Toward high-performance stereo- and sequence-defined block copolymers via site-monomer specific recognition of chiral three-site organocatalyst

Xiaowei Geng,[1] Ziheng Liu,[1] Chengjian Zhang,[1] and Xinghong Zhang[1,2]

[1]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, International Research Center for X Polymers, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027 (China)

[2]Center of Chemistry for Frontier Technologies, Zhejiang University, Hangzhou 310027 (China)

Corresponding authors: chengjian.zhang@zju.edu.cn (Chengjian Zhang); xhzhang@zju.edu.cn (Xinghong Zhang)

Abstract

The development of high-performance sustainable polymers as candidates to replace petroleum-based plastics is a priority, but still a grand challenge. Here, we report a series of stereo- and sequence-defined copolymers with isotactic polylactide and alternating/regioregular polythiocarbonate blocks from one-pot, metal-free, and switchable copolymerization of *rac*-lactide, COS, and epoxides. The highly active organocatalyst incorporating boron and chiral thiourea and tertiary amine groups is developed based on the site-monomer specific recognition mechanism, in short, the boron site selectively activates epoxides through B-O bonds and the thiourea site selectively activates lactide through hydrogen bonds. Such block copolymers manifest impressive toughness and ductility owing to their isotactic polylactide fragments and high molecular weights, such as **P8** with an ultimate tensile strength of 54 ± 3 MPa and an elongation at break of 270 ± 10%. Our strategy provides distinctive insights into designing robust organocatalysts and promising sustainable polymers.

Introduction

Plastics make modern life better, with an annual output of more than 300 million tons. However, the vast majority come from non-renewable petrochemicals.[1,2] There is a growing demand for sustainable polymeric materials derived from renewable monomers or waste.[3-7] Unfortunately, their practical application has invariably been limited by underwhelming performance. For this issue, copolymerization extends the scope of physical properties accessed by the polymer.[8] Especially, learn from nature and biology, precise control over complex sequences in synthetic polymers can tailor properties and applications, which is highly desirable but also challenging.[9,10]

The evolution of new and versatile catalytic methods for sequence control continues to drive innovation in polymer science. A versatile approach to synthesize sustainable sequence-defined polymers is to conjoin ring-opening polymerization (ROP) of lactones and ring-opening copolymerization (ROCOP) of epoxide/heteroallene.[11-19] As an example, Williams and co-workers developed a state-of-the-art *switch catalysis* strategy whereby a unimodal catalyst can switch between ROP and ROCOP to deliver block copolymers from mixed monomers.[20-23] The key is to construct robust catalysts capable of simultaneously adapting to the different mechanisms of ROP and ROCOP.

Organocatalysts are increasingly applied in polymerizations owing to their environmental friendliness, low toxicity, and inexpensiveness, resulting in desirable metal-free polymers.[24-26] Based on the cooperative dual activation of monomers and chain ends, mono- or bicomponent bifunctional catalytic systems consisting of electrophilic and nucleophilic moieties have been extensively demonstrated for ROP and ROCOP.[6,27] In particular, thiourea and boron groups demonstrate exceptional activation of lactones and epoxides, respectively, disclosed by Hedrick,[28] Waymouth,[29-31] Gnanou,[32] Feng,[33] our group,[34-36] and others.[37-40] To develop versatile catalysts for switchable ROP and ROCOP, we sought to integrate two electrophilic sites (thiourea and boron) and one nucleophilic site (tertiary amine) in one molecule, based on the intramolecular synergy and the hypothesized specific monomer/chain-end activation: boron activates epoxides via B−O bonds, thiourea and amine activate lactones and chain ends via hydrogen bonds, respectively (Fig. 1).

Here, we report the synthesis of block copolymers from switchable ROP of *rac*-lactide (LA) and ROCOP of propene oxide (PO)/carbonyl sulfide (COS) using unimolecular trifunctional catalysts (Fig. 1). Polylactide (PLA) is among the most attractive bio-based aliphatic polyesters owing to its biodegradability and biocompatibility.[16,41] PO is one of the most important epoxides with an annual global production of ~ 10 million tons. COS is an emerging monomer for the synthesize of sulfur-containing polymers, produced industrially from abundant CO and elemental sulfur (waste from oil refineries and gas purification).[42-45] ROCOP of PO/COS, first reported by our group in 2013,[46] has been demonstrated to be a facile route to produce polythiocarbonates with approving optical and mechanical properties.[47-49] Block copolymers bearing PLA and polythiocarbonate fragments promise to integrate the superior properties of each block. In addition, there are several stereo-, regio-, and chemoselective regulation in ROP of *rac*-LA[50] and ROCOP of PO/COS.[47] Remarkably, chiral catalyst **4** delivered block copolymers containing isotactic PLA and alternating/regioregular polythiocarbonate blocks.

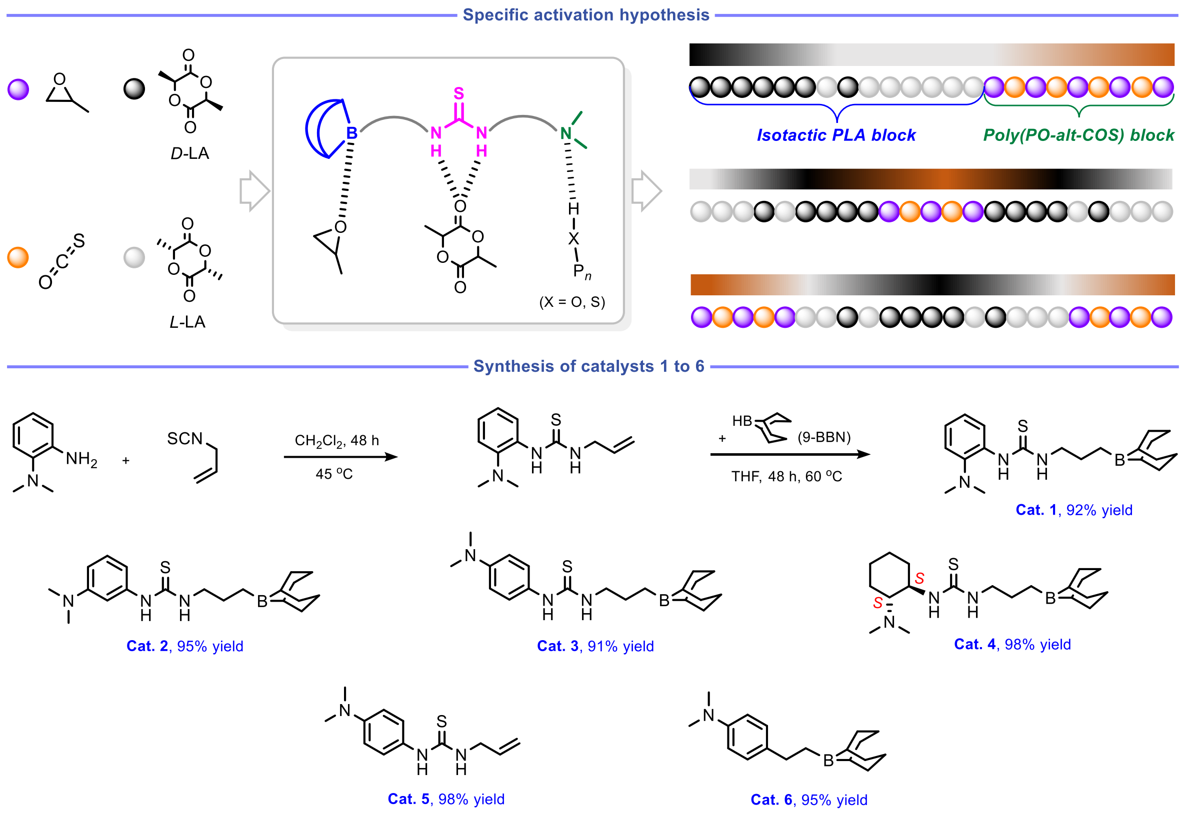

Fig. 1 Trifunctional catalysts for the synthesis of PLA-polythiocarbonate block copolymers. Synthesis of catalysts **1** to **4** via two steps of amine-thioisocyanate Michael addition and hydroboration reaction. Chiral catalyst **4** for the synthesis of isotactic PLA block copolymers.

Results and discussion

Synthesis of catalysts 1 to 6. We synthesized three-site organocatalysts **1** to **4** in > 90% yields via two efficient and easy-to-handle steps of amine-thioisocyanate Michael addition and hydroboration (Figs. 1 and S1-S9, Supplementary Information). These catalysts integrate Takemoto's catalyst[51] and a boron group in one molecular. The boron moiety is derived from the common borohydride reagent of 9-borabicyclo[3.3.1]nonane (9-BBN). The amine and thiourea groups in catalysts **1** to **3** are designed at the *ortho*, *meta*, and *para* positions of the benzene ring, respectively. We also synthesized catalyst (*S*, *S*)-**4** bearing chiral amine and thiourea moieties to form isotactic PLA blocks given their crystallinity and enhanced mechanical properties.[50,52-54] Recently, Dove, Coulembier, Taton, and co-workers reported the isoselective ROP of *rac*-LA using a chiral Takemoto's catalyst.[55] In addition, bifunctional catalysts **5** and **6** were synthesized as controls.

Catalysts 1 to 6 for ROP of LA. We next applied catalysts **1** to **6** toward ROP of LA and ROCOP of COS/PO, respectively (Table 1). Exhibited activities of catalysts **1** to **4** in the ROP and ROCOP are in the same order, that is, **4** > **1** > **2** > **3**. Catalyst **4** manifested the highest catalytic activity owing to its highest alkalinity, based on *N*,*N*-dimethylcyclohexylamine (pK_a ~ 10.7 in H_2O) with a higher basicity than *N*,*N*-dimethylbenzeneamine (pK_a ~ 5.2 in H_2O). In the case of catalysts **1** to **3**, the tighter Lewis acid and base groups are believed to make the synergistic catalytic effect more pronounced, *i.e.*, **1** > **2** > **3**. This order was consistent with the order of exhibited catalytic activity, indicative of a positive effect of synergistic catalysis.

Table 1. ROP of LA and ROCOP of PO/COS using catalysts **1** to **6** [a]

entry	Cat.	initiator[b]	$[M]_0/[C]/[I]_0$	T (°C)	t (h)	Conv. (%)[c]	M_n^{Theo} (kDa)[d]	M_n^{GPC} (kDa)[e]	$Đ$[e]
ROP of LA									
1	**1**	BnOH	100/1/2	25	6	70	5.0	4.7	1.20
2	**2**	BnOH	100/1/2	25	6	64	4.6	5.3	1.18
3	**3**	BnOH	100/1/2	25	6	45	3.2	3.6	1.20
4	**4**	BnOH	100/1/2	25	6	86	6.2	6.2	1.06
5	**5**	BnOH	100/1/2	25	6	18	-	-	-
6	**6**	BnOH	100/1/2	25	6	0	-	-	-
7	**4**	BDM	100/1/1	25	6	95	13.7	16.3	1.05
8	**4**	BDM	100/1/1	40	1	92	13.2	11.7	1.11
9	**4**	BDM	100/1/1	80	5 min	93	13.3	15.9	1.05
10	**4**	BDM	500/1/2	40	5	90	32.4	42.3	1.08
11	**4**	BDM	1000/1/2	40	10	95	68.4	62.4	1.08
ROCOP of COS with PO									
12	**1**	BDM	1000/1/2	40	8	54	31.9	32.2	1.03
13	**2**	BDM	1000/1/2	40	8	44	26.0	23.0	1.04
14	**3**	BDM	1000/1/2	40	8	38	22.4	20.2	1.04
15	**4**	BDM	1000/1/2	40	8	92	54.3	59.1	1.05
16	**5**	BDM	1000/1/2	40	8	0	-	-	-
17	**6**	BDM	1000/1/2	40	8	26	15.3	15.5	1.05
18	**4**	BnOH	1000/1/2	40	8	93	54.9	57.5	1.12
19	**4**	BDM	1500/1/2	40	15	95	84.1	72.5	1.12
20	**4**	BDM	2000/1/2	40	15	95	112.1	110.8	1.08

[a] ROP of LA was performed using PO as a solvent with $[LA]_0 = 1.38$ mol ml^{-1}, ROCOP of PO/COS was performed in bulk with $[COS]_0:[PO]_0 = 1.2:1.0$; [b] Using benzyl alcohol (BnOH) and 1,4-benzenedimethanol (BDM) as initiators; [c] Conversion determined by ^{1}H NMR; [d] Theoretical M_n^{Theo} calculated by $MW_{mon} \times [M]_0/[I]_0 \times$ Conv.; [e] Determined by GPC in THF for PLA and in DMF for poly(PO-*alt*-COS), calibrated with polystyrene standards.

For ROP of LA, with $[LA]_0$:[catalyst]:$[BnOH]_0$ = 100:1:2, at 25 °C for 6 h, catalysts **1** to **4** achieved LA conversions of 70, 64, 45, and 86%, respectively, affording PLA with predictable molecular weight (M_n^{GPC} of 3.6 to 6.2 kDa) and narrow dispersity ($Đ = M_w/M_n \leq 1.20$, entries 1 to 4 in Table 1). Catalyst **5**, which did not contain boron groups, yielded 18% of

LA conversion (entry 5 in Table 1), while catalyst **6** without thiourea groups showed no catalysis for ROP of LA (entry 6 in Table 1). Thus, the activation of LA by the three-site catalyst appears to be mainly through the thiourea moiety, in agreement with the hypothesized specific activation mechanism. Ofial and co-workers also disclosed little activation effect of ester carbonyl groups by boron compounds due to the weak Lewis basicity of carbonyls.[56]

By increasing the reaction temperature to 80 °C, the use of catalyst **4** yielded 93% LA conversion within only 5 min (entry 9 in Table 1). Low loading of catalyst **4** ($[LA]_0$:[catalyst]:$[BDM]_0$ = 1000:1:2) also resulted in high conversion of 95% and yielded PLA with a high M_n of 62.4 kDa ($Đ$ = 1.08, entry 11 in Table 1). By varying the feeding amount of BnOH, we obtained PLA with tailored molecular weights (Figs. S10 and S11). The resulting PLA also possesses a well-defined structure with α-OBn and ω-OH terminals, as revealed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS, Fig. S12). These results suggested that ROP of LA with catalyst **4** is in an efficient and controlled manner.

Notably, catalyst **4** produced isotactic-enriched PLA from ROP of *rac*-LA, which could be attributed to the synergistic catalysis of chiral thiourea and amine groups. The stacked homonuclear decoupled ^{1}H NMR (Fig. S13a) revealed the obtained PLA at 25 °C (entry 4 in Table 1) with tetrad ratios of [rmr] = 0.054, [mmr] = 0.065, [rmm] = 0.092, and [mrm] = 0.080, inconsistent with neither the chain-end control (CEC, expected [mrm] = [rmm] ≠ [rmr]) nor the site enantiomorphic control (ESC, expected [rmr] = [mmr] = [rmm] = [mrm]/2) mechanisms (Fig. S14).[50,53] To provide further evidence for the stereoselective mechanism, we monitored the kinetics of *rac*-, *L*-, and *D*-LA polymerization, respectively (Fig. S15). Kinetic studies suggested that catalyst **4** preferentially polymerizes *D*-LA from *rac*-LA. Furthermore, polarimetry analysis of unreacted LA (at 82% LA conversion) revealed an enantiomeric excess (*ee*) of 34% for L-LA (Fig. S16). Thereby, we figured out that CEC and ESC mechanisms occurred concomitantly in the ROP of LA, similar to the results reported by Dove and co-workers using a chiral Takemoto's catalyst.[55] The PLA obtained (entry 4 in Table 1) possesses a probability of forming *meso* dyads (P_m) of 0.84, as determined by the stacked homonuclear decoupled ^{1}H NMR spectrum based on ESC statistics (Fig. S13a), and 0.88 calculated according to the ^{13}C NMR spectrum (Fig. S13b). Owing to the high stereoregularity, the resulting PLA is crystalline and exhibits a melting temperature (T_m) of 146 °C, as determined by differential scanning calorimeter (DSC, obtained from first scan, Fig. S17). The PLA obtained at 40 and 80 °C (entries 8 and 9 in **Table 1**) also possess high P_m values of 0.83 and 0.80, respectively, as determined by ^{13}C NMR (Figs. S18 and S19).

Catalysts 1 to 6 for ROCOP of PO/COS. With $[PO]_0$:[catalyst]:$[BDM]_0$ = 1000:1:2, at 40 °C for 8 h, catalysts **1** to **4** realized PO conversions of 54, 44, 38, and 92%, respectively, affording poly(PO-*alt*-COS) with alternating sequences, predictable M_n of 20.2 to 59.1 kDa, and narrow $Đ \leq 1.05$ (entries 12 to 15 in Table 1). The copolymerization exhibited a regioselective manner, that is, the C=S double bond of COS and the methylene of PO are selectively attacked by growing anions,[47] yielding copolymers with tail-to-head diads according to NMR analysis (Figs. S20 and S21). No any side reactions including formation of cyclic thiocarbonates and homopolymerization of PO were observed.[46] Catalyst **6** without thiourea groups resulted in 26% PO conversion (entry 17 in Table 1), while catalyst **5** without boron groups showed no catalysis (entry 16 in Table 1). Thereby, the activation of PO by the three-site catalyst appears to be mainly through the boron moiety, in agreement with hypothesized specific recognition. Although it has been reported that thiourea groups can activate epoxides,[57,58] the activation is insufficient compared to the activation by boron groups in this study.

By varying the feeding amount of BnOH, we obtained poly(PO-*alt*-COS) with designed molecular weights (Figs. S22 and S23). The copolymer also possesses precise structures with α-OBn and ω-OH terminals, as revealed by MALDI-TOF MS (Fig. S24). With $[PO]_0$:[catalyst **4**]:$[BDM]_0$ of 1000:1:2, we obtained poly(PO-*alt*-COS) with a high M_n of 100.8 kDa ($Đ = 1.08$, entry 20 in Table 1). As a result, the ROCOP of PO/COS with catalyst **4** exhibits efficient and controlled features.

Computational calculations and NMR characterization for the specific recognition mechanism. In addition to the above comparative experimental results, the proposed site-monomer specific recognition was further identified by DFT calculations (Supplementary Information). As shown in Fig. 2a, PO and LA are bound to catalyst **4** via B−O bonds and hydrogen bonds, respectively, to form the trimolecular complex with 1.8 kcal mol^{-1} slightly higher energy than reactants. The B−O and hydrogen bonds possess lengths of 1.75 and ~ 2.2 Å, respectively. In the spatial position, PO and LA are combined on opposite side of the catalyst framework, eliminating the inability to combine due to steric hindrance.

The calculation results were further corroborated by NMR characterization. By comparing the ^{17}O NMR spectra of PO mixed with catalysts **3**, **5**, and **6** (Fig. 2b), we observed that catalysts **3** and **6** deshield the oxygen atom on PO with shifted chemical shifts (Δδ) of +0.86 and +0.81 ppm, respectively, while catalyst **5** shows slight effect to PO with Δδ of +0.04 ppm. By comparing the ^{13}C NMR spectra (Fig. 2c) of LA mixed with catalysts **3**, **5**, and **6**, catalysts **3** and **5** deshield the ester carbonyl on LA with Δδ of +0.16 and +0.11 ppm, while catalyst **6** shows little effect to LA with Δδ of -0.03 ppm. Accordingly, the site-monomer specific activation mechanism was comprehensibly demonstrated by comparative experiments, DFT calculations, and NMR characterization.

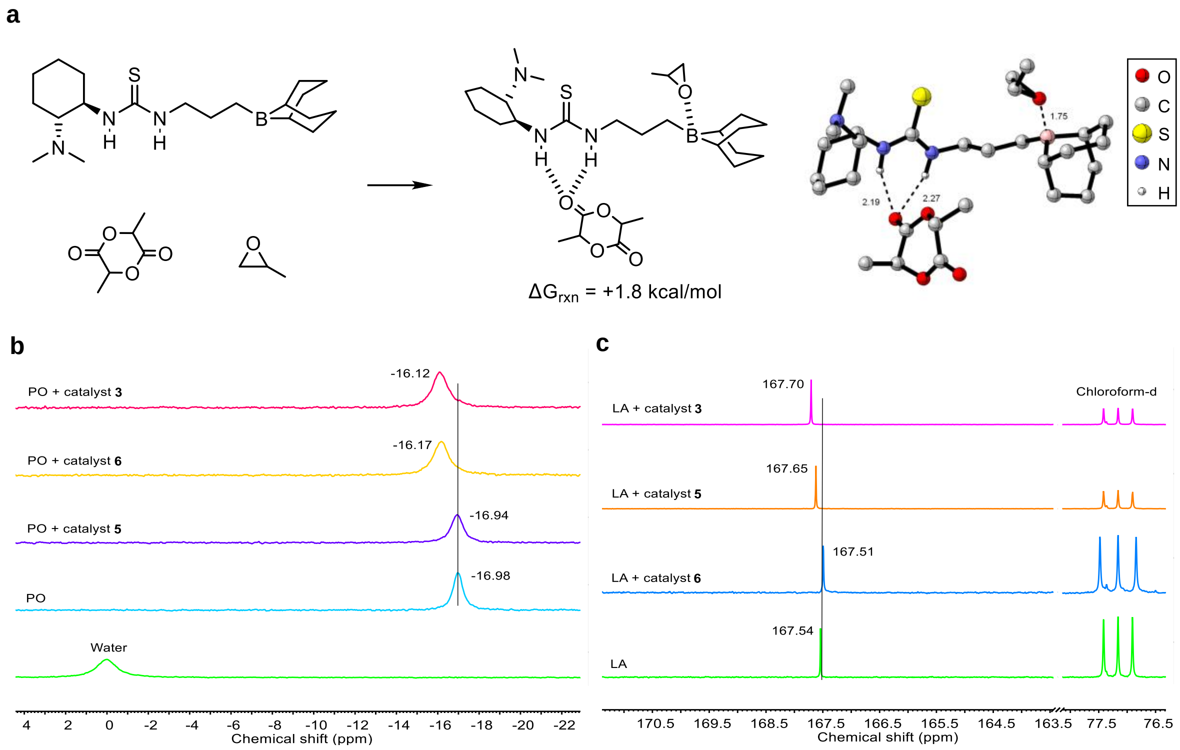

Fig. 2 Computational calculations and NMR characterization for the mechanism. **a** DFT computation optimized structures of the combination of PO, LA, and catalyst **4**. **b** ^{17}O NMR spectra of catalyst **3**/PO ([catalyst **3**] = 0.85 M), catalyst **5**/PO ([catalyst **5**] = 0.85 M), catalyst **6**/PO ([catalyst **6**] = 0.85 M), PO, and H_2O (as external standard at 0 ppm). **c** ^{13}C NMR spectra of catalyst **3**/LA (1/1, [catalyst **3**] = 0.42 M), catalyst **5**/LA (1/1, [catalyst **5**] = 0.42 M), catalyst **6**/LA (1/1, [catalyst **6**] = 0.42 M), and LA.

Switch catalysis for forming block copolymers with catalyst 4. In view of the favorable activity and controllability exhibited by catalyst **4** for either ROP of LA or ROCOP of PO/COS, we developed an intramolecular site switching method to synthesize copolymers with precise sequences from PO, *rac*-LA, and COS in one pot. As our expectation, catalyst **4** exhibited a switchable feature[22] toward the mixture of PO, *rac*-LA, and COS (Fig. 3a). Only ROCOP of PO/COS occurred from the mixture of PO, LA, and COS, while only ROP of LA occurred in the absence of COS. This phenomenon could be ascribed to the rapid binding of COS to the oxyanion to form a thiocarbonate anion, which can ring open PO but not LA, as revealed by the control experiments ($k_1 > k_3 > k_2$, Figs. 3a and S25).

From the mixture of PO and LA, under a nitrogen atmosphere, at 40 °C for 0.8 h, PLA was firstly synthesized with an M_n of 3.9 kDa and LA conversion of 30% (Fig. 3b). When COS ($[COS]_0:[PO]_0$ = 1.2:1.0) was charged into the system, ROCOP of PO/COS was triggered whereas ROP of LA was completely turned off, affording a triblock copolymer with an M_n of 33.4 kDa at the sixth hour (Fig. S26). After draining COS and charging N_2, ROP of LA restarted, delivering a pentablock copolymer with an M_n of 42.1 kDa at the eighth hour, as revealed by unimodal GPC peaks (Fig. 3c) and diffusion-ordered NMR (Fig. S27). The PLA block was highly isotactic with a P_m of 0.82 according to ^{13}C NMR (Fig. 3d). The polythiocarbonate block had alternating and regioregular structures, as determined by NMR analysis (Fig. S28).

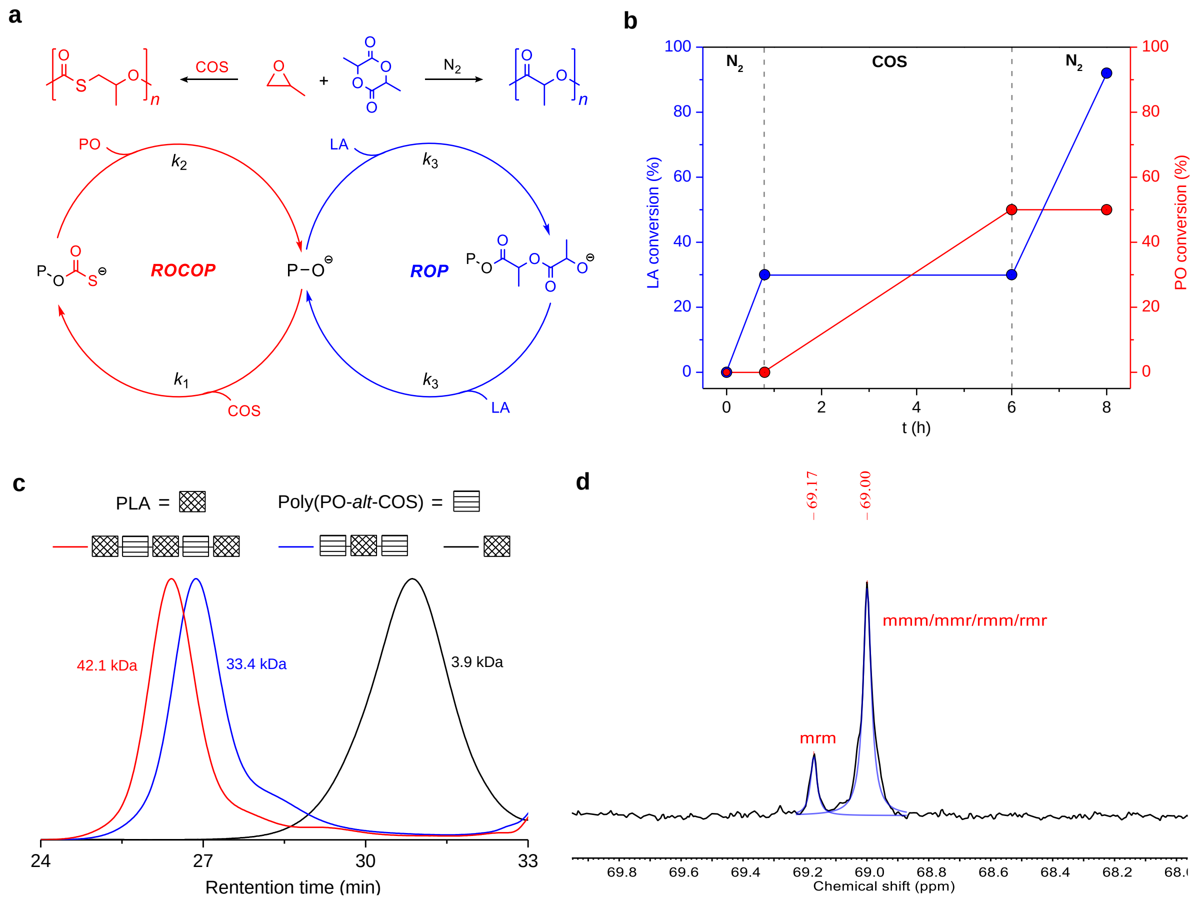

Fig. 3 Chemoselective polymerization control from COS, PO, and LA mixtures. **a** Illustration of heterocycle ROCOP and ROP pathways. Only ROCOP occurs under a COS atmosphere, while only ROP occurs under a nitrogen atmosphere without COS. **b** Reaction conversion versus time plot, with $[PO]_0:[LA]_0:[catalyst\ \mathbf{4}]:[BDM]_0 = 1000:200:1:2$, at 40 °C. **c** GPC curves of the obtained (co)polymers from the switch copolymerization. **d** Quantitative ^{13}C NMR spectrum (126 MHz in $CDCl_3$) of the methine region of the obtained block copolymer.

Synthesis of various block copolymers with catalyst 4. Based on the switchable feature of this catalytic method, we next synthesized various sulfur-containing block copolymers in one pot via ROP and ROCOP two steps (Table 2, Figs. S29-S40). Using BnOH and BDM as initiators, we delivered diblock copolymers **P1** to **P4** and triblock copolymers **P5** to **P8** (PLA block in the middle), respectively, by ROP first and then ROCOP. Conversely, by ROCOP first and then ROP, we synthesized triblock polymers **P9** to **P12** (polythiocarbonate block in the middle). The switch between ROP and ROCOP is through simple inflation and deflation operations (Supplementary Information). By changing the amount of monomer and initiator added, we could easily regulate the molecular weight and the length of each block. The resulting block copolymers have high M_n up to 144.8 kDa ($Đ$ ~ 1.1).

Thermal properties of block copolymers. In these copolymers, the PLA blocks are highly isotactic with $P_m \geq 0.80$ according to ^{13}C NMR (Figs. S41-S52). The block copolymers (**P3**, **P4**, **P7**, **P8**, **P11**, and **P12**) with a high content of PLA blocks exhibit T_m of 41 to 54 °C (Figs. S53-S64). In addition, **P5** shows distinctly two glass-transition temperatures (T_g) of 29.4 and 57.2 °C (Fig. S57a), suggestive of the weak miscibility of PLA and poly(PO-*alt*-COS) blocks. The microphase-separated bulk structure was further revealed by atomic force miscroscope images of the spin-coated thin film (Fig. S65). Moreover, such block copolymers demonstrate high thermal stability with $T_{d,5\%}$ (decomposition temperature of 5% in mass fraction) of 233 to 274 °C, as determined by thermogravimetric analysis (Figs. S53-S64).

Table 2. Synthesis of block copolymers using catalyst **4** from *rac*-LA, COS, and PO [a]

P	initiator	$[PO]_0/[LA]_0$ $/[C]/[I]_0$	t (h)[b]	PO/LA Conv.(%)[c]	[thiocarbonate] /[PLA][d]	M_n^{Theo} (kDa)[e]	M_n^{GPC} (kDa)[f]	$Đ$[f]	P_m[g]	σ_B (MPa)[h]	ε_B (%)[h]
PLA-*b*-Poly(PO-*alt*-COS) [i]											
P1	BnOH	1000/150/1/3	2+8	66/97	67/33	39.1	46.5	1.07	0.81	-	-
P2	BnOH	2000/200/1/2	4+15	84/>99	87/13	113.5	102.4	1.08	0.82	6±1	780±20
P3	BnOH	1000/1000/1/2	10+8	48/95	58/42	125.0	122.7	1.03	0.80	32±1	260±20
P4	BnOH	500/1000/1/2	4+8	57/96	30/70	111.5	103.7	1.06	0.83	51±2	220±40
Poly(PO-*alt*-COS)-*b*-PLA-*b*-Poly(PO-*alt*-COS) [i]											
P5	BDM	1000/150/1/3	2+8	>99/98	80/20	32.4	51.8	1.14	0.80	-	-
P6	BDM	2000/200/1/2	4+15	91/>99	84/16	126.5	133.4	1.09	0.82	7±1	950±50
P7	BDM	1000/1000/1/2	10+8	46/94	39/61	120.5	131.5	1.11	0.80	39±4	215±65
P8	BDM	500/1000/1/2	4+8	53/90	29/71	102.1	98.2	1.05	0.82	54±3	270±10
PLA-*b*-Poly(PO-*alt*-COS)-*b*-PLA [j]											
P9	BDM	1000/150/1/3	2+8	90/80	85/15	40.0	31.0	1.08	0.85	-	-
P10	BDM	2000/200/1/2	4+15	>99/80	87/13	129.5	139.6	1.09	0.80	5±1	1040±100
P11	BDM	1000/1000/1/2	10+8	77/92	32/68	157.2	144.8	1.08	0.82	-	-
P12	BDM	500/1000/1/2	4+8	62/97	28/72	109.3	100.5	1.07	0.89	-	-

[a] Reactions were performed at 40 °C; [b] Reaction time of ROP + ROCOP; [c] Conversion of PO/LA, determined by ^{1}H NMR; [d] Molar ratio of thiocarbonate/PLA in the obtained block copolymer, determined by ^{1}H NMR; [e] Theoretical M_n^{Theo} calculated by $MW_{mon} \times [M]_0/[I]_0 \times$ conv.; [f] Determined by GPC in DMF, calibrated with polystyrene standards; [g] Determined by ^{13}C NMR, based on ESC statistics, $[mrm] = [P_m(1-P_m)]$; [h] Determined by stress-strain experiments; [i] ROP first, then ROCOP; [j] ROCOP first, then ROP.

Mechanical properties of block copolymers. Notably, the resulting high-MW block copolymers exhibit remarkable mechanical properties, as determined by stress-strain experiments on specimens formed by melt processing (Fig. 4, Figs. S66-S73). Polymers **P3**, **P4**, **P7**, and **P8** with high content of isotactic PLA segments (≥ 42 mol%) demonstrate impressive toughness, with σ_B values of 32 ± 1, 51 ± 2, 39 ± 4, 54 ± 3 MPa and ε_B values of 260 ± 20, 220 ± 40, 215 ± 65, and 270 ± 10%, respectively (Fig. 4b). Polymers **P11** and **P12** were too fragile to be applied in tensile experiments probably due to the dispersed short PLA fragments. Compared with poly(PO-*alt*-COS) (M_n = 110.8 kDa, σ_B = 2.3 ± 0.5 MPa, ε_B = 1260 ± 40%), polymers **P2**, **P6**, and **P10** with low content of PLA segments (13 ~ 16 mol%) exhibit 2 ~ 3 times σ_B values of 6 ± 1, 7 ± 1, and 5 ± 1 MPa and slight sacrifice of ε_B values of 780 ± 20, 950 ± 50, and 1040 ± 100%, respectively (Fig. 4c).

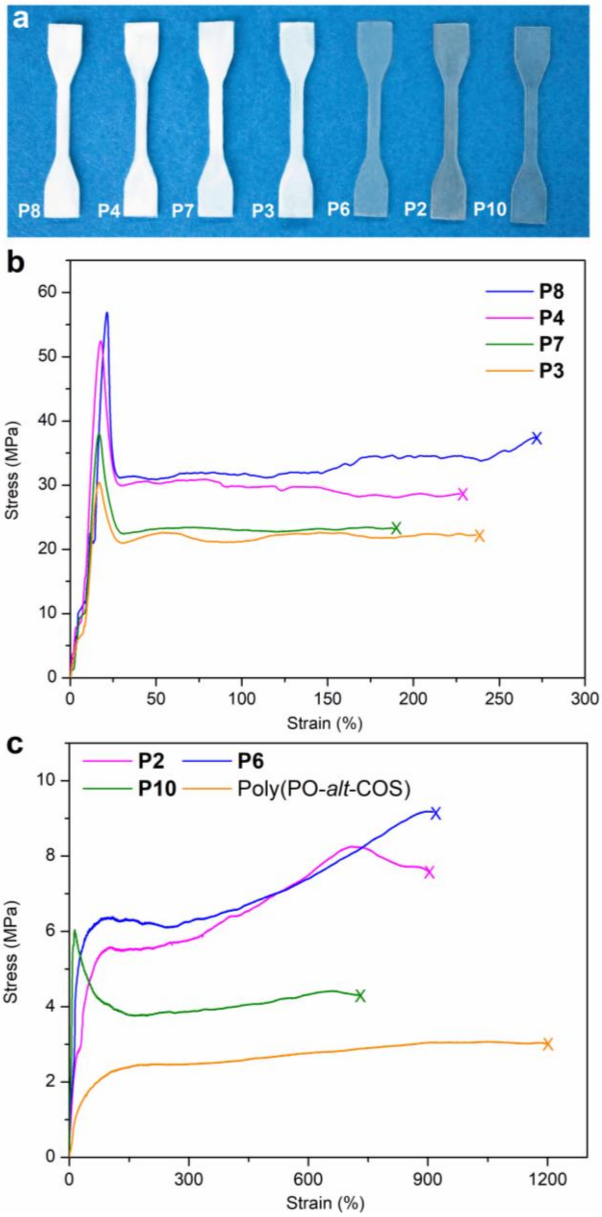

Fig. 4 Tensile properties of obtained block copolymers. **a** Image of specimens formed by hot pressing. **b** Stress-strain curves of **P3**, **P4**, **P7**, and **P8**. **c** Stress-strain curves of **P2**, **P6**, **P10**, and poly(PO-*alt*-COS).

Optical properties of block copolymers. Our method is also a convenient way to synthesize sulfur-containing block copolymers. Sulfur atoms endow block copolymers with desirable optical properties. As the polythiocarbonate content increases from 33 to 91 mol%, the refractive index (n_d) of the diblock increases from 1.47 to 1.58 (at wavelength of 587.6 nm), as determined by spectroscopic ellipsometer (Fig. S74). By contrast, the PLA homopolymer has a lower n_d of 1.47. The outstanding optical and mechanical properties demonstrate broad application prospects of these materials in the field of optoelectronics.

Conclusion

In summary, a series of high-performance, stereo-, regio- and sequence-defined block copolymers were synthesized from commercially available monomers of *rac*-LA, PO, and COS. Catalyst **4**, installing boron and chiral thiourea and amine groups, not only exhibited high efficiency and excellent controllability for ROP and ROCOP, but also achieved stereoselective ROP of *rac*-LA and switch catalysis of mixed monomers. The unique mechanism of site-monomer specific recognition was built and applied to the synthesis of sustainable block polymers. The resulting block copolymers have tailor-made structures, the isotactic PLA block ($P_m \geq 0.8$), the alternating and regioregular polythiocarbonate block, and high M_n up to 144.8 kDa ($Đ$ ~ 1.1). Desirable mechanical properties of such block copolymers were readily tuned by regulating the content of each block. Generally, our findings are expected to provide graceful guidance in two areas: (1) development of cooperative multifunctional organocatalysts for ROP/ROCOP of cyclic monomers; (2) design of unprecedented sustainable block copolymers to meet practical needs.

Acknowledgment

We acknowledge the financial support of the National Science Foundation of China (51973190 and 21774108) and Zhejiang Provincial Department of Science and Technology (2020R52006).

Author Contributions

Chengjian Zhang and Xinghong Zhang conceived, designed, and directed the investigations, and revised the manuscript. Xiaowei Geng carried out most of experiments and analysis and wrote the draft. Ziheng Liu analyzed the polymerization mechanism.

Additional Information

Supplementary information is available. The authors declare no competing interests.

References

(1) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, use, and fate of all plastics ever made. *Science Advances* **2017**, *3*, e1700782.

(2) Jehanno, C.; Alty, J. W.; Roosen, M.; De Meester, S.; Dove, A. P.; Chen, E. Y. X.; Leibfarth, F. A.; Sardon, H. Critical advances and future opportunities in upcycling commodity polymers. *Nature* **2022**, *603*, 803-814.

(3) Haque, F. M.; Ishibashi, J. S. A.; Lidston, C. A. L.; Shao, H.; Bates, F. S.; Chang, A. B.; Coates, G. W.; Cramer, C. J.; Dauenhauer, P. J.; Dichtel, W. R.; Ellison, C. J.; Gormong, E. A.; Hamachi, L. S.; Hoye, T. R.; Jin, M.; Kalow, J. A.; Kim, H. J.; Kumar, G.; LaSalle, C. J.; Liffland, S.; Lipinski, B. M.; Pang, Y.; Parveen, R.; Peng, X.; Popowski, Y.; Prebihalo, E. A.; Reddi, Y.; Reineke, T. M.; Sheppard, D. T.; Swartz, J. L.; Tolman, W. B.; Vlaisavljevich, B.; Wissinger, J.; Xu, S.; Hillmyer, M. A. Defining the macromolecules of tomorrow through synergistic sustainable polymer research. *Chemical Reviews* **2022**, *122*, 6322-6373.

(4) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable polymers from renewable resources. *Nature* **2016**, *540*, 354.

(5) Hillmyer, M. A. The promise of plastics from plants. *Science* **2017**, *358*, 868-870.

(6) Zhang, X.; Fevre, M.; Jones, G. O.; Waymouth, R. M. Catalysis as an enabling science for sustainable polymers. *Chemical Reviews* **2018**, *118*, 839-885.

(7) Wang, Z.; Yuan, L.; Tang, C. Sustainable elastomers from renewable biomass. *Accounts of Chemical Research* **2017**, *50*, 1762-1773.

(8) Scott, A. J.; Penlidis, A.: Copolymerization. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*; Elsevier, 2017.

(9) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. Multiblock polymers: Panacea or pandora's box? *Science* **2012**, *336*, 434-440.

(10) Matyjaszewski, K. Architecturally complex polymers with controlled heterogeneity. *Science* **2011**, *333*, 1104-1105.

(11) Plajer, A. J.; Williams, C. K. Heterocycle/heteroallene ring-opening copolymerization: selective catalysis delivering alternating copolymers. *Angewandte Chemie International Edition*, **2022**, *61*, e202104495.

(12) Ji, H.-Y.; Wang, B.; Pan, L.; Li, Y.-S. One-step access to sequence-controlled block copolymers by self-switchable organocatalytic multicomponent polymerization. *Angewandte Chemie International Edition* **2018**, *57*, 16888-16892.

(13) Liu, S.; Bai, T.; Ni, K.; Chen, Y.; Zhao, J.; Ling, J.; Ye, X.; Zhang, G. Biased Lewis pairs: A general catalytic approach to ether-ester block copolymers with unlimited ordering of sequences. *Angewandte Chemie International Edition* **2019**, *58*, 15478-15487.

(14) Huang, Y.; Hu, C.; Pang, X.; Zhou, Y.; Duan, R.; Sun, Z.; Chen, X. Electrochemically controlled switchable copolymerization of lactide, carbon dioxide, and epoxides. *Angewandte Chemie International Edition* **2022**, *61*, e202202660.

(15) Darensbourg, D. J.; Wu, G.-P. A one-pot synthesis of a triblock copolymer from propylene oxide/carbon dioxide and lactide: Intermediacy of polyol initiators. *Angewandte Chemie International Edition* **2013**, *52*, 10602-10606.

(16) Hillmyer, M. A.; Tolman, W. B. Aliphatic polyester block polymers: Renewable, degradable, and sustainable. *Accounts of Chemical Research* **2014**, *47*, 2390-2396.

(17) Meimoun, J.; Sutapin, C.; Stoclet, G.; Favrelle, A.; Roussel, P.; Bria, M.; Chirachanchai, S.; Bonnet, F.; Zinck, P. Lactide lactone chain shuttling copolymerization mediated by an aminobisphenolate

supported aluminum complex and Al(OiPr)$_3$: Access to new polylactide based block copolymers. *Journal of the American Chemical Society* **2021**, *143*, 21206-21210.

(18) Jeske, R. C.; Rowley, J. M.; Coates, G. W. Pre-rate-determining selectivity in the terpolymerization of epoxides, cyclic Anhydrides, and CO$_2$: A one-step route to diblock copolymers. *Angewandte Chemie International Edition* **2008**, *47*, 6041-6044.

(19) Kernbichl, S.; Reiter, M.; Adams, F.; Vagin, S.; Rieger, B. CO$_2$-controlled one-pot synthesis of AB, ABA block, and statistical terpolymers from β-butyrolactone, epoxides, and CO$_2$. *Journal of the American Chemical Society* **2017**, *139*, 6787-6790.

(20) Romain, C.; Williams, C. K. Chemoselective polymerization control: From mixed-monomer feedstock to copolymers. *Angewandte Chemie International Edition* **2014**, *53*, 1607-1610.

(21) Stößer, T.; Mulryan, D.; Williams, C. K. Switch catalysis to deliver multi-block polyesters from mixtures of propene oxide, lactide, and phthalic anhydride. *Angewandte Chemie International Edition* **2018**, *57*, 16893-16897.

(22) Deacy, A.; Gregory, G.; Sulley, G.; Chen, T.; Williams, C. Sequence control from mixtures: Switchable polymerization catalysis and future materials applications. *Journal of the American Chemical Society* **2021**, *143*, 10021-10040.

(23) Romain, C.; Zhu, Y.; Dingwall, P.; Paul, S.; Rzepa, H. S.; Buchard, A.; Williams, C. K. Chemoselective polymerizations from mixtures of epoxide, lactone, anhydride, and carbon dioxide. *Journal of the American Chemical Society* **2016**, *138*, 4120-4131.

(24) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. Organocatalytic ring-opening polymerization. *Chemical Reviews* **2007**, *107*, 5813-5840.

(25) Mespouille, L.; Coulembier, O.; Kawalec, M.; Dove, A. P.; Dubois, P. Implementation of metal-free ring-opening polymerization in the preparation of aliphatic polycarbonate materials. *Progress in Polymer Science* **2014**, *39*, 1144-1164.

(26) Zhang, C.-J.; Zhang, X.-H. Organocatalytic polymerization. *Science China Chemistry* **2019**, *62*, 1087.

(27) Dove, A. P. Organic catalysis for ring-opening polymerization. *ACS Macro Letters* **2012**, *1*, 1409-1412.

(28) Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G.; Waymouth, R. M.; Hedrick, J. L. Thiourea-based bifunctional organocatalysis: Supramolecular recognition for living polymerization. *Journal of the American*

Chemical Society **2005**, *127*, 13798-13799.

(29) Zhang, X.; Jones, G. O.; Hedrick, J. L.; Waymouth, R. M. Fast and selective ring-opening polymerizations by alkoxides and thioureas. *Nature Chemistry* **2016**, *8*, 1047-1053.

(30) Lin, B.; Hedrick, J. L.; Park, N. H.; Waymouth, R. M. Programmable high-throughput platform for the rapid and scalable synthesis of polyester and polycarbonate libraries. *Journal of the American Chemical Society* **2019**, *141*, 8921-8927.

(31) Jadrich, C. N.; Pane, V. E.; Lin, B. H.; Jones, G. O.; Hedrick, J. L.; Park, N. H.; Waymouth, R. M. A cation-dependent dual activation motif for anionic ring-opening polymerization of cyclic esters. *Journal of the American Chemical Society* **2022**, *144*, 8439-8443.

(32) Zhang, D.; Boopathi, S. K.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. Metal-free alternating copolymerization of CO_2 with epoxides: Fulfilling “green” synthesis and activity. *Journal of the American Chemical Society* **2016**, *138*, 11117-11120.

(33) Boopathi, S. K.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. Direct access to poly(glycidyl azide) and its copolymers through anionic (co-)polymerization of glycidyl azide. *Nature Communications* **2019**, *10*, 293.

(34) Zhang, C.-J.; Wu, S.-Q.; Boopathi, S.; Zhang, X.-H.; Hong, X.; Gnanou, Y.; Feng, X.-S. Versatility of boron-mediated coupling reaction of oxetanes and epoxides with CO_2: Selective synthesis of cyclic carbonates or linear polycarbonates. *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 13056-13063.

(35) Yang, J.-L.; Wu, H.-L.; Li, Y.; Zhang, X.-H.; Darensbourg, D. J. Perfectly alternating and regioselective copolymerization of carbonyl sulfide and epoxides by metal-free Lewis pairs. *Angewandte Chemie International Edition* **2017**, *56*, 5774-5779.

(36) We designed bifunctional catalysts containing borane and quaternary ammonium salt for COS(CO_2)/epoxide ROCOP in the proposal of 2017 NSF of China (no. 21774108).

(37) Xu, J.; Wang, X.; Liu, J.; Feng, X.; Gnanou, Y.; Hadjichristidis, N. Ionic H-bonding organocatalysts for the ring-opening polymerization of cyclic esters and cyclic carbonates. *Progress in Polymer Science* **2022**, *125*, 101484.

(38) Zhang, J.; Wang, L.; Liu, S.; Li, Z. Synthesis of diverse polycarbonates by organocatalytic copolymerization of CO_2 and epoxides: From high pressure and temperature to ambient conditions. *Angewandte Chemie International Edition*, **2022**, *61*, e202111197.

(39) Yang, G.-W.; Zhang, Y.-Y.; Wu, G.-P. Modular organoboron catalysts enable transformations with

unprecedented reactivity. *Accounts of Chemical Research* **2021**, *54*, 4434-4448.

(40) Li, M.; Zhang, S.; Zhang, X.; Wang, Y.; Chen, J.; Tao, Y.; Wang, X. Unimolecular anion-binding catalysts for selective ring-opening polymerization of O-carboxyanhydrides. *Angewandte Chemie International Edition* **2021**, *60*, 6003-6012.

(41) Tian, H.; Tang, Z.; Zhuang, X.; Chen, X.; Jing, X. Biodegradable synthetic polymers: Preparation, functionalization and biomedical application. *Progress in Polymer Science* **2012**, *37*, 237-280.

(42) Ferm, R. J. The chemistry of carbonyl sulfide. *Chemical Reviews* **1957**, *57*, 621-640.

(43) Farrell, W. S.; Zavalij, P. Y.; Sita, L. R. Metal-catalyzed “on-demand” production of carbonyl sulfide from carbon monoxide and elemental sulfur. *Angewandte Chemie International Edition* **2015**, *54*, 4269-4273.

(44) Tian, T.; Hu, R.; Tang, B. Z. Room temperature one-step conversion from elemental sulfur to functional polythioureas through catalyst-free multicomponent polymerizations. *Journal of the American Chemical Society* **2018**, *140*, 6156-6163.

(45) Zhang, C.-J.; Zhu, T.-C.; Cao, X.-H.; Hong, X.; Zhang, X.-H. Poly(thioether)s from closed-system one-pot reaction of carbonyl sulfide and epoxides by organic bases. *Journal of the American Chemical Society* **2019**, *141*, 5490-5496.

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

(47) Luo, M.; Zhang, X.-H.; Darensbourg, D. J. Poly(monothiocarbonate)s from the alternating and regioselective copolymerization of carbonyl sulfide with epoxides. *Accounts of Chemical Research* **2016**, *49*, 2209-2219.

(48) Zhang, C.-J.; Wu, H.-L.; Li, Y.; Yang, J.-L.; Zhang, X.-H. Precise synthesis of sulfur-containing polymers via cooperative dual organocatalysts with high activity. *Nature Communications* **2018**, *9*, 2137.

(49) Yue, T.-J.; Bhat, G. A.; Zhang, W.-J.; Ren, W.-M.; Lu, X.-B.; Darensbourg, D. J. Facile synthesis of well-defined branched sulfur-containing copolymers: One-pot copolymerization of carbonyl sulfide and epoxide. *Angewandte Chemie International Edition* **2020**, *59*, 13633-13637.

(50) Tang, X.; Chen, E. Y. X. Toward infinitely recyclable plastics derived from renewable cyclic esters. *Chem* **2019**, *5*, 284-312.

(51) Crosby, O.: Takemoto's catalyst. In *Catalysis from A to Z.*

(52) Sanchez-Sanchez, A.; Rivilla, I.; Agirre, M.; Basterretxea, A.; Etxeberria, A.; Veloso, A.; Sardon,

H.; Mecerreyes, D.; Cossío, F. P. Enantioselective ring-opening polymerization of *rac*-lactide dictated by densely substituted amino acids. *Journal of the American Chemical Society* **2017**, *139*, 4805-4814.

(53) Liu, S.; Li, H.; Zhao, N.; Li, Z. Stereoselective ring-opening polymerization of *rac*-lactide using organocatalytic cyclic trimeric phosphazene base. *ACS Macro Letters* **2018**, *7*, 624-628.

(54) Zhu, J.-B.; Chen, E. Y. X. From *meso*-lactide to isotactic polylactide: Epimerization by B/N Lewis pairs and kinetic resolution by organic catalysts. *Journal of the American Chemical Society* **2015**, *137*, 12506-12509.

(55) Orhan, B.; Tschan, M. J. L.; Wirotius, A.-L.; Dove, A. P.; Coulembier, O.; Taton, D. Isoselective ring-opening polymerization of *rac*-lactide from chiral Takemoto's organocatalysts: Elucidation of stereocontrol. *ACS Macro Letters* **2018**, *7*, 1413-1419.

(56) Mayer, R. J.; Hampel, N.; Ofial, A. R. Lewis acidic boranes, Lewis bases, and equilibrium constants: A reliable scaffold for a quantitative Lewis acidity/basicity scale. *Chemistry-A European Journal* **2021**, *27*, 4070-4080.

(57) Martín, C.; Fiorani, G.; Kleij, A. W. Recent advances in the catalytic preparation of cyclic organic carbonates. *ACS Catalysis* **2015**, *5*, 1353-1370.

(58) Sopeña, S.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Pushing the limits with squaramide-based organocatalysts in cyclic carbonate synthesis. *ACS Catalysis* **2017**, *7*, 3532-3539.