

Facile Synthesis of Polycarbonate Diol *via* Copolymerization of CO₂ and Cyclohexene Oxide Catalysed by a Combination of One-Component Phosphonium Borane Lewis Pair and Water

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 Electronic Supplementary Information

Abstract Well-defined polycarbonate diol was successfully synthesized through a strategy using a combination of organocatalyst and water. Such strategy was less developed in organocatalyzed polymerization and frequently regarded as side reactions. Herein, one-component phosphonium borane Lewis pairs **PB1**–**PB8** were successfully applied in the copolymerization of CO₂ and cyclohexene oxide (CHO) to generate poly(CHO-*alt*-CO₂) carbonate (PCHC). Parameters of linker length and counter anion effects on the catalyst activity were investigated. It was found that Lewis pair **PB3** served as a dual initiator and catalyst in the copolymerization of CHO and CO₂ with or without the presence of water. In contrast, Lewis pair **PB8** can serve as a true catalyst for the preparation of well-defined α,ω -hydroxyl PCHC diols. This was achieved by introducing a labile CF₃COO group as counter anion through anion exchange reaction while water molecules acted as chain transfer agents. The function of trifluoroacetate group in the polymerization process was investigated in detail and possible mechanism was proposed. Upon changing the amount of water and catalyst loading, PCHC diols with varied molecular weight (1.5 kg/mol to 7.5 kg/mol), low dispersities ($D < 1.2$) and carbonate content (>99%) could be easily obtained. The low molecular weight PCHC diol was used as a bifunctional macroinitiator for the ring-opening polymerization of L-lactide (LLA) to afford ABA triblock copolymer in one-pot synthesis.

Keywords Polycarbonate; Phosphonium borane Lewis pair; CO₂ utilization; Organocatalysis; Ring-opening polymerization

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INTRODUCTION

The sustainability and low carbon emission demand of current society have stimulated the usage of renewable sources to manufacture fine chemicals or products.^[1] With respect to the huge amounts of petroleum-based plastics, partial replacement of them with degradable polymers would offer the opportunity to reduce the burden of energy and environment. CO₂, a renewable C1 resource, is nontoxic and abundant in industrial plants. Therefore, utilization of CO₂ for the production of aliphatic polycarbonates as degradable materials could offer the opportunity to cater the sustainability of modern society.^[2]

An attractive approach to prepare aliphatic polycarbonates was the copolymerization of CO₂ with epoxides, which was pioneered by Inoue *et al.* in 1969.^[3] Delicate work of co-

polymerization of CO₂ with epoxides using both heterogeneous and homogeneous metal complexes was contributed by Prof. Wang and coworkers.^[4–8] Since then, a variety of homogeneous and heterogeneous metal-based catalysts had been reported to achieve copolymerization of CO₂ and epoxides.^[9–12] Homogeneous catalysts based on cobalt,^[13–15] zinc,^[16–18] chromium,^[19] magnesium^[20] and aluminium^[21,22] usually showed great catalytic behavior in the generation of aliphatic polycarbonates. In these cases, the generated aliphatic polycarbonates possessed moderate to high carbonate contents and varied dispersities. In terms of epoxides, propylene oxide (PO) and cyclohexene oxide (CHO) were the frequently investigated monomers due to the large production of PO and model reaction activity of CHO. Copolymerization of PO or CHO with CO₂ afforded poly(PO-*alt*-CO₂) (PPCs)^[23–29] or poly(CHO-*alt*-CO₂) (PCHCs),^[30–35] respectively. Generally, higher molecular weight aliphatic polycarbonates showed a higher glass transition temperature, reasonable tensile strength and better mechanical properties.^[36] Nevertheless, the development of low molecular weight aliphatic polycar-

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bonates, especially, telechelic aliphatic polycarbonate diols ($M_n < 10$ kg/mol) with well-defined structure and highly efficient catalysts was also highly attractive. They could serve as macromonomers for polyurethane/other copolymer production.^[20,37–39] Up to now, several highly active homogeneous meal-based catalysts had been reported for the preparation of low molecular weight polycarbonate diols.^[40–42] Although metal-based catalysts contributed a big progress in the preparation of low molecular weight polycarbonate diols, they faced several challenges, *e.g.*, tedious synthesis, high cost or metal residue issues, especially for low molecular weights diols requiring higher catalyst loading.

In recent years, organocatalysts became promising catalysts in the ring-opening polymerization (ROP) of cyclic monomers.^[43–45] In terms of copolymerization of CO₂ with epoxides, Feng *et al.* firstly reported BEt₃/onium halides binary system as organocatalyst to synthesize aliphatic polycarbonates.^[46] In dry CO₂ condition, BEt₃/onium chloride and BEt₃/tetrabutylammonium carbonate system can prepare high molecular weight and functional polycarbonates, respectively.^[47–51] Kerton *et al.* investigated different Lewis acidic triarylboranes used in such binary system to control the selectivity between cyclic carbonate/polycarbonate products.^[45] Zhang *et al.* reported tertiary amine/trialkyl borane worked as highly selective catalysts for the CO₂ and PO copolymerization *via* zwitterionic growth mechanism.^[52] Wu *et al.* developed a bifunctional organocatalyst that showed intramolecular cooperative catalysis and exhibited extremely high efficiency (TON up to 13000) towards copolymerization of CO₂ and CHO.^[53] Subsequently, the same group reported pinwheel-shaped tetranuclear organoboron catalysts realized the challenging copolymerization of epichlorohydrin with CO₂.^[54] The above-mentioned systems were not purely catalytic system because the polymerization process was initiated either by introduced nucleophilic anion or amine. Very recently, Li and coworkers reported copolymerization of various epoxides with CO₂ using phosphazene/BEt₃/initiator under atmospheric CO₂ pressure.^[55]

In brief, organo-catalyzed copolymerization of epoxides and CO₂ to generate polycarbonate is still in its early stage. The preparation of well-defined α,ω -hydroxyl polycarbonate telechelics using organo-catalysts is rather limited, especially in the case of less dried CO₂ condition. Up to now, there have been two pathways to afford α,ω -hydroxyl polycarbonate telechelics in a metal-free manner, *i.e.*, bifunctional initiator/BEt₃^[49,50] and phosphazene/diol/BEt₃ systems.^[55] Furthermore, BEt₃, frequently used in above mentioned systems, is highly sensitive to water and its hydrolysis leads to deactivation of the polymerization process. Therefore, development of moisture tolerant organo-catalysts will not only simplify the polymerization set-up, but also reduce the time and costs for the purification of epoxides and CO₂ frequently required in the copolymerization. Inspired by the success of bifunctional catalyst systems,^[53] we were interested in the design of one-component Lewis pairs and their synergistic and catalytic behavior in ROP. Previously, we reported that one-component phosphonium bisborane Lewis pair **PBB** behaved as a highly active and efficient ini-

tiator/catalyst for homopolymerization of PO. Moreover, **PBB** could afford well-defined α,ω -hydroxyl polyether in the presence of H₂O.^[56] These results prompted us to extend such concept for the copolymerization of CO₂ with CHO using one-component synergistic phosphorus borane Lewis pairs (**PB**). Preliminary investigation of the copolymerization of CO₂ and PO using **PB** resulted in the exclusive formation of cyclic carbonate. Herein, we explored the preparation poly(CHO-*alt*-CO₂) carbonate (PCHC) diols using **PB1–PB8** as catalysts.

EXPERIMENTAL

Materials

Diethyl ether, acetonitrile, methanol, dichloromethane, ethyl acetate, chloroform and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydride (NaH), calcium hydride (CaH₂), sodium acetate (CH₃COONa), sodium trifluoroacetate (CF₃COONa) and deuterated solvents were purchased from Macklin Co., Ltd. Cyclohexene oxide (CHO), 3-bromo-1-propene, 4-bromo-1-butene, 5-bromo-1-pentene, 6-bromo-1-hexene, 5-iodo-1-pentene, 9-borabicyclo[3.3.1]nonane (9-BBN) were purchased from Energy Chemical Co., Ltd. Tetrahydrofuran (THF), *n*-hexane were purchased as SuperDry solvent from Energy Chemical Co., Ltd. CO₂ were purchased from Qingdao Ludong Gas Company with 99.999% purity. Amberlite(R) IRA-400 (Cl) resin was purchased from Energy Chemical Co., Ltd. Detailed syntheses of Lewis pairs **PB1–PB6** were synthesized according to our previous report.^[57]

Synthesis of Phosphonium Borane Lewis Pair **PB7**

To a 10 mL Schlenk vessel, **PB3** (107 mg, 0.2 mmol, 1 equiv.) and sodium acetate (32.8 mg, 0.4 mmol, 2.0 equiv.) was charged in a glovebox. CH₂Cl₂ (4 mL) was added and the reaction mixture was stirred at r.t. for 48 h. After that, the reaction mixture was filtered and the filtrate was collected. Removal of the solvent under vacuum gave the product as white solid powder in 91% yield (93.0 mg, 0.18 mmol).

Synthesis of Phosphonium Borane Lewis Pair **PB8**

To a 10 mL Schlenk vessel, **PB3** (107 mg, 0.2 mmol, 1 equiv.) and sodium trifluoroacetate (54.4 mg, 0.4 mmol, 2.0 equiv.) was charged in a glovebox. CH₂Cl₂ was added and the reaction mixture was stirred at r.t. for 48 h. After that, the reaction mixture was filtered and the filtrate was collected. Removal of the solvent under vacuum gave the product as white solid powder in 93% yield (105 mg, 0.185 mmol).

Copolymerization of CHO and CO₂

Polymerization was performed in a 10 mL stainless steel micro autoclave (MS-10-316L, Anhui Kemi Machinery Technology Co., Ltd., Hefei, China) for each run. In a glovebox, CHO (0.51 mL, 5 mmol) and **PB3** (5.3 mg, 10 μ mol) were introduced into a 10 mL autoclave equipped with a magnetic stirrer before taken out of the glovebox. The sealed autoclave was charged with CO₂ to reach a pressure of 15×10^5 Pa and placed in an oil bath at a preset temperature. The polymerization reaction reacted for 12 h before quenched by adding a few drops of dilute HCl solution (1 mol/L ethanol solution) and 3 mL of CHCl₃ was added. Subsequently, an aliquot of the solution was sampled to for ¹H-NMR characterization. The resultant PCHC was precipitated in methanol and dried under vacuum at 40 °C overnight.

Synthesis of PLA-Poly(CHO-*alt*-CO₂)-PLA

Low molecular weight poly(CHO-*alt*-CO₂) ($M_n=3300$ g/mol) was synthesized in a molar ratio of CHO:H₂O:PB8=200:2:1. In a glovebox, CHO (1020 μ L, 5 mmol, 200 equiv.), H₂O (1.8 μ L, 0.1 mmol, 2 equiv.) and PB8 (28.3 mg, 50 μ mol, 1 equiv.) were introduced into a 10 mL autoclave equipped with a magnetic stirrer before being taken out of the glovebox. The sealed autoclave was charged with CO₂ to reach a pressure of 15×10^5 Pa and placed in an oil bath at 80 °C. The polymerization reaction reacted for 2 h. Afterwards, an aliquot of the solution was sampled to GPC and ¹H-NMR spectroscopy to determine the molecular weight of obtained PCHC diol and conversion, respectively. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (6 μ L, 0.04 mmol, 1 equiv.), L-lactide (273.6 mg, 1.9 mmol, 25 equiv. per OH group, 50 equiv. total) and 1 mL of CH₂Cl₂ were subsequently added to the above reaction mixture. The autoclave was sealed and the reaction mixture was allowed to react at r.t. for 1 h and subsequently recorded by ¹H-NMR spectroscopy. The reaction was terminated with 0.1 mol/L HCl (ethanol solution) and the polymer was precipitated by addition of hexane (25 mL). The polymer was filtered and dried under vacuum at 40 °C overnight.

RESULTS AND DISCUSSION

Synthesis of Lewis Pairs PB7 and PB8

Lewis pairs PB1–PB6 were synthesized by hydroboration of alkenyl phosphonium salts with 9-BBN in good yields (>90%).^[57] PB7 and PB8 having carboxylic counter-anion were obtained by anion exchange of PB3 with 2 equiv. of carboxylic salt in CH₂Cl₂ for 48 h in good yield (Fig. 1) and were characterized by NMR spectroscopy. Long reaction time was required due to the low solubility of carboxylic salt precursor. The acetic group of PB7 displayed typical signals at 1.95 ppm in ¹H-NMR spectrum (Fig. S34 in the electronic supplementary information, ESI). The ¹⁹F{¹H} NMR spectrum of PB8 in CDCl₃ displayed single resonance at –75.3 ppm, indicating existence of trifluoroacetate (Fig. S40 in ESI). It had been reported by Williams *et al.* that

trifluoroacetate coordinated bimetallic zinc complexes was a good catalyst to prepare PCHC diol in the presence of water.^[38] The good leaving and easy hydrolysis properties of trifluoroacetate group in the polymerization condition allowed the exclusive formation of PCHC diol. Therefore, we assume PB8 bearing trifluoroacetate anion would facilitate the preparation of exclusive PCHC diol.

Catalytic Behaviors of Lewis Pairs PB1–PB8

The catalytic performance of PB3 for the copolymerization of CHO and CO₂ was firstly evaluated. We studied the temperature effects on the catalytic behaviors of PB3 in the copolymerization of CHO and CO₂ (Table S1 in ESI). In all cases, the selectivity remained high for both PCHC (>99%) and carbonate linkages (>99%). Increasing the temperature from 60 °C to 80 °C led to an increase of conversion and M_n , while the molecular weight distributions were relatively narrow (Table S1, runs 1 and 2, in ESI). Further elevating temperature from 80 °C to 150 °C caused both decrease of conversion and M_n of PCHCs, while the \bar{D} values of obtained PCHCs increased (Table S1, runs 3–5, in ESI). Therefore, we chose 80 °C for subsequent investigations. The polymerization was performed with a molar ratio of [CHO]/[catalyst]=500/1 under 15×10^5 Pa CO₂ pressure, and the results were presented in Table 1.

Interestingly, all the Lewis pairs PB1–PB8 exhibited >99% polymer selectivity and >99% carbonate linkages for the resultant PCHCs, verified by ¹H-NMR characterization (Fig. S43–S50 in ESI). Although the GPC curves of produced PCHCs were bimodal, the \bar{D} values for the obtained PCHCs were relatively narrow. The molecular weight (M_n) determined by GPC was much lower than the theoretical values possibly due to the residual water molecules acting as chain transfer agents. The M_n^{GPC} of obtained PCHC was also lower than the M_n^{theo} under dried CO₂ condition (Table 1, run 7), which might be ascribed to the chain transfer to other impurities in the system.^[17]

To explain the bimodal characteristic of GPC curves and identify end-group fidelity of obtained PCHCs, low molecular weights of PCHCs were prepared (Table 1, runs 7 and 8). Spe-

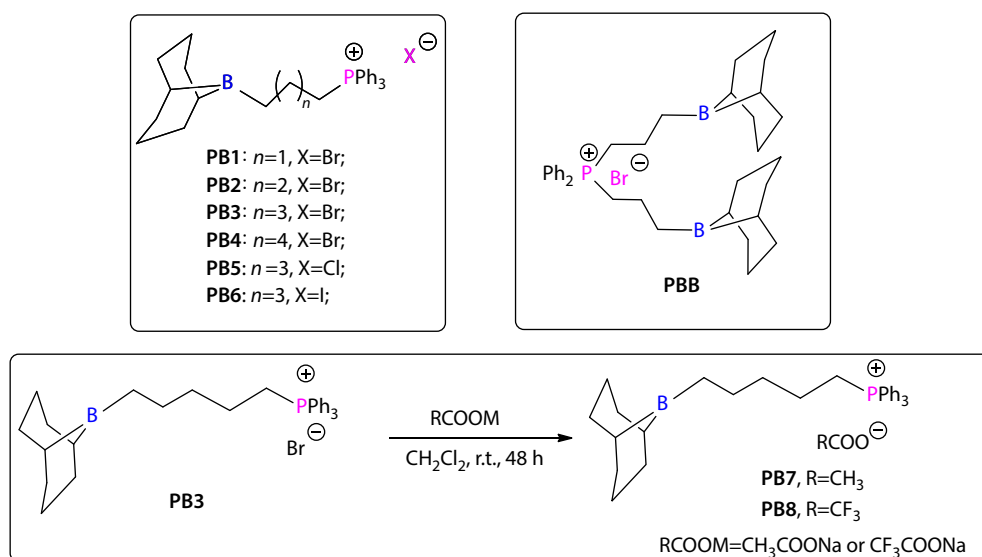


Fig. 1 Chemical structures of Lewis pairs PB1–PB6, PBB and preparation of Lewis pairs PB7 and PB8 via anion exchange.

Table 1 Copolymerization of CHO and CO₂ catalysed by Lewis pairs **PB1**–**PB8**.

Run ^a /PCHC	Catalyst	[CHO]/[Catalyst]	Time (h)	Conversion ^b (%)	TOF ^c (h ⁻¹)	$M_n^{\text{theo.}}$ ^d (kg/mol)	M_n^{GPC} ^e (kg/mol)	\bar{D} ^e
1/ PCHC-1	PB1	500	12	53	22.1	37.6	8.3	1.20
2/ PCHC-2	PB2	500	12	70	29.2	49.7	13.9	1.20
3/ PCHC-3	PB3	500	12	78	32.5	55.4	14.2	1.25
4/ PCHC-4	PB4	500	12	76	31.7	54.0	12.0	1.25
5/ PCHC-5	PB5	500	12	77	32.1	54.7	14.7	1.30
6/ PCHC-6	PB6	500	12	76	31.7	54.0	13.0	1.38
7 ^f / PCHC-7	PB3	200	1	53	106	15.1	6.3	1.17
8/ PCHC-8	PB3	500	2	35	87.5	24.9	4.5	1.18
9/ PCHC-9	PB3	500	4	67	83.8	47.6	12.0	1.15
10/ PCHC-10	PB7	200	1	55	110	15.6	4.2	1.18
11/ PCHC-11	PB7	500	4	70	87.5	49.7	15.6	1.23
12/ PCHC-12	PB8	200	1	57	114	16.7	7.5	1.19
13/ PCHC-13	PB8	500	4	69	86.3	49.0	15.3	1.22
14/ PCHC-14	PB8	1000	12	70	58	99.4	20.2	1.30
15/ PCHC-15	PB8	2000	12	53	88	150.6	18.7	1.19
16/ PCHC-16	PB8	5000	24	45	94	319.6	18.2	1.11
17/ PCHC-17	B2/BrPPh₄	500	12	38	15.8	27.0	6.8	3.93

^a All the polymerizations were performed in 10 mL autoclave under 15×10^5 Pa of commercial CO₂ at 80 °C unless otherwise mentioned. All obtained polymers exhibited > 99% PCHC/CHC selectivity; ^b Conversion is calculated by ¹H-NMR spectroscopy; ^c TOF = turnover frequency; ^d $M_n^{\text{theo.}} = 142.06 \times [\text{CHO}]_0/[\text{cat.}]_0 \times \text{conversion} + M_n(\text{end group})$; ^e Determined by GPC in THF with polystyrene standard; ^f CO₂ was dried with P₂O₅.

cifically, low molecular weights of PCHCs named **PCHC-7** and **PCHC-8** were obtained by **PB3** with or without CO₂ purification, respectively. **PCHC-7** was analyzed by the MALDI-ToF MS (Fig. 2a), in which only α -Br, ω -OH end capped PCHC was observed, thus indicating Br⁻ was the dominating initiation species under dried CO₂ atmosphere. Likewise, analysis of **PCHC-8** by the MALDI-ToF MS (Fig. 2b) revealed two polymer series: α -Br/ ω -OH groups capped PCHCs units (red square and blue square, major fraction) and α -OH/ ω -OH dihydroxy groups capped PCHCs units (black circle, minor fraction). These results clearly showed that both Br⁻ and water can initiate the copolymerization of CHO and CO₂. In this case, water can be regarded as chain transfer agents to produce dihydroxyl end-capped PCHC chains. The narrow dispersity of

both fractions indicated that the chain transfer is fast and reversible. Moreover, the end-group fidelity of PCHC strongly depended on the water to catalyst molar ratio *vide infra*.^[20]

MALDI-ToF MS revealed that both α -acetate/ ω -OH and α -OH/ ω -OH end groups were present in the obtained PCHC generated by **PB7** (Fig. S30 in ESI). The major fraction of produced PCHC featuring α -acetate/ ω -OH end group indicated acetate group dominated the initiation process. The presence of acetate group capped **PCHC-7** was proved by ¹H-NMR spectroscopy, which showed resonance signal at 4.10 ppm ascribed to the methine proton (H_d) attached to acetate group. The methine proton (H_a) on the terminal cyclohexyl ring attached with -OH group showed resonance at 3.58 ppm (Fig. S53 in ESI).^[20,58] In contrast, α -trifluoroacetate end group was not observed for the PCHC samples prepared by

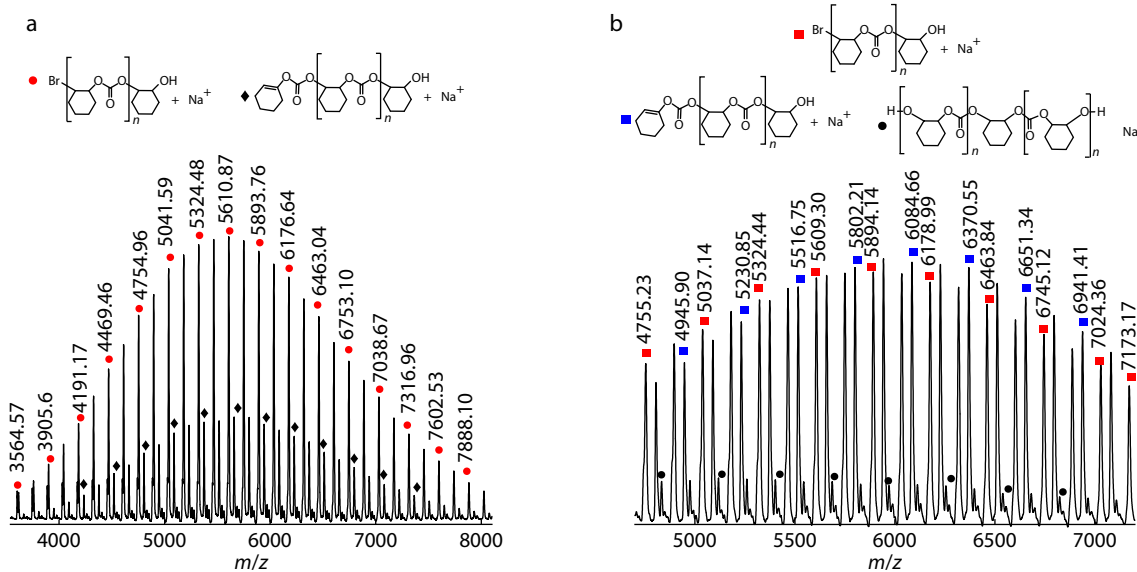


Fig. 2 (a) MALDI-ToF MS of low molecular weight PCHC (**PCHC-7**) obtained by **PB3** under dried CO₂ pressure (Table 1, run 7); (b) MALDI-ToF MS of low molecular weight PCHC (**PCHC-8**) obtained by **PB3** under undried CO₂ pressure (Table 1, run 8).

PB8 using analytical methods, e.g., NMR spectroscopy and MALDI-ToF MS. The silent resonance signal in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of the **PCHC-12** indicated the absence of trifluoroacetate terminal groups (Fig. S54 in ESI). Moreover, the ^1H -NMR spectrum of **PCHC-12** produced by **PB8** does not show any resonance signal at 3.76 ppm, indicating no methine proton (H_α) attached to CF_3COO group. Interestingly, terminal methine protons capped with dihydroxyl group showed resonance at 3.55 ppm and terminal methine protons of CHO carbonate linkage showed resonance at 4.38 ppm, which were in good agreement with the generation of telechelic PCHC diol (Fig. S56 in ESI). MALDI-ToF MS of **PCHC-12** afforded by **PB8** showed two distributions, while the major distribution of peaks revealed α,ω -dihydroxyl PCHC diol formation (Fig. 3, more details, see Figs. S33a and S33b in ESI). In contrast, MALDI-ToF MS of PCHC samples afforded by **PB8** in the presence of water showed one distribution of peaks revealed α,ω -dihydroxyl PCHC diol formation (Fig. 3b, more details, see Fig. S33c in ESI). These results illustrated that **PB8** showed enhanced selectivity for α,ω -dihydroxyl PCHC formation. Detailed explanations for selective α,ω -dihydroxyl PCHC diol formation were discussed later. **PB1** and **PB2** showed inferior catalytic activity than **PB3** (Table 1, runs 1–3). **PB4** having linker length of 6 showed comparable activity performance with **PB3** (Table 1, runs 3 and 4). Given the relatively high activity and higher molecular weight PCHC ($M_n=14.2$ kg/mol) obtained by **PB3**, we hence chose pentamethylene $-(\text{CH}_2)_5-$ as the optimized linker between B and P^+ in the following catalyst optimization. We next studied the counteranion effects on the polymerization behavior. The anions of Cl^- , Br^- , and I^- show marginal difference in the activity of copolymerization of CHO and CO_2 , while **PB3** outperformed **PB5-PB6** in terms of producing relatively high M_n of PCHCs with relatively low \bar{D} (Table 1, runs 3, 5, 6). Replacing Br^- with either CH_3COO^- or CF_3COO^- had almost no influence on the activity of polymerization, while an increase of M_n and broadening of \bar{D} values were observed (Table 1, runs 9, 11 and 13). Increasing the molar ratio of CHO/**PB8** from 500/1 to 1000/1,

2000/1, 5000/1 resulted in an increase of M_n s from 15.3 kg/mol to 20.2 kg/mol, 18.1 kg/mol, 18.2 kg/mol, respectively. The \bar{D} s of generated PCHCs were in the range of 1.11–1.22 (Table 1, runs 13–16). The independence of the molecular weight to CHO/catalyst ratio implied that the residual water in the polymerization system determined the M_n s of obtained PCHCs. An investigation of the impact of CO_2 pressure on the copolymerization might provide some useful information about the catalytic mechanism. Copolymerization of CHO and CO_2 were performed by using **PB3** under 1×10^5 – 20×10^5 Pa CO_2 atmosphere. The results were summarized in Table S2 (in ESI). Apparently, variation of the CO_2 pressure had negligible effect on activity of the polymerization, which indicated a pseudo-zero order in CO_2 pressure.

To show synergistic effect of one-component Lewis pair, control experiments with binary system were performed under identical conditions. In contrast to **PB3**, copolymerization of CHO and CO_2 using binary system **B2/BrPPH₄** led to a lower conversion and the generated PCHC had relatively lower molecular weight and broader \bar{D} (Table 1, runs 3 and 17). These results highlighted the importance of structural design strategy and necessity of Lewis acid and Lewis base integrated in one molecule.

Copolymerization of CHO and CO_2 Using **PB8** in the Presence of Water

The exclusive PCHC diol afforded by Lewis pair induced us to further explore the catalytic behavior of **PB8** in the copolymerization of CHO and CO_2 . These results were summarized in Table 2.

The molar ratios of water/**PB8** were varied from 2 to 5, the molecular weights of the generated PCHCs gradually decreased (Table 2, runs 19 and 20) and further reflected by GPC curves of the obtained PCHCs. The bimodal molecular weight distributions of PCHC became mono-modal distribution with narrow \bar{D} when water was added, thus revealing successful chain transfer reactions (Fig. 4a). Comparison of the theoretical and actual molecular weights of the resulting PCHC diols

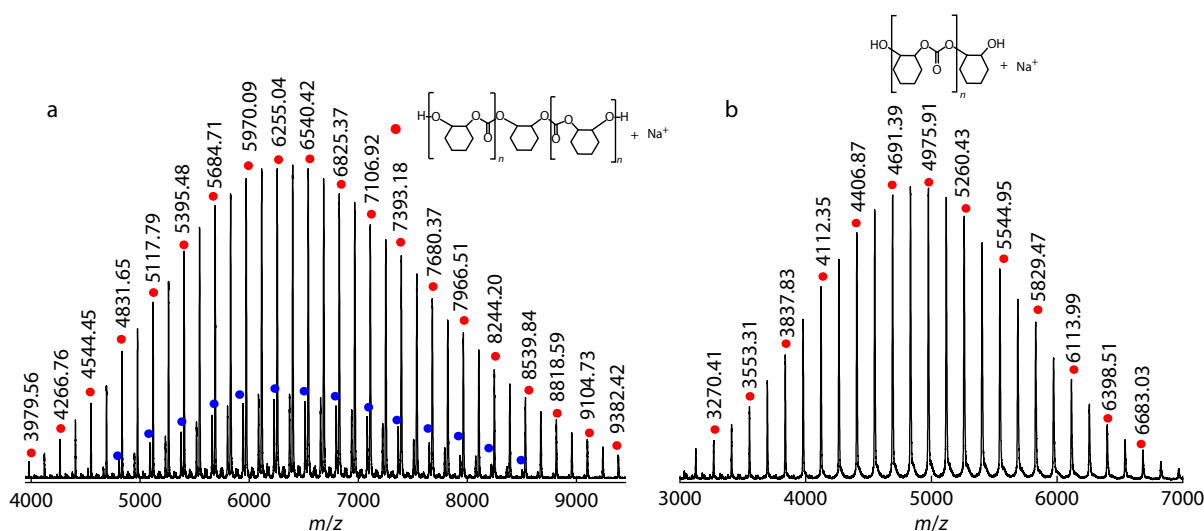


Fig. 3 (a) MALDI-ToF MS of low molecular weight PCHC obtained by **PB8** under CO_2 pressure (Table 1, run 12), the peaks of blue circle cannot be assigned; (b) MALDI-ToF MS of low molecular weight PCHC obtained by **PB8** under CO_2 pressure in the presence of water (Table 2, run 21).

Table 2 Copolymerization of CHO and CO₂ using **PB8** in the presence of water.

Run ^a	[M]/[H ₂ O]/ PB8	Time (h)	Conversion ^b (%)	TOF ^c (h ⁻¹)	PCHC/CHC ^b (%)	M _n ^{theo.} ^d (kg/mol)	M _n ^{GPC} ^e (kg/mol)	D ^e
18	200:0:1	1	57	114	>99	16.2	7.5	1.19
19	200:2:1	2	60	20	>99	5.6	3.3	1.15
20	200:5:1	2	60	12	94	3.3	1.8	1.22
21	200:2:0.5	2	55	28	>99	7.8	4.3	1.12
22	200:2:0.2	2	19	9	98	2.5	1.5	1.17
23	200:2:0.1	2	0	–	–	–	–	–

^a All the polymerizations were carried out in 10 mL autoclave under 15×10⁵ Pa of commercial CO₂ at 80 °C unless otherwise mentioned; ^b Conversion is calculated by ¹H-NMR spectroscopy; PCHC/CHC means the ratio of polycarbonate/cyclohexane carbonate; ^c TOF = turnover frequency; ^d M_n^{theo.} = 142.06 × [CHO]₀/([**PB8**]₀ + [H₂O]₀) × conversion% + M_w(end group). ^e Determined by GPC in THF with polystyrene standard.

indicated that excess water remained in the reaction system serving as chain transfer agents. (Table 2, runs 18–20). In the presence of excess of water, e.g., 5 equiv., a tiny amount of cyclohexene carbonate was observed in the coupling product of CHO and CO₂, thus leading to PCHC with 94% polymer selectivity and 99% carbonate linkages (Table 2, run 20, Fig. S55 in ESI). The formation of cyclohexene carbonate indicated that excess water might facilitate the leaving tendency of CF₃COO⁻ and the probability of back-biting in the polymerization. Keeping the ratio of [CHO]₀/[H₂O]₀ as a constant, the molar amount of **PB8** could be reduced one-tenth of H₂O, potentially indicated that the water tolerance of **PB8** (Table 2, run 22). The shift to low molecular weight PCHC diols was reflected by GPC curves (Fig. 4b). The ¹H-NMR spectrum of the PCHC diol showed resonances at 3.55 ppm which corresponded to the methine proton on the OH end group. A resonance at 3.76 ppm was not observed, thus indicating the absence of CF₃COO⁻ end capped PCHCs (Fig. 5).

For the formation of telechelic dihydroxyl PCHC generated by **PB8**, we therefore proposed water serve as chain transfer agents to facilitate the hydrolysis of CF₃COO⁻ group, thus leading to a hydroxyl group end-capped PCHC diol and regeneration of the CF₃COO⁻ group.^[18,20,59] The selective formation of α,ω-dihydroxyl PCHC diol might be ascribed to the following reasons. It was known that trifluoroacetic group is a good leaving group and susceptible to hydrolysis in the presence of water. Williams *et al.* reported that the trifluoroacetic ester can be hydrolyzed to trifluoroacetic acid in the presence of excess water during the cyclohexene oxide/CO₂ poly-

merization process using well-defined magnesium complex.^[20] To rationalize the actual role of water in current polymerization process and the role of CF₃COO⁻ in the production of PCHC diol, we performed detailed mechanistic investigation.

Mechanistic Study on Copolymerization of CHO and CO₂ Catalyzed by **PB8**

To elucidate the leaving property of CF₃COO group under water or basic condition, we attempted to synthesize *cis*-2-hydroxycyclohexyl-2,2,2-trifluoroacetate,^[60] which can be generated *in situ* (Fig. S62 in ESI). In ¹H-NMR spectrum, the resonance at 3.76 ppm corresponded to the methine proton on the terminal cyclohexyl ring connected with CF₃COO group. The proton attached to OH group showed signal at 4.79 ppm. All attempts to isolate this compound failed. However, when water was added to the generated *cis*-2-hydroxycyclohexyl-2,2,2-trifluoroacetate in CH₂Cl₂, the resonance at 3.76 ppm disappeared (Fig. S63 in ESI) and resulted in the formation of *cis*-1,2-dihydroxycyclohexane (Fig. S64 in ESI). The generation of *cis*-1,2-dihydroxycyclohexane indicated that CF₃COO group was readily hydrolyzed in the presence of water, thus indicating that the hydrolysis of CF₃COO⁻ end group was prior to occurring at the early stage of the copolymerization. Moreover, ¹¹B{¹H} NMR spectra offered useful information of the generated species in the polymerization process and were tentatively assigned (Fig. S61 in ESI). Based on the experimental results, the polymerization mechanism was proposed in Scheme 1. Coordination of CHO with **PB8** afforded **INT-1**, the coordinated

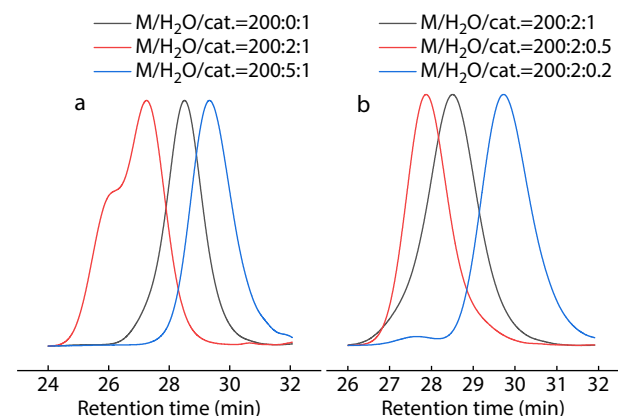


Fig. 4 (a) GPC curves of PCHCs produced by **PB8** with and without addition of water; (b) GPC curves of PCHCs produced by **PB8** at fixed CHO/H₂O molar ratio (200/2), while the catalyst loading was reduced.

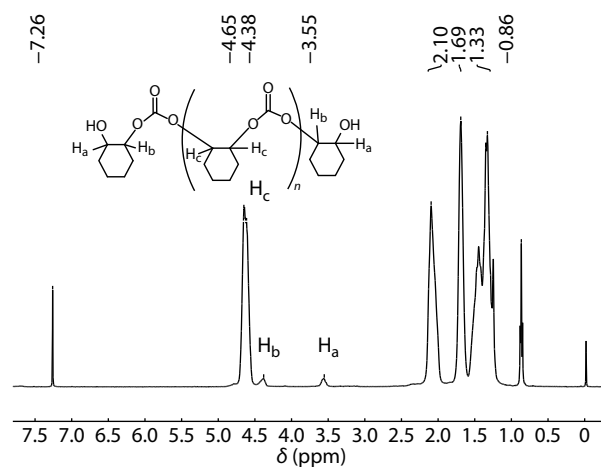
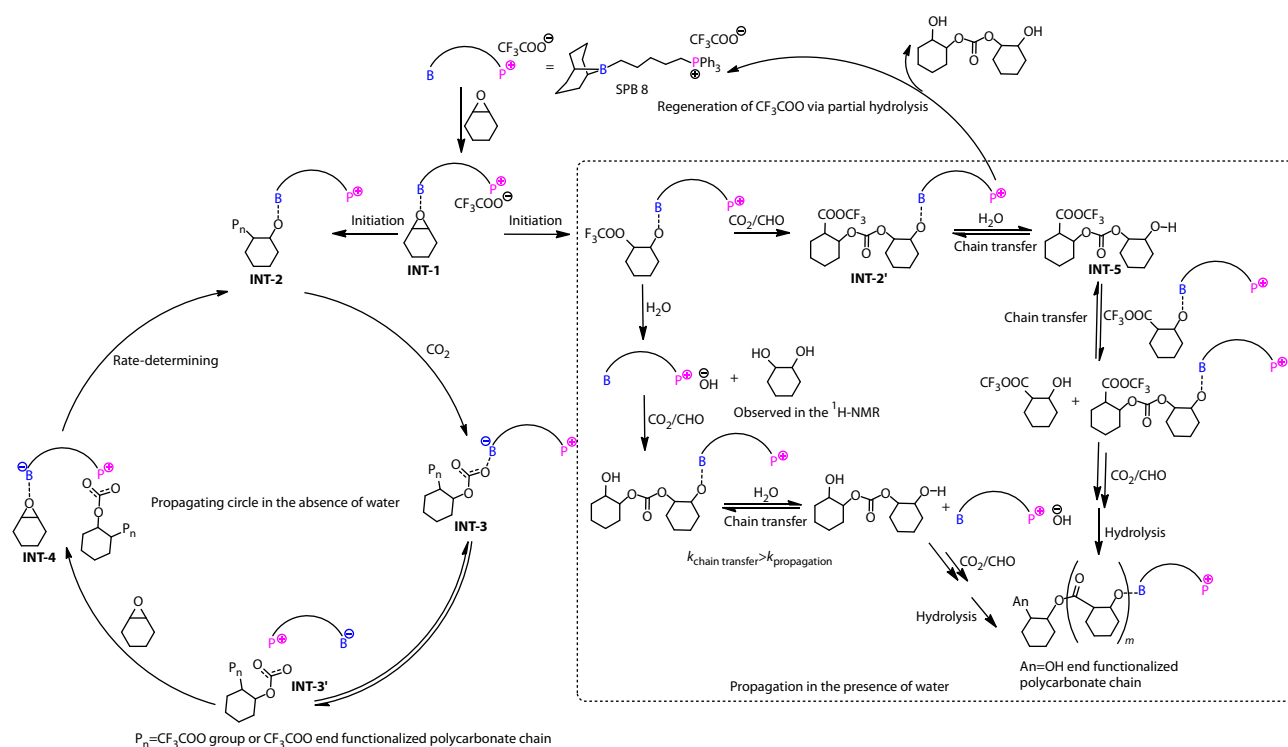


Fig. 5 ¹H-NMR (400 MHz, CDCl₃, 25 °C) of neat PCHC produced by **PB8** (Table 1, run 12).



Scheme 1 Proposed mechanism for the copolymerization of CHO and CO_2 catalyzed by **PB8** in the presence of H_2O .

CHO was then ring-opened by trifluoroacetate anion to give **INT-2**. Insertion of CO_2 into **INT-2** produced the carboxylic species **INT-3**, which was interconverted with **INT-3'**. Further coordination of CHO with **INT-3'** gave **INT-4**, subsequent ring-opening of CHO generated **INT-2**. In the presence of water, the trifluoroacetate end-capped nucleophilic anion bound to the boron center deprotonates water to afford a neutral polymer chain end-capped with a hydroxyl group (**INT-5**). We assumed partial hydrolysis of **INT-5** generated **PB8** at a relatively low concentration, which could initiate a new catalytic circle to afford **INT-2'**. Fast and reversible chain transfer between **INT-5** and alkoxide active species assured the unimodal characteristic of GPC curve of obtained PCHC in the presence of water. The partial hydrolysis characteristic of trifluoroacetate group and maintaining at low concentration during the copolymerization made **PB8** as a true catalyst in the copolymerization of CHO and CO_2 . Nevertheless, it is possible that OH^- ion can be generated during the chain transfer reaction with water. Then OH^- ion of **PB8** then can also initiate the copolymerization to generate diols. Because the rate of chain transfer reaction to water is faster than the propagation rate, many diols are generated until the complete consumption of water in the reaction system. Therefore, the linear relationship between M_n and molar ratio of monomer to water is hold.

Block Copolymer Prepared by PCHC Diol and L-lactide

To demonstrate the application of PCHC diols generated by **PB8**, the low molecular weight PCHCs diols were used as bifunctional initiator for the construction of ABA block copolymer. DBU was reported as an efficient catalyst for the polymerization of lactide in the presence of alcohol.^[31] Therefore, the telechelic PCHC diols ($M_n=3.3\text{--}3.5$ kg/mol)

without purification produced by **PB8** were combined with DBU and applied for the ring-opening of L-lactide (LLA, 25 equiv. per OH group, 50 equiv. total, Table S3 in ESI). The reaction completed within 1 h at room temperature and afforded an ABA triblock copolymer (Fig. S65 in ESI). GPC analysis of the triblock copolymer showed a unimodal distribution with a molecular weight of 9.8 kg/mol (Fig. 6). The trace amount of diblock copolymer cannot be ruled out. However, it is well known that the rate of chain transfer in such polymerization is faster than propagation. The hydroxyl groups of the PCHC diol are in identical environments, the only expected product would be ABA triblock copolymer. In $^1\text{H-NMR}$ spectrum, the resonances assigned to the terminal PCHC methine protons (3.55 ppm, a, Fig. 7) were not observed in the triblock copolymer, likely due to

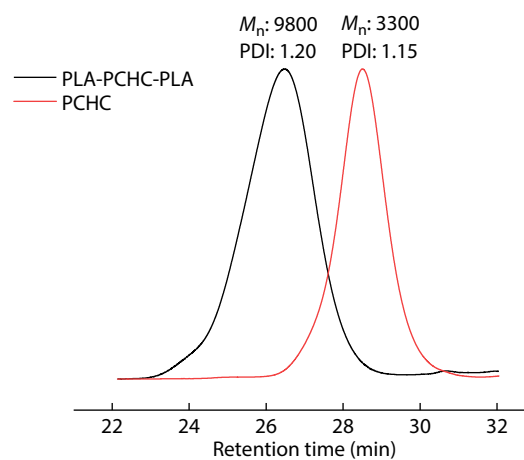


Fig. 6 Expanded overlaid GPC traces of PCHC and PLA-PCHC-PLLA (Table S3 in ESI) using THF as an eluent.

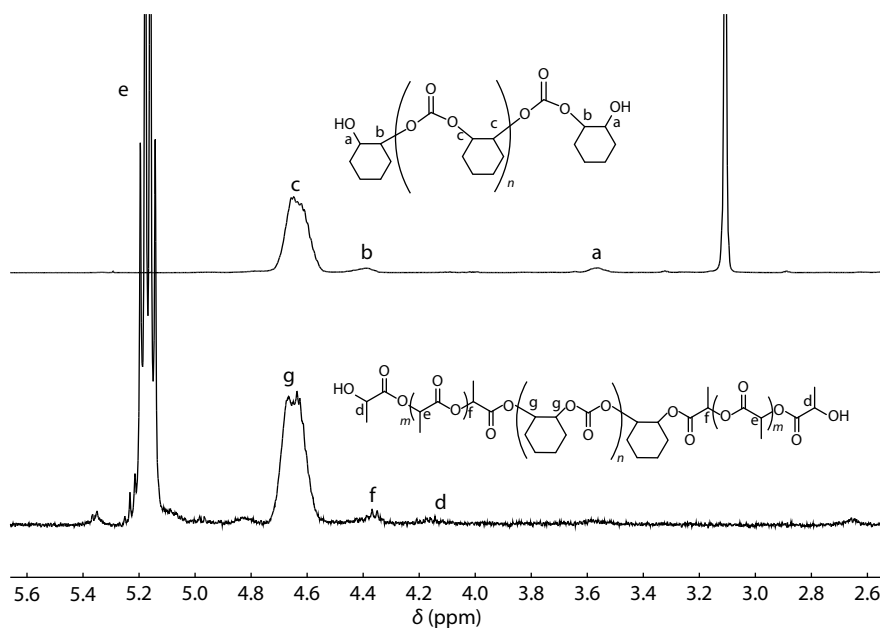


Fig. 7 $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectra of the generated copolymer.

the de-shielding by the adjacent ester group leading to them being masked by the PCHC resonances (g). Terminal methine protons of poly(lactide) showed resonance at 4.14 ppm (d) and methine protons within the linkage of PCHC-lactide unit exhibited resonance at 4.35 ppm (f). We therefore proposed that complete consumption of the terminal alcohol groups occur. The two hydroxyl terminal groups were deprotonated simultaneously and reacted with LLA at the same rate.

CONCLUSIONS

In conclusion, we reported an active organocatalyst for the copolymerization of CHO and CO_2 based on one-component Lewis pair design strategy. These organocatalysts were readily accessible, active at 80 $^\circ\text{C}$ under 15×10^5 Pa CO_2 atmosphere and produced PCHC with >99% carbonate linkages selectivity. Moreover, these catalysts were robust in terms of their tolerance to excess quantities of water (10 equiv.). Interestingly, **PB8** having CF_3COO anion solely generated telechelic PCHC diol in the presence of water. Chain transfer or hydrolysis reactions with water accounted for the exclusive generation of telechelic PCHC diol. The telechelic PCHC diol can serve as a macroinitiator for subsequent ROP of LLA to prepare ABA type triblock copolymer.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2925-3>.

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