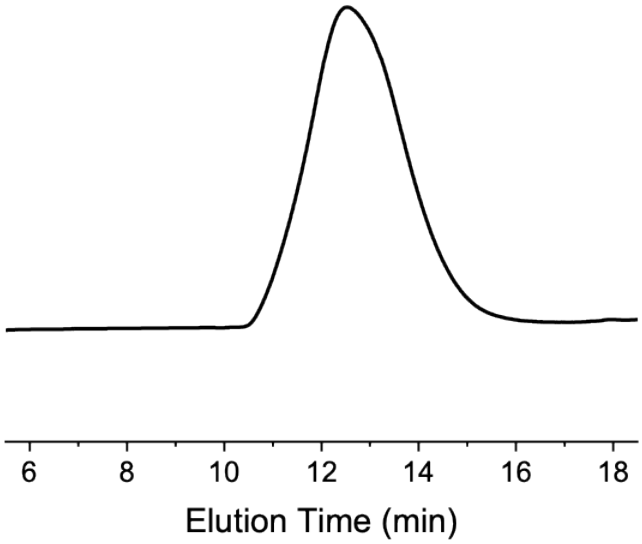

Fig. S19 SEC trace of PMCL produced from a ratio of [MCL]:[[La(OBn)$_3$]$_x$] = 1000:1. (M_n = 470 kDa, $Đ$ = 1.46).

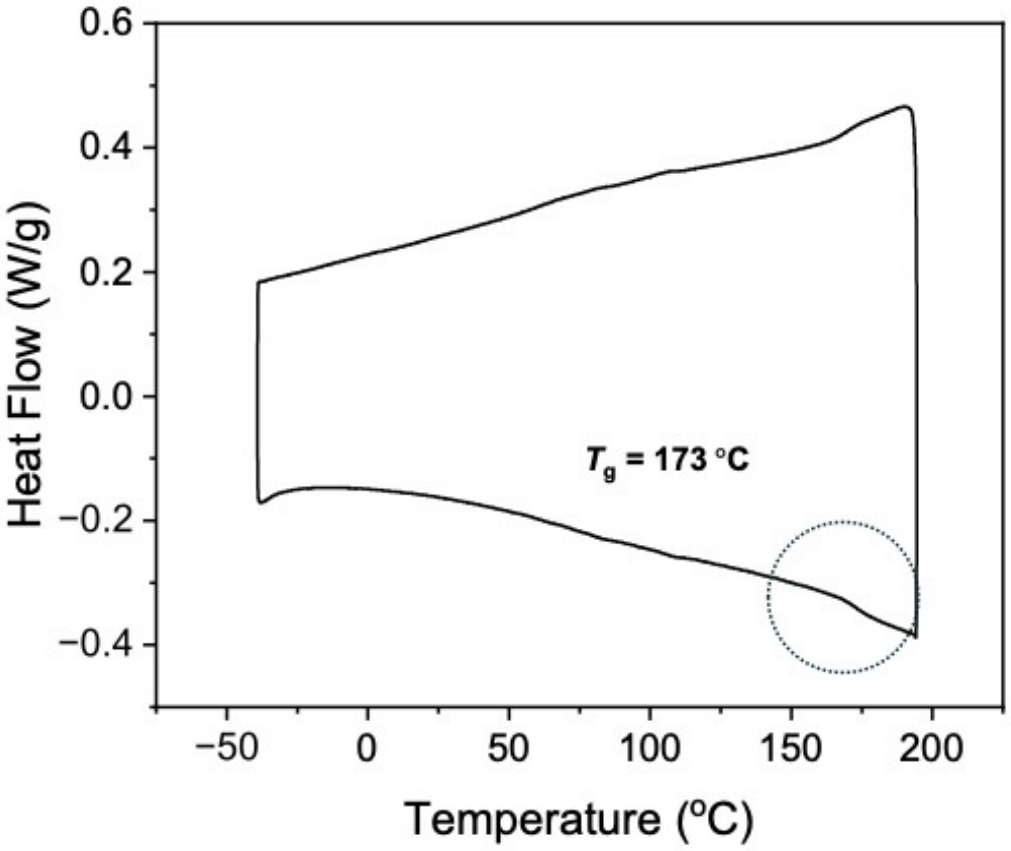

Fig. S20 DSC curve of PMCL produced from a ratio of [MCL]:[[La(OBn)$_3$]$_x$] = 1000:1 (M_n = 470 kDa, $Đ$ = 1.46).

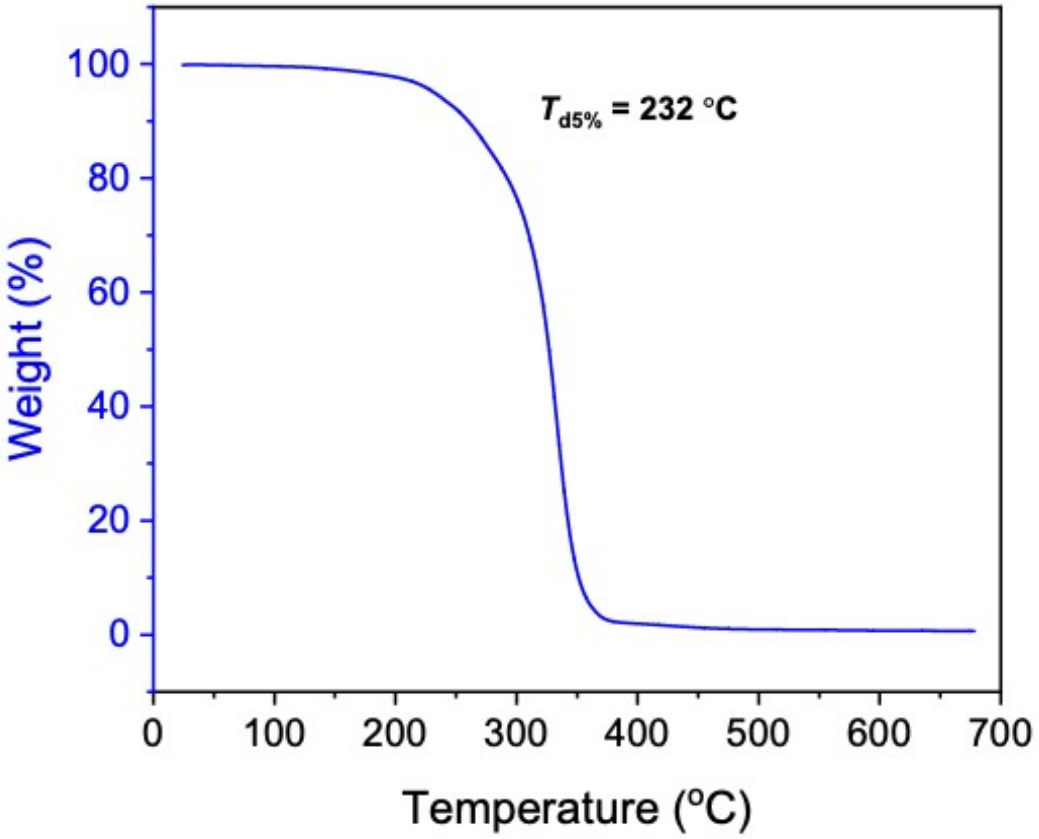

Fig. S21 TGA curve of PMCL produced from a ratio of [MCL]:[[La(OBn)$_3$]$_x$] = 1000:1 (M_n = 470 kDa, $Đ$ = 1.46).

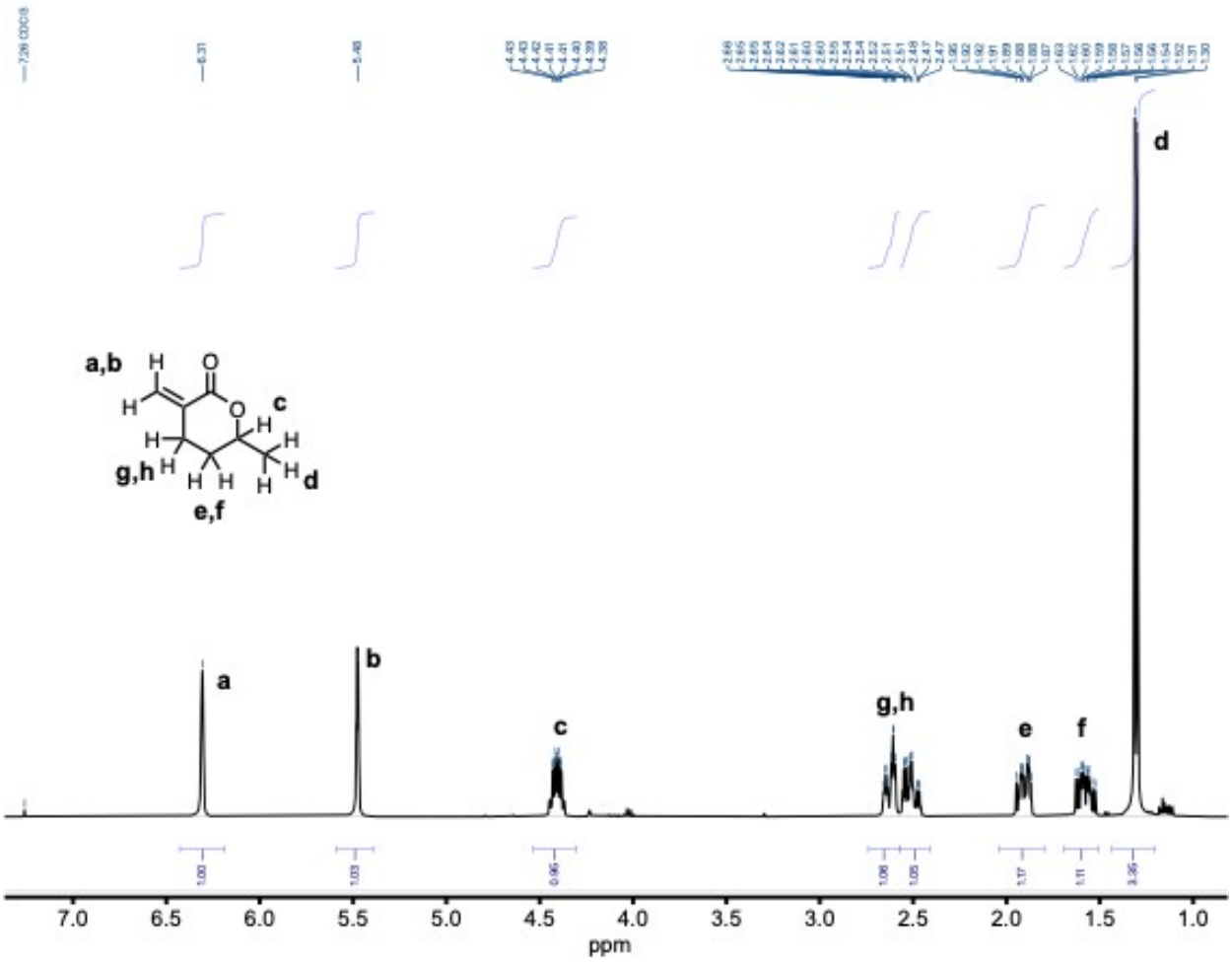

Fig. S22 ^{1}H NMR spectrum ($CDCl_3$, 23 °C) of MCL synthesized following the organic synthesis procedure as a reference for polymerization.

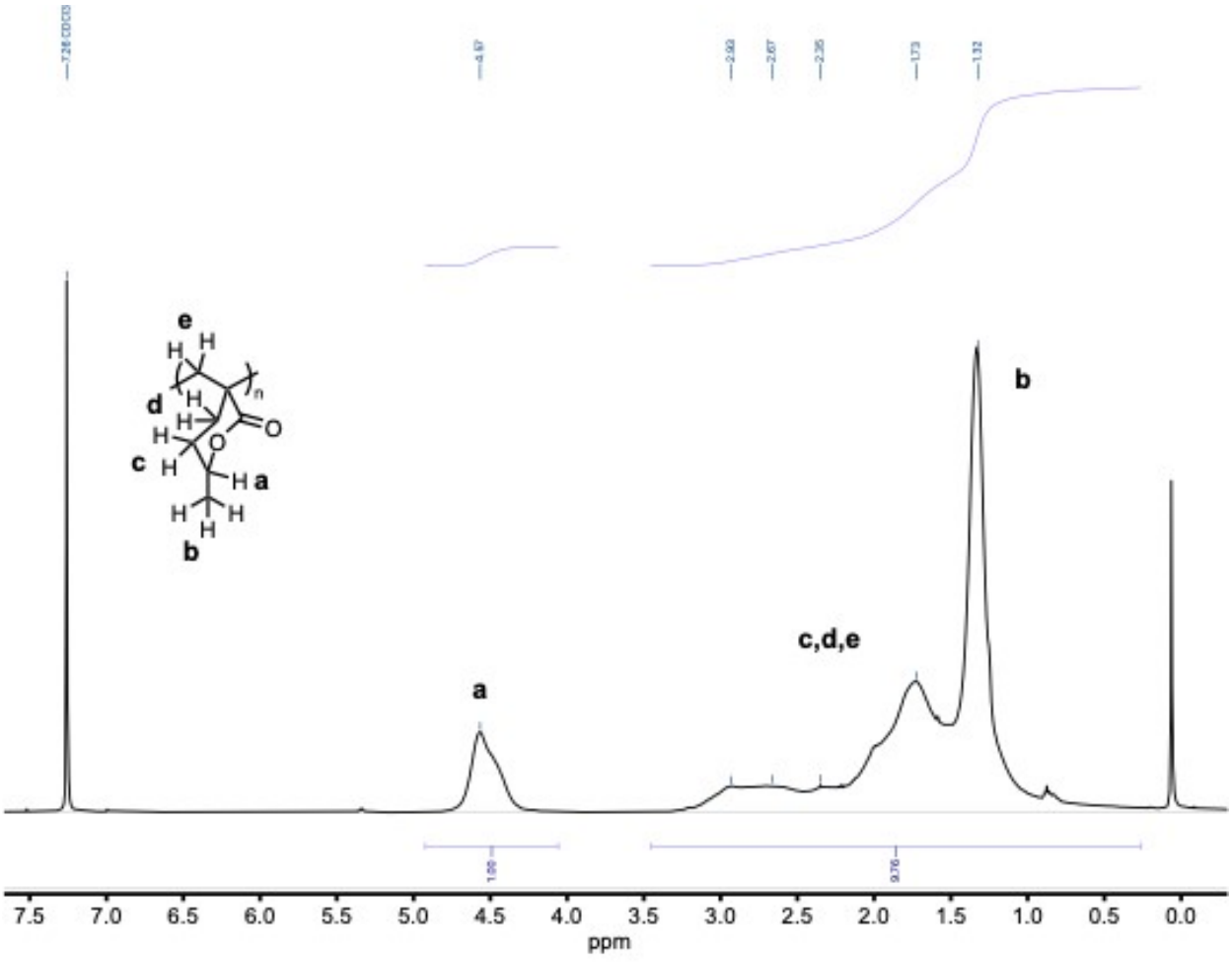

Fig. S23 ^{1}H NMR spectrum ($CDCl_3$, 23 °C) of purified PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 65.5 kDa, $Đ$ = 1.96) using MCL synthesized following the organic synthesis procedure.

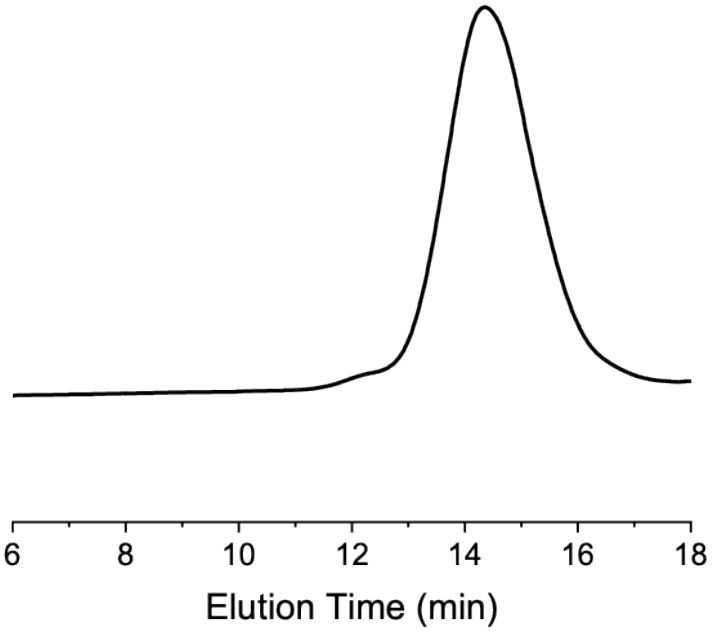

Fig. S24 SEC trace of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 65.5 kDa, $Đ$ = 1.96) using MCL synthesized following the organic synthesis procedure.

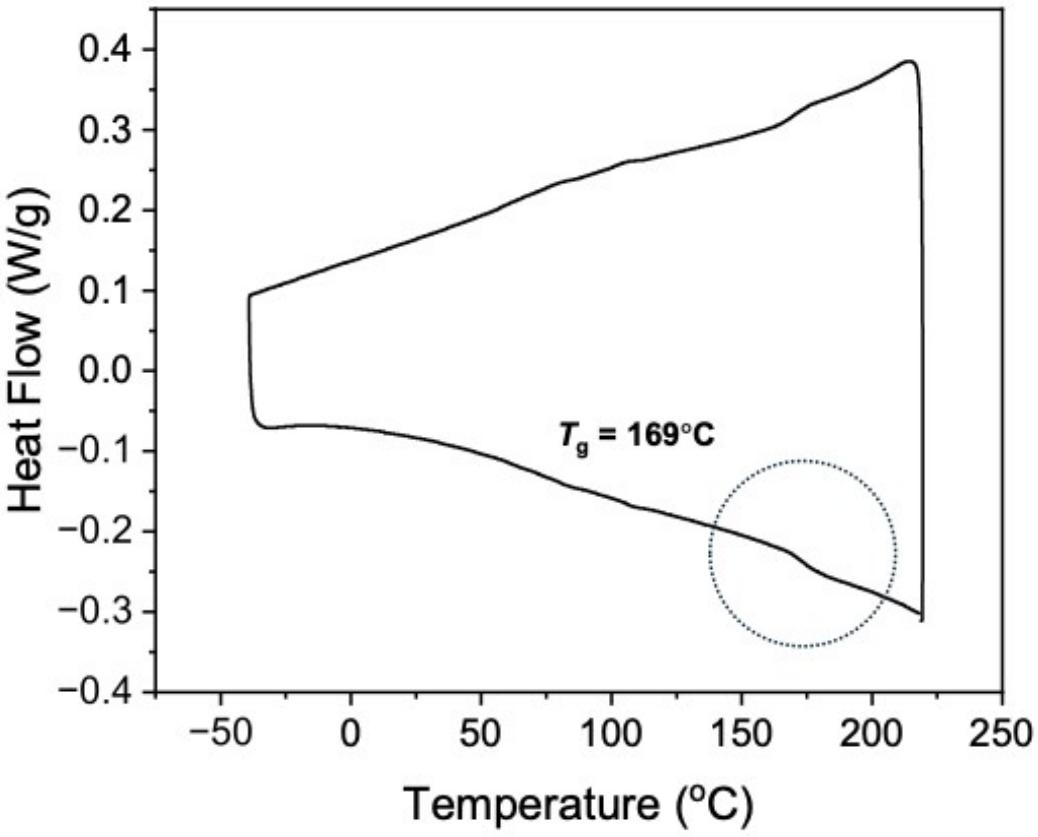

Fig. S25 DSC curve of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 65.5 kDa, $Đ$ = 1.96) using MCL synthesized following the organic synthesis procedure.

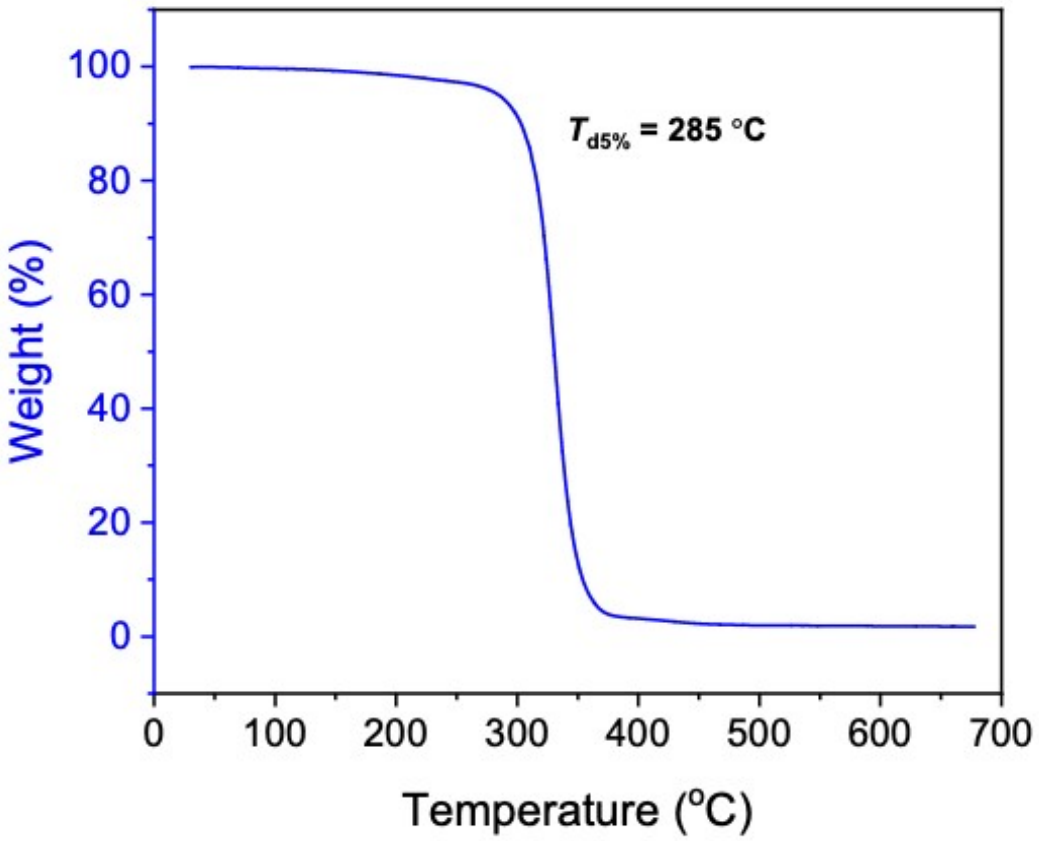

Fig. S26 TGA curve of PMCL produced from a ratio of [MCL]:[AIBN] = 1000:1 (M_n = 65.5 kDa, $Đ$ = 1.96) using MCL synthesized following the organic synthesis procedure.

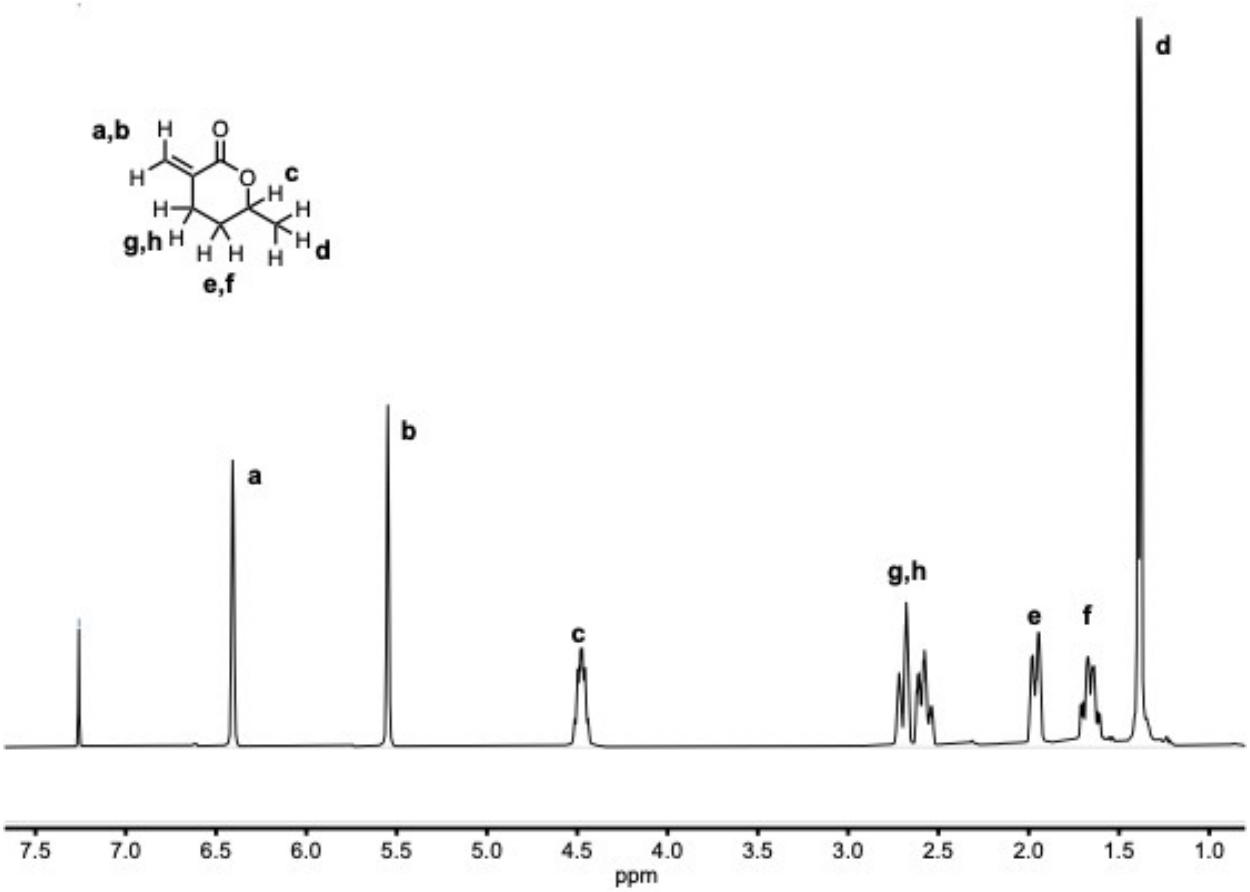

Fig. S27 ^{1}H NMR ($CDCl_3$, 23 ˚C) of pure MCL collected from reactive distillation experiment at 220 ˚C.

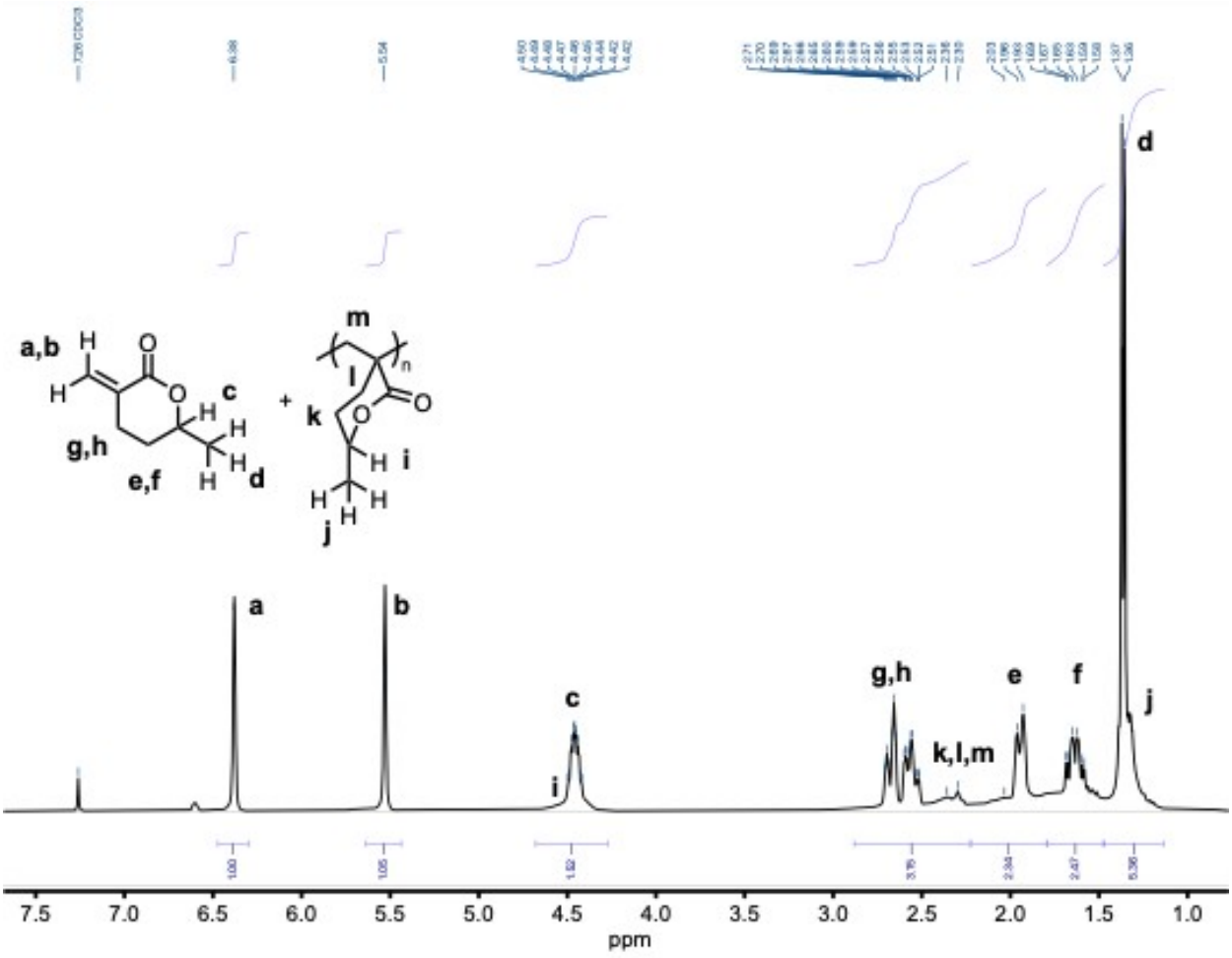

Fig. S28 ^{1}H NMR ($CDCl_3$, 23 °C) of MCL and PMCL oligomers remaining in the reaction flask following depolymerization at 220 ˚C over 11 h. Some structural hydrogens are omitted for clarity. Monomer and polymer peaks overlap.