Precise synthesis of sulfur-containing polymers via cooperative dual organocatalysts with high activity

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Metal-free and controlled synthesis of sulfur-containing polymer is still a big challenge in polymer chemistry. Here, we report a metal-free, living copolymerization of carbonyl sulfide (COS) with epoxides via the cooperative catalysis of organic Lewis pairs including bases (e.g.: phosphazene, amidine, and guanidine) and thioureas as hydrogen-bond donors, afford well-defined poly(monothiocarbonate)s with 100% alternating degree, >99% tail-to-head content, controlled molecular weights (up to 98.4 kg/mol), and narrow molecular weight distributions (1.13–1.23). The effect of the types of Lewis pairs on the copolymerization of COS with several epoxides is investigated. The turnover frequencies (TOFs) of these Lewis pairs are as high as 112 h⁻¹ at 25 °C. Kinetic and mechanistic results suggest that the supramolecular specific recognition of thiourea to epoxide and base to COS promote the copolymerization cooperatively. This strategy provides commercially available Lewis pairs for metal-free synthesis of sulfur-containing polymers with precise structure.
The finding of fresh monomers and the development of active catalysts are the central topics in synthetic polymer chemistry. Carbonyl sulfide (COS), a key intermediate of the atmospheric sulfur cycle and the most abundant sulfur-containing gas in the troposphere, causes haze, acid rain, and ozonosphere damage, and is also a one-carbon (C1) hetero-containing gas in the troposphere, causes haze, acid rain, and ozonosphere damage. Recent synthetic advances provide metal catalytic strategies for making a variety of COS-derived poly(monothiocarbonate)s that have good solubility in organic solvents, superior optical properties, and excellent chemical resistance. Zinc-cobalt(III) double-metal cyanide complexes and (salen)CrX+onium salts (Lewis bases, LBs, Fig.1a) have been discovered to catalyze the COS/epoxide copolymerization. Unfortunately, metal-contaminated or colored copolymers are resulted and severely impede their applications in optical, optoelectronic, photochemical, or biomedical materials. Organic Lewis pairs composed of triethylborane (TEB) and LBs, including amidine, quinidine, quaternary onium salts could generate poly(monothiocarbonate)s from COS and epoxides (Fig. 1b). However, the TEB/LB pairs often led to relative broad polydispersity (PDI) and higher molecular weights than the calculated one. Meanwhile, only TEB, which is toxic and spontaneous combustion in air, was effective to COS/epoxide copolymerization.

The above-mentioned catalysts have the coordination bonds that are responsible to the activation of the monomers. Whereas very few of reports suggested an anionic copolymerization process involved C1 monomers. For example, Nozaki et al., disclosed that [PPN]Cl could solely catalyze the carbon-disulfide (CS2)/propylene sulfide copolymerization. Feng and Gnanou et al. presented that alkoxide/benzyl alcohol (BnOH) could effectively initiate the CO2/epoxide copolymerization. However, anionic copolymerization of COS with epoxides remains unexplored. In contrast with the CO2/epoxide copolymerization that is often expected to attain fully alternating structure and no production of side cyclic carbonate (i.e., 100% polycarbonate), the chemistry of COS/epoxide copolymerization is more complicated.

![Diagram of catalyst systems for COS/epoxide copolymerization](image_url)

**Fig. 1** The catalyst systems for COS/epoxide copolymerization. a Metal catalysts (zinc-cobalt(III) double-metal cyanide complexes and (salen)CrX+onium salts), b TEB/LB pairs (triethylborane/Lewis bases), c TU/base pairs in this study (TU-1: diisopropyl thiourea; TU-2: 1-cyclohexyl-3-phenylthiourea; TU-3: 1-[3,5-bis(trifluoromethyl)phenyl]-3-cyclohexylthiourea; DBU: 8-diazabicyclo[5.4.0]undec-7-ene; MTBD: N-methyl-1,5,7-triazabicyclodecene; 1Bu-P4: P4, 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis [tris(dimethylamino)-phosphoranylidene]-25,4S-catenadi(phosphazene); 1Bu-P2: P2, 1-tert-Butyl-2,2,4,4,4-pentakis(dimethylamino)-25,4S-catenadi(phosphazene); and 1Bu-P1, tert-butylimino-tris(dimethylamino) phosphorene)
Table 1 COS/PO copolymerization catalyzed by TU-1/organic base pairs at 25 °C

| Entry | LB  | [PO]: [LB]: [TU-1]: [I] | TOF (h⁻¹) | Copolymer selectivity | Alternating degree | T-H diad content (%) | O/S ER | Mₙ (kg/mol) | PDI |
|-------|-----|------------------------|-----------|----------------------|-------------------|---------------------|--------|------------|------|
| 1     | DBU | 250:1:0:0              | 4         | 93/7                 | 100               | >99                 | N.F.   | 38.3       | 1.35 |
| 2     | P4  | 1000:1:0:0             | 23        | 60/40                | 92/8              | >99                 | N.F.   | 29.4       | 1.58 |
| 3     | P2  | 250:1:0:0              | 4         | 98/2                 | 100               | >99                 | N.F.   | 45.1       | 1.14 |
| 4     | P1  | 250:1:0:0              | 1         | >99                  | 100               | >99                 | N.F.   | 9.0        | 1.05 |
| 5     | MTBD| 250:1:0:0              | 3         | 96/4                 | 100               | >99                 | N.F.   | 46.0       | 1.20 |
| 6     | DBU | 2000:1:0:1             | 10        | 92/8                 | 100               | >99                 | N.F.   | 13.9       | 1.20 |
| 7     | P4  | 2000:1:0:1             | 55        | 99/1                 | 100               | >99                 | N.F.   | 42.5       | 1.23 |
| 8     | P2  | 2000:1:0:1             | 29        | 99/1                 | 100               | >99                 | N.F.   | 35.6       | 1.15 |
| 9     | P4  | 2000:1:1:0             | 41        | 97/3                 | 100               | >99                 | N.F.   | 31.3       | 1.16 |
| 10    | P2  | 1000:1:1:0             | 24        | >99                  | 100               | >99                 | N.F.   | 34.3       | 1.16 |
| 11    | DBU | 250:1:0:0              | 7         | 93/7                 | 100               | >99                 | N.F.   | 30.2       | 1.13 |
| 12    | MTBD| 250:1:0:0              | 4         | 95/5                 | 100               | >99                 | N.F.   | 36.1       | 1.16 |
| 13    | MTBD| 1000:1:1:0             | 10        | 98/2                 | 100               | >99                 | N.F.   | 98.4       | 1.14 |
| 14    | P4  | 4000:1:1:1             | 75        | >99                  | 100               | >99                 | N.F.   | 21.3       | 1.21 |
| 15    | P4  | 4000:1:5:5             | 112       | 98/2                 | 100               | >99                 | N.F.   | 9.9        | 1.13 |
| 16    | P2  | 2000:1:1:1             | 35        | >99                  | 100               | >99                 | N.F.   | 19.3       | 1.13 |
| 17    | DBU | 2000:1:1:1             | 22        | 94/6                 | 100               | >99                 | N.F.   | 11.3       | 1.19 |
| 18    | MTBD| 2000:1:1:1             | 17        | 97/3                 | 100               | >99                 | N.F.   | 12.0       | 1.23 |

The copolymerization results under other conditions (including controls), representative NMR spectra and corresponding calculations are in Supplementary Figs. 2–11 and 35, and the Methods.

*Turnover of frequency (TOF), (Mol epoxide consumed)/(mol LB h), PO conversion was determined by 1H NMR spectroscopy.

aReactions were run at 25 °C in neat PO (1.0 ml; COS: PO = 100:1) in a 10 ml autoclave, 24 h.

bReaction temperature (°C), [COS]: [PO] = 1:1, ([TU] = 1:1), ([I] = 0:0) was determined by 13C NMR spectroscopy.

cDetermined by gel permeation chromatography in THF, calibrated with polystyrene standards.

dDetermined by 1H NMR spectroscopy. O/S ER = oxygen-sulfur exchange reaction. N.F. = not found (dithiocarbonate and carbonate units).

eDetermined by gel permeation chromatography in THF, calibrated with polystyrene standards.

One is the possible occurrence of oxygen/sulfur exchange reactions (O/S ERs), which cause the production of CO₂ and thirane intermediate, will produce randomly distributed dithiocarbonate and carbonate units in the final copolymer.8,25–27. The other is that the copolymerization of structurally asymmetric COS with a terminated epoxide, will generate four consecutive mono-thiocarbonate diads, i.e., head-to-tail (H–T), tail-to-head (T–H), tail-to-tail (T–T), and head-to-head (H–H) diads.6 As a result, the metal-free catalyst for anionic COS/epoxide copolymerization should avoid O/S ER, attain highly regioselectivity involved two asymmetric monomers and be precisely controlled by varying the monomer to initiator ratios under mild condition.

Herein, we have developed a living copolymerization of COS with various epoxides with high activity, using commonly available thioureas (TUs) and organic LBs (DBU, MTBD, P4, P2, and P1, Fig. 1c). This catalyst system was developed based on the hypothesis that the cooperative catalytic process of Lewis pairs composed of TU and base, undergoing a non-covalent mode to activate and stabilize the alcohol initiator/chain end for controlling the anionic copolymerization.26,28–31. The resulting poly(monothiocarbonate)s have perfectly alternating structure with regioregularity, controlled molecular weights and narrow PDI values (Supplementary Fig. 1).

Results

Anionic COS/propylene oxide (PO) copolymerization. Previous studies have shown that the organic bases, e.g., amidine and guanidine widely employed as the cocatalysts for metal complex for catalyzing CO₂/epoxide copolymerization.8,32–34. In this scenario, the organic bases often exhibited no activity towards CO₂/epoxide copolymerization.9–24,32–34. Since COS is more reactive than CO₂ and the expected thiocarbonate anion [OC(=O)S⁻] is more nucleophilic than carbonate anion [OC(=O)O⁻]8, we performed the sole catalysis of LBs (DBU, MTBD, P4, P2, and P1) for COS/PO copolymerization as controls (entries 1–5 in Table 1) for comparatively studying the catalytic performance of the designed Lewis pairs of TU/LB (entries 9–18 in Table 1). Unexpectedly, we observed that DBU could solely catalyze COS/PO copolymerization in a high PO/DBU feed ratio of 250/1 at ambient temperature (25 °C) for a long time of 24 h (entry 1, Table 1). Poly(propylene monothiocarbonate)s (PPMTCs) were obtained with a number-average molecular weight (Mₐ) of 38.3 kg/mol with production of 7% of cyclic monothiocarbonate. P4, a phosphazene with the strongest basicity,35 was active for the anionic ROP of epoxides, cyclic esters, and caprolactam,26,36–39, was also effective to the COS/PO copolymerization with a TOF of 23 h⁻¹ even under a PO/P4 feed ratio (1000/1). However, the copolymer selectivity was only 60%, and 8% polyether was detected (entry 2 in Table 1, Supplementary Fig. 2). The sole catalysis of P2, P1, and MTBD for the copolymerization exhibited high copolymer selectivity (>96%), but low TOFs (1–4 h⁻¹), entries 3–5 in Table 1). Concurrently, high reaction temperatures (≥70 °C) or the use of TBD (at 20 °C) only afforded cyclic products (entry 6 in Supplementary Table 2; entry 10 in Supplementary Table 1). PPMTCs obtained by these organic bases had Mₐ of 29.4–46.0 kg/mol and PDIs of 1.20–1.58. This result exclusively suggested that the COS/PO copolymerization could be performed in an anionic manner.

The activity and selectivity of the above LB-catalyzed COS/PO copolymerization were clearly enhanced by introducing TU-1 (entries 9–12 in Table 1), while TU-1 did not catalyze the reaction alone (entry 11 in Supplementary Table 1). For example, P4/TU-1 and P2/TU-1 pairs afforded improved TOFs (41 and 24 h⁻¹), copolymer selectivity (97/3 and >99%) even in high monomer/ pair feed ratios of 2000/1 and 1000/1/1, respectively, (entries 9–10, Table 1). Concurrently, COS/PO copolymerization via the catalysis of DBU/TU-1 or MTBD/TU-1 pairs led to a slight improvement of TOF (4–7 h⁻¹) and the copolymer selectivity (93/7 and 95/5) while the P1/TU-1 pair had low TOF (1 h⁻¹), but perfect copolymer selectivity (>99%) (entry 5, Supplementary
Table 1). Of note, the use of TU-1 caused a slight decrease of $M_n$ (30.2–36.1 kg/mol) and narrower PDIs of 1.13–1.16, suggesting the generation of larger amounts of active centers when TU-1 was introduced. Of special interest, MTBD/TU-1 pair catalysis provided a copolymer with a remarkably high $M_n$ of 98.4 kg/mol with PDI of 1.14 after 72 h reaction (entry 13, Table 1), which can be ascribed to a longer lifespan of the active species.

The addition of benzyl alcohol (BnOH) to the COS/PO copolymerization catalyzed by either single LB (entries 6–8 in Table 1, entries 3, 6, and 8 in Supplementary Table 1) or TU-1/LB pairs (entries 14–18 in Table 1, entries 2, 4, 7, and 9 in Supplementary Table 1) led to a dramatic improvement of TOF without the sacrifice of the copolymer selectivity, even in a rather low catalyst loading. For example, adding equimolar BnOH to P4 and P4/TU-1-catalyzed copolymerizations presented improved TOFs of 55 and 75 h$^{-1}$, respectively (entries 7 and 14 in Table 1). In addition, high loading of TU-1 and BnOH ($P_4$/TU-1/BnOH = 1/5/5) led to a dramatic increase of TOF to 112 h$^{-1}$ (entry 15 in Table 1). Introducing equimolar BnOH to the DBU/TU-1 pair led to a clear promotion of TOF (22 h$^{-1}$) even in a low PO/DBU/TU-1 feed ratio of 2000/1/1 (entry 17 in Table 1). In contrast, no copolymers were afforded in the absence of BnOH in PO/DBU feed ratio of 2000/1 under the same reaction conditions (entry 12 in Supplementary Table 1). Actually, LB could activate BnOH...
Chain microstructures of COS/PO copolymers. The perfectly alternating structure and regioregularity of the PPTMCs were also revealed by MALDI-TOF MS spectroscopy (Fig. 2). Figure 2a showed one distribution of α-ΟΗ, ω-ΟΗ-terminated [H + (PO + COS)]m+n + n (PS + COS) + PO + OH + K+] copolymer, i.e., a single PPTMC with two –OH end groups and one dithiocarbonate unit (Mn: 6.5 kg/mol; PDI: 1.15). Furthermore, high-resolution 1H (13C) NMR spectra (Supplementary Fig. 13a, b) revealed that the copolymer contained two secondary –OH end groups with minimal regio-defect (one dithiocarbonate unit). 40 These results were indicative of inclusively regioselective attack of the sulfur anion to the CH2 site of PO, and thus the sole production of the T–H diad via the organocatalysis. 40 In the presence of BnOH, only one distribution of α-OBn, ω-ΟΗ copolymer-terminated [BnO + (PO + COS)]n + H + K+] (Fig. 2b) with >99% T–H diad content (Supplementary Fig. 13c, d) was obtained without dithiocarbonate unit (Mn: 4.4 kg/mol; PDI: 1.14), meant that BnOH was a very efficient initiator and depressed the production of the dithiocarbonate unit.

Living COS/PO copolymerization catalyzed by Lewis pairs. Remarkably, the TU/LB pair catalysis allowed for the copolymerization exhibiting the living features. Take the TU-1/DBU pair-catalyzed COS/PO copolymerization with or without using BnOH (Fig. 3a, b) as instances: linear increase of α-ΟΗ end groups and one dithiocarbonate unit (Mn: 4.4 kg/mol; PDI: 1.14), meant that BnOH was a very efficient initiator and depressed the production of the dithiocarbonate unit.
microstructure (Supplementary Table 4 and Figs. 20–22). As a result, such TU/LB pairs are robust for the copolymerization under mild conditions.

We further explored the chain extension reaction via tandem synthesis (Fig. 3d and Supplementary Fig. 23). PO and COS were copolymerized firstly using TU-1/DBU pair without using BnOH ([PO]: [COS]: [TU-1]: [DBU] = 50: 60: 1: 1) at 25 °C for 10 h. After slowly venting the unreacted COS, PO was totally consumed according to the 1H NMR spectra, and the resultant PPTMC exhibited unimodal peak with a $M_n$ of 8.6 kg/mol and a PDI of 1.19. Then, 1.0 ml PO and 1.18 g COS (COS: PO = 25 °C. PO conversion was 88% according to 1H NMR spectra. PPTMC exhibited unimodal peak with a $M_n$ of 22.3 kg/mol with a PDI of 1.26, as revealed by that GPC curve shifted overall to high molecular weight. The result of the chain extension reaction also confirmed the living mode of TU-1/DBU pair-catalyzed COS/PO copolymerization.

**Kinetic and mechanistic study.** The cooperative catalysis of TU-1/LB pair for the COS/PO copolymerization was firmly supported by the kinetic studies (Fig. 4a). The apparent rate constant ($k_{app}$) obtained from the slopes of the best-fit lines to the plots of PO conversion vs. time, is well proportional to [TU-1] + [DBU] in the absence or presence of BnOH, suggesting that the TU-1/DBU pair behaved as a discreet catalyst species ([a] in Fig. 6). As expected, $k_{app}$ of the TU-1/P2 pair was $13.6 \pm 0.3 \times 10^{-2}\text{ h}^{-1}$ and higher than that of TU-1/DBU pair ($5.7 \pm 0.8 \times 10^{-2}\text{ h}^{-1}$) for the copolymerization under the same conditions due to the stronger basicity of P2. This result is in agreement with the binding constant via 1H NMR dilution (see Methods, Supplementary Fig. 24) that was $10.3 \pm 2.5$ for TU-1/DBU pair and $21.2 \pm 2.2$ for TU-1/P2 pair in equilibrium in CDCl$_3$ at 25 °C (Fig. 4b). Because the H-bond interaction could be weakened by elevating the temperature, the TU-1/DBU pair catalysis for COS/PO copolymerization at high temperatures ($\geq 55 ^\circ\text{C}$) produced considerable amounts of the cyclic products (Supplementary Table 2), which is consistent with the catalysis involving only the bases for the coupling reaction of COS with PO.

We have further studied the combining capabilities of TU-1, DBU, COS, and PO in CDCl$_3$ using 1H NMR spectra (Fig. 5 and Supplementary Fig. 25). In a high concentration of TU-1 and DBU (0.5 M), the H-bond interaction was clearly revealed by the proton signal of NH group (5.65 ppm) of TU-1 disappearing while the six protons (NCH$_2$) of DBU became chemically equivalent (Supplementary Fig. 25). Of interest, TU-1 was shown to solely activate PO and did not interact with COS in CDCl$_3$ (Fig. 5a). Conversely, DBU could only activate COS owing to a clear deshielding effect of protons of NCH$_2$ of DBU (from 2.38 to 2.77 ppm) and appearance of chemical equivalent protons of...
NCH₂ of DBU rather than activate PO (Fig. 5b). Such supramolecular specific recognition of TU-1 to PO and DBU to COS in TU-1/DBU pair promoted the copolymerization cooperatively.

The introduction of BnOH into the polymerization system led to the prior formation of the BnOC(O)S⁻…DBUH⁺ owing to the deprotonation of BnOH by DBU, generated species (b) and (c) in Fig. 6, as revealed by ¹H NMR spectra (Supplementary Fig. 24-26). Since PO was activated by TU-1 through H-bond [species (d) in Fig. 6, revealed by Fig. 5b], the chain growth could be accelerated (Table 1). On the other hand, in the absence of BnOH, trace water (i.e., R=H, Fig. 6) could also initiate the copolymerization via the similar activation route of BnOH by TU/LB pair. Such H₂O initiation led to the formation of the end –S(O=C)–OH group, which was thermodynamically unstable and thus converted to –SH group via decarboxylation process⁶,⁴⁰. Since the end –SH group has the stronger acidity than –OH group, it was rapidly deprotonated, generating bifunctional initiator for further chain growth, a copolymer with two end secondary –OH groups and one dithiocarbonate unit (f) was produced, which was clearly revealed by Fig. 2a (Supplementary Figs. 13 and 22).

**The impact of Lewis pairs on COS/epoxides copolymerizations.** Different Lewis pairs including other thioureas were also investigated for the copolymerization of COS with several epoxides. Two other thioureas, TU-2 and TU-3 were synthesized⁴³ and successfully utilized for the COS/PO copolymerization (entries 1–4 in Table 2). H-bond interactions of both TU-2 and TU-3 with DBU are similar to that of the DBU/TU-1 pair (Supplementary Fig. 28). The TU-3/DBU pair was more active than TU-1 (TU-2)/DBU pairs for the copolymerization, but with a slightly lower copolymer selectivity of 93%. Both TU-2 and TU-3 paired with P₂ showed the same TOFs (29 h⁻¹, entries 3–4, Table 2) for the COS/PO copolymerization. Totally, TU-3 with more electron-withdrawing group resulted in the production of slightly more amounts of cyclic products. In addition, two epoxides, glycidyl phenyl ether (PGE) and cyclohexene oxide (CHO) were copolymerized with COS by using P₂/TU-1, P₄/TU-1 pairs, affording fully alternating copolymers (entries 5–8, Table 2). Thereof, the COS/PGE copolymerization were fully regioselective with T–H diad content of >99% (Supplementary Fig. 29), while COS/CHO copolymerization could proceed at 40 °C, afforded well-defined copolymer with perfect alternating degree and >99% copolymer selectivity (Supplementary Fig. 30). These results illustrate the use of several low-cost thioureas for the copolymerization of COS and epoxides with different structures.

**Discussion**

We have described the synthesis of perfectly alternating and regioregular poly(monothiocarbonate)s from COS and epoxides by employing thioureas and organic bases under mild conditions. Of importance, the use of thioureas and BnOH led to living/controlled COS/epoxide copolymerization, improved catalytic activity and copolymer selectivity than previous systems. One of the key features of such metal-free catalyst systems is that it can
be applied to a variety of epoxides. Due to the ease of tailoring the molecular structures of these organic thioureas and bases, this strategy is a promising alternative to get metal-free well-defined sulfur-containing polymers with high activity and selectivity. Our ongoing efforts are to seek a better understanding of the mechanistic aspects of such catalytic processes, and to develop chiral TU/LB pairs for the copolymerization.

### Methods

**Materials.** Propylene oxide (PO), glycidyl phenyl ether (PGE), and cyclohexene oxide (CHO) were purified by distillation after stirring with calcium hydride for 3 days. 1,3-Disopropyl-2-thiourea (TU-1) was purchased from Sigma Aldrich and sublimed before use. 1-cyclohexyl-3-phenylthiourea (TU-2) and 1-[3,5-bis(trifluoromethyl)phenyl]-3-cyclohexylthiourea (TU-3) were synthesized according to literature. 1H NMR spectra of TU-2 and TU-3 are shown in Supplementary Fig. 27. Tert-butylmino-tris(dimethylamino) phosphine (‘Bu-P3, P1, 97%), 1-tert-Butyl-2,2,4,4,4-pentakis(dimethylamino)-2,4,6-tri-2-catenadi(phosphazene) (‘Bu-P2, P2, ~2.0 M in THF) and 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2,2-tris(dimethylenimino)-phosphoranylidenediamino)-2,4,6-tri-2-catenadi(phosphazene) (‘Bu-P4, P4, ~0.8 M in hexane) were purchased from Sigma and used directly. 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) was purchased from Aldrich Chemical Laboratories. CH₃COOK was used as the matrix for MALDI-TOF mass spectrometric measurements. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometric measurements were performed on a Waters MALDI Micro MX mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Dithranol (97%, Aldrich), was used as the matrix. CH₃COOK (≥ 98%, Aladdin) was added for ion formation.

### Characterization

1H and 13C NMR spectra were performed on a Bruker Advance DMX 400 MHz or 600 MHz spectrometer. And chemical shift values were referred to 2,2-dimethyl-2-silapentane-5-sulfonic acid (DSS). All other data is available within the paper and its Supplementary Information File. All other data is available from the authors upon reasonable request.

### Data availability

The authors declare that the data supporting this study are available within the paper and its Supplementary Information File. All other data is available from the authors upon reasonable request.

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**Table 2 The copolymerization of COS with various epoxides by using various TU/LB pairs**

| Entry | Epoxide | TU/LB | Epoxide: | TOF (h⁻¹) | Copolymer selectivity | Alternating degree (%) | T-H diad content (%) | O/S ER product | Mₚ (kg/mol) | PDI |
|-------|---------|-------|----------|-----------|----------------------|-----------------------|---------------------|----------------|-------------|------|
| 1     | PO      | TU-2/DBU | 50:00:1:1 | 6         | 97/3                 | 100                    | >99                 | N.F.           | 21.9        | 1.15 |
| 2     | PO      | TU-3/DBU | 50:00:1:1 | 10        | 93/7                 | 100                    | >99                 | N.F.           | 21.9        | 1.18 |
| 3     | PO      | TU-2/P2  | 1000:1:1  | 29        | 98/2                 | 100                    | >99                 | N.F.           | 19.8        | 1.10 |
| 4     | PO      | TU-3/P2  | 1000:1:1  | 29        | 96/4                 | 100                    | >99                 | N.F.           | 32.2        | 1.20 |
| 5     | PGE     | TU-1/P2  | 1000:1:1  | 22        | 96/4                 | 100                    | >99                 | N.F.           | 29.3        | 1.26 |
| 6     | PGE     | TU-1/P4  | 4000:1:1  | 52        | 96/4                 | 100                    | >99                 | N.F.           | 17.5        | 1.18 |
| 7     | CHO     | TU-1/P2  | 250:1:1   | 2         | >99                  | 100                    | —                   | N.F.           | 15.8        | 1.19 |
| 8     | CHO     | TU-1/P4  | 250:1:1   | 5         | >99                  | 100                    | —                   | N.F.           | 13.4        | 1.16 |

**Representative NMR spectra are in Supplementary Figs. 29, 30.**

**PGE glycidyl phenyl ether, CHO cyclohexene oxide.**

**Reaction conditions and characterization methods were the same with Table 1 (40 °C).**

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**Calculation of copolymer selectivity, PO conversion and TOF.** Copolymer selectivity and PO conversion were calculated based on the 1H NMR spectrum of the crude product. Taking entry 11 in Table 1 as an example, spectrum of the crude product was showed in Supplementary Fig. 35. Protons with chemical shifts at 4.80, 3.52, 3.26 and 1.51 ppm belong to the methenyl (–CH₂–), methene (–CH=), and methyl (–CH₃) groups, respectively. The peak area ratio of these protons was determined from linear regression.

The TOF (h⁻¹) = PO conversion × [PO]/[LB] / t

Thus, the TOF (h⁻¹) = PO conversion × [PO]/[LB] / t

**Data availability.** The authors declare that the data supporting this study are available within the paper and its Supplementary Information File. All other data is available from the authors upon reasonable request.
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References
1. Bates, F. S. (Workshop Chair) et al. Frontiers in Polymer Science and Engineering, Report of a 2016 NSF Workshop (Frontiers in Polymer Science and Engineering, University of Minnesota–Twin Cities, Minneapolis, 2017).

2. Hong, M. & Chen, E. Y. X. Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of gamma-butyrolactone. Nat. Chem. 8, 42–49 (2016).

3. Longo, J. M., Sanford, M. I. & Coates, G. W. Ring-opening copolymerization of epoxides and cyclic anhydrides with discrete metal complexes: structure–property relationships. J. Polym. Sci. Part A 116, 15167–15197 (2016).

4. Zhang, X., Fevre, M., Jones, G. O. & Waymouth, R. M. Catalysis as an enabling science for sustainable polymers. Chem. Rev. 118, 839–885 (2017).

5. Rasmussen, R. A., Khalil, M. A. K., Dalluge, R. W., Pennett, S. A. & Jones, B. Carbonyl sulfide and carbon disulfide from the eruptions of Mount St. Helens. Science 215, 665–667 (1982).

6. Luo, M., Zhang, X.-H. & Darenbourg, D. J. Poly(monothiocarbonate)s from the alternating and regioselective copolymerization of carbon disulfide with epoxides. Acc. Chem. Res. 49, 2209–2219 (2016).

7. Wu, H.-L. et al. Poly(trimethylene monothiocarbonate) from the alternating copolymerization of COS and oxetane: A semicrystalline copolymer. Macromolecules 49, 8863–8868 (2016).

8. Zhang, X.-H. et al. Atom-exchange coordination polymerization of carbon disulfide and propylene oxide by a highly effective double-metal cyanide complex. Macromolecules 41, 1587–1590 (2008).

9. Luo, M., Zhang, X.-H., Du, B.-Y., Wang, Q. & Fan, Z.-Q. Regioselective and alternating copolymerization of carbon sulfide with racemic propylene oxide. Macromolecules 46, 5899–5904 (2013).

10. Ren, W.-M., Liu, Y., Xin, A.-X., Fu, S. & Lu, X.-B. Single-site bifunctional catalysts for CO2/epoxide copolymerization by using weight using weight.

11. Bates, F. S. (Workshop Chair) et al. Frontiers in Polymer Science and Engineering, Report of a 2016 NSF Workshop (Frontiers in Polymer Science and Engineering, University of Minnesota–Twin Cities, Minneapolis, 2017).

12. Hong, M. & Chen, E. Y. X. Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of gamma-butyrolactone. Nat. Chem. 8, 42–49 (2016).

13. Longo, J. M., Sanford, M. I. & Coates, G. W. Ring-opening copolymerization of epoxides and cyclic anhydrides with discrete metal complexes: structure–property relationships. J. Polym. Sci. Part A 116, 15167–15197 (2016).

14. Zhang, X., Fevre, M., Jones, G. O. & Waymouth, R. M. Catalysis as an enabling science for sustainable polymers. Chem. Rev. 118, 839–885 (2017).

15. Bates, F. S. (Workshop Chair) et al. Frontiers in Polymer Science and Engineering, Report of a 2016 NSF Workshop (Frontiers in Polymer Science and Engineering, University of Minnesota–Twin Cities, Minneapolis, 2017).

16. Kober, M. R., Buchard, A. & Waymouth, R. M. Catalysis as an enabling science for sustainable polymers. Chem. Rev. 118, 839–885 (2017).

17. Bates, F. S. (Workshop Chair) et al. Frontiers in Polymer Science and Engineering, Report of a 2016 NSF Workshop (Frontiers in Polymer Science and Engineering, University of Minnesota–Twin Cities, Minneapolis, 2017).

18. Kober, M. R., Buchard, A. & Waymouth, R. M. Catalysis as an enabling science for sustainable polymers. Chem. Rev. 118, 839–885 (2017).

19. Bates, F. S. (Workshop Chair) et al. Frontiers in Polymer Science and Engineering, Report of a 2016 NSF Workshop (Frontiers in Polymer Science and Engineering, University of Minnesota–Twin Cities, Minneapolis, 2017).

20. Bates, F. S. (Workshop Chair) et al. Frontiers in Polymer Science and Engineering, Report of a 2016 NSF Workshop (Frontiers in Polymer Science and Engineering, University of Minnesota–Twin Cities, Minneapolis, 2017).

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Author contributions
X.-H.Z. conceived, designed and directed the investigations, and revised the manuscript. C.-Y.Z. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L. carried out all experiments and analyses, contributed much for the sole catalysis of organic bases for the copolymerization and wrote the draft. H.-L.W. and J.-Y.L.
out some NMR, MALDI-TOF-MS characterizations and analyses, and discussed with Y. L. for mechanism and kinetic study.

**Additional information**

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