ChemComm

ROYAL SOCIETY OF CHEMISTRY

FEATURE ARTICLE

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2025, **61**, 46

Terpolymerization reactions of epoxides, CO_2, and the third monomers toward sustainable CO_2-based polymers with controllable chemical and physical properties

Koichi Nakaoka and Tadashi Ema *

Carbon dioxide (CO_2) serves as a cheap, abundant, and renewable C1 building block for the synthesis of organic compounds and polymers. Selective and efficient CO_2 fixation processes are still challenging because of the kinetic and thermodynamic stability of CO_2. Among various CO_2 fixation processes, the ring-opening copolymerization (ROCOP) of epoxides and CO_2 gives aliphatic polycarbonates with high atom economy, although the chemical and physical properties of the resulting polycarbonates are not necessarily satisfactory. Introducing the third monomers into this ROCOP system provides new terpolymers, and the thermal, optical, mechanical or degradation properties can be added or tuned by incorporating new polymer backbones derived from the third monomers at the expense of the CO_2 content. Here we review the terpolymerization reactions of epoxides, CO_2, and the third monomers such as cyclic anhydrides, lactones, lactides, heteroallenes, and olefins. The development of catalysts and the control of the polymer structures are described together with the chemical and physical properties of the resulting polymers.

Received 7th September 2024,
Accepted 28th October 2024

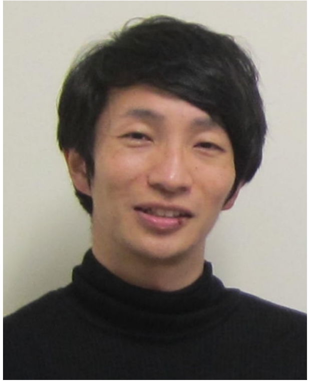
DOI: 10.1039/d4cc04615c

rsc.li/chemcomm

1. Introduction

Carbon dioxide (CO_2) is a cheap, abundant, and renewable C1 building block, while it is a greenhouse gas causing severe damage to the global environment. The effective utilization of CO_2 as well as the mitigation of CO_2 emission is required to realize sustainable carbon-neutral societies based on resource circulation.[1] On the other hand, the accumulation of plastics in the environment and living organisms is also a big problem to be solved. More environmentally benign plastics should be developed and used. The creation of CO_2-based polymers will contribute to finding the solution to these global issues.

Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan.
E-mail: ema@cc.okayama-u.ac.jp

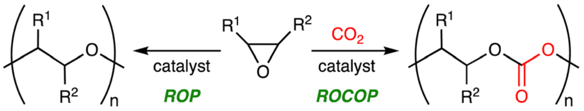


Koichi Nakaoka

Koichi Nakaoka was born in Osaka, Japan in 1988. He received his bachelor's degree in 2011 and master's degree in 2013 from Osaka University under the supervision of Professor Akio Baba. He joined Asahi KASEI in 2013 and was promoted to a team leader in 2020. He obtained his doctor's degree from Okayama University under the supervision of Professor Tadashi Ema in 2024. He moved to PPG Japan in 2024. His research interest is in the design and synthesis of sustainable materials based on green chemistry.

Tadashi Ema

Tadashi Ema was born in Gifu, Japan in 1966. He received his bachelor's degree from Kyoto University in 1989, and he obtained his master's degree in 1991 and doctor's degree in 1994 from Kyoto University under the supervision of Professor Hisanobu Ogoshi. He was appointed as an Assistant Professor at Okayama University in 1994 and was promoted to an Associate Professor in 2002 and a Full Professor in 2012. His research interest is in the design and synthesis of unique molecular catalysts for sustainable organic synthesis.



Scheme 1 ROCOP of epoxides and CO$_2$ and ROP of epoxides.

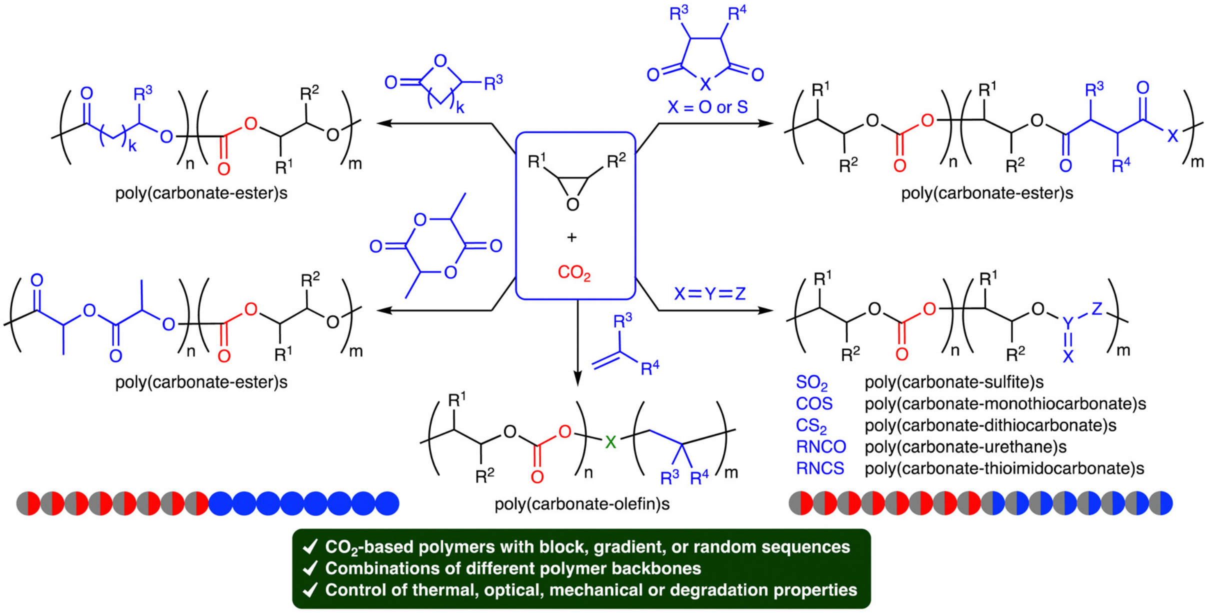
Because CO$_2$ is the most oxidized form of carbon with high stability, the effective and efficient conversion of CO$_2$ into useful compounds and polymers is still challenging. The thermodynamic stability of CO$_2$ can be overcome by using high-energy chemicals, heat, or electric current, while the kinetic stability of CO$_2$ can be overcome by lowering activation barriers using catalysts.

Ring-opening copolymerization (ROCOP) of epoxides and CO$_2$ can produce aliphatic polycarbonates in a highly atom-economical manner (Scheme 1).[2,3] Because the ROCOP of epoxides and CO$_2$ occasionally competes with the ring-opening polymerization (ROP) of epoxides to give polyethers (Scheme 1), selective catalysts for the ROCOP of epoxides and CO$_2$ are needed, and much progress has been made. On the other hand, the chemical or physical properties of the resultant aliphatic CO$_2$-based polycarbonates are rather limited. When the polycarbonates have unsatisfactory properties, there is an option of employing the third monomer at the expense of the CO$_2$ content.[4] The terpolymerization strategy may be quite effective and even essential for the creation of more useful and practical polymers. The terpolymerization reactions of epoxides, CO$_2$, and the third monomers, such as cyclic anhydrides,[5] lactones,[6] lactides,[7] heteroallenes,[8,9] and olefins,[10] are effective strategies for the development of new CO$_2$-based polymers (Scheme 2). The thermal, optical, mechanical, adhesive, or degradation properties can be added or tuned by not only incorporating different polymer backbones derived from the third monomers but also controlling the sequence structures such as block, gradient, and random structures.[11] Controlling these factors is important for the modulation of heat resistance, mechanical strength, elasticity, or biodegradability, leading to the creation of functional materials such as heat-resistant resins, tough plastics, elastomers, adhesives, and environmentally benign plastics. Two catalytic cycles, which may be switchable, need to proceed, and the development of the selective and controllable catalysts for terpolymerization reactions is challenging and important for the further advancement of CO$_2$-based polymers.

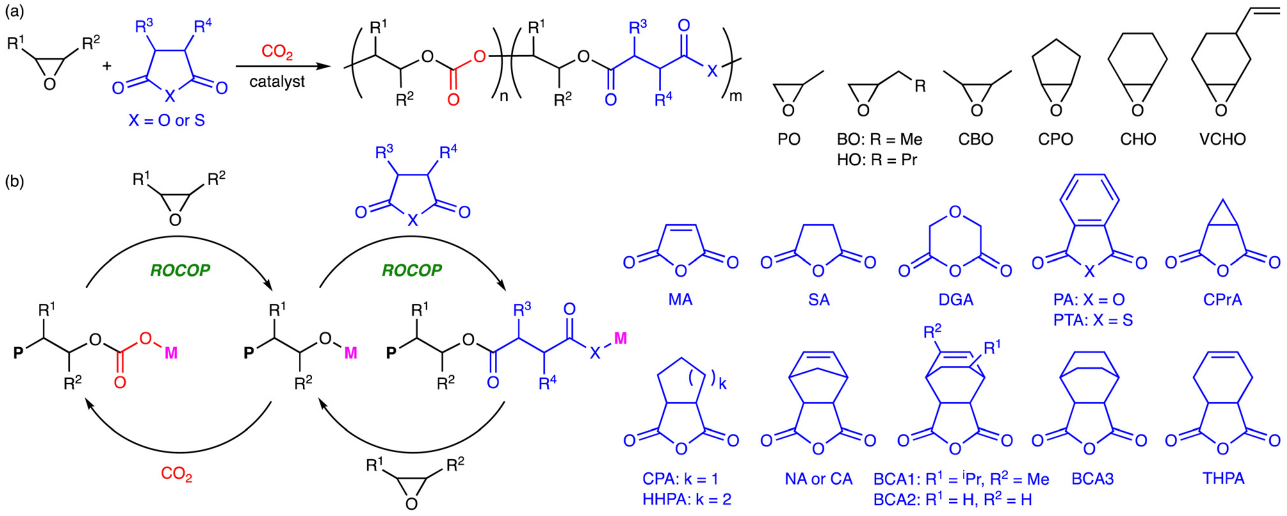
Here we provide an overview of the terpolymerization reactions of epoxides, CO$_2$, and the third monomers for the synthesis of CO$_2$-based polymers made up of different polymer backbones, which are suitable for the improvement or control of chemical and physical properties. The terpolymerization reactions of two different epoxides and CO$_2$ or epoxides, CO$_2$, and cyclic carbonates are not included herein, although the resulting polycarbonates often have excellent properties.[12,13] Polymerization reactions with the stepwise feeding of different monomers such as epoxides and lactones are also excluded, whereas terpolymerization reactions with gas switching, for example, between CO$_2$ and N$_2$ are introduced herein. The reactions, catalysts, and chemical or physical properties of the resulting CO$_2$-based polymers are concisely summarized one by one. Herein, one will find the beneficial effects, potential, and challenging aspects of the catalytic terpolymerization strategy to create new CO$_2$-based polymers with excellent chemical and physical properties.

2. Terpolymerization reactions of epoxides, CO$_2$, and cyclic anhydrides

The terpolymerization reactions of epoxides, CO$_2$, and cyclic anhydrides give poly(carbonate-ester)s (Scheme 3a). Because



Scheme 2 Terpolymerization reactions of epoxides, CO$_2$, and the third monomers.



Scheme 3 (a) Representative reactions and (b) catalytic cycles. **P** simply represents a part of a polymer chain that may differ in each step, while **M** represents a Lewis acid catalyst.

the carbonate and ester linkages show different biodegradabilities, it is possible to adjust the degradability of the poly(carbonate-ester)s by regulating the ratio of the polyester linkage to the polycarbonate linkage. In addition, the chemical and physical properties of the terpolymers can be altered by changing the structures and proportions of the monomers. The representative catalytic cycles, catalysts, and reaction conditions for the terpolymerization reactions of epoxides, CO_2, and cyclic anhydrides are shown in Scheme 3b, Fig. 1 and Table 1, respectively.

In 2006, Huang and co-workers reported the terpolymerization of propylene oxide (PO), CO_2, and maleic anhydride (MA) by using polymer-supported bimetallic (PBM) complex **1** as a catalyst.[5a] The viscosity, glass transition temperature (T_g), and decomposition temperature of the terpolymers were much higher than those of poly(propylene carbonate) (PPC). The terpolymers also showed a higher degradability than PPC, and their degradation rates increased with increasing content of MA in the terpolymers.

Coates and co-workers developed an excellent homogeneous catalytic system using β-diiminate (BDI) Zn^{II} complex **2**, which enabled the first block terpolymerization of cyclohexene oxide (CHO) or 4-vinyl-1-cyclohexene-1,2-epoxide (VCHO), CO_2, and diglycolic anhydride (DGA) or succinic anhydride (SA) in a one-step procedure.[5b] Diblock terpolymers with very little tapering were obtained. This discovery led to the development of several other selective catalysts.

Meng and co-workers found that the Zn^{II} glutarate catalyst (ZnGA) **3** prepared from zinc oxide and glutaric acid acted as a good catalyst for the terpolymerization of PO, CO_2, and MA.[5c] The T_g values of the terpolymers increased with increasing molecular weights. The decomposition temperatures of the terpolymers were enhanced in proportion to the MA content because the double bonds derived from MA readily underwent crosslinking at high temperature. Tensile tests also indicated that the mechanical properties of the terpolymers increased with increasing molecular weight. The same group also reported the terpolymerization of PO, CO_2, and phthalic anhydride (PA) using ZnGA **3**.[5h] In this system, CO_2 was much more reactive than PA. The incorporation of a small amount of PA enhanced the thermal properties of the terpolymers. They also reported the terpolymerization of PO, CO_2, and MA using Zn^{II} adipate (ZnAA) **4**, and the sulfonation of the resulting terpolymers afforded new biodegradable surfactants.[5k] The terpolymer with comparable hydrophilic and hydrophobic segments exhibited the best surface activity.

Zhang and co-workers achieved the terpolymerization of CHO, CO_2, and MA using heterogeneous Zn–Co double metal cyanide (DMC) **5** to obtain poly(ester-carbonate) with a low content of ether units.[5d] THF used as a solvent dramatically inhibited the polyether formation owing to the coordination of THF to the Zn^{II} center. Moreover, the polycarbonate chain containing a small amount of the polyester linkage showed a slightly higher decomposition temperature than the fully alternating polycarbonate.

Duchateau and co-workers achieved the terpolymerization of CHO, CO_2, and cyclic anhydride using Cr(TPP)Cl **6a** or Cr(salophen)Cl **7** as a catalyst and 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) as a co-catalyst.[5e] SA, cyclopropane-1,2-dicarboxylic acid anhydride (CPrA), cyclopentane-1,2-dicarboxylic acid anhydride (CPA) or PA was used as an anhydride monomer. Both **6a** and **7** in combination with DMAP afforded poly(ester-carbonate)s with completely alternating structures because the presence of CO_2 suppressed the formation of the polyether linkage associated with the homopolymerization of CHO. Chisholm and co-workers reported the terpolymerization of PO, CO_2, and SA using **6a** and bis(triphenylphosphine)iminium chloride (PPNCl) as a catalyst and a co-catalyst, respectively, to give poly(ester-*b*-carbonate).[5g] The preferential reactivity of SA over CO_2 was ascribed to the higher concentration of SA relative to CO_2 dissolved in the reaction mixture.

Darensbourg and co-workers studied the kinetics of the terpolymerization of CHO, CO_2, and PA using Cr(salen)Cl **8**

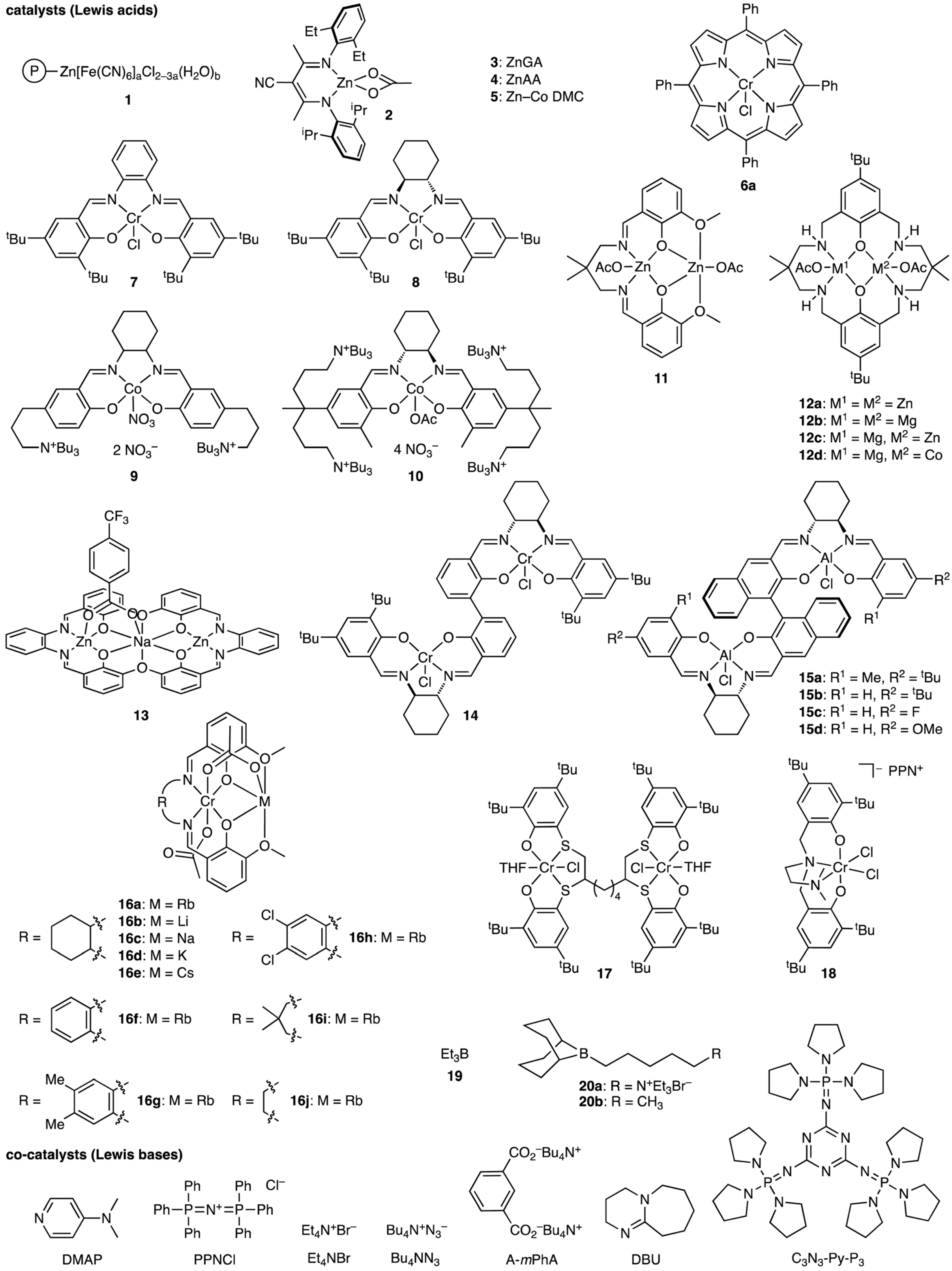
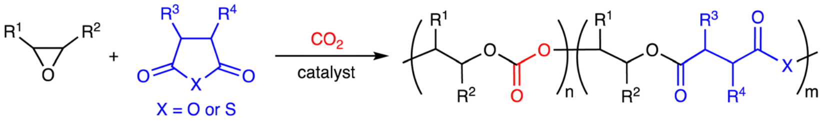


Fig. 1 Catalysts and co-catalysts for the terpolymerization reactions of epoxides, CO_2, and cyclic anhydrides.

and PPNCl as a catalyst and a co-catalyst, respectively, to afford diblock copolymers with very little tapering.[5f] The polyester formation was much faster than the polycarbonate formation. In the latter case, the epoxide ring opening was much slower,

Table 1 Terpolymerization reactions of epoxides, CO$_2$, and cyclic anhydrides



Entry	Epoxide	Anhydride	CO$_2$ (MPa)	Cat.	Co-cat.	T (°C)	M_n[a] (kg mol^{-1})	Sequence[b]	Ref.
1	PO	MA	3.5–4	**1**	—	50–80	78.1	R	5*a*
2	CHO, VCHO	DGA, SA	0.34–5.5	**2**	—	50–55	37.0	B	5*b*
3	PO	MA	5.2	**3**	—	60	67.1	R	5*c*
4	PO	PA	0.5–5.0	**3**	—	75	221	R	5*h*
5	PO	MA	2.5–5.0	**4**	—	75	152	G	5*k*
6	CHO	MA	1.0–4.0	**5**	—	75–90	14.1	R, B	5*d*
7	CHO	SA, CPrA, CPA, PA	5.0	**6a**, **7**	DMAP	80	16	B	5*e*
8	PO	SA	4.0–5.0	**6a**	PPNCl	25	—	B	5*g*
9	CHO	PA	3.4	**8**	PPNCl	80	—	B	5*f*
10	PO	NA	3.0	**9**	—	60	94.4	B	5*i*
11	PO	PA	3.5	**10**	—	80	381	G, B	5*j*
12	CHO	PA	3.0	**11**	—	100	7.1	B	5*l*
13	CHO	PA	0.10	**12a**	—	100	—	B	5*m*
14	CHO	BCA1–3, CA, THPA	0.10	**12a–b**	—	100	11.8	B	5*n*
15	CHO	PA, BCA1	0.10–2.0	**12**	—	100	19.4	R, B	5*q*
16	CHO	PA	0.10	**13**	—	90–100	4.06	B	5*r*
17	CHO	PA	1.0	**14**	PPNCl	80	10.2	B	5*o*
18	CBO, CPO, CHO	PA	0.5–2.0	**15**	PPNCl	0–60	30.0	R	5*w*
19	CHO	PTA	0.4	**16**	—	100	16.9	R	5*y*
20	PO, CHO, VCHO, HO	PA	2.0	**17**	PPNCl	45–80	10.3	B	5*z*
21	CHO	PA	4.0	**18**	—	100, 60	17.6	B	5*aa*
22	PO	PA	0.5–3.0	**19**	PPNCl	60–100	58.3	R, B	5*s*
23	EO	PA	1.0	**19**	A-*m*PhA	40–45	273	G	5*v*
24	CHO, PO, BO	PA	1.0	**19**	PPNCl	80	29.8	B	5*t*
25	CHO	PA	1.0	**19**	C_3N_3-Py-P_3	80	15.5	R, G, B	5*x*
26	CHO, PO	SA, PA	1.0	**19**	Bu_4NN_3, PPNCl	60–80	22.7	R, G, B	5*u*
27	PO, CHO	PA, SA, HHPA	2.0	**19**	DBU	60	12.0	B	5*ab*
28	CHO	PA	0.15–4.0	**20a**	—	60–120	62.3	G, B	5*ac*

[a] Maximum value. [b] Sequence structures of polymers. R: random, G: gradient, B: block.

and CO$_2$ insertion into the metal–alkoxide bond was highly reversible.

Liu and co-workers performed the terpolymerization of PO, CO$_2$, and norbornene anhydride (NA) using bifunctional Co(salen)NO$_3$ tethering two quaternary ammonium salts **9** as a catalyst.[5i] The reaction afforded diblock copolymers containing reactive norbornene moieties, which could be applied to the thiol–ene click reaction. Lee and co-workers reported that bifunctional Co(salen)OAc tethering four quaternary ammonium salts **10** showed a high catalytic activity of 2.2 kg-polymer per g-catalyst for the terpolymerization of PO, CO$_2$, and PA.[5j] The T_g value of the terpolymer was higher than that of the PO/CO$_2$ alternating copolymer, PPC, and lower than that of the PO/PA alternating copolymer.

Williams and co-workers used dinuclear Zn$^{\text{II}}$ complex **11** for the terpolymerization of CHO, CO$_2$, and PA. The polyester was initially produced selectively, and poly(cyclohexene carbonate) (PCHC) was then formed, delivering poly(ester-*b*-carbonate)s in a one-step manner.[5l] They also studied the block-selective copolymerization from a mixture of CHO and PA under 1 atm CO$_2$ using dinuclear Zn$^{\text{II}}$ complex **12a** to obtain poly(ester-*b*-carbonate)s.[5m] CHO/PA copolymerization proceeded first until the complete consumption of PA, and CHO/CO$_2$ copolymerization then occurred. DFT calculations indicated that PA insertion into CHO was more favorable than CO$_2$ insertion into CHO. The same group also used sterically congested tricyclic anhydrides (BCA1–3), carbic anhydride (CA), and 1,2,3,6-tetrahydrophthalic anhydride (THPA) as the third monomers in the terpolymerization, and both catalysts **12a** and **12b** showed excellent catalytic performances to synthesize block copolymers from bio-derived anhydride BCA1, CHO, and CO$_2$.[5n] Interestingly, Zn$^{\text{II}}$-based catalyst **12a** initially catalyzed CHO/BCA1 polymerization, after which alternating CHO/CO$_2$ polymerization occurred to give poly(ester-*b*-carbonate)s. In sharp contrast, more active Mg$^{\text{II}}$-based catalyst **12b** formed the polycarbonate block, and after the removal of CO$_2$, CHO/BCA1 copolymerization proceeded to give poly(carbonate-*b*-ester)s. This unusual selectivity of **12b** was ascribed to the rigidity and steric hindrance of the tricyclic anhydrides. DSC analysis demonstrated that the T_g values of the polymers could be controlled by the carbonate/ester block ratios. Later, different block structures were realized with a series of dinuclear catalysts **12**.[5q] Zn$^{\text{II}}$Zn$^{\text{II}}$ complex **12a** yielded poly(ester-*b*-carbonate)s, Mg$^{\text{II}}$Mg$^{\text{II}}$ complex **12b** or Mg$^{\text{II}}$Co$^{\text{II}}$ complex **12d** gave poly(carbonate-*b*-ester)s, and Mg$^{\text{II}}$Zn$^{\text{II}}$ complex **12c** furnished random copolymers from CHO, CO$_2$, and BCA1. The most active and selective Mg$^{\text{II}}$Co$^{\text{II}}$ catalyst **12d** also delivered triblock (ABA), pentablock (BABAB), and heptablock (ABABABA) polymers by switching the atmosphere between CO$_2$ and N$_2$. They also reported that trinuclear Zn$^{\text{II}}$Na$^{\text{I}}$Zn$^{\text{II}}$ catalyst **13** catalyzed CHO/PA ROCOP, CHO/CO$_2$ ROCOP, and CHO

ROP from mixtures of CHO and PA by using the atmosphere of CO_2 or N_2.[5r]

Liu, Lu, and co-workers reported the terpolymerization of CHO, CO_2, and PA with dinuclear Cr^{III} complex **14**. PA was consumed completely within 2 h to give polyesters, and then the polymerization entered the second phase, leading to the formation of poly(ester-*b*-carbonate)s without forming the polyether segments.[5o] More recently, they achieved the asymmetric terpolymerization reactions of *meso*-epoxides, CO_2, and PA using chiral bimetallic Al^{III} complex **15**, giving terpolymers with a random distribution of carbonate and ester segments, which differed from that observed for tapered or gradient terpolymers.[5w] All the catalysts exhibited good catalytic activities to afford enantioenriched terpolymers with high enantioselectivity and narrow polydispersity. Especially, catalyst **15b** gave the terpolymer with the highest molecular weight and enantiomeric purity. Various epoxides such as CHO, cyclopentene oxide (CPO), and *cis*-2,3-butene oxide (CBO) were reactive, and the terpolymerization of the epoxides, CO_2, and PA proceeded with excellent enantioselectivities of up to 99% ee.

Plajer and co-workers reported the terpolymerization of CHO, CO_2, and phthalic thioanhydride (PTA) forming random poly(ester-thioester-carbonate) by employing heterobimetallic Cr^{III}-based catalysts **16**.[5y] The ratios of the ester, thioester, and carbonate linkages varied, depending on the structures of the catalysts (alkali metals and backbones). Interestingly, the ratios of the thioester to ester linkages were always lower than 1, implying the loss of the S atoms and the enrichment of the O atoms in the polymer backbones, which is due to the O/S exchange at the chain end followed by the release of thiirane (cyclohexene sulfide). The terpolymers degraded into oligomers under UV irradiation as a result of the selective cleavage of the thioester linkages. The quaterpolymerization of CHO, CO_2, PA, and PTA was also achieved, where the terpolymerization of CHO, CO_2, and PA occurred until PA was consumed, and the subsequent terpolymerization of CHO, CO_2, and PTA proceeded to produce poly(ester-thioester-carbonate) with some tapering.

Capacchione and co-workers developed dinuclear Cr^{III} complexes, among which **17** was the most active for the terpolymerization reactions of epoxides, CO_2, and PA as well as the copolymerization reactions of epoxides and CO_2.[5z] The ^1H and ^{13}C NMR spectra showed no polycarbonate sequences in the polyester segments, suggesting the formation of diblock poly(ester-*b*-carbonate) copolymers. It is considered that after the faster reaction of the epoxides with PA to fully consume PA, the carbonate block was elongated by the slower reaction of the epoxides with CO_2. Kozak and co-workers conducted two-step polymerization with Cr^{III} ate complex **18** to synthesize block copolymers.[5aa] Poly(ester-*b*-carbonate) was obtained by the ROCOP of CHO and PA under N_2 at 100 °C followed by the ROCOP of CHO and CO_2 at 60 °C.

Metal-free catalysts have also been developed since the discovery of ROCOP of epoxides/CO_2 with Et_3B (**19**) and onium salts by Gnanou, Feng, and co-workers.[3b] Xiao, Meng, and co-workers performed the terpolymerization of PO, CO_2, and PA using **19** and PPNCl.[5s] A random poly(ester-carbonate) segment formed first, and a long PPC-enriched segment grew after the full consumption of PA, which afforded poly[(ester-carbonate)-*b*-carbonate]. The terpolymer with an aromatic polyester content of 43 mol% displayed a T_g value of 47 °C, which was higher than that of PPC (38 °C). The terpolymers exhibited tensile strengths of up to 37.6 MPa, which was much higher than that of PPC (9 MPa, M_n = 28 kg mol^{-1}). The terpolymers also exhibited satisfactory degradation behaviors under the standard composting conditions. They also reported the quaterpolymerization of CHO, PO, CO_2, and PA using **19** and PPNCl to obtain polymers with an M_n of up to 77.7 kg mol^{-1}.[5p] They succeeded in changing T_g values between 86 and 116 °C and enhancing tensile strengths to 54.8 MPa by modulating the monomer ratios. They also reported that gradient terpolymers were successfully synthesized by the terpolymerization of ethylene oxides (EO), CO_2, and PA using **19** and the tetrabutylammonium salt of *m*-phthalic acid (A-*m*PhA).[5v] Thermal gravimetric analysis (TGA) indicated that the terpolymers had two fast decomposition stages: the first weight loss peak corresponded to the decomposition of the poly(ethylene carbonate) (PEC) sequence, and the second weight loss peak was assigned to the thermal degradation of the EO/PA polyester. The terpolymers had a higher thermal stability than PEC. Liu, Kang, Li, and co-workers achieved the terpolymerization of CHO, CO_2, and PA with **19** and PPNCl to deliver diblock copolymers with little tapering in a one-pot one-step manner.[5t] Furthermore, the ROCOP of CHO and PA and the ROCOP of CHO and CO_2 were done in a sequential one-pot manner by changing the atmosphere from N_2 to CO_2 to synthesize well-defined diblock poly(ester-*b*-carbonate)s. Other epoxides such as PO and 1,2-butylene oxide (BO) were also used to construct diblock poly(ester-*b*-carbonate)s. All materials showed single T_g values between the T_g values for the corresponding polyester and polycarbonate homopolymers. Liu, Zhong, Li, and co-workers reported the chemoselective terpolymerization of CHO, CO_2, and PA using **19** and phosphazene C_3N_3-Py-P_3 as binary organocatalysts.[5x] The terpolymers with block, tapered, or random structures could be selectively synthesized by changing the molar ratio of C_3N_3-Py-P_3 to **19**. DFT calculations clarified the effect of the molar ratio of C_3N_3-Py-P_3 to **19** on the chemoselectivity. Gnanou, Feng, and co-workers demonstrated the terpolymerization of PO or CHO, CO_2, and SA or PA in the presence of **19** and PPNCl or tetrabutylammonium azide (Bu_4NN_3).[5u] Only single glass transition temperature was observed for all the terpolymers, and the T_g value could be tuned by varying the ester contents. Wang and co-workers found a combination of **19** and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) showing the self-switchable polymerization of PO, PA, and CO_2 to afford poly(propylene phthalate)-*b*-poly(propylene carbonate) with linear and hyperbranched architectures.[5ab] The linear and hyperbranched topologies were realized by employing benzyl alcohol and 1,2,4-benzene tricarboxylic anhydride as a polymerizable chain transfer agent, respectively, and the effect of the polymeric topology on viscosity, glass transition temperature, and thermal stability was revealed. For example, the T_g values of the linear and hyperbranched polymers were 50.1 °C and 44.2 °C, respectively.

Yang, Wu, and co-workers observed that bifunctional organoborane **20a** with quaternary ammonium bromide produced gradient terpolymers from CHO, CO_2, and PA, while the corresponding binary catalyst, **20b**, and Et_4NBr, afforded diblock terpolymers with tapering segments.[5ac] DFT calculations rationalized the experimental results; in the case of **20a**, synergistic electrostatic interactions operate in the transition state, leading to the more competitive formation of the polyester and polycarbonate linkages. The gradient terpolymers with different polyester contents ranging from 5 mol% to 64 mol% had T_g values in the range of 114 °C to 128 °C, although the gradient terpolymers had a decomposition temperature ($T_d^{5\%}$) at 280 °C, which was lower than that of the diblock terpolymers (298 °C).

3. Terpolymerization reactions of epoxides, CO_2, and lactones

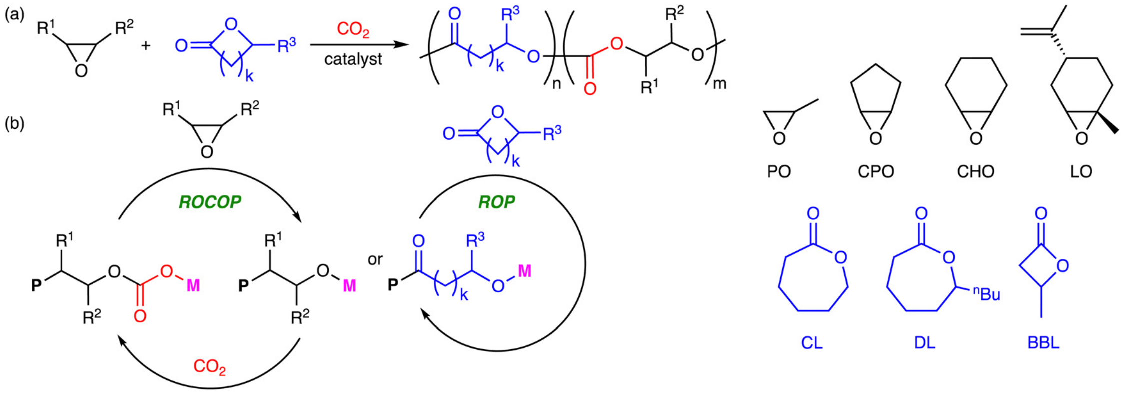
Polymers containing the carbonate and ester linkages can also be obtained by the terpolymerization reactions of epoxides, CO_2, and lactones, where the ROCOP and ROP mechanisms are involved (Scheme 4a). This approach is accessible to polymers that cannot be synthesized by the terpolymerization reactions of epoxides, CO_2, and cyclic anhydrides. The representative catalytic cycles, catalysts, and reaction conditions for the terpolymerization reactions of epoxides, CO_2, and lactones are shown in Scheme 4b, Fig. 2 and Table 2, respectively.

In 2003, Ree and co-workers carried out the terpolymerization of PO, CO_2, and ε-caprolactone (CL) using ZnGA **3** as a catalyst to produce poly(propylene carbonate-caprolactone)s, PPC-PCL, with improved biodegradability.[6a,6b] All the terpolymers showed a single T_g originating from the polycarbonate blocks and a single T_m originating from the polyester blocks. The terpolymers underwent enzymatic degradation in the presence of a lipase in a phosphate buffer (pH 7.0) at 37 °C for 10 days. Huang and co-workers reported the terpolymerization of PO, CO_2, and CL with PBM complex **1**.[6c] The incorporation of CL into the polymer skeletons increased the viscosity, glass transition temperature, and the degradation rate of the terpolymers.

Williams and co-workers reported the selective synthesis of poly(cyclohexene carbonate-caprolactone)s, PCHC-PCL, from CHO, CO_2, and CL using dinuclear Zn^{II} complex **12a**,[6d] which also catalyzed the terpolymerization reactions of epoxides, CO_2, and cyclic anhydrides as mentioned above. This is the first example of a single catalyst that not only promoted two distinct polymerization reactions but also switched them by the addition of exogeneous switching reagents, epoxide or CO_2. The catalytic mechanism was elucidated by experiments and DFT calculations.[6h] The same terpolymerization was catalyzed by dinuclear Zn^{II} complex **12e**, and ABA block polymers, PCL-*b*-PCHC-*b*-PCL, were prepared in one pot.[6e] The ROCOP of CHO and CO_2 occurred first to produce polycarbonates, and after removal of CO_2, the subsequent ROP of CL on both sides of the polymer chains produced the triblock copolymers. These polymers showed controllable T_g values from −54 °C to 34 °C, depending on the block compositions. The one-pot switchable catalysis (reverse procedure) was also applied to the synthesis of PCHC-*b*-PDL-*b*-PCHC triblock polymers from CHO, CO_2, and ε-decalactone (DL) with heterodinuclear $Zn^{II}Mg^{II}$ catalyst **21**.[6k] The block polymers showed not only excellent mechanical properties and thermal stability but also good degradation behaviors upon gentle heating under acidic conditions.

Xiao, Meng, and co-workers reported the terpolymerization of CHO, CO_2, and CL with Schiff base trinuclear Zn^{II} complexes **22**.[6f] **22b** was more active than **22a**. In this terpolymerization system, CL was much more reactive than the CHO/CO_2 pair, and the resulting terpolymers had high molecular weights.

Zhang and co-workers achieved the highly efficient terpolymerization of CHO, CO_2, and CL with binary catalysts, Zn–Co DMC **5** and stannous octoate (**23**).[6g] The ROCOP of CHO and CO_2 with **5** and the ROP of CL with **23** occurred independently with matched polymerization rates to give PCHC and PCL, respectively, and the two independently growing chains underwent the cross-chain exchange reaction to produce multiblock copolymers, which are the first examples of biodegradable polycarbonate-polyester multiblock copolymers. In addition,



Scheme 4 (a) Representative reactions and (b) catalytic cycles. **P** simply represents a part of a polymer chain that may differ in each step, while **M** represents a Lewis acid catalyst.

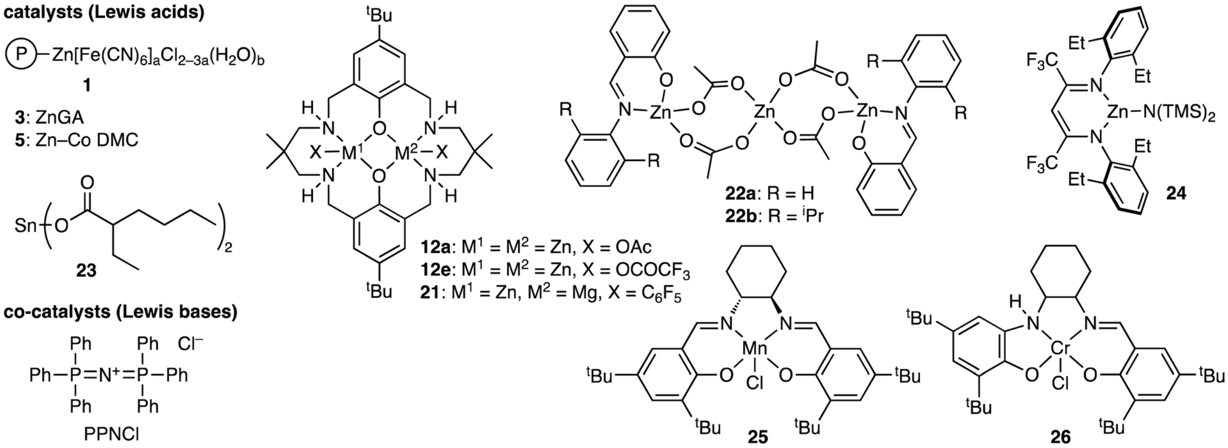
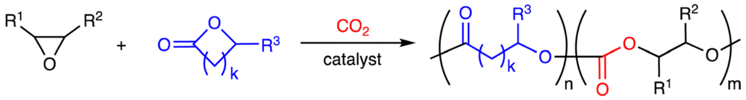


Fig. 2 Catalysts and co-catalysts for the terpolymerization reactions of epoxides, CO_2, and lactones.

Table 2 Terpolymerization reactions of epoxides, CO_2, and lactones



Entry	Epoxide	Lactone	CO_2 (MPa)	Cat.	Co-cat.	T (°C)	M_n[a] (kg mol^{-1})	Sequence[b]	Ref.
1	PO	CL	2.8	**3**	—	60	275	B	6*a*,6*b*
2	PO	CL	4.0	**1**	—	50–90	73.6	N/A	6*c*
3	CHO	CL	0.10	**12a**	—	80	4.81	B	6*d*
4	CHO	CL	0.10	**12e**	—	80	13.8	B	6*e*
5	CHO	DL	2.0	**21**	—	80	71.9	B	6*k*
6	CHO	CL	5.0	**22**	—	70–100	234.3	G	6*f*
7	CHO	CL	4.0	**5, 23**	—	100	35.2	B	6*g*
8	CHO, CPO	BBL	0.1–5.0	**24**	—	50–60	174	R, G, B	6*i*
9	CHO, CPO, LO	BBL	0.3–4.0	**24**	—	40–60	233	R, B	6*j*
10	CHO	CL	1.5	**25**	PPNCl	80	41.8	B	6*l*
11	CHO	CL	1.0–4.0	**26**	PPNCl	60–100	67.1	G	6*m*

[a] Maximum value. [b] Sequence structures of polymers. R: random, G: gradient, B: block, N/A: data not available.

improved chemical and physical properties were confirmed in glass transition temperature, melting temperature, and tensile tests. For example, the film material of the multiblock copolymers showed an elongation at break of 22.8%, which was much higher than those of PCHC (3.3%) and a PCHC/PCL blend (1.8%).

Rieger and co-workers achieved the terpolymerization reactions of epoxides, CO_2, and *rac*-β-butyrolactone (BBL), which is less reactive than CL or lactide.[6i] Catalyst **24** could switch between the ROP of BBL and the ROCOP of epoxides and CO_2, and the following three terpolymerization procedures were established. The first procedure provided the block structures by the ROP of BBL in the beginning followed by the addition of 40 bar CO_2 initiating the ROCOP of epoxides and CO_2. The second one was the reverse procedure starting from the ROCOP of epoxides and CO_2 followed by the ROP of BBL after complete CO_2 release. In the third procedure, lowering the CO_2 pressure to 3 bar afforded random terpolymers composed of epoxides, CO_2, and BBL. Not only CHO and CPO but also limonene oxide (LO), a bio-based monomer, was successfully used for the terpolymerization.[6j] Although the terpolymers with a block structure showed two T_g values because of the phase separation, only one T_g was observed for those with a random structure. As for mechanical behaviors, the Young's modulus of each of the block and random polymers was smaller than that of PCHC because of the incorporation of soft poly(3-hydroxybutyrate) segments.

Pang and co-workers synthesized AB-type diblock copolymers and ABA-type triblock copolymers by the terpolymerization of CHO, CO_2, and CL using Mn(salen)Cl **25**.[6l] In this catalyst system, cyclic anhydrides were also used as monomers, and the one-pot switchable copolymerization of anhydrides, epoxides, CO_2, and CL delivered AB, ABA, and ABC-type block copolymers. They also reported a facile method for the synthesis of gradient poly(carbonate-ester), PCHC-*g*-PCL, from a mixture of CHO, CO_2, and CL with Cr^{III} complex **26**.[6m] Compared with a symmetrical Cr(salen)Cl complex, this catalyst had an exceptional ability to synthesize biodegradable terpolymers with gradient character. The polymerization initially produced a PCHC segment, which then changed to a PCL-enriched segment by a cross-propagation reaction, and the chain configurations could be modulated by adjusting the reaction conditions. When the proportion of the PCL in the terpolymers was increased, a melting peak appeared and the degradation temperature increased.

4. Terpolymerization reactions of epoxides, CO_2, and lactides

Polylactide (PLA), which can be derived from renewable resources, has a T_g of 60 °C, high crystallinity, and biodegradability, but the brittleness of PLA restricts potential applicability. On the other hand, poly(carbonate-ester)s synthesized by the terpolymerization reactions of epoxides, CO_2, and lactides (Scheme 5a) may have excellent properties originating from both PLA and polycarbonates. The representative catalytic cycles, catalysts, and reaction conditions for the terpolymerization reactions of epoxides, CO_2, and lactides are shown in Scheme 5b, Fig. 3 and Table 3, respectively.

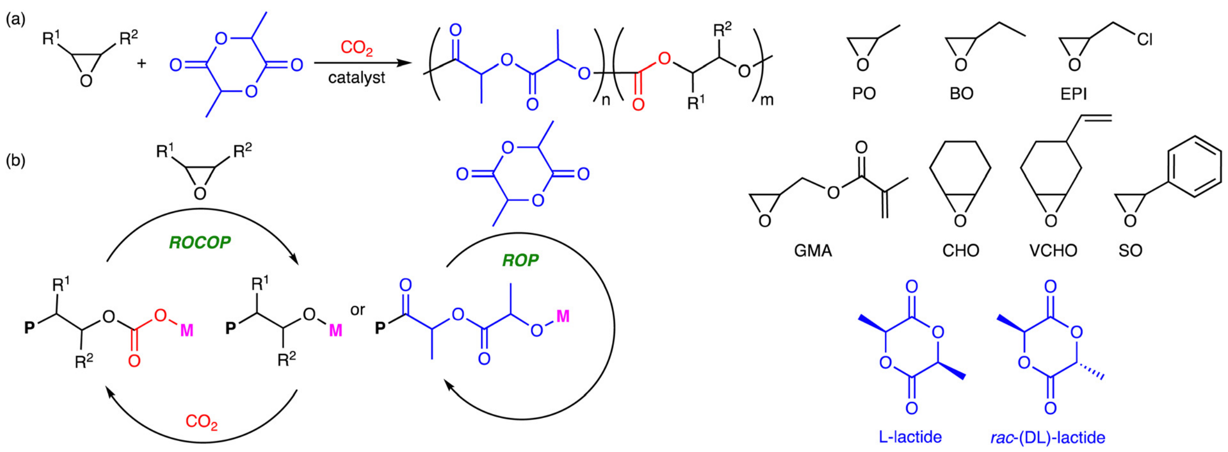
In 2006, Kröger, Döring, and co-workers reported the first example of the terpolymerization of CHO, CO_2, and lactides with Zn^{II} complexes **27** for the synthesis of poly(cyclohexene carbonate-lactide)s whose composition was adjusted by monomer feeding.[7a] The T_g values of the terpolymers fell between those of pure PLA and pure PCHC and increased with increasing the PCHC content, indicating the random structures of the terpolymers.

Liu and co-workers synthesized terpolymers from PO, CO_2, and *rac*-lactides by using PBM **1** as a catalyst.[7b] The terpolymers showed a much higher hydrolytic degradability in tris buffer (pH 7.4) over 10 weeks than PPC. Wang and co-workers conducted the terpolymerization of PO, CO_2, and L-lactide using $Y(CCl_3CO_2)_3$-$ZnEt_2$-glycerin ternary catalyst **28**.[7c] The resulting terpolymers showed a decomposition temperature T_d of up to 242.9 °C, which was much higher than that of pure PPC (197.1 °C), and the elongation at break of the terpolymers reached 40.5%, which was three times larger than that of pure PPC.

Wang, Meng, and co-workers reported the synthesis of carbonate-ester terpolymers with a long L-lactide-rich sequence *via* the terpolymerization of PO, CO_2, and L-lactide using ZnAA **4**.[7e] The thermal stability of the terpolymers was greatly improved; the decomposition temperature ($T_d^{5\%}$) of the terpolymers was modulated from 235.9 °C to 258.6 °C, which was much higher than that for pure PPC (219.9 °C) and close to that for pure PLA (257.0 °C). This is because the zipper-like depolymerization reaction of PPC was suppressed by the L-lactide-rich sequence; the activation energy for PLA decomposition (280 kJ mol^{-1}) is much higher than that for PPC decomposition (80 kJ mol^{-1}). Regarding the mechanical properties, all terpolymers exhibited greater tensile strengths than PPC; the tensile strength of the terpolymers increased from 27.1 MPa to 49.5 MPa upon increasing the crystalline PLA segment. The same catalyst system was also reported by Sakharov and co-workers.[7d]

The one-pot regioselective and stereoselective terpolymerization of PO, CO_2, and *rac*-lactide was reported by Xie and co-workers.[7f] Interestingly, M(TPP)Cl **6** and PPNCl catalyzed the polymerization to produce PPC–PLA–PPO (poly(propylene oxide)) multiblock copolymers with good regioregularity (head-to-tail structure) in the PPC block and good stereoregularity (isotacticity) in the PLA block despite the use of the achiral catalyst and racemic starting materials. They also reported the terpolymerization of VCHO, CO_2, and *rac*-lactide with **6c**.[7k] The glass transition temperature of the resulting polymers could be adjusted by changing the molar ratio of the monomers, reaction temperature, CO_2 pressure, and the amount of the catalyst.

Pang, Chen, and co-workers developed a switchable system with **29a** and DBU to achieve chemoselective block copolymerization between lactide ROP and PO/CO_2 ROCOP in one pot.[7g] This catalyst system is based on the reversible adsorption of CO_2 onto DBU and the chain shuttling polymerization using *i*-PrOH as a chain shuttling reagent. Pang and co-workers also devised a ternary catalyst system comprising the Co^{II} complex (**29b**, **29c**, or **30a**), the Co^{III} complex (**29d**, **29e**, or **30b**), and PPNCl, which produced poly(ester-carbonate)s with no polyether structures from a mixture of PO, CO_2, and L-lactide.[7h] The resultant



Scheme 5 (a) Representative reactions and (b) catalytic cycles. **P** simply represents a part of a polymer chain that may differ in each step, while **M** represents a Lewis acid catalyst.

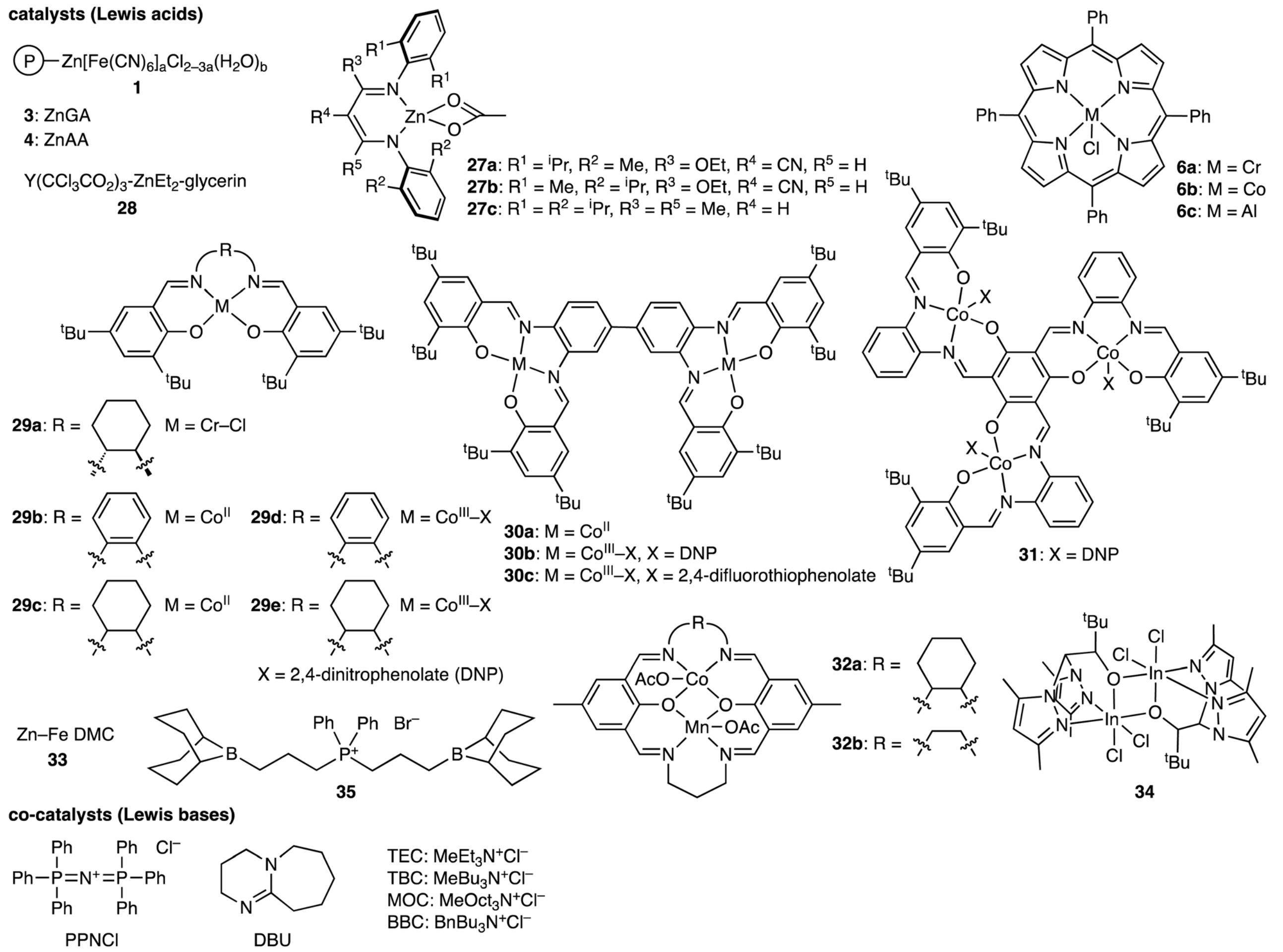
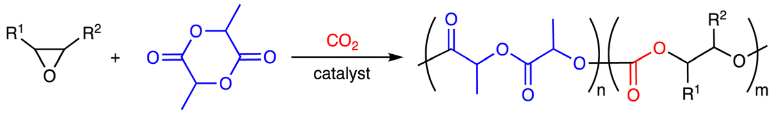


Fig. 3 Catalysts and co-catalysts for the terpolymerization reactions of epoxides, CO$_2$, and lactides.

Table 3 Terpolymerization reactions of epoxides, CO$_2$, and lactides



Entry	Epoxide	Lactide	CO$_2$ (MPa)	Cat.	Co-cat.	T (°C)	M_n^{a} (kg mol^{-1})	Sequence^b	Ref.
1	CHO	*rac*, L	4.0	**27**	—	90	41.6	R	*7a*
2	PO	*rac*	3.5	**1**	—	70	14.3	N/A	*7b*
3	PO	L	4.0	**28**	—	60–80	156	R, B	*7c*
4	PO	L	5.0	**4**	—	60–90	132	B	*7e*
5	PO	L	CO$_2$: PO = 1 : 1	**4**	—	70	68	B	*7d*
6	PO	*rac*	0.1–4.0	**6**	PPNCl	23–60	14.7	B	*7f*
7	VCHO	*rac*	0.10–4.0	**6c**	PPNCl	25–70	8.2	B	*7k*
8	PO	L	2.0	**29a**	DBU	rt, 40	7.15	B	*7g*
9	PO, SO, CHO	L	2.0	**29b–e, 30a–b**	PPNCl	60	13.6	B	*7h*
10	PO	L	3.0	**31**	—	25–60	15.3	B	*7i*
11	PO, EPI, GMA	—^{c}	1.0–4.0	**32**	PPNCl	60	49.3	B	*7n*
12	PO, BO	L	0.20–2.0	**30b, 3**	PPNCl	60	698	B	*7l*
13	PO, BO	L	0.20–2.0	**30**	PPNCl, O$_2$	60	28.7	B	*7m*
14	PO	*rac*	3.5	**33**	TEC, TBC, MOC, BBC	55	11.3	N/A	*7j*
15	CHO	L	0.5–4.0	**34**	—	60	9.1	R, B	*7o*
16	CHO	L	0.5–0	**35**	—	45	8.6	B	*7p*

[a] Maximum value. [b] Sequence structures of polymers. R: random, G: gradient, B: block, N/A: data not available. [c] Stereochemistry of lactide not indicated.

polymers were biodegradable, and the T_g values were tunable between 38 °C and 52 °C, which contrasts with pure PPC having a T_g value of 35–40 °C. The mechanistic investigation revealed that the Co^{III} and Co^{II} complexes catalyzed PO/CO_2 ROCOP and lactide ROP, respectively, and the combined polymers were formed *via* the transfer of the growing chains. Styrene oxide (SO) and CHO were also reactive in this copolymerization. They also developed trinuclear Co^{III} complex **31** for the terpolymerization of PO, CO_2, and L-lactide to produce multiblock copolymers.[7i] The lactide ROP and PO/CO_2 ROCOP were separately catalyzed by **31** without any co-catalyst to give the terpolymers in one pot. Recently, Pang, Chen, and co-workers developed an electrochemically controlled switchable copolymerization system with redox-active heteronuclear complex **32** for the synthesis of multi-block copolymers.[7n] When the catalyst was in a reduced state, the ROP of lactide proceeded (ON), and the ROCOP of epoxide and CO_2 did not occur (OFF). In contrast, when the catalyst underwent the electrochemical oxidation, the ROCOP of epoxide and CO_2 proceeded (ON), and the ROP of lactide did not occur (OFF). The electrochemical switching between the active (ON) and dormant (OFF) states of the catalyst realized the synthesis of the multi-block copolymers.

Pang, Deng, and co-workers reported a heterogeneous ternary catalyst system composed of dinuclear Co^{III} complex **30b**, ZnGA **3**, and PPNCl for the terpolymerization of epoxides, CO_2, and L-lactide.[7l] Interestingly, **30b** could not catalyze the PO/CO_2 ROCOP and the lactide ROP simultaneously because the strong coordination of CO_2 prevented the latter, while **3** was also inactive for the ROP of lactide. The intermolecular cooperation between the two metal catalysts realized the terpolymerization, forming PLA/PPC multiblock copolymers with high molecular weights of up to 698 kg mol^{-1}. Several homogeneous ternary catalyst systems (TCSs) were also developed.[7m] TCS I was composed of **30a**, **30b**, and PPNCl, while TCS III_a consisted of **30b**, **30c**, and PPNCl, and TCS III_b comprised **30b**, O_2, and PPNCl. TCS III_a and TCS III_b showed a higher catalytic activity than TCS I.

Lin, Zhu, and co-workers reported Zn–Fe DMC **33** and quaternary ammonium salts for the terpolymerization of PO, CO_2, and lactide.[7j] The catalyst systems were synthesized from $ZnBr_2$, $K_3Fe(CN)_6$, and quaternary ammonium salts *via* ball grinding, and the combination of Zn–Fe DMC and triethylmethylammonium chloride (TEC) showed the highest catalytic activity.

Castro-Osma, Lara-Sánchez, and co-workers developed bimetallic In^{III} complex **34** for the terpolymerization of CHO, CO_2, and L-lactide.[7o] Terpolymers were obtained without any co-catalyst, and the degree of CO_2 incorporation could be modulated by changing the CO_2 pressure and the monomer amounts. The terpolymers exhibited single T_g values between those of pure PLA and pure PCHC, which suggested the formation of random copolymers, and the T_g values increased as the ratio of CHO to L-lactide increased. The terpolymer with the highest ratio of CHO to L-lactide showed good thermal stability (a $T_d^{5\%}$ of up to 244 °C) because of the higher PCHC content.

Wang, Xia, Li, and co-workers employed bifunctional organoboron **35** for the one-pot two-step synthesis of poly(carbonate-*b*-ester).[7p] When a mixture of CHO, L-lactide, and **35** was subjected to CO_2 (5 bar) at 45 °C for 1 h, the ROCOP of CHO and CO_2 proceeded selectively to form PCHC in 99% conversion. The release of CO_2 allowed the ROP of L-lactide to produce the PCHC-*b*-PLA block polymer. In contrast, this type of block polymer could not be obtained when a similar experiment was done at a higher CO_2 pressure (20 bar); the ROP of L-lactide did not proceed probably because the polymer end was capped with CO_2 to form a carbonate anion, a weak nucleophile for the ring-opening of L-lactide.

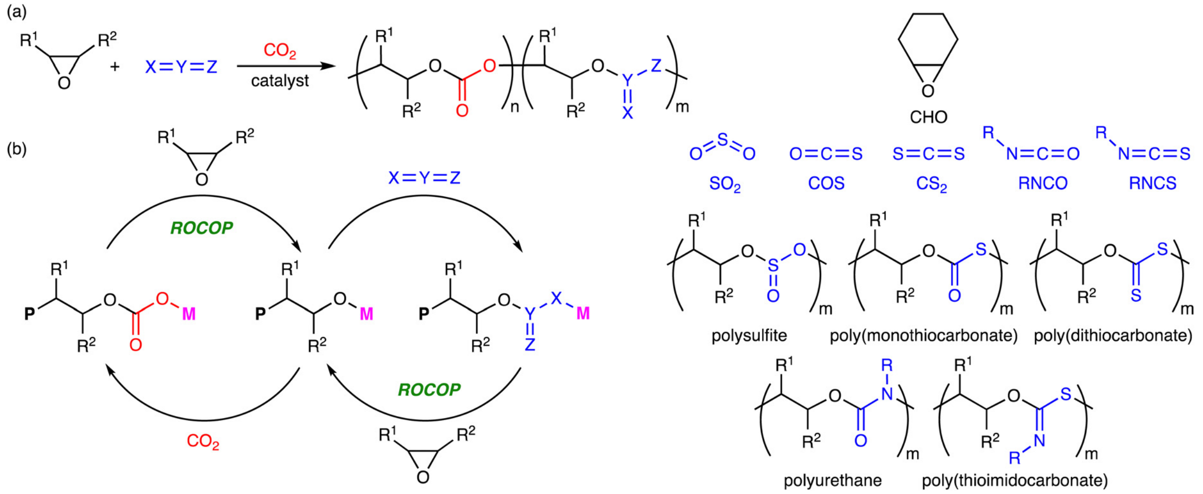
5. Terpolymerization reactions of epoxides, CO_2, and heteroallenes

Heteroallenes such as CO_2, sulfur dioxide (SO_2), carbonyl sulfide (COS), and carbon disulfide (CS_2), isocyanates (RNCO), and isothiocyanates (RNCS) are important reagents for organic synthesis. The ROCOP of epoxides and heteroallenes can incorporate new linkages into the main chains of the polymers, which may improve their chemical and physical properties. Therefore, the terpolymerization reactions of epoxides, CO_2, and heteroallenes provide new opportunities to create new CO_2-based polymers (Scheme 6a), even if they are challenging because of the difference in reactivity between CO_2 and heteroallenes.[8] In fact, there are only several reports on this type of terpolymerization. The representative catalytic cycles, catalysts, and reaction conditions for the terpolymerization reactions of epoxides, CO_2, and heteroallenes are shown in Scheme 6b, Fig. 4 and Table 4, respectively.

In 2019, Jia, Shan, and co-workers achieved the terpolymerization of CHO, CO_2, and SO_2 with Cr^{III}(salen)Cl **8** to synthesize poly(carbonate-sulfite)s.[9a] Interestingly, no nucleophilic co-catalyst was needed to promote this terpolymerization because SO_2 acted as a nucleophile as well as a reactant. TGA indicated that the first weight loss appeared at 211.4–242.7 °C, corresponding to the degradation of the sulfite units. The second weight loss appeared at 242.7–327.7 °C, corresponding to the decomposition of the carbonate and ether units.

Ren, Darensbourg, and co-workers synthesized terpolymers with tunable randomly distributed sulfur atoms from CHO, CO_2, and COS using **36** or **37** as a catalyst.[9b] By changing the CO_2 pressure, random polycarbonates with different COS contents in the terpolymers could be prepared, and the polymers showed good optical properties such as the Abbe number as high as 48.6 and a refractive index of 1.501. The optical parameters of the terpolymers exceeded those of homopolymer blends or diblock copolymers with equal sulfur compositions.

Neale, Plajer, and co-workers reported the terpolymerization of CHO, CO_2, and CS_2 with heterobimetallic catalyst **16a**.[9c] The mechanism of O/S scrambling is proposed to rationalize the oxygen enrichment in the terpolymers. For example, the alkoxide chain end attacks the adjacent dithiocarbonate linkage (–OC(=S)S–) to generate the thiolate chain end and the monothiocarbonate linkage (–OC(=S)O–), which is followed by the release of thiirane, as supported by DFT calculations. Although the terpolymers had T_g values and refractive indexes that were



Scheme 6 (a) Representative reactions and (b) catalytic cycles. **P** simply represents a part of a polymer chain that may differ in each step, while **M** represents a Lewis acid catalyst.

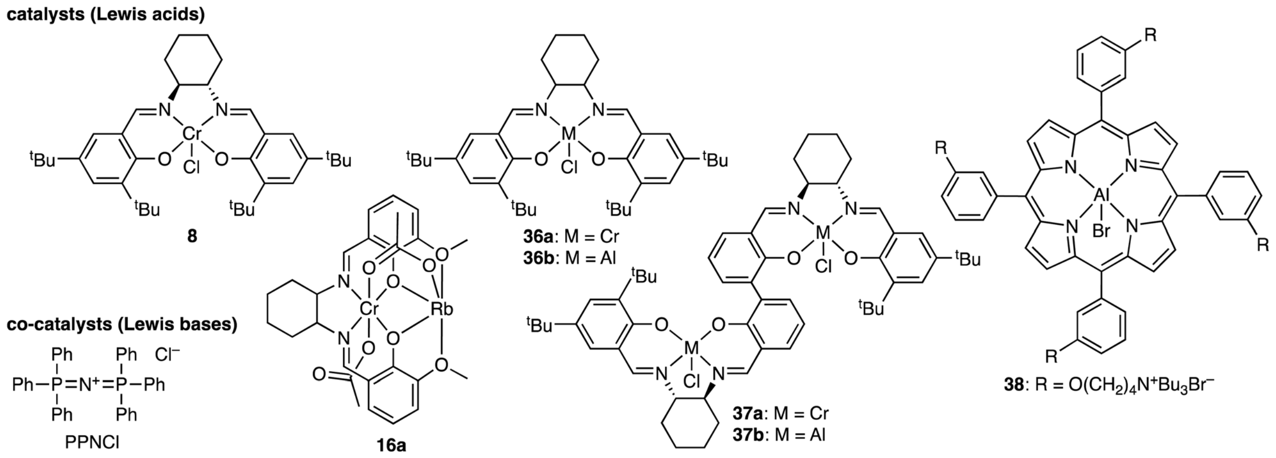
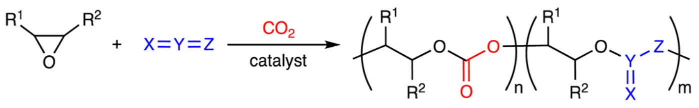


Fig. 4 Catalysts and co-catalysts for the terpolymerization reactions of epoxides, CO_2, and heteroallenes.

Table 4 Terpolymerization reactions of epoxides, CO_2, and heteroallenes



X=Y=Z	polymers
SO_2	poly(carbonate-sulfite)s
COS	poly(carbonate-monothiocarbonate)s
CS_2	poly(carbonate-dithiocarbonate)s
RNCO	poly(carbonate-urethane)s
RNCS	poly(carbonate-thioimidocarbonate)s

Entry	Epoxide	Heteroallene	CO_2 (MPa)	Cat.	Co-cat.	T (°C)	M_n[a] (kg mol^{-1})	Sequence[b]	Ref.
1	CHO	SO_2	$SO_2 : CO_2 = 1:4$–16	**8**	—, PPNCl	40–90	9.99	B	9*a*
2	CHO	COS	0.6–3.0	**36, 37**	PPNCl	25–80	50.2	R, G	9*b*
3	CHO	CS_2	0.4	**16a**	—	100	12.7	R	9*c*
4	CHO	RNCO	0.1	**38**	—	80–100	7.4	R	9*d*
5	CHO	RNCS	0.5–2.0	**38**	—	80–100	183	G, B	9*d*

[a] Maximum value. [b] Sequence structures of polymers. R: random, G: gradient, B: block.

similar to those of PCHC, the sulfur-containing terpolymers were susceptible to oxidative and photolytic cleavage. The terpolymers degraded into oligomers under aqueous H_2O_2 or UV irradiation owing to the selective degradation of the dithiocarbonate units, which is in contrast to the corresponding all-oxygen CHO/CO_2 copolymers being fully intact under the same conditions.

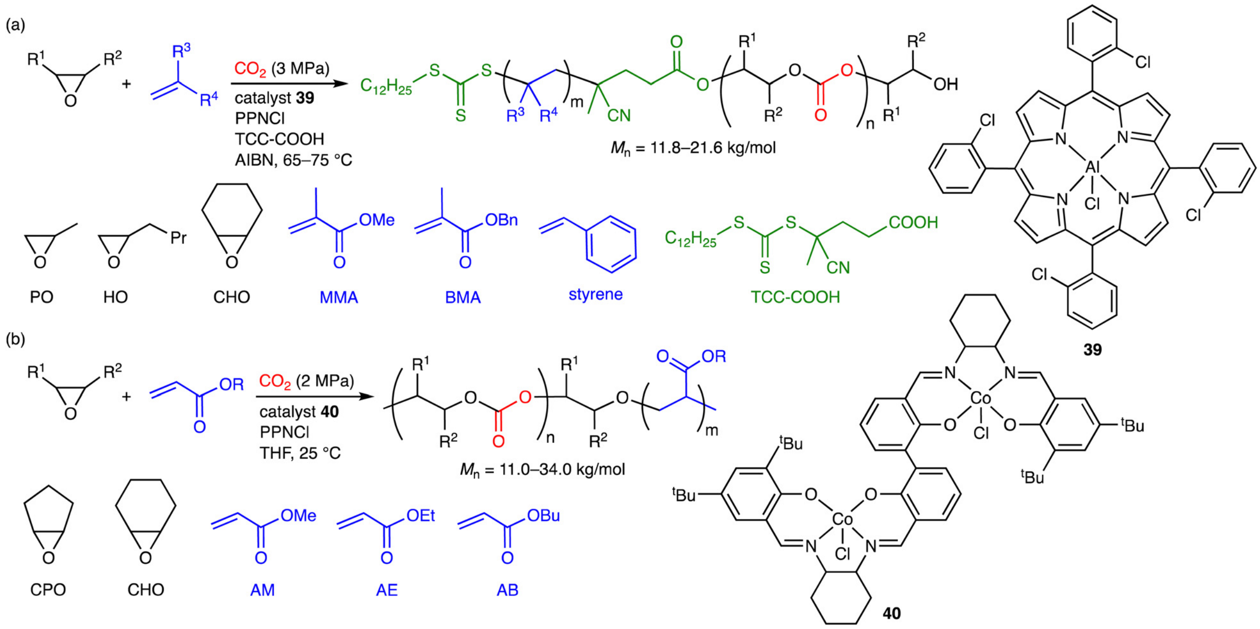
Ema and co-workers achieved the terpolymerization of CHO, CO_2, and aryl isothiocyanates to produce poly(carbonate-thioimidocarbonate)s with gradient character, and the ratio of the polythioimidocarbonate to the polycarbonate units in the terpolymers could be controlled by the CO_2 pressure.[9d] When the scope of aryl isothiocyanates was explored, *p*-tolyl isothiocyanate was modestly incorporated into the terpolymer, while aryl isothiocyanates with electron-withdrawing groups showed higher reactivity to give terpolymers with higher polythioimidocarbonate contents. On the other hand, the terpolymerization of CHO, CO_2, and aryl isocyanates furnished poly(carbonate-urethane)s with random sequences. It should be noted that these terpolymerization reactions were catalyzed by a single catalyst, bifunctional Al^{III} porphyrin **38**. This fact clearly demonstrates that cooperative catalysis with the metal center and the quaternary ammonium salts of bifunctional Al^{III} porphyrins is effective for polymer synthesis.[14,15] Poly(carbonate-thioimidocarbonate)s underwent partial degradation upon acid treatment or UV irradiation to give polycarbonates, while poly(carbonate-urethane)s were stable under the same conditions.

6. Terpolymerization reactions of epoxides, CO_2, and olefins

The terpolymerization reactions of epoxides, CO_2, and olefins have been achieved by ingenious strategies. In 2018, Xie, Wang, and co-workers reported the unprecedented terpolymerization of epoxides, CO_2, and olefins using Al^{III} porphyrin **39** as a catalyst (Scheme 7a).[10a] Well-defined CO_2-based diblock copolymers were obtained in one step by the simultaneous ROCOP of epoxides and CO_2 and the reversible addition–fragmentation chain transfer (RAFT) polymerization of olefin monomers using TTC-COOH and 2,2′-azobis(isobutyronitrile) (AIBN) as a chain transfer agent with the trithiocarbonate (TTC) group and a radical initiator, respectively. More recently, Yue, Ren, and co-workers achieved the terpolymerization reactions of epoxides, CO_2, and acrylate esters with dinuclear Co^{III} catalyst **40** (Scheme 7b).[10b] In the presence of CO_2, various polycarbonate-*b*-polyacrylates, which had a wide range of M_n and T_g values, were obtained successfully. In contrast, in the absence of CO_2, the copolymerization of epoxides and acrylates proceeded in a sequence-controlled manner, delivering polyether-*b*-polyacrylates; the polyether formation occurred first to consume most of the epoxides, and the non-catalytic anionic polymerization of acrylate esters took place from the alkoxide ends of the growing polymers (not shown). Several examples of stepwise terpolymerization reactions have also been reported,[16] although they are not described herein.

7. Conclusions and outlook

The mitigation of CO_2 emission is crucially important because one of the most urgent issues is global warming caused by greenhouse gases such as CO_2, while the effective and efficient utilization of CO_2 is also considerably important from the viewpoint of resource circulation aimed at carbon neutrality. In addition, the accumulation of plastics in the environment and living organisms is also a big problem to be solved. More environmentally benign and sustainable plastics should be created and used. The creation of CO_2-based polymers can contribute to finding the solution to these global issues. Among various CO_2-based polymers, aliphatic polycarbonates synthesized by the copolymerization of epoxides and CO_2 are fascinating from the viewpoint of high CO_2 contents and good chemical and physical properties, and biomass-based epoxides can also



Scheme 7 Terpolymerization reactions of epoxides, CO_2, and olefins.

be employed. Nevertheless, synthetic efficiencies and polymer functions are often insufficient for practical use. The incorporation of the third monomer may be effective for the improvement of the latter (polymer functions), although the former (synthetic efficiencies) may become more difficult to achieve. Here we provided an overview of the terpolymerization reactions of epoxides, CO_2, and the third monomers such as cyclic anhydrides, lactones, lactides, heteroallenes, and olefins. They present promising routes to new CO_2-based polymers with altered chemical and physical properties. Especially, we focused on the catalysts/cocatalysts, reaction conditions, and tunable polymer properties. The incorporation of various monomers not only improves the thermal and mechanical properties of the terpolymers but also adjusts the degradation rates. In addition, the precise control of polymer sequences enhances the ability to tailor the properties of materials for specific applications. Further studies and efforts are required for the further improvement of synthetic efficiencies and the exploration of new CO_2-based polymers. The terpolymerization reactions of epoxides, CO_2, and the third monomers will contribute significantly to the development of environmentally benign and sustainable polymers.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 Recent reviews: (*a*) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, *Chem. Rev.*, 2018, **118**, 434–504; (*b*) C. Hepburn, E. Adlen, J. Beddington, E. A. Carter, S. Fuss, N. M. Dowell, J. C. Minx, P. Smith and C. K. Williams, *Nature*, 2019, **575**, 87–97; (*c*) C. Kim, C.-J. Yoo, H.-S. Oh, B. K. Min and U. Lee, *J. CO2 Util.*, 2022, **65**, 102239; (*d*) P. Challa, G. Paleti, V. R. Madduluri, S. B. Gadamani, R. Pothu, D. R. Burri, R. Boddula, V. Perugopu and S. R. R. Kamaraju, *Catal. Surv. Asia*, 2022, **26**, 80–91; (*e*) L.-Q. Qiu, X. Yao, Y.-K. Zhang, H.-R. Li and L.-N. He, *J. Org. Chem.*, 2023, **88**, 4942–4964.

2 Reviews: (*a*) M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163; (*b*) S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479; (*c*) X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462–1484; (*d*) M. Taherimehr and P. P. Pescarmona, *J. Appl. Polym. Sci.*, 2014, **131**, 41141; (*e*) D. J. Darensbourg and A. D. Yeung, *Polym. Chem.*, 2014, **5**, 3949–3962; (*f*) G. Trott, P. K. Saini and C. K. Williams, *Phil. Trans. R. Soc., A*, 2016, **374**, 20150085; (*g*) S. J. Poland and D. J. Darensbourg, *Green Chem.*, 2017, **19**, 4990–5011; (*h*) Y. Wang and D. J. Darensbourg, *Coord. Chem. Rev.*, 2018, **372**, 85–100; (*i*) C. M. Kozak, K. Ambrose and T. S. Anderson, *Coord. Chem. Rev.*, 2018, **376**, 565–587; (*j*) M. Scharfenberg, J. Hilf and H. Frey, *Adv. Funct. Mater.*, 2018, **28**, 1704302; (*k*) D. J. Darensbourg, *Green Chem.*, 2019, **21**, 2214–2223; (*l*) A. J. Kamphuis, F. Picchioni and P. P. Pescarmona, *Green Chem.*, 2019, **21**, 406–448; (*m*) V. Paradiso, V. Capaccio, D. H. Lamparelli and C. Capacchione, *Catalysts*, 2020, **10**, 825; (*n*) J. Huang, J. C. Worch, A. P. Dove and O. Coulembier, *ChemSusChem*, 2020, **13**, 469–487; (*o*) G. A. Bhat and D. J. Darensbourg, *Green Chem.*, 2022, **24**, 5007–5034; (*p*) C. A. L. Lidston, S. M. Severson, B. A. Abel and G. W. Coates, *ACS Catal.*, 2022, **12**, 11037–11070; (*q*) F. Siragusa, C. Detrembleur and B. Grignard, *Polym. Chem.*, 2023, **14**, 1164–1183; (*r*) G. A. Bhat and D. J. Darensbourg, *Coord. Chem. Rev.*, 2023, **492**, 215277.

3 Selected examples: (*a*) S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287–292; (*b*) D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, *J. Am. Chem. Soc.*, 2016, **138**, 11117–11120; (*c*) M. Reiter, S. Vagin, A. Kronast, C. Jandl and B. Rieger, *Chem. Sci.*, 2017, **8**, 1876–1882; (*d*) Z. Huang, Y. Wang, N. Zhang, L. Zhang and D. J. Darensbourg, *Macromolecules*, 2018, **51**, 9122–9130; (*e*) H. Nagae, R. Aoki, S. Akutagawa, J. Kleemann, R. Tagawa, T. Schindler, G. Choi, T. P. Spaniol, H. Tsurugi, J. Okuda and K. Mashima, *Angew. Chem., Int. Ed.*, 2018, **57**, 2492–2496; (*f*) R. Duan, C. Hu, Z. Sun, H. Zhang, X. Pang and X. Chen, *Green Chem.*, 2019, **21**, 4723–4731; (*g*) N. G. Patil, S. K. Boopathi, P. Alagi, N. Hadjichristidis, Y. Gnanou and X. Feng, *Macromolecules*, 2019, **52**, 2431–2438; (*h*) H. Asaba, T. Iwasaki, M. Hatazawa, J. Deng, H. Nagae, K. Mashima and K. Nozaki, *Inorg. Chem.*, 2020, **59**, 7928–7933; (*i*) W. Lindeboom, D. A. X. Fraser, C. B. Durr and C. K. Williams, *Chem. Eur. J.*, 2021, **27**, 12224–12231; (*j*) R. Zhang, Q. Kuang, H. Cao, S. Liu, X. Chen, X. Wang and F. Wang, *CCS Chem.*, 2022, **5**, 750–760; (*k*) G.-W. Yang, C.-K. Xu, R. Xie, Y.-Y. Zhang, C. Lu, H. Qi, L. Yang, Y. Wang and G.-P. Wu, *Nat. Synth.*, 2022, **1**, 892–901; (*l*) Y.-N. Li, H.-H. Yang and X.-B. Lu, *J. Polym. Sci.*, 2022, **60**, 2078–2085; (*m*) H. Nagae, S. Matsushiro, J. Okuda and K. Mashima, *Chem. Sci.*, 2023, **14**, 8262–8268.

4 Reviews on terpolymerizations: (*a*) J. Liang, S. Ye, S. Wang, M. Xiao and Y. Meng, *Polym. J.*, 2021, **53**, 3–27; (*b*) D. H. Lamparelli and C. Capacchione, *Catalysts*, 2021, **11**, 961.

5 (*a*) Y. Liu, K. Huang, D. Peng and H. Wu, *Polymer*, 2006, **47**, 8453–8461; (*b*) R. C. Jeske, J. M. Rowley and G. W. Coates, *Angew. Chem., Int. Ed.*, 2008, **47**, 6041–6044; (*c*) P. F. Song, M. Xiao, F. G. Du, S. J. Wang, L. Q. Gan, G. Q. Liu and Y. Z. Meng, *J. Appl. Polym. Sci.*, 2008, **109**, 4121–4129; (*d*) X.-K. Sun, X.-H. Zhang, S. Chen, B.-Y. Du, Q. Wang, Z.-Q. Fan and G.-R. Qi, *Polymer*, 2010, **51**, 5719–5725; (*e*) S. Huijser, E. H. Nejad, R. Sablong, C. de Jong, C. E. Koning and R. Duchateau, *Macromolecules*, 2011, **44**, 1132–1139; (*f*) D. J. Darensbourg, R. R. Poland and C. Escobedo, *Macromolecules*, 2012, **45**, 2242–2248; (*g*) A. Bernard, C. Chatterjee and M. H. Chisholm, *Polymer*, 2013, **54**, 2639–2646; (*h*) Y. Liu, M. Xiao, S. Wang, L. Xia, D. Hang, G. Cui and Y. Meng, *RSC Adv.*, 2014, **4**, 9503–9508; (*i*) Z. Duan, X. Wang, Q. Gao, L. Zhang, B. Liu and I. Kim, *J. Polym. Sci.*, 2014, **52**, 789–795; (*j*) J. Y. Jeon, S. C. Eo, J. K. Varghese and B. Y. Lee, *Beilstein J. Org. Chem.*, 2014, **10**, 1787–1795; (*k*) Y. Liu, K. Deng, S. Wang, M. Xiao, D. Han and Y. Meng, *Polym. Chem.*, 2015, **6**, 2076–2083; (*l*) A. Thevenon, J. A. Garden, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2015, **54**, 11906–11915; (*m*) C. Romain, Y. Zhu, P. Dingwall, S. Paul, H. S. Rzepa, A. Buchard and C. K. Williams, *J. Am. Chem. Soc.*, 2016, **138**, 4120–4131; (*n*) P. K. Saini, G. Fiorani, R. T. Mathers and C. K. Williams, *Chem. Eur. J.*, 2017, **23**, 4260–4265; (*o*) Y. Liu, J.-Z. Guo, H.-W. Lu, H.-B. Wang and X.-B. Lu, *Macromolecules*, 2018, **51**, 771–778; (*p*) S. Ye, W. Wang, J. Liang, S. Wang, M. Xiao and Y. Meng, *ACS Sustainable Chem. Eng.*, 2020, **8**, 17860–17867; (*q*) G. Rosetto, A. C. Deacy and C. K. Williams, *Chem. Sci.*, 2021, **12**, 12315–12325; (*r*) A. J. Plajer and C. K. Williams, *Angew. Chem., Int. Ed.*, 2021, **60**, 13372–13379; (*s*) J. Liang, S. Ye, W. Wang, C. Fan, S. Wang, D. Han, W. Liu, Y. Cui, L. Hao, M. Xiao and Y. Meng, *J. CO2 Util.*, 2021, **49**, 101558; (*t*) J. Zhang, L. Wang, S. Liu, X. Kang and Z. Li, *Macromolecules*, 2021, **54**, 763–772; (*u*) V. K. Chidara, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, *Macromolecules*, 2021, **54**, 2711–2719; (*v*) S. Ye, Y. Ren, J. Liang, S. Wang, S. Huang, D. Han, Z. Huang, W. Liu, M. Xiao and Y. Meng, *J. CO2 Util.*, 2022, **65**, 102223; (*w*) G.-H. He, B.-H. Ren, S. Wang, Y. Liu and X.-B. Lu, *Angew. Chem., Int. Ed.*, 2023, **62**, e202304943; (*x*) Y. Ma, X. You, J. Zhang, X. Wang, X. Kou, S. Liu, R. Zhong and Z. Li, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303315; (*y*) M. R. Stühler, C. Gallizioli, S. M. Rupf and A. J. Plajer, *Polym. Chem.*, 2023, **14**, 4848–4855; (*z*) F. Niknam, A. Denk, A. Buonerba, B. Rieger, A. Grassi and C. Capacchione, *Catal. Sci. Technol.*, 2023, **13**, 4684–4692; (*aa*) C. W. Vos, J. Beament

and C. M. Kozak, *Polym. Chem.*, 2023, **14**, 5083–5093; (*ab*) M. Zhao, S. Zhu, G. Zhang, Y. Wang, Y. Liao, J. Xu, X. Zhou and X. Xie, *Macromolecules*, 2023, **56**, 2379–2387; (*ac*) R. Xie, Y. Wang, S. Li, B. Li, J. Xu, J. Liu, Y. He, G.-W. Yang and G.-P. Wu, *Angew. Chem., Int. Ed.*, 2024, **63**, e202404207.

6 (*a*) Y. Hwang, J. Jung, M. Ree and H. Kim, *Macromolecules*, 2003, **36**, 8210–8212; (*b*) Y. Hwang, H. Kim and M. Ree, *Macromol. Symp.*, 2005, **224**, 227–237; (*c*) S. Liu, H. Xiao, K. Huang, L. Lu and Q. Huang, *Polym. Bull.*, 2006, **56**, 53–62; (*d*) C. Romain and C. K. Williams, *Angew. Chem., Int. Ed.*, 2014, **53**, 1607–1610; (*e*) S. Paul, C. Romain, J. Shaw and C. K. Williams, *Macromolecules*, 2015, **48**, 6047–6056; (*f*) Y. Xu, S. Wang, L. Lin, M. Xiao and Y. Meng, *Polym. Chem.*, 2015, **6**, 1533–1540; (*g*) Y. Li, J. Hong, R. Wei, Y. Zhang, Z. Tong, X. Zhang, B. Du, J. Xu and Z. Fan, *Chem. Sci.*, 2015, **6**, 1530–1536; (*h*) C. Romain, Y. Zhu, P. Dingwall, S. Paul, H. S. Rzepa, A. Buchard and C. K. Williams, *J. Am. Chem. Soc.*, 2016, **138**, 4120–4131; (*i*) S. Kernbichl, M. Reiter, F. Adams, S. Vagin and B. Rieger, *J. Am. Chem. Soc.*, 2017, **139**, 6787–6790; (*j*) S. Kernbichl, M. Reiter, J. Mock and B. Rieger, *Macromolecules*, 2019, **52**, 8476–8483; (*k*) G. S. Sulley, G. L. Gregory, T. T. D. Chen, L. P. Carrodeguas, G. Trott, A. Santmarti, K.-Y. Lee, N. J. Terrill and C. K. Williams, *J. Am. Chem. Soc.*, 2020, **142**, 4367–4378; (*l*) Z. Yang, C. Hu, F. Cui, X. Pang, Y. Huang, Y. Zhou and X. Chen, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117533; (*m*) Y. Zhou, Z. Gao, C. Hu, S. Meng, R. Duan, Z. Sun and X. Pang, *Macromolecules*, 2022, **55**, 9951–9959.

7 (*a*) M. Kröger, C. Folli, O. Walter and M. Döring, *Adv. Synth. Catal.*, 2006, **348**, 1908–1918; (*b*) S. Liu, J. Wang, K. Huang, Y. Liu and W. Wu, *Polym. Bull.*, 2011, **66**, 327–340; (*c*) L. Gu, Y. Qin, Y. Gao, X. Wang and F. Wang, *Chin. J. Chem.*, 2012, **30**, 2121–2125; (*d*) Z. N. Nysenko, E. E. Said-Galiev, M. I. Buzin, Y. E. Belevtsev, M. M. Ilin, G. G. Nikiforova and A. M. Sakharov, *Mendeleev Commun.*, 2014, **24**, 236–238; (*e*) L. Tang, W. Luo, M. Xiao, S. Wang and Y. Meng, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1734–1741; (*f*) D. Xie, Z. Yang, L. Wu, C. Zhang and M. H. Chisholm, *Polym. Int.*, 2018, **67**, 883–893; (*g*) C. Hu, R. Duan, S. Yang, X. Pang and X. Chen, *Macromolecules*, 2018, **51**, 4699–4704; (*h*) X. Li, C. Hu, X. Pang, R. Duan and X. Chen, *Catal. Sci. Technol.*, 2018, **8**, 6452–6457; (*i*) R. Duan, C. Hu, Z. Sun, H. Zhang, X. Pang and X. Chen, *Green Chem.*, 2019, **21**, 4723–4731; (*j*) N. Liu, C. Gu, M. Chen, J. Zhang, W. Yang, A. Zhan, K. Zhang, Q. Lin and L. Zhu, *ChemistrySelect*, 2020, **5**, 2388–2394; (*k*) Y. Chen, W. Wang, D. Xie, L. Wu and C. Zhang, *J. Polym. Sci.*, 2021, **59**, 1528–1539; (*l*) X. Li, R.-L. Duan, C.-Y. Hu, X. Pang and M.-X. Deng, *Polym. Chem.*, 2021, **12**, 1700–1706; (*m*) X. Li, C.-Y. Hu, R.-L. Duan, Z.-Z. Liang, X. Pang and M.-X. Deng, *Polym. Chem.*, 2021, **12**, 3124–3131; (*n*) Y. Huang, C. Hu, X. Pang, Y. Zhou, R. Duan, Z. Sun and X. Chen, *Angew. Chem., Int. Ed.*, 2022, **61**, e202202660; (*o*) M. Martínez de Sarasa Buchaca, F. de la Cruz-Martínez, L. F. Sánchez-Barba, J. Tejeda, A. M. Rodríguez, J. A. Castro-Osma and A. Lara-Sánchez, *Dalton Trans.*, 2023, **52**, 3482–3492; (*p*) Y. Li, X. Kou, X. Wang, L. Xia and Z. Li, *Polym. Chem.*, 2024, **15**, 2476–2481.

8 Z. Li, R. J. Mayer, A. R. Ofial and H. Mayr, *J. Am. Chem. Soc.*, 2020, **142**, 8383–8402.

9 (*a*) Y. Zhi, Y. Miao, W. Zhao, J. Wang, Y. Zheng, H. Su, Q. Jia and S. Shan, *Polymer*, 2019, **165**, 11–18; (*b*) T.-J. Yue, B.-H. Ren, W.-J. Zhang, X.-B. Lu, W.-M. Ren and D. J. Darensbourg, *Angew. Chem., Int. Ed.*, 2021, **60**, 4315–4321; (*c*) J. Stephan, M. R. Stühler, S. M. Rupf, S. Neale and A. J. Plajer, *Cell Rep. Phys. Sci.*, 2023, **4**, 101510; (*d*) K. Nakaoka, S. Muranaka, I. Yamamoto and T. Ema, *Polym. Chem.*, 2024, **15**, 707–713.

10 (*a*) Y. Wang, Y. Zhao, Y. Ye, H. Peng, X. Zhou, X. Xie, X. Wang and F. Wang, *Angew. Chem., Int. Ed.*, 2018, **57**, 3593–3597; (*b*) X.-Y. Fu, T.-J. Yue, B.-H. Ren, H. Wang, W.-M. Ren and X.-B. Lu, *Angew. Chem., Int. Ed.*, 2024, **63**, e202401926.

11 (*a*) Y.-Y. Zhang, G.-P. Wu and D. J. Darensbourg, *Trends Chem.*, 2020, **2**, 750–763; (*b*) A. C. Deacy, G. L. Gregory, G. S. Sulley, T. T. D. Chen and C. K. Williams, *J. Am. Chem. Soc.*, 2021, **143**, 10021–10040.

12 Selected examples: (*a*) D. J. Darensbourg and Y. Wang, *Polym. Chem.*, 2015, **6**, 1768–1776; (*b*) F. W. Shaarani and J. J. Bou, *Sci. Total Environ.*, 2017, **598**, 931–936; (*c*) W. Mo, C. Zhuo, H. Cao, S. Liu, X. Wang and F. Wang, *Macromol. Chem. Phys.*, 2022, **223**, 2100403; (*d*) M. Sengoden, G. A. Bhat and D. J. Darensbourg, *Macromolecules*, 2023, **56**, 2362–2369; (*e*) S. Tang, H. Suo, R. Qu, H. Tang, M. Sun and Y. Qin, *Polymers*, 2023, **15**, 748; (*f*) W. Mo, C. Zhuo, S. Liu, X. Wang and F. Wang, *Polym. Chem.*, 2023, **14**, 152–160.

13 Selected examples: (*a*) Z. N. Nysenko, E. E. Said-Galiev, G. G. Nikiforova, M. I. Buzin, A. A. Glazkov, M. M. Ilin, G. A. Belyaev, V. V. Rusak and A. M. Sakharov, *Russ. Chem. Bull.*, 2022, **71**, 1770–1776; (*b*) Z. Gao, B. Gao, S. Meng, Z. Yang, Z. Liang, Z. Sun, Y. Zhou and X. Pang, *Macromolecules*, 2023, **56**, 2062–2069.

14 (*a*) J. Deng, M. Ratanasak, Y. Sako, H. Tokuda, C. Maeda, J. Hasegawa, K. Nozaki and T. Ema, *Chem. Sci.*, 2020, **11**, 5669–5675; (*b*) C. Maeda, H. Inoue, A. Ichiki, T. Okihara and T. Ema, *ACS Catal.*, 2022, **12**, 13042–13049; (*c*) C. Maeda, K. Kawabata, K. Niki, Y. Sako, T. Okihara and T. Ema, *Polym. Chem.*, 2023, **14**, 4338–4343.

15 T. Ema, *Bull. Chem. Soc. Jpn.*, 2023, **96**, 693–701.

16 Selected examples: (*a*) Y.-Y. Zhang, G.-W. Yang and G.-P. Wu, *Macromolecules*, 2018, **51**, 3640–3646; (*b*) H.-J. Zhou, G.-W. Yang, Y.-Y. Zhang, Z.-K. Xu and G.-P. Wu, *ACS Nano*, 2018, **12**, 11471–11480; (*c*) Y. Zhao, Y. Wang, X. Zhou, Z. Xue, X. Wang, X. Xie and R. Poli, *Angew. Chem., Int. Ed.*, 2019, **58**, 14311–14318.