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Terpolymerizations of cyclohexene oxide, CO_2, and isocyanates or isothiocyanates for the synthesis of poly(carbonate–urethane)s or poly(carbonate–thioimidocarbonate)s†

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Terpolymerization of cyclohexene oxide (CHO), CO_2, and aryl isothiocyanates produced poly(carbonate–thioimidocarbonate)s with gradient character, while that of CHO, CO_2, and aryl isocyanates furnished poly(carbonate–urethane)s with random sequences. The former underwent partial degradation upon acid treatment or UV irradiation, while the latter was stable under the same conditions.

Introduction

The ring-opening copolymerization (ROCOP) of epoxides and carbon dioxide (CO_2) for the synthesis of aliphatic polycarbonates is a green and sustainable synthetic technology with 100% atom economy, and it has been intensively studied.[1–3] On the other hand, the terpolymerization of epoxides, CO_2, and comonomers, such as lactones,[4] lactides,[5] cyclic acid anhydrides,[6] and heteroallenes,[7,8] is an effective strategy for the development of new CO_2-based polymers (Scheme 1a). The thermal, optical, mechanical, or degradation properties can be added or tuned by incorporating new polymer backbones derived from the comonomers at the expense of the CO_2 content. The scope of comonomers and the tunability of the physical properties are important factors in the terpolymerizations. Heteroallenes used as comonomers have been limited to SO_2 and COS,[7,8] which are gases to be carefully used, while isocyanates or isothiocyanates have never been used to prepare CO_2-based polymers despite the commercial availability, good reactivity, and tunability with substituents.[9] The terpolymerizations of epoxides, CO_2, and isocyanates or isothiocyanates may open up a new way for the development of novel CO_2-based polymers.

In 2020, two groups independently achieved the first epoxide/isocyanate ROCOP (without CO_2) to obtain new polyurethanes (PUs) with tertiary carbamate linkages,[10*a*,*b*] which are almost inaccessible *via* the conventional synthetic method with diisocyanates and diols. There are only several reports on this type of ROCOP partly because of the difficulty in using highly reactive isocyanates,[10] which readily trimerize into isocyanurates.[11] On the other hand, the epoxide/isothiocyanate ROCOP for the synthesis of poly(thioimidocarbonate)s (PTICs) was reported by three groups independently in 2021, and strong bases were used to activate isothiocyanates with poor reactivity as compared with isocyanates.[12] These pioneering works suggest that the terpolymerizations of epoxides, CO_2, and isocyanates or isothiocyanates might be difficult to achieve especially with a single catalyst because the ideal reaction conditions for the epoxide/CO_2 ROCOPs are quite different from those for the epoxide/iso(thio)cyanate ROCOPs.

Previously, bifunctional Mg^{II} or Zn^{II} porphyrin catalysts showed high activity for the synthesis of cyclic carbonates from epoxides and CO_2,[13] while bifunctional Al^{III} porphyrin catalysts **1** promoted the ROCOP of epoxides and CO_2 efficiently to produce polycarbonates (Scheme 1b).[14,15] The cooperative actions of the metal center and the quaternary ammonium halides led to the high activity and selectivity in both cases.[16] More recently, we have also succeeded in the selective conversions of oxetanes and CO_2 into trimethylene carbonates or poly(trimethylene carbonate)s with **1d**.[17] We envisioned that isocyanates or isothiocyanates could be used as comonomers in our catalytic system. Here we report the terpolymerizations of epoxide, CO_2, and isocyanates or isothiocyanates for the first time (Scheme 1c). The terpolymerization of cyclohexene oxide (CHO), CO_2 (2 MPa), and aryl isothiocyanates produced poly(carbonate–thioimidocarbonate)s with gradient character, while that of CHO, CO_2 (1 atm), and aryl isocyanates afforded poly(carbonate–urethane)s with random sequences. The former underwent partial degradation upon acid treatment or UV irradiation to give polycarbonates, while the latter was stable under the same conditions.

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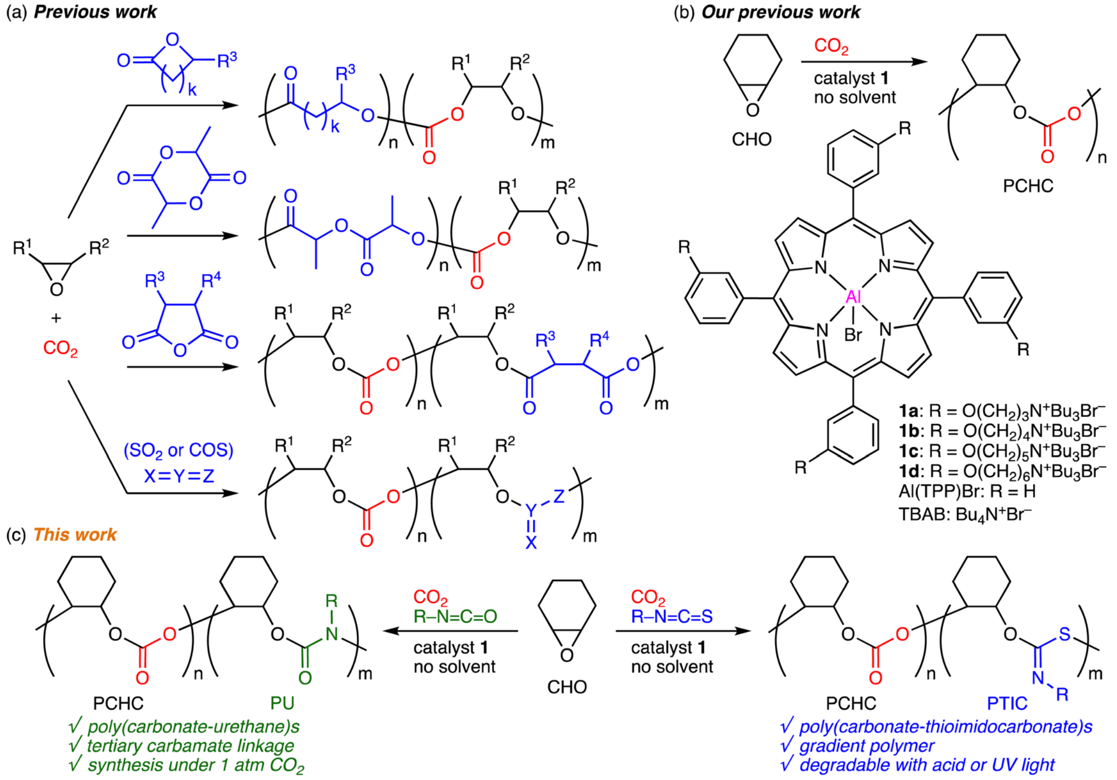
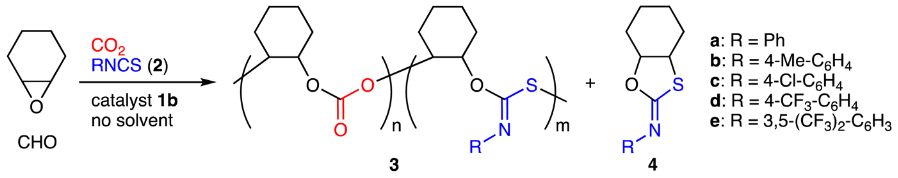


Scheme 1 (a) Previous work on terpolymerization of epoxides, CO_2, and comonomers. (b) Our previous work. (c) This work.

Results and discussion

We investigated the terpolymerization of CHO, CO_2 (2 MPa), and phenyl isothiocyanate (**2a**) with **1b**, which showed the highest activity for the ROCOP of CHO and CO_2.[15] As a result, terpolymer **3a** containing the poly(cyclohexene carbonate) (PCHC) and PTIC units were successfully obtained at 90 °C (Table 1, entry 1). **3a** was isolated by reprecipitation (chloro-

Table 1 Terpolymerization of CHO, CO_2, and **2** with **1b**[a]



			Conv.[c] (%)			3			4
Entry	2	S/C[b]	CHO	2	TON[c]	n : m[d]	M_n[e] (kg mol^{-1})	PDI[e]	Yield[c] (%)
1	**2a**	6250	94	75	5400	4 : 1	83/34	1.1/1.1	6
2	**2a**	20 000	93	46	12 400	5 : 1	164/63	1.0/1.3	3
3[f]	**2a**	20 000	83	71	15 600	3 : 1	167/55	1.1/1.3	7
4[g]	**2a**	20 000	80	85	9000	2 : 1	85/22	1.1/1.4	10
5	**2a**	40 000	87	30	31 600	8 : 1	183/57	1.1/1.5	3
6	**2b**	40 000	89	39	29 600	9 : 1	121/41	1.1/1.4	0
7	**2c**	40 000	90	71	27 600	3 : 1	74/25	1.1/1.3	0
8	**2d**	40 000	91	77	23 500	4 : 1	132/45	1.1/1.4	0
9	**2e**	40 000	80	>99	33 100	2 : 1	164/59	1.1/1.2	0

[a] Reaction conditions: CHO (12.5 mmol), **2** (3.1 mmol), **1b** (quantity indicated above), CO_2 (2.0 MPa), 90 °C, 24 h, in an autoclave. [b] Ratio of CHO to **1b**. [c] Determined by ^1H NMR analysis of the crude reaction mixture. TON for the formation of **3**. The yields of **4** were calculated based on **2**. [d] Determined by ^1H NMR analysis of the purified polymer. [e] Determined by SEC analysis of the purified polymer using THF as an eluent and polystyrene as a molecular-weight standard. Peaks had bimodal shapes. [f] CO_2 (1.0 MPa). [g] CO_2 (0.5 MPa).

form/methanol) and characterized by ^{1}H NMR spectroscopy; the broad signals for the methine groups of the PCHC units appeared at 4.6 ppm, and those for the PTIC units were observed at 6.6–7.4 ppm (Fig. S6a, ESI†). Size-exclusion chromatography (SEC) indicated that **3a** had high molecular weights with a bimodal distribution (Fig. S6c, ESI†). Bimodal molecular weight distributions are often observed for copolymerizations of epoxides and CO_2, and higher-molecular-weight polymers are twice as large as lower-molecular-weight polymers.[14] In the present terpolymerization, interestingly, the former was more than twice as large as the latter. The IR spectrum showed two strong absorptions at 1624 and 1759 cm^{-1} corresponding to the C=N and C=O stretching vibrations, respectively (Fig. S6d, ESI†). The MALDI-TOF mass spectrum of **3a** showed two *m*/*z* intervals of 142 and 233 corresponding to the PCHC and PTIC units, respectively (Fig. S8, ESI†). The formation of terpolymers rather than blends was also confirmed by diffusion-ordered spectroscopy (DOSY) (Fig. S7, ESI†). Furthermore, we also synthesized a model compound to confirm the structure of **3a**, and the NMR and IR spectra showed good similarities between **3a** and the model compound (Fig. S13, ESI†).

The reaction conditions were optimized. Higher temperature promoted the formation of byproduct **4a**, while lower temperature resulted in a lower conversion of **2a**; 90 °C was optimal (Table S1, entries 1–3, ESI†). When the molar ratio of CHO to **2a** was set to 4 : 1, both the molecular weight of the polymer and the conversion of **2a** were high (entries 2, 4–6). When the amount of catalyst **1b** decreased from 0.016 to 0.0025 mol% (S/C = 40 000), turnover numbers (TONs) increased from 5400 to 31 600 to give high-molecular-weight polymers, and both the conversion of **2a** and the PTIC content (n : m) decreased (Table 1, entries 1, 2 and 5). Interestingly, lower CO_2 pressure led to a higher PTIC content (entries 2–4). These results suggest that although the formation of the PTIC units is slower than that of the PCHC units, the former becomes favorable as CO_2 is consumed. This trend is consistent with the electrophilicity parameters reported for heteroallenes; isothiocyanates are less electrophilic than CO_2.[18] The linker length of catalysts **1** had a significant effect on the catalytic activity, and **1b** exhibited the best result (Table S2, entries 1–4, ESI†). We consider that catalysts **1c** and **1d** have longer linkers that may hinder the polymer elongation owing to steric bulkiness, while catalyst **1a** has shorter linkers that cannot assist well the ring-opening of CHO and/or the insertion of CO_2 or **2a**. In sharp contrast, a binary catalytic system composed of Al(TPP)Br and tetrabutylammonium bromide (TBAB) showed little or no activity for the PTIC formation under otherwise the same conditions (entry 5), which clearly demonstrates the importance of cooperative catalysis with bifunctional catalyst **1b**.[13–17]

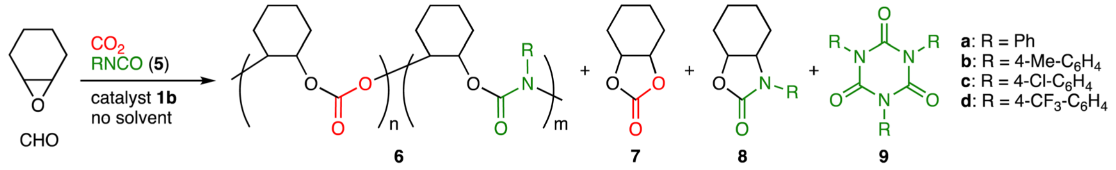
The scope of aryl isothiocyanates **2** was explored under the optimized conditions with **1b**. Isothiocyanate **2b** with the methyl group at the *para* position was modestly incorporated to form terpolymer **3b** (Table 1, entry 6). In contrast, isothiocyanates **2c–e** with electron-withdrawing groups showed much higher reactivity, and terpolymers **3c–e** with higher PTIC contents were successfully obtained (entries 7–9).

We next examined the reactivity of aryl isocyanates **5**. In view of the facile conversion of **5a** into isocyanurate **9a**, we employed a syringe-pump for the slow dropwise addition of **5a** *via* syringe under atmospheric CO_2 pressure (balloon), which allowed us to optimize the reaction conditions for the terpolymerization of CHO, CO_2, and **5a** (Table S3, ESI†). Terpolymer **6a** containing both the PCHC and PU units was obtained most efficiently with a catalyst loading of 0.016 mol% (S/C = 6250) (entries 1–3). The formation of byproduct **9a** was minimal at 90 °C, although the formation of cyclohexene carbonate (**7**) and 2-oxazolidone **8a** was suppressed at 80–100 °C (entries 2, 4 and 5). A faster dropwise addition of **5a** resulted in the formation of a significant amount of **9a** (entry 6). The use of 10 equiv. of CHO relative to **5a** was better than that of 5 or 15 equiv. of CHO (entries 2, 7 and 8). The linker length of **1** had a crucial effect on the catalytic activity; **1b** was the best catalyst (Table S4, entries 1–4, ESI†). In sharp contrast, a binary catalytic system composed of Al(TPP)Br and TBAB showed poor polymerization activity (entry 5), which demonstrates the advantage of bifunctional catalyst **1b**.

Pure terpolymer **6a** was obtained by reprecipitation (chloroform/methanol), and **6a** was characterized by ^{1}H NMR spectroscopy (Fig. S20a, ESI†). In addition to the broad signals at 4.6 ppm for the methine groups of the PCHC units, broad signals appeared at 6.9–7.5 ppm, which clearly indicates the incorporation of **5a**. The ^{13}C NMR spectrum showed the signals for the carbonyl groups of the PCHC and PU units at 153–154 ppm (Fig. S20b, ESI†). The IR spectrum showed two peaks for the C=O stretching vibrations of the PU and PCHC units at 1707 and 1749 cm^{-1}, respectively (Fig. S20d, ESI†). The structure of **6a** was also analyzed by MALDI-TOF mass spectroscopy (Fig. S22a, ESI†); *m*/*z* intervals of 142 and 217 corresponding to the PCHC and PU units, respectively, were observed. DOSY also supported the formation of **6a** (Fig. S21, ESI†). The analysis of hydrolysis products as well as the comparison of the NMR spectra between **6a** and a model compound also supported the existence of the PCHC and PU units (Fig. S26 and S27, ESI†). Because **6a** was prepared by the dropwise addition of **5a** and because no systematic changes were seen in the ratios between the PCHC and PU units of **6a** over the reaction time (data not shown), we consider that **6a** had random sequences.

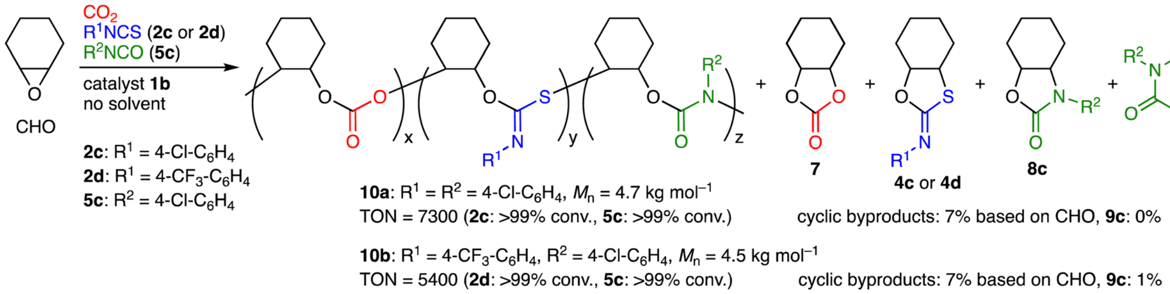
The scope of aryl isocyanates **5** was examined (Table 2). Isocyanate **5b** with the methyl group at the *para* position was incorporated into terpolymer **6b** accompanied with **9b**. 4-Chlorophenyl isocyanate (**5c**) was successfully used to make **6c**, while 4-(trifluoromethyl)phenyl isocyanate (**5d**) led to the formation of **6d** with a larger molecular weight; byproduct **8d** seems to result from the backbiting of the highly electrophilic carbonyl group of the PU unit by the adjacent terminal alkoxide ion. We also challenged the quaterpolymerizations of CHO, CO_2, **2c** or **2d**, and **5c** (Scheme 2 and Fig. S28–S33, ESI†). A mixture of **5c** and CHO was added dropwise with the syringe-pump to a mixture of CHO, **2c** or **2d**, and **1b** under

Table 2 Terpolymerization of CHO, CO_2, and **5** with **1b**[a]



Entry	5	Conv.[b] (%)		6				Byproduct[b] (%)		
		CHO	5	TON[b]	n : m[c]	M_n[d] (kg mol^{-1})	PDI[d]	7	8	9
1	**5a**	81	>99	3200	6 : 1	7.1	1.4	3	0	8
2	**5b**	85	>99	1900	2 : 1	4.2	1.4	1	0	29
3[e]	**5c**	79	>99	3100	3 : 1	7.4	1.5	3	0	2
4[e]	**5d**	80	>99	4200	9 : 1	14	1.3	4	8	12

[a] A mixture of CHO (1.2 mmol) and **5** (1.2 mmol) was added dropwise to a mixture of CHO (11.2 mmol) and **1b** (S/C = 6250 for CHO, 0.016 mol%) at 15 μL h^{-1} with a syringe-pump under CO_2 (1 atm, balloon) at 90 °C, and the mixture was then stirred at 90 °C for 2 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. TON for the formation of **6**. The yields of **7** were calculated based on CHO, and those of **8** and **9** were calculated based on **5**. [c] Determined by ^{1}H NMR analysis of the purified polymer. [d] Determined by SEC analysis of the purified polymer using THF as an eluent and polystyrene as a molecular-weight standard. [e] Addition at 24 μL h^{-1}.

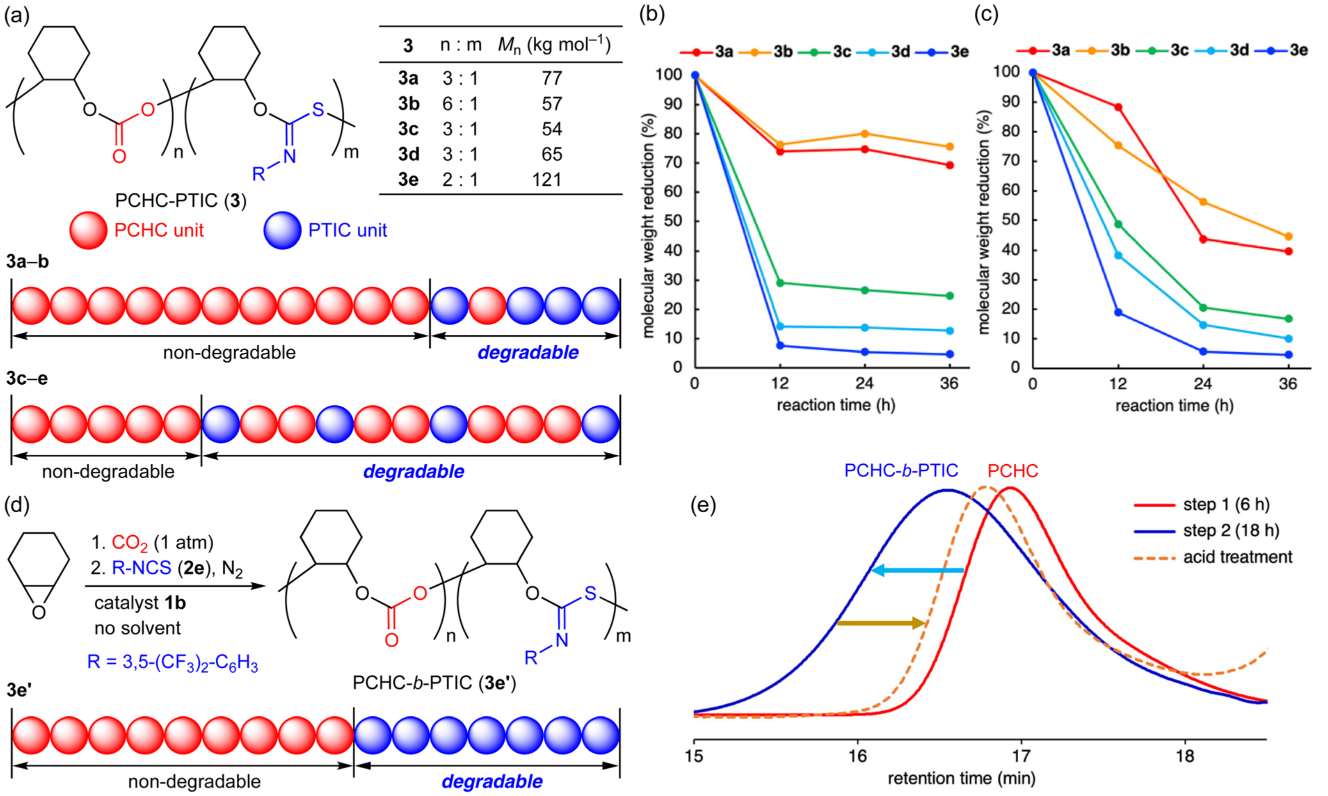


Scheme 2 Quaterpolymerizations of CHO, CO_2, **2c** or **2d**, and **5c**.

CO_2 (1 atm); as a result, quaterpolymers **10a** with a M_n of 4.7 kg mol^{-1} and **10b** with a M_n of 4.5 kg mol^{-1} were produced with the quantitative conversions of the comonomers (**2c**, **2d**, and **5c**). NMR, DOSY, IR, and mass spectra of the purified polymers indicated that the PCHC, PTIC, and PU units were contained in the polymer chains. When alkyl isocyanates were used instead of aryl isocyanates, the corresponding terpolymers **6** could not be obtained efficiently (data not shown). This is partly due to the rapid formation of the corresponding isocyanurates **9**.

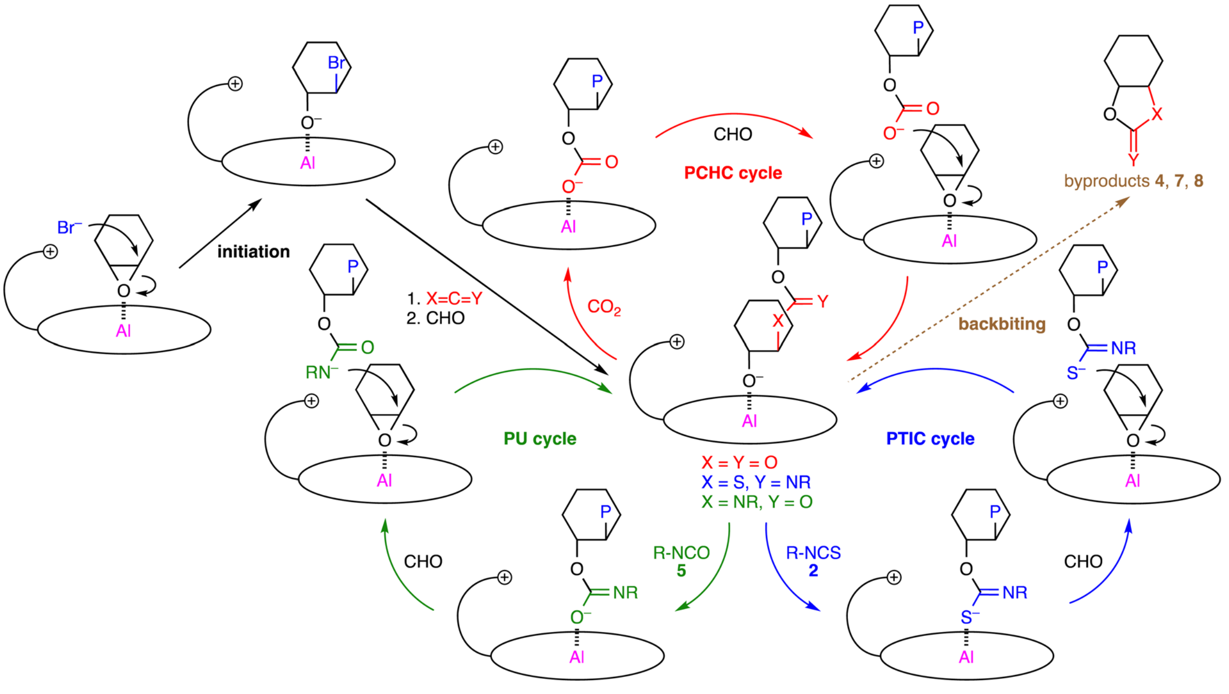
Recently, degradable polymers have attracted much attention from the viewpoint of the promotion of chemical recycling and the mitigation of plastic pollution.[19] Although sulfur-containing polymers are known to be susceptible to UV light or chemicals,[19a] there are no reports on the degradability of PTICs to our knowledge. We envisioned that terpolymers **3** containing the PTIC units might be degradable upon acid treatment or UV light irradiation. To our delight, **3** did undergo partial degradation by acid exposure or UV irradiation (Fig. 1a–c). Reprecipitation (chloroform/methanol) of the degradation mixtures and spectroscopic characterizations indicated that pure PCHCs were formed by the selective degradation of the PTIC linkages in both cases (Fig. S35 and S39, ESI†). Interestingly, Fig. 1b and c strongly suggests that terpolymers **3** have gradient character in composition (ratio of the PTIC to PCHC units);[20] **3c–e** with electron-withdrawing groups showed larger decrease in molecular weight upon acid treatment or UV light irradiation than **3a** and **3b**. Accordingly, kinetic studies indicated that **2d** was converted into the terpolymers faster than **2a** (Fig. S14, ESI†). For comparison, block copolymer PCHC-*b*-PTIC (**3e′**) was synthesized in a one-pot two-step manner, which was confirmed to exhibit the selective degradation of the PTIC moiety (Fig. 1d, e and S42–S44, ESI†), while copolymer PTIC that was synthesized from CHO and **2e** and purified in a similar manner was completely degraded (Fig. S49, ESI†). In sharp contrast, both PCHC and terpolymer **6a** showed little or no degradability under the same conditions, which indicates that the PCHC and PU linkages are more robust (Fig. S37 and S41, ESI†).

Plausible catalytic cycles for the **1b**-catalyzed polymerizations of CHO, CO_2, and isothiocyanates/isocyanates are shown in Scheme 3. The nucleophilic attack of the counter anion on CHO activated by the Al center of **1b** makes a new PCHC/PTIC/PU linkage, generating the alkoxide intermediate



3	n : m	M_n (kg mol^{-1})
3a	3 : 1	77
3b	6 : 1	57
3c	3 : 1	54
3d	3 : 1	65
3e	2 : 1	121

Fig. 1 (a) Illustration of gradient character of **3**. The molecular weights of **3** are average values for two peaks in SEC charts. Degradation of **3** upon (b) acid treatment and (c) UV irradiation. (d) One-pot two-step synthesis of block copolymer **3e'**. (e) Synthesis and partial degradation of **3e'** monitored by SEC.



Scheme 3 Plausible catalytic cycles, where P simply represents a part of a polymer chain that may differ in each step.

shown in the center. The subsequent insertion of CO_2/isothiocyanate/isocyanate into the Al–O bond gives the carbonate/thioimidocarbonate/imidocarbonate anion, which then forms an ion pair with the quaternary ammonium ion of **1b** upon CHO coordination. The S and N atoms of the thioimidocarbonate and carbamate anions, respectively, are more nucleophilic because the negatively charged atom with less electronegativity is more labile, which is the key determinant for the selective formation of the PTIC or PU linkage. In the PTIC cycle, the reaction of the alkoxide anion with isothiocyanate **2** is considered to be the rate-determining step, judging from the substituent effect of **2** on the ratio of the PTIC to PCHC units (Table 1), degradation behaviors with gradient character (Fig. 1), and kinetic studies (Fig. S14, ESI†). In the PU cycle, the PU linkage formation may be the rate-determining step, although the situation is complicated owing to the side reactions such as the formation of **9**. Cyclic byproducts **7**, **4**, and **8** are formed by the backbiting of the terminal alkoxide ions just after the construction of the PCHC, PTIC, and PU linkages, respectively.

The molecular weights of terpolymers **6** and quaterpolymers **10** synthesized at 1 atm CO_2 pressure (Table 2 and Scheme 2) were much smaller than those of terpolymers **3** synthesized at 2.0 MPa CO_2 pressure (Table 1). In the synthesis of **6** and **10**, isocyanates **5** were added dropwise to minimize the formation of byproducts **9**. It is likely that **6** and **10** growing at 1 atm CO_2 pressure have the alkoxide anions at the ends, which may experience backbiting and protonation. In contrast, **3** growing at the high CO_2 pressure can undergo the rapid addition of CO_2 to the alkoxide anions to form the carbonate anions, which leads to the smooth ring-opening of CHO rather than backbiting or protonation. If **5** could be added dropwise at the high CO_2 pressure, **6** and **10** with higher molecular weights would be obtained.

Conclusions

We have achieved terpolymerizations of epoxide, CO_2, and isocyanates or isothiocyanates to synthesize new terpolymers for the first time. These terpolymerizations are fascinating because the reactions can proceed with 100% atom economy if no cyclic byproducts are formed. Herein, CHO was used as an epoxide because of the excellent physical properties of the resulting polycarbonates,[15] while aryl iso(thio)cyanates were used because of the controllable reactivities. The terpolymerization of CHO, CO_2, and isothiocyanates produced poly(carbonate–thioimidocarbonate)s showing degradability for acids and UV light. The ratio of the PTIC to PCHC units in the terpolymers could be controlled by the CO_2 pressure, and the terpolymers had gradient character in composition. A block copolymer, poly(carbonate-*b*-thioimidocarbonate), was also synthesized in a one-pot two-step manner. On the other hand, the terpolymerization of CHO, CO_2, and isocyanates yielded poly(carbonate–urethane)s; the slow addition of isocyanates under atmospheric CO_2 pressure suppressed the formation of cyclic byproducts and enabled the formation of terpolymers with random sequences. It should be noted that all the terpolymerizations were catalyzed by a single catalyst, bifunctional Al^{III} porphyrin **1b**, which demonstrates that cooperative catalysis with the metal center and the quaternary ammonium salts is effective for the conversions of the monomers with different reactivities into the terpolymers. The results reported here will be useful for the design and creation of environmentally benign polymers. Further studies on the application of the polymers and the creation of new CO_2-based polymers are currently underway in our group.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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