

Chemoselective Polymerization of Fully Biorenewable α -Methylene- γ -Butyrolactone Using Organophosphazene/Urea Binary Catalysts Toward Sustainable Polyesters

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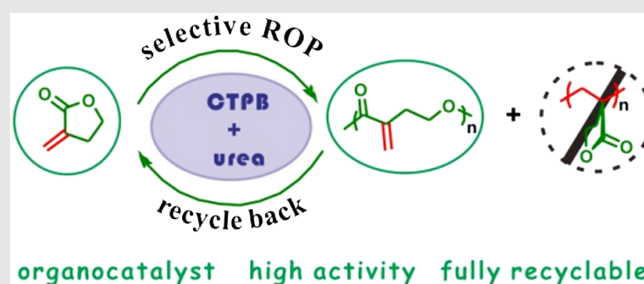
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Despite the great potential of biorenewable α -methylene- γ -butyrolactone (MBL) to produce functional, recyclable polyester, the ring-opening polymerization (ROP) of MBL remains a challenge due to the competing polymerization of the highly reactive exocyclic double bond and low-strained five-membered ring. In this contribution, we present the first organocatalytic chemoselective ROP of MBL to exclusively produce functional unsaturated polyester by utilizing a phosphazene base/urea binary catalyst. We show that delicate chemoselectivity can be realized by controlling the temperature and using selected urea catalysts. The obtained polyester can be completely recycled back to its monomer by chemolysis under mild conditions. Experimental and theoretical calculations provide mechanistic insights and indicate that

the ROP pathway is kinetically favored by using urea with stronger acidity at low temperatures.



Keywords: organocatalyst, ring-opening polymerization, polyester, sustainable polymer, recyclability

Introduction

Sustainable polymers derived from renewable feedstocks have attracted increasing attention due to growing concerns over the eventual consumption of finite fossil fuels and the concomitant environmental pollution caused by the production and disposal of petroleum-based polymeric materials.^{1–4} Aliphatic polyesters are probably the most intensively investigated sustainable polymers, such as poly(ϵ -caprolactone) (PCL), poly(glycolic acid) (PGA), and poly(L-lactide) (PLLA).⁵ Although these aliphatic polyesters can be readily degraded to CO₂ and water in nature, recycling remains as a challenge. For example, the thermal or chemical depolymerization of PLLA produces a mixture of lactide stereoisomers, cyclic oligomers, and other impurities, which require tedious purification before recycled L-LA can be reused.^{6–8} An approach to address the end-of-use issue of polymeric materials is to develop chemical recyclable polymers with closed-loop life cycles that can be completely depolymerized to their monomers under mild and energy efficient conditions.^{9,10}

One emerging frontier in chemical recyclable polymers is the design and preparation of polyesters using lactones with five-membered rings as building blocks.^{11–18} For example, Hong and Chen¹¹ realized the ring-opening polymerization (ROP) of γ -butyrolactone (γ BL) under readily accessible conditions by utilizing La- or Y-based organometallic catalysts. Organophosphazene superbases, such as *tert*-Bu-P₄ and a new cyclic trimetric phosphazene superbase (CTPB; Figure 1), were later demonstrated to be effective organocatalysts for the ROP of γ BL.^{12,13} Significantly, the resultant polyester, P γ BL, can be selectively and quantitatively depolymerized to its monomer γ BL by

simply heating the bulk material or chemolysis with a catalyst. A *trans*-cyclohexyl-ring-fused γ BL (3,4-T6GBL) at the α and β positions with increased ring strain energy relative to γ BL was recently developed, which can be readily polymerized into a high molecular weight polymer under room temperature and solvent-free conditions.^{14,15} The obtained polymer can also be recycled back to its monomer and successfully establish a circular life cycle. The same group recently presented the organocatalytic ROP of similar six-five bicyclic lactone (4,5-T6GBL) to produce high molecular weight recyclable polyesters utilizing organobase/(thio)urea binary catalysts.¹⁹

Despite the success achieved in recyclable polymers over the past several years, fully recyclable polymeric materials are still limited, especially those with functional groups. Lu et al.²⁰ recently developed recyclable polythioesters from biomass-sourced bridged bicyclic thio-lactones with side chain allyl functional groups, which can be further modified and provide opportunities to adjust the polythioesters' properties. Another functionalizable monomer with potential chemical recyclability is MBL, the simplest derivative of γ BL bearing a low-strained five-membered ring and an exocyclic double bond. MBL is naturally found in tulips and can be produced from biosourced feedstocks.²¹ MBL has been intensively investigated as a sustainable alternative to the petroleum-based methyl methacrylate (MMA) monomer due to a higher glass transition temperature and better solvent durability of the MBL-derived polymer compared with poly(methyl methacrylate) (PMMA).²² However, most studies have reported the vinyl-addition polymerization (VAP) of MBL through Michael-type addition across the exocyclic double bond to produce

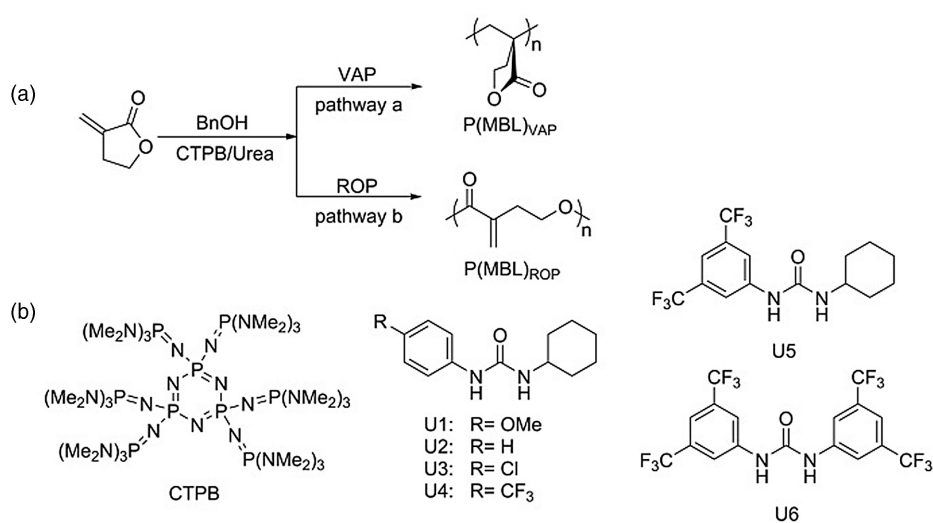


Figure 1 | (a) Two different polymerization pathways of MBL and (b) the chemical structures of CTPB and ureas used in this study.

P(MBL)_{VAP} (Figure 1a, pathway a) that is not fully degradable or recyclable.²²⁻²⁷ The selective ROP of MBL to produce recyclable polyesters is even more challenging compared with the ROP of γ BL due to the competing polymerization between the highly reactive exocyclic double bond and the low-strained five-membered lactone ring. To the best of our knowledge, the only selective ROP of MBL was performed by Chen et al. by utilizing La[N(SiMe₃)₂]₃ or yttrium-based catalysts. Intriguingly, the ROP product of MBL, P(MBL)_{ROP} (Figure 1a, pathway b), has been shown to be recyclable to MBL in the presence of a simple catalyst, LaCl₃.²⁸ Considering the high functional group tolerance, metal-free nature, and facile removal of catalyst residues from polymers, organocatalysts will be highly desirable for the chemoselective ROP of MBL.²⁹ Herein, we have reported the first organocatalytic chemoselective ROP of MBL to produce exclusively unsaturated recyclable P(MBL)_{ROP} by utilizing an organophosphazene base in combination with ureas as cocatalysts, which makes (PMBL)_{ROP} a metal-free sustainable polyester.

Experimental Methods

General polymerization procedure

A typical polymerization procedure (Table 1, run 5) is described as follows. A flame-dried Schlenk tube was charged with (0.05 mmol, 5.2 μ L) benzyl alcohol (BnOH), (0.05 mmol, 59.9 mg) CTPB, (0.15 mmol, 42.95 mg) U4, and 0.187 mL tetrahydrofuran (THF) in a glove box. The Schlenk tube was sealed with a septum and immersed into a cooling bath set to -50 °C. After equilibrium at -50 °C for 10 min, (5 mmol, 0.44 mL), MBL was injected into the Schlenk tube via a gastight syringe to begin the polymerization. The polymerization was conducted at -50 °C for 4 h before quenching via the addition of a few drops of acetic acid. About 3 mL dichloromethane (DCM) was used to dissolve the product. An aliquot of solution was withdrawn and used for MBL conversion determination with ¹H NMR measurement. The remaining solution was poured into excess cold methanol (-20 °C). The obtained precipitate was washed with cold methanol

Table 1 | Results of ROP of MBL with CTPB/Urea as Catalysts^a

Run	Initiator	Urea	[M]/[B]/[U]/[I]	Sol.	Temperature (°C)	Time (h)	C(ROP) (%) ^b	C(VAP) (%) ^b	Mn (kDa) ^c	\bar{D} ^c
1	BnOH		100/1/0/1	THF	-50	4	0	20	n.d.	n.d.
2	BnOH	U1	100/1/3/1	THF	-50	4	0	100	n.d.	n.d.
3	BnOH	U2	100/1/3/1	THF	-50	4	54	24	n.d.	n.d.
4	BnOH	U3	100/1/3/1	THF	-50	4	51	4	5.2	1.57
5	BnOH	U4	100/1/3/1	THF	-50	4	50	0	5.9	1.29
6	BnOH	U5	100/1/3/1	THF	-50	4	18	0	2.3	1.25
7 ^d	BnOH	U4	100/1/3/1	THF	-50	4	12	0	n.a.	n.a.
8	BnOH	U4	100/1/3/1	THF	-50	2	35	0	4.0	1.19
9	BnOH	U4	100/1/3/1	THF	-50	8	62	0	6.1	1.46
10	BnOH	U4	100/1/3/1	TOL	-50	4	16	0	n.a.	n.a.
11	BnOH	U4	100/1/3/1	DMF	-50	4	9	0	n.a.	n.a.
12	BnOH	U4	100/1/3/1	THF	-20	4	0	0	n.a.	n.a.
13	BnOH	U4	100/1/3/1	THF	25	4	0	37	n.d.	n.d.
14	BnOH	U4	100/1/2/1	THF	-50	4	65	0	5.2	1.34
15 ^e	BnOH	U4	100/1/1/1	THF	-50	4	n.d.	n.d.	n.d.	n.d.
16	BnOH	U4	100/1/3/5	THF	-50	4	47	0	3.2	1.31
17	BnOH	U4	100/1/3/2	THF	-50	4	52	0	4.4	1.33
18	BnOH	U4	100/1/3/0.67	THF	-50	4	45	0	6.7	1.34
19	BnOH	U4	200/2/6/1	THF	-50	4	43	0	6.4	1.56
20	ⁱ PrOH	U4	100/1/3/1	THF	-50	4	49	0	5.4	1.28
21	Ph ₂ CHOH	U4	100/1/3/1	THF	-50	4	35	0	5.8	1.32
22 ^f	-	U4	100/1/3	THF	-50	4	32	0	6.0	1.35

^a Conditions: (5 mmol, 490 mg) MBL was used. CTPB was used as the base. The polymerization was conducted at [MBL] = 8 M in THF. n.d.= not determined (M_n and \bar{D} not determined due to poor solubility in THF). n.a. = not available (no polymer precipitation occurred).

^b Determined by ¹H NMR.

^c Determined by SEC in THF relative to PS standards.

^d The MBL concentration was 6 M.

^e The conversions were not determined due to cross-linking.

^f No initiator was added.

once more and then dried under vacuum at room temperature to give PMBL as a white powder with 41.2% (202 mg) yield.

^1H NMR (DMSO- d_6 , 400 MHz): δ (ppm): 6.10 (s, 1H, =CH₂), 5.71 (s, 1H, =CH₂), 4.20 (t, 2H, J = 6.2 Hz, -OCH₂-), 2.58 (t, 2H, J = 6.2 Hz, -CH₂-). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ (ppm): 165.69, 136.32, 127.41, 62.66, and 30.76.

Depolymerization of P(MBL)_{ROP}

A flame-dried Schlenk tube was charged with (0.005 mmol, 6 mg) CTPB, (0.015 mmol, 7.2 mg) U6, and 1 mL THF in a glove box. About 49 mg P(MBL)_{ROP} (produced by MBL/KOMe/U4 = 100/1/3, M_n = 6.5 kDa, \bar{D} = 1.49) was then added into the aforementioned solution. The Schlenk tube was then immersed into an oil bath at 50 °C for 48 h. An aliquot of solution was then withdrawn and used for ^1H NMR measurement.

Postfunctionalization of P(MBL)_{ROP}

A mixture of 39.2 mg P(MBL)_{ROP} (M_n = 6.1 kDa, prepared by CTPB/U4), (5 equiv., 2 mmol, 174 μL) benzyl mercaptan, and (0.05 equiv., 0.02 mmol, 2.8 μL) triethylamine was dissolved in 0.4 mL dimethyl sulfoxide (DMSO). The reaction was conducted at 40 °C for 5 h. An aliquot of reaction mixture was withdrawn and used to determine the conversion by ^1H NMR measurement. The remaining mixture was poured into excess cold methanol (-20 °C). The obtained precipitate was washed with cold methanol twice and then dried under vacuum at room temperature.

^1H NMR (CDCl₃, 400 MHz): δ (ppm): 7.27 (br, 5H, Ph-), 4.05 (br, 2H, -OCH₂-), 3.66 (br, 2H, PhCH₂-), 2.65 (br, 2H, -SCH₂-), 2.53 (br, 1H, -CH<), 1.90 (br, 2H, -CH₂-). ^{13}C NMR (CDCl₃, 100 MHz): δ (ppm): 173.51, 137.97, 128.99, 128.67, 127.27, 62.53, 42.42, 36.68, 33.05, 30.38.

Results and Discussion

Chemoselective ROP of MBL

To realize the selective ROP of MBL, one should activate the low-strained five-membered γBL ring while inhibiting the VAP of the highly reactive exocyclic double bond simultaneously. Waymouth and coworkers reported the rapid and highly selective ROP of cyclic lactones, lactides, and carbonates by utilizing alkoxides in combination with (thio)ureas as catalysts.^{30,31} Interestingly, the (thio)urea anions generated by deprotonation of (thio)ureas with alkoxides are more effective at the activation of cyclic lactones compared to linear open-chain esters.^{30,31} Very recently, our group and others have successfully prepared high molecular weight P γBL with a strong base/(thio)urea binary catalytic system, in which (thio)urea anions were shown to also effectively activate the γBL ring.^{32–34} The strong base/(thio)urea binary

catalysts also showed high activity toward the ROP of other cyclic monomers.^{35,36} According to previous studies, we believe that urea anions can also effectively promote the ROP of MBL through activation of the γBL ring. On the other hand, the VAP pathway of MBL is proposed to proceed via the generation of a carbanion intermediate, which requires catalysts with considerably stronger basicity than those suitable for the ROP pathway. As such, we speculate that MBL may undergo chemoselective ROP by judicious selection of suitable combinations of organobases and ureas.

As a proof of concept, a series of ureas bearing a cyclohexyl group and a substituted phenyl group was designed and screened for the chemoselective ROP of MBL since ureas with asymmetric structures were proven to be more effective at γBL ring activation (Figure 1b, see Supporting Information Figures S1–S5).³⁴ It was reported that the ROP of MBL gave an enthalpy change of $\Delta H = -5.9 \text{ kJ mol}^{-1}$ and an entropy change of $\Delta S = -40.1 \text{ J mol}^{-1} \text{ K}^{-1}$, which corresponded to a ceiling temperature of -14 °C at $[\text{MBL}]_0 = 8 \text{ M}$ or -52 °C at $[\text{MBL}]_0 = 5 \text{ M}$.²⁸ To achieve the ROP of MBL, the polymerization should be conducted at a low temperature to meet the thermodynamic requirements. As a consequence, the experiments were first conducted at low temperature (-50 °C) and high monomer concentration (8 M) in THF to favor the ROP of MBL in the presence of BnOH as the initiator. As a control experiment, the polymerization conducted with CTPB in the absence of urea achieved a low MBL conversion of 20%, exclusively producing VAP product P(MBL)_{VAP} (Table 1, run 1). A urea with a 4-methoxyphenyl group (U1) was then attempted in combination with CTPB as the base for the polymerization of MBL at a feeding molar ratio of MBL/CTPB/U1/BnOH = 100/1/3/1. The polymerization achieved 100% MBL conversion within 4 h but still proceeded exclusively through the VAP pathway (Table 1, run 2). By changing the substituent at the *para*-position of the phenyl ring from methoxy to hydrogen and chloro, a mixture of P(MBL)_{VAP} and P(MBL)_{ROP} was obtained, and the accompanying MBL conversion through the VAP pathway decreased from 100% to 24% and 4% (runs 3 and 4), respectively. The exclusive ROP of MBL was achieved with U4 as a cocatalyst, which features a 4-trifluoromethylphenyl group. An MBL conversion of 50% was obtained within 4 h, producing P(MBL)_{ROP} with a molecular weight of $M_n = 5.9 \text{ kDa}$ and a relatively narrow distribution of $\bar{D} = 1.29$ (run 5). The basicity of the deprotonated urea anions was expected to sequentially decrease from U1 to U4, considering the gradual increase of the electron-withdrawing effect of the substitution group on the aromatic ring. Thus, the aforementioned results appear to agree well with our initial hypothesis on using a weaker basic catalyst to favor the ROP of MBL and inhibit the VAP pathway in the meantime. Nevertheless, although cocatalyst U5 bearing a more

electron-withdrawing substituent of 3,5-bis(trifluoromethyl)phenyl group also produced P(MBL)_{ROP} exclusively, the MBL conversion dropped to only 18% and the resulting polymer showed a decreased $M_n = 2.3$ kDa (run 6). This result indicated that while a less basic urea anion can generally improve ROP selectivity, it may also result in decreased catalytic activity.^{30,37} Next, we focused on U4 for further optimization because it appeared to give balanced selectivity and catalytic activity.

The polymerization was further investigated with CTPB/U4 as the catalyst under different conditions. The polymerization conducted at a lower initial monomer concentration of 6 M resulted in much lower MBL conversions, and no polymers were obtained by precipitation (run 7). An extended polymerization time to 8 h led to a slightly higher MBL conversion to 62% and a comparable molecular weight of $M_n = 6.1$ kDa but with a broader polydispersity of $\mathcal{D} = 1.46$, which is likely due to the intra- or intermolecular transesterification (run 9). Switching the solvent from THF to toluene (TOL) or *N,N*-dimethylformamide (DMF) still led to good chemoselectivity through the ROP pathway but resulted in lower MBL conversions (run 10 and 11). The decreased MBL conversion in TOL is probably due to the decreased solubility of CTPB/U4 in TOL. Of note, the MBL conversions for the polymerizations conducted in THF can exceed the thermodynamic equilibrium limit because the resulting polymer can precipitate out of the reaction system. In contrast, the same polymerization in DMF gave a lower monomer conversion because the polymerization remained as a homogeneous system. The polymerization was then conducted at different temperatures to investigate the effect of temperature on chemoselectivity. No polymerization was observed either via the VAP or ROP pathway at -20 °C (run 12). Further elevating the polymerization temperature to 25 °C resulted in the exclusive formation of P(MBL)_{VAP} (run 13). These results suggested that low temperature was necessary to provide negative Gibbs free energies to thermodynamically drive the ROP of the γ BL ring as discussed earlier.¹¹ The molar ratio of CTPB/urea also plays a critical role on the conversion of MBL and polymerization chemoselectivity. For example, a slightly higher MBL conversion of 65% through the ROP pathway can be obtained at CTPB/U4 = 1/2 at -50 °C (run 14), but a further decrease in the U4 amount to CTPB/U4 = 1/1 resulted in formation of cross-linked networks probably due to the coexistence of the VAP and ROP pathways (run 15). It was reported that the urea anions can activate the propagating chain end by hydrogen bonding.³⁰ The addition of excess neutral ureas might reduce the activity of propagating chains by forming hydrogen bonding with urea anions.³⁰ Here, we speculate that the basicity and catalytic activity of the U4/U4 pair were subtly adjusted by the amount of neutral U4, which served as not only an acid but also a hydrogen bonding donor

participating in the polymerization.^{30,37} Overall, the polymerizations prefer to proceed via the ROP pathway at a lower temperature and excess U4 can effectively inhibit the VAP pathway.

P(MBL)_{ROP} with varied molecular weights can be successfully prepared by adjusting the feeding molar ratio of MBL to BnOH. The molecular weight of P(MBL)_{ROP} increased from 3.2 to 4.4 kDa and 6.7 kDa as MBL/BnOH increased from 100/5 to 100/2 and 100/0.67 (see Supporting Information Figure S7), respectively. Two other alcohol initiators, isopropanol (*i*PrOH) and diphenylmethanol (Ph₂CHOH), also resulted in exclusive formation of P(MBL)_{ROP}. *i*PrOH as an initiator gave similar results as BnOH, whereas Ph₂CHOH with bulkier groups gave lower MBL conversion (runs 20 and 21). The polymerization conducted in the absence of initiator also led to chemoselective ROP of MBL but resulted in lower MBL conversion (run 22). In addition to CTPB, the chemoselective ROP of MBL can also be achieved by utilizing common inorganic bases in combination with U4, such as KOMe and NaOMe (see Supporting Information Table S1).

It is worth pointing out that the CTPB/U4 binary catalyst described herein showed a higher turnover frequency (TOF) compared to the previously reported lanthanum complex La[N(SiMe₃)₂]₃.²⁸ For example, the polymerization conducted at the same conditions utilizing La[N(SiMe₃)₂]₃ as the catalyst achieved a lower MBL conversion of 19%, producing P(MBL)_{ROP} with a lower $M_n = 2.2$ kDa (see Supporting Information Table S2). On the other hand, the previously reported yttrium-based catalyst exhibited the best catalytic activity so far as indicated by its ability to produce high molecular weight P(MBL)_{ROP} up to $M_n = 21.0$ kDa.²⁸ In our laboratory, more effort is being devoted to improving the molecular weight of P(MBL)_{ROP} utilizing the current organophosphazene base/urea catalytic system.

The well-defined structure of the obtained P(MBL)_{ROP} was further examined collaboratively with NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). As shown in Figure 2, the ¹H NMR spectra of the obtained P(MBL)_{ROP} clearly displays characteristic double bond resonances at 6.10 and 5.71 ppm without the presence of any P(MBL)_{VAP} contamination, which is expected to show two broad peaks at 4.34 and 2.10 ppm. Moreover, the clear assignments of chain end groups suggest that the obtained P(MBL)_{ROP} samples were dominantly initiated by BnOH, *i*PrOH, and Ph₂CHOH, as designed. The representative ¹³C NMR spectrum of P(MBL)_{ROP} shown in Supporting Information Figure S8 is also in good agreement with a ring-opened structure rather than a vinyl-addition structure. The MALDI-TOF mass spectra of P(MBL)_{ROP} confirm the linear structure of obtained P(MBL)_{ROP} with expected chain ends, which is consistent with the aforementioned NMR analyses (see Supporting Information

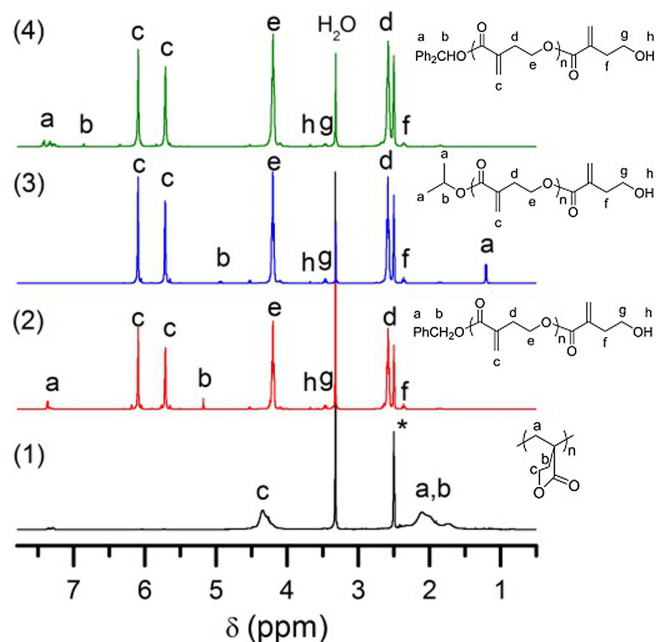


Figure 2 | Stacked ^1H NMR spectra of (1) $\text{P}(\text{MBL})_{\text{VAP}}$ and $\text{P}(\text{MBL})_{\text{ROP}}$ initiated by (2) BnOH , (3) $i\text{PrOH}$, and (4) Ph_2CHOH measured in DMSO-d_6 (the residual solvent peak marked as *).

Figures S9–S11). For example, the MALDI-TOF mass spectrum of a low molecular weight $\text{P}(\text{MBL})_{\text{ROP}}$ initiated by BnOH displays two series of molecular ion peaks, in which the major peaks are assigned as linear $\text{P}(\text{MBL})_{\text{ROP}}$ with BnO/H chain ends and the minor peaks are assigned as linear $\text{P}(\text{MBL-co-}\gamma\text{BL})_{\text{ROP}}$ copolymers with BnO/H chain

ends (see Supporting Information Figure S9). Notably, the presence of a trace amount of $\text{P}(\text{MBL-co-}\gamma\text{BL})$ copolymers is also confirmed by the ^1H NMR spectrum (see Supporting Information Figure S12), which is ascribed to the small amount of γBL impurity existing in the purchased MBL reagent (see Supporting Information Figure S13).

Thermal properties and postfunctionalization of $\text{P}(\text{MBL})_{\text{ROP}}$

The thermal properties of the obtained $\text{P}(\text{MBL})_{\text{ROP}}$ were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses. Supporting Information Figure S14 compares the TGA and DTG curves of two $\text{P}(\text{MBL})_{\text{ROP}}$ samples with different molecular weights as well as a $\text{P}(\text{MBL})_{\text{VAP}}$ sample (see Supporting Information). Both $\text{P}(\text{MBL})_{\text{ROP}}$ samples displayed a multistep degradation profile, which is consistent with a previous report.²⁸ The temperature at 5% weight loss ($T_{\text{d}, 5\%}$) improved from 229 to 261 °C as the molecular weight of $\text{P}(\text{MBL})_{\text{ROP}}$ increased from 4.4 to 5.9 kg mol^{-1} . On the other hand, both $\text{P}(\text{MBL})_{\text{ROP}}$ samples gave a temperature at maximum degradation rate ($T_{\text{d}, \text{max}}$) near 340 °C. In contrast, the $\text{P}(\text{MBL})_{\text{VAP}}$ sample exhibited a one-step degradation profile with a much higher $T_{\text{d}, 5\%}$ of 338 °C and a $T_{\text{d}, \text{max}}$ of 406 °C. A series of $\text{P}(\text{MBL})_{\text{ROP}}$ samples with varied molecular weights were subjected to DSC analyses, and the related results are summarized in Supporting Information Table S3. The $\text{P}(\text{MBL})_{\text{ROP}}$ samples were found to be semicrystalline polyester although there were no melting transitions observed at a 10 °C/min heating rate probably due to their slow crystallization (Figure 3).

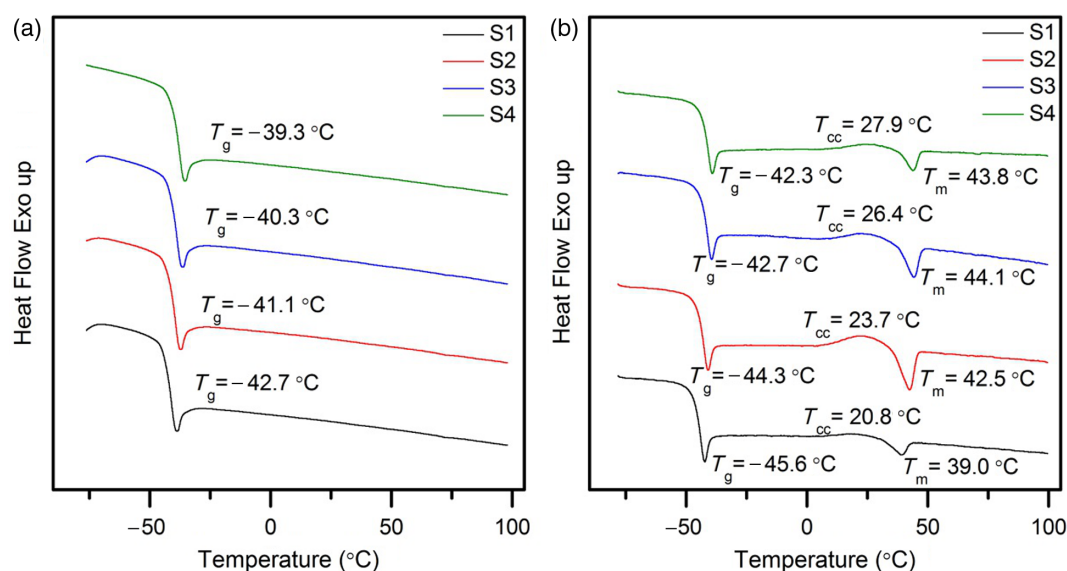


Figure 3 | DSC curves for second heating scans of $\text{P}(\text{MBL})_{\text{ROP}}$ samples with variable molecular weights at different heating rates: (a) 10 °C/min and (b) 2 °C/min. S1: Table 1, run 16; S2: Table 1, run 17; S3: Table 1, run 5; S4: Table 1, run 18.

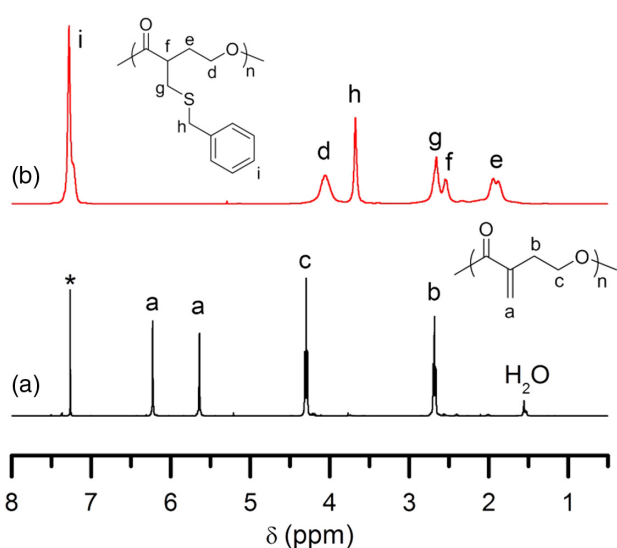


Figure 4 | Overlay of ¹H NMR spectra measured in CDCl₃ of (a) P(MBL)_{ROP} (M_n = 6.1 kDa, prepared by CTPB/U4) and (b) the obtained thiolated polyester P(MBL)_{ROP}-SR produced by thiol-Michael addition reaction (residual solvent peak marked as *).

All samples gave a glass transition temperature T_g in the range of -42 to -46 °C at a 2 °C/min heating rate. A cold crystallization transition temperature T_{cc} and a melting temperature T_m in the range from 20.8 to 27.9 °C and from 39.0 to 44.1 °C, respectively, can be observed at a 2 °C/min heating rate. As the molecular weights of the P(MBL)_{ROP} samples increased, the T_g , T_{cc} , and T_m slightly increased.

The pendent double bond of P(MBL)_{ROP} can be further functionalized by UV-triggered cross-linking or a photo-catalyzed thiol-ene click reaction as reported before.²⁸ Herein, we presented the postfunctionalization of P(MBL)_{ROP} by a thiol-Michael addition reaction. Benzyl mercaptan was used as a representative thiol to react with P(MBL)_{ROP} in DMSO at 40 °C in the presence of triethylamine as the catalyst. The disappearance of double bond signals, as shown in the ¹H NMR spectrum, suggests the complete conversion of P(MBL)_{ROP} to produce a thiolated polyester P(MBL)_{ROP}-SR (Figure 4).

Chemical recycling of P(MBL)_{ROP}

Similar to P(MBL)_{ROP} generated by the La or Y metal-based catalysts, the P(MBL)_{ROP} obtained herein by organocatalytic ROP can also be completely recycled back to its starting monomer MBL. Although simple metal catalysts, such as LaCl₃, have been used for chemolysis of P(MBL)_{ROP},²⁸ our interest focuses on the depolymerization of P(MBL)_{ROP} mediated by an organophosphazene base/urea catalyst. Initial attempts with CTPB/U4 or CTPB/U5 as the catalyst at 25 °C failed to recycle MBL as indicated by the formation of P(MBL)_{VAP}.

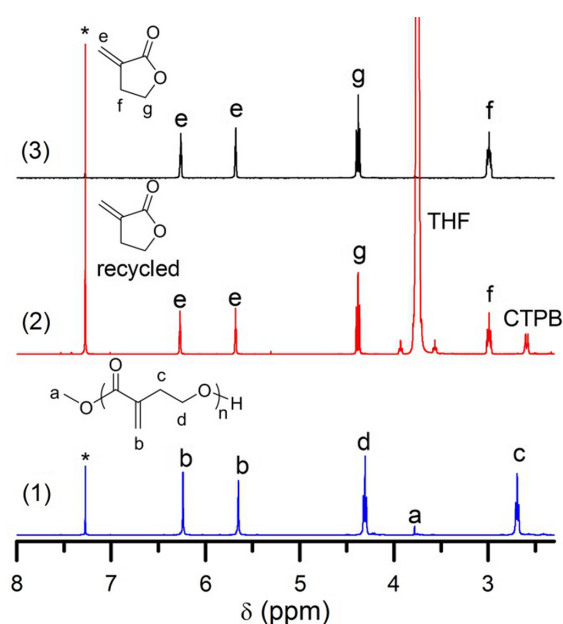


Figure 5 | Overlay of ¹H NMR spectra measured in CDCl₃ of (1) P(MBL)_{ROP} (M_n = 6.5 kDa, prepared by KOMe/U4); (2) the obtained reaction mixture after heating P(MBL)_{ROP} in the presence of CTPB/U6 = 1/3 in THF at 50 °C for 48 h; (3) the original MBL monomer for comparison (residual solvent peak marked as *).

To inhibit the VAP pathway, a urea with more electron-withdrawing substituents, U6, was used as a cocatalyst in combination with CTPB (see Supporting Information Figure S6). Quantitative recycling of clean MBL monomer can be achieved by heating a 0.5 M solution of P(MBL)_{ROP} in THF at 50 °C within 48 h in the presence of CTPB/U6 = 1/3 (0.01 equiv. CTPB relative to repeating units) as evidenced by the ¹H NMR spectra (Figure 5). More experiments are still occurring in our group to further optimize the chemolysis conditions.

Mechanistic considerations

To give more details regarding the binary catalyst-mediated ROP of MBL, NMR experiments were then conducted to investigate the interactions of CTPB, urea, and BnOH. Figure 6 gives the stacked ¹H NMR spectra of BnOH, U4, CTPB/U4 = 1/1, CTPB/U4/BnOH = 1/1/1, and CTPB/U4/BnOH = 1/3/1, measured in THF-*d*₈ at room temperature. The deprotonation of U4 by CTPB to generate urea anions was evidenced by the disappearance of half of the urea protons (see Supporting Information Figure S15) and the concomitant shift of other proton resonances of U4 (d, e, g, and h) to upfield, which is consistent with previous reports.^{34,38} Upon addition of BnOH, the formation of hydrogen bonding between BnOH and the U4 anion rather than the formation of the BnO⁻ anion was indicated by the downfield shift of the methylene proton resonance (b)

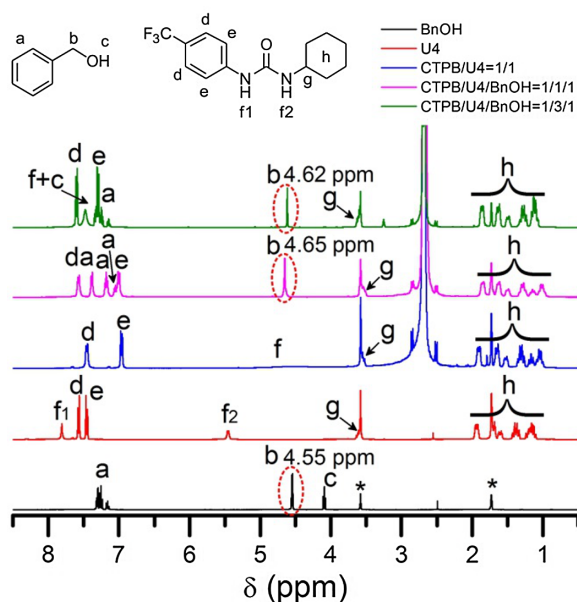


Figure 6 | Overlay of ^1H NMR spectra of BnOH, U4, CTPB/U4=1/1, CTPB/U4/BnOH=1/1/1, and CTPB/U4/BnOH=1/3/1 measured in THF- d_8 at room temperature (residual solvent peak marked as *).

from 4.55 to 4.65 ppm as well as the broadening of the hydroxyl proton (c) signal (see Supporting Information Figure S16). The addition of excess U4 led to the reduced deshielding effect to methylene proton (b) of BnOH as evidenced by the slightly upfield shift of proton resonance (b) from 4.65 to 4.62 ppm. This result suggested weaker hydrogen bonding interactions, as well as weaker activation of the hydroxyl groups of BnOH in the mixture of CTPB/U4/BnOH=1/3/1 compared to the case of CTPB/U4/BnOH=1/1/1. In comparison, ^1H NMR of CTPB/U1/BnOH=1/1/1 showed that the same methylene proton resonance (b) shifted to 4.81 ppm (see Supporting Information Figure S17), suggesting stronger activation of the hydroxyl group of BnOH by the U1 anion. This is not surprising if we consider that the *p*-CF₃-substituted U4 anion has weaker basicity than the *p*-MeO-substituted U1 anion.

We next studied the chain initiation and propagation steps of both ROP and VAP pathways with DFT calculations to better understand polymerization chemoselectivity. To simplify the calculation, a methoxy chain end was used and U4 was considered fully deprotonated in the model reaction. Figure 7 gives the intermediates (INT) and transition states (TS) involved in the chain initiation and propagation steps for ROP and VAP pathways as well as the corresponding free energies when U4⁻ was used as the catalyst. Notably, the chain initiation and propagation of the ROP pathway were essentially the same process, both

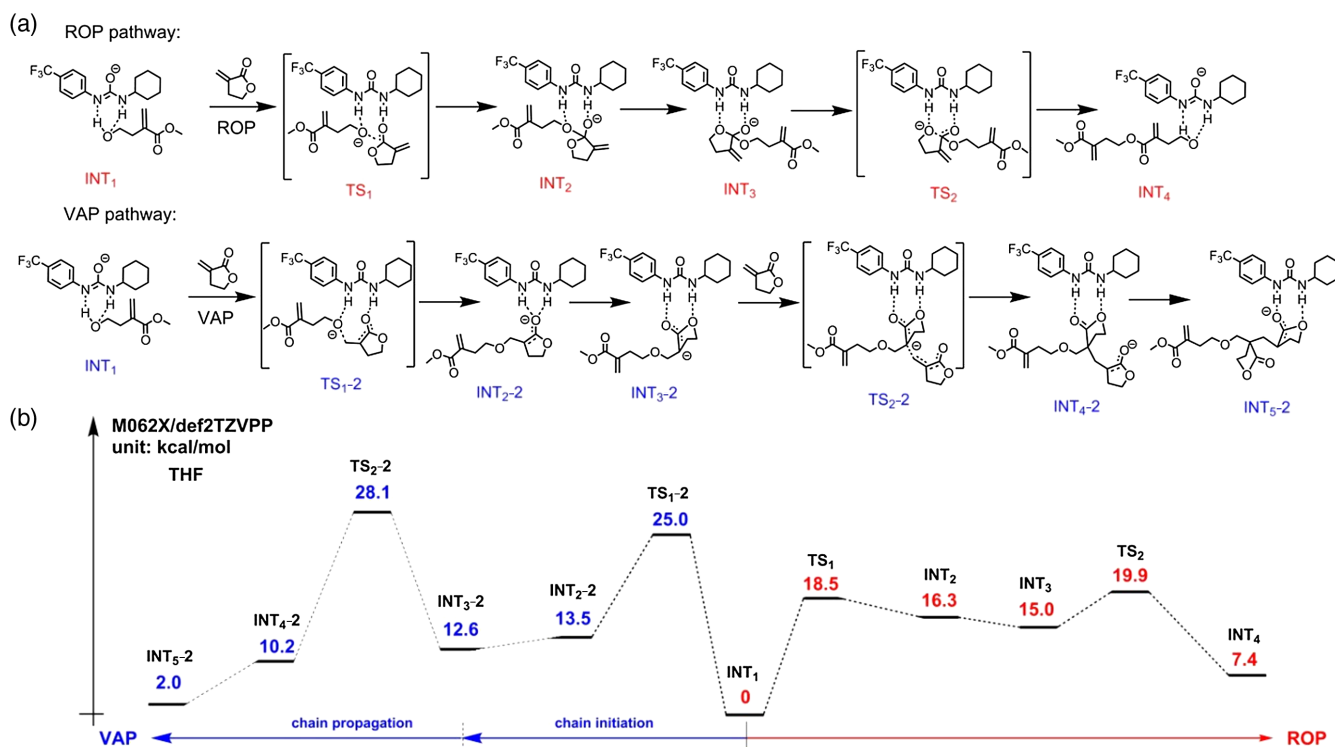


Figure 7 | (a) Proposed intermediates (INT) and transition states (TS) in the chain propagation step for the ROP and VAP pathway of MBL. (b) Free energy profiles (kcal mol^{-1} in THF) for each INT and TS calculated by DFT.

mediated by the complex of primary alcohol/U4⁻ (Figure 7a, INT₁ to INT₄); however, for the VAP pathway, the chain initiation was the Michael-type addition of the primary alcohol to the double bond to form a carbanion (Figure 7a, INT₁ to INT₃₋₂), and the following chain propagation was mediated by a carbanion/U4 complex (INT₃₋₂ to INT₅₋₂). The calculated energy barrier for the ROP pathway (INT₁ to TS₂) was +19.9 kcal mol⁻¹ and the net free energy change was +7.4 kcal mol⁻¹ (INT₁ to INT₄) in THF. On the other hand, to switch from the ROP to the VAP pathway, the energy barrier (INT₁ to TS₁₋₂) for initiation was as high as +25.0 kcal mol⁻¹ in THF and the free energy change (INT₁ to INT₃₋₂) was +12.6 kcal mol⁻¹. Thus, although the VAP pathway is overall thermodynamically more favorable (free energy change from INT₃₋₂ to INT₅₋₂ is -10.6 kcal mol⁻¹), switching from the ROP pathway to the VAP pathway requires a considerable higher energy barrier (19.9 vs 25.0 kcal mol⁻¹), which makes the ROP pathway kinetically favored. Overall, the DFT calculations and the ¹H NMR study collaboratively suggest that the kinetically controlled ROP pathway is favored at low temperatures using less basic urea anion (U4⁻), whereas the thermodynamically controlled VAP pathway would dominate at elevated temperatures and/or using stronger basic urea anions (U1⁻). These results agree well with our experimental data in which both the temperatures and selection of ureas played important roles on the polymerization chemoselectivity.

Conclusions

The selective polymerization of MBL via the ROP pathway is an important approach toward functional aliphatic polyesters for sustainable applications. However, due to the unfavorable thermodynamic characteristics and competing VAP pathway, the chemoselective ROP of MBL has only been recently achieved using organometallic catalysts²⁸, whereas a large number of attempts using organocatalysts all afforded P(MBL)_{VAP}.³⁹⁻⁴¹ Here, the chemoselective ROP of MBL to exclusively produce unsaturated P(MBL)_{ROP} polyester without contamination of the VAP product was successfully realized by utilizing a unique CTPB/urea binary catalyst. Different alcohols can be used as initiators, and the well-defined chain end fidelity was characterized with NMR and MALDI-TOF MS spectra. Although MBL cannot be completely polymerized through ROP pathway due to the intrinsic low strain energy of its five-membered ring and the related unfavorable thermodynamics, the conversion of MBL by an organobase/urea catalyst is comparable to previous organometallic catalysts.²⁸ In addition, the unconverted MBL can be easily recovered by distillation from the reaction medium, which minimizes loss of material value. Quantitative recycling of obtained P(MBL)_{ROP} back to its monomer was achieved under mild conditions. The DSC results indicated the obtained P(MBL)_{ROP} was a semicrystalline polyester with

a slow crystallization rate. The chain initiation and propagation mechanism through either ROP or VAP pathway was investigated with NMR experiments and DFT calculations, which suggested that the ROP pathway was kinetically more favored, whereas the competing VAP pathway was thermodynamically favored. The key to the chemoselective ROP of MBL, uncovered by both our experimental and DFT calculation results, is the prevention of the propagating chain switching from anionic alkoxide to carbanion. In our study, we achieved this by judicious selection and screening of cocatalyst urea. Following this rule, we realized similar chemoselective ROP of MBL using a CH₃O⁻M⁺ (M⁺ = Na⁺ or K⁺)/U4 binary system. Compared with previously reported organometallic catalysts, the organobase/urea binary system features a number of advantages including lower cost, better stability, scalability, and biocompatibility, which is beneficial for future scalability and industrialization. Although the molecular weight needs further improvement in this study, the P(MBL)_{ROP} bearing well-defined chain end (see supra) is expected to be a useful precursor for polyurethane preparation. In addition, the pendent double bond of P(MBL)_{ROP} can be facilely postfunctionalized by thiol-Michael addition reaction, which holds promises constructing useful materials such as drug delivery carriers or elastomers. Overall, this work offers molecular understanding and mechanistic insights on controlling the chemoselective polymerization of MBL using binary organocatalysts, which may lay the foundation for a wide range of organocatalytic systems for the synthesis of high molecular weight sustainable P(MBL)_{ROP} and functional, recyclable polyesters.

Supporting Information

Supporting Information is available.

Conflict of Interest Statement

There is no conflict of interest to report.

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