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Binary Catalyst Manipulating the Sequences of Poly(ester-carbonate) Copolymers in Metal-Free Terpolymerization of Epoxide, Anhydride, and CO_2

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Cite This: *Precis. Chem.* 2025, 3, 35−42

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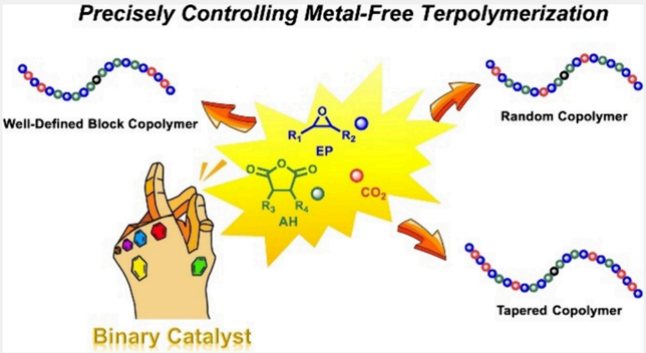
ABSTRACT: The one-pot terpolymerization of epoxide (EP), anhydride (AH), and CO_2 to synthesize polyester-polycarbonate copolymers with precise sequences remains a significant challenge in polymer chemistry. In this study, promising progress was achieved by utilizing a cyclic trimeric phosphazene base (CTPB) and triethylboron (TEB) as a binary catalyst, enabling the synthesis of both well-defined block and truly random poly(ester-carbonate) copolymers through the one-pot terpolymerization of EP/AH/CO_2. By adjusting the molar ratio of CTPB/TEB to 1/0.5, remarkable chemoselectivity for ring-opening alternating copolymerization (ROAC) of propylene oxide (PO) and phthalic anhydride (PA) was achieved, followed by the ROAC of PO/CO_2. This sequential control allowed for the synthesis of well-defined block poly(ester-carbonate) copolymers, containing three possible sequences, ester−ester sequence (EE)/ester-carbonate sequence (EC)/carbonate-carbonate sequence (CC) = 59/4/37, from a mixture of PO, PA, and CO_2. Moreover, the versatility of this CTPB/TEB catalyst in regulating chemoselectivity was demonstrated, with a ratio of 1/3 facilitating the simultaneous ROAC of PO/PA and PO/CO_2 with compatible rates, resulting in the production of random poly(ester-carbonate) copolymers, in which three possible sequences (EE/EC/CC = 26/50/24) are very close to theoretical values. This metal-free catalytic system and its flexible chemoselectivity regulation strategy proved to be applicable to a wide range of epoxides (PO, cyclohexene oxide (CHO)) and anhydrides (PA, diglycolic anhydride (DGA), and succinic anhydride (SA)), enabling the successful synthesis of poly(ester-carbonate) copolymers with diverse sequences and compositions.



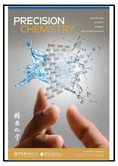
KEYWORDS: *Binary catalyst, Chemoselective terpolymerization, Block copolymer, Random copolymer, CO_2-based copolymer*

INTRODUCTION

The surging popularity of CO_2-based biodegradable polymers is driven by their pivotal role in advancing sustainability.[1−8] By addressing critical concerns like global warming and white plastic pollution, these polymers offer a promising solution toward a greener future. In 1969, Inoue and colleagues successfully prepared aliphatic polycarbonate by ring-opening alternating copolymerization (ROAC) of CO_2 and propylene oxide (PO), a groundbreaking achievement that propelled the development of CO_2-based polymers.[9] However, the range of widely studied epoxide monomers has remained limited to PO and cyclohexene oxide (CHO) over the past 50 years, thus restricting the performance and applications of CO_2-based polymers. To overcome this limitation and to create CO_2-based polymers with diverse structures and superior properties, incorporating a third monomer through terpolymerization has emerged as a promising solution.[10,11] Apart from polycarbonates, polyesters are also a complementary class of polymers that can be synthesized from cyclic esters or a combination of epoxides and anhydrides.[12−14] By exploring terpolymerization strategy that combine epoxide (EP), anhydride (AH), and CO_2, the synthesis of CO_2-based poly(ester-carbonate) copolymers holds great potential.[15]

Copolymers with precise and specific sequences represent a highly valuable class of materials that offer customized properties.[16,17] Block copolymers, for instance, are composed of different segments and find versatile applications as thermoplastic elastomers (TPEs).[18−21] On the other hand, random copolymers are equally significant, because the random structure can provide two distinct polymers that are mutually complementary to the maximum extent.[22−25] In the terpolymerization process involving epoxides, anhydrides, and

Received: July 22, 2024
Revised: October 10, 2024
Accepted: October 11, 2024
Published: October 21, 2024



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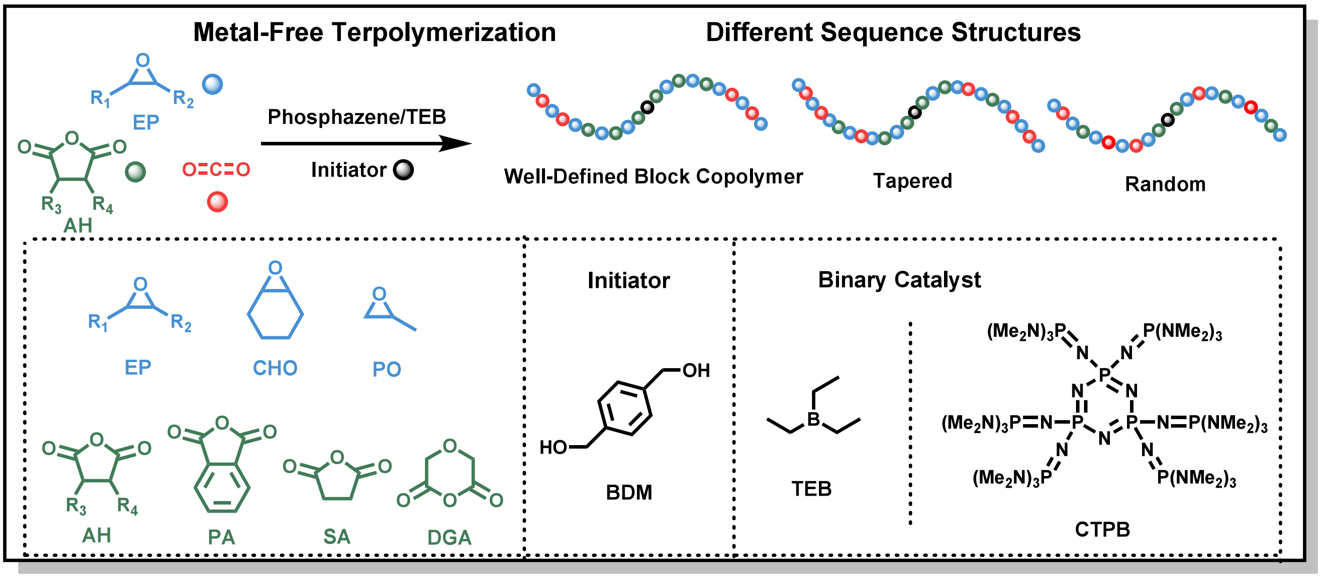
https://doi.org/10.1021/prechem.4c00062

Scheme 1. Binary Catalyst CTPB/TEB toward EP/AH/CO_2 Terpolymerization



CO_2, the choice of catalysts and polymerization conditions can yield either block or random poly(ester-carbonate) copolymers.[10] In a significant advancement in 2008, Coates and colleagues utilized homogeneous zinc catalysts to conduct chemoselective terpolymerization of CHO/diglycolic anhydride (DGA)/CO_2, resulting in the synthesis of block polyester-polycarbonate copolymers via a prerate-determining mechanism.[26] This innovative method took advantage of the reactivity of CHO/DGA over CHO/CO_2. Following this, a range of mononuclear and dinuclear metal catalysts have been developed to enable the selective synthesis of block polyester-polycarbonate copolymers by chemoselective terpolymerization.[27−37]

On the other hand, significant progress has been made in the metal-free ROAC of CO_2 with epoxides since the discovery by Gnanou and Feng in 2016, utilizing a binary system of organic bis(triphenylphosphine)iminium chloride (PPNCl)/triethylboron (TEB).[38] This PPNCl/TEB binary catalytic system also demonstrated efficiency in the ROAC of epoxide/anhydride,[39−41] leading to the synthesis of block or random poly(ester-carbonate) copolymers through one-pot terpolymerization by adjusting the feed ratios of epoxide and anhydride.[42] Further advancements in the field include the synthesis of block polyester-polycarbonate quadripolymers via ROAC of CHO/PO/PA/CO_2 using similar catalytic systems.[43−45] However, these reports showed that the block copolymers always contain a small amount of tapered structure or gradient copolymers were obtained by a bifunctional catalyst,[46] necessitating the sequential ROAC of CHO/PA followed by ROAC of CHO/CO_2 for the synthesis of well-defined block polyester-polycarbonate copolymers.[47] As a binary catalyst, the catalytic properties including activity and selectivity are highly dependent on the basicity, Lewis acidity, and ratios of base to Lewis acid.[48] Thus, phosphazenes with tunable basicity and structures are particularly interesting to construct binary catalysts in combination with TEB. Recently, we achieved the synthesis of well-defined block polyester-polycarbonate copolymers via the one-pot terpolymerization of CHO/PA/CO_2 employing highly chemoselective C_3N_3-Py-P_3/TEB as the catalyst.[49] Interestingly, the chemoselectivity can be adjusted by varying molar ratios of C_3N_3-Py-P_3/TEB, allowing for the preparation of tapered and random copolymers. However, the latter was not a truly random copolymer, as the distributions of three possible sequences (ester−ester sequence (EE), ester-carbonate sequence (EC), and carbonate-carbonate sequence (CC)) were far from theoretical values of 25/50/25.[50] The resultant copolymer was predominantly composed of polycarbonate (PC), and the contents of PC in all the random copolymers are higher than 75 mol %, suggesting the rate for ROAC of CHO/CO_2 was far over that for ROAC of CHO/PA.

To synthesize truly random copolymers from terpolymerization of EP/AH/CO_2, it is necessary to balance the reactivity for ROAC of EP/AH and EP/CO_2, namely increasing the former or decreasing the latter. According to our previous report, cyclic trimeric phosphazene base (CTPB) showed a much lower activity than C_3N_3-Py-P_3 in the presence of TEB for ROAC of EP/CO_2, due to its relatively higher basicity (pK_a of 33.3 vs pK_a of 26.5 in MeCN).[51] Therefore, in this study we systematically studied CTPB/TEB as a binary catalyst for metal-free terpolymerization of EP/AH/CO_2 (Scheme 1). Remarkably, both well-defined block and truly random CO_2-base poly(ester-carbonate) copolymers were successfully synthesized with only one catalytic system via the one-pot methodology, depending on the precisely choosing molar ratios of CTPB and TEB. Particularly, with CTPB/TEB = 1/3 for terpolymerization of PO/PA/CO_2, a conversion of 65% PA was achieved within 4 h, and the sequence distributions of EE, EC, and CC were 26 mol %, 50 mol %, and 24 mol %, close to the theoretical ratio of 25:50:25 for a perfect random copolymer. Moreover, the binary catalyst and the strategy to adjust chemoselectivity are versatile for different anhydrides (PA, DGA, and succinic anhydride (SA)) and epoxides (PO and CHO), leading to the synthesis of a large family of CO_2-base poly(ester-carbonate) copolymers.

Table 1. One-Pot Terpolymerization of PO/PA/CO_2 with CTPB/TEB[a]

run	CTPB/TEB	*t* (h)	PA conv.[b] (%)	sequence distribution[b] (mol %)			PC/(PE + PC)[b] (mol %)	cc/(cc + PC)[b] (mol %)	polymer type	$M_{n,GPC}$[c] (kDa)	*Đ*[c]
				EE	EC	CC					
1	1/0.5	3	39	>99	0	0	0	0	Polyester	n.d.[d]	n.d.[d]
2	1/0.5	6	84	>99	0	0	0	0	Polyester	3.4	1.55
3	1/0.5	6.5	99	>99	0	0	0	0	Polyester	5.3	1.51
4	1/0.5	7	>99	86	6	8	10	60	Block	8.5	1.20
5	1/0.5	9	>99	83	4	13	15	58	Block	10.1	1.16
6	1/0.5	15	>99	59	4	37	39	56	Block	12.1	1.12
7	1/1	3	98	88	9	3	11	0	Tapered	4.9	1.75
8	1/2	3	76	80	13	7	13	0	Tapered	2.3	1.98
9	1/2	4	88	66	23	11	23	0	Tapered	2.6	2.44
10	1/3	3	52	28	51	21	50	0	Random	1.3	2.35
11	1/3	4	65	26	50	24	50	0	Random	1.9	2.45
12	1/3	6	85	19	50	31	62	0	Random	4.0	2.43
13	1/5	4	43	12	48	40	64	0	Random	4.3	1.67
14	1/5	9	96	11	49	40	65	trace	Random	13.4	1.33

[a] Conditions: [PO]/[PA]/[BDM]/[CTPB] = 500/100/1/1, PA was 1 mol L^{-1} in THF, 1 MPa CO_2, 60 °C. [b] Determined by ^1H NMR; EE = ester−ester sequence, EC = ester-carbonate sequence, CC = carbonate-carbonate sequence, and cc = cyclic carbonate. [c] Determined by GPC at 40 °C in THF relative to polystyrene standards. [d] Not determined.

■ RESULTS AND DISCUSSION

Synthesis of Poly(ester-carbonate) Copolymers via One-Pot Terpolymerization of PO/PA/CO_2 by CTPB/TEB

We first explored the terpolymerizatoin of PO/PA/CO_2, considering PO is the most used epoxide monomer in both academia and industry. It was reported that the terpolymerization of PO/PA/CO_2 tended to generate thermodynamically stable cyclic carbonates (cc) at 80 °C and above.[49] Therefore, the terpolymerizations of PO/PA/CO_2 were carried out at 60 °C under 1 MPa CO_2 with PO/PA/BDM/CTPB = 500/100/1/1 and an initial PA concentration of 1 mol L^{-1} in THF (Table 1). According to previous reports, the low loading of TEB usually resulted in high chemoselectivity.[47,49] Thus, a ratio of CTPB/TEB = 1/0.5 was first investigated for terpolymerization (Table 1 runs 1−6). The progress of the terpolymerization at various time points was monitored using NMR spectroscopy (Figures 1 and S1−S6), allowing for the easy tracking and analysis of PA conversion, as well as determining the formation of polyester (PE) and polycarbonate (PC) products. It was not surprising that the activity of CTPB/TEB was relatively lower than that of C_3N_3-Py-P_3/TEB,[49] but PA was still completely consumed within 6.5 h, achieving a conversion of 99% (Table 1 run 3). The peaks at 8.02 and 7.92 ppm that are typical for PA monomer gradually decreased, whereas the characteristic resonance at 5.40 ppm for polyester increased (Figure 1). Notably, there was no PC formation, as indicated by the absence of the peak around 5.00 ppm. However, as the reaction time progressed from 6.5 to 15 h, a new signal emerged at 5.00 ppm, signifying the conversion of PO with CO_2 to yield poly(propylene carbonate) (PPC) alongside cyclic carbonate (cc) formation. From 6.5 to 7 h to 9 to 15 h (Table 1 runs 3−6), the signals for PPC steadily increased and the contents of PC in copolymers increased from 0 to 10 to 15 to 39 mol %, respectively. These findings suggested that the CTPB/TEB catalytic system in a ratio of 1/0.5 exhibited a high chemoselectivity toward the terpolymerization of PO/PA/CO_2, with the reaction of PO and PA taking precedence and CO_2 engaging in the reaction only after PA had been consumed completely (at least >99%).

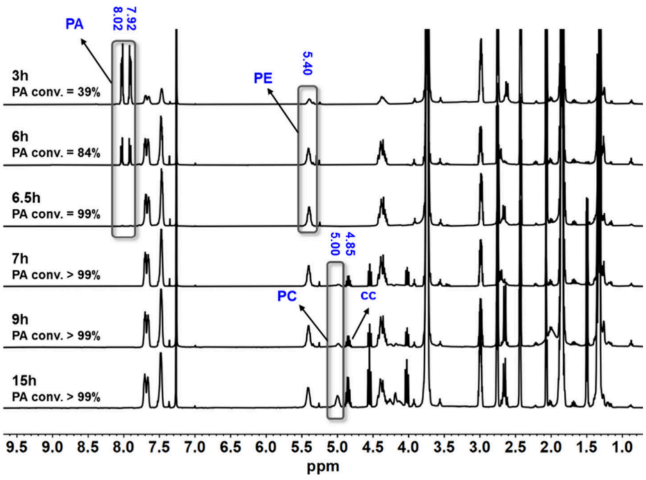


Figure 1. Stacked ^1H NMR spectra ($CDCl_3$) of the crude reaction mixtures from terpolymerizations of PO/PA/CO_2 at different reaction times (Table 1 runs 1−6).

The structure of poly(PO-*alt*-PA)-*b*-PPC block copolymer was confirmed through detailed ^1H NMR and ^{13}C NMR analysis of isolated polymer (Figure S7 and Figure S8; Table 1 run 6). In the ^1H NMR spectrum (Figure S7), two major resonances at 5.40 ppm (a) and 4.99 ppm (b) were found for PE block and PC block,[52] while the signals (a' and b') for the junctions between blocks were minor. In the ^{13}C NMR spectrum (Figure S8), distinctive resonances were observed at 166.90 ppm for the ester carbonyl and 154.32 ppm for the carbonate carbonyl group. Through further characterization with DOSY NMR (Figure 2a), only one logarithm of the diffusion coefficient (log *D*) was detected for the same sample (Table 1 run 6). Additionally, the molar masses (M_ns) of the resulting copolymers were found to increase with polymerization time, as shown in Figure 2b. It was interesting that the molar mass distributions became narrow once CO_2 was copolymerized. To investigate the initiation process, the

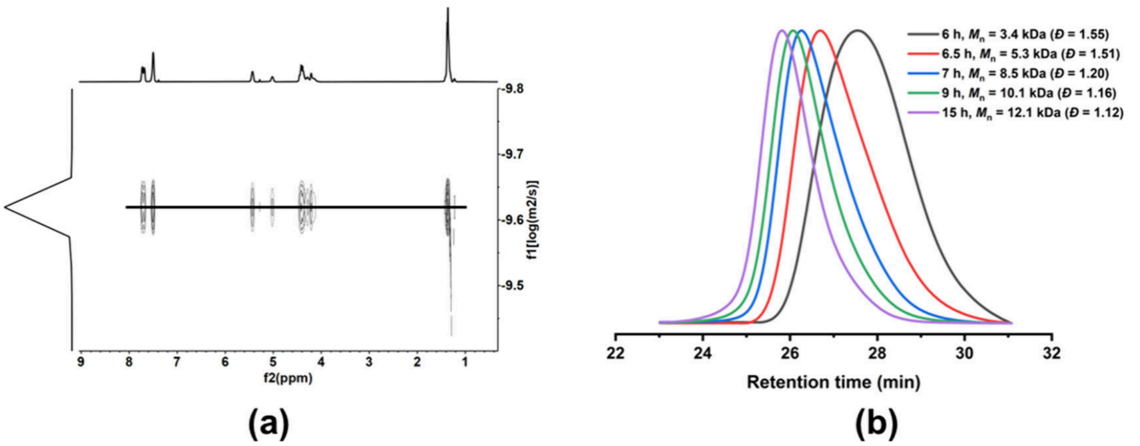


Figure 2. (a) DOSY NMR spectrum ($CDCl_3$) of block poly(PA-*alt*-PO)-*b*-PPC obtained by one-pot terpolymerization of PO/PA/CO_2 (Table 1 run 6); (b) GPC traces of the polymers from terpolymerizations of PO/PA/CO_2 with PO/PA/BDM/CTPB/TEB = 500/100/1/1/0.5 at different reaction times (Table 1 runs 2–6).

polymer sample obtained in Table 1 run 3 with a low M_n of 5.3 kDa and a broad $Đ$ of 1.51 was characterized by MALDI-TOF (Figure S36), showing that all polymer chains were initiated by BDM and assigned to poly(PA-*alt*-PO)s. This result was consistent with the NMR analysis that no PC was formed (Table 1 run 3). The broad molecular weight distribution could attribute to significant transesterification for copolymerization of PA and PO because of the high basicity of CTPB (pK_a of 33.3 in MeCN), while copolymerization of PO and CO_2 showed minor transesterification and led to narrow distributions. These comprehensive findings conclusively establish the successful synthesis of well-defined block poly(PA-*alt*-PO)-*b*-PPC copolymers, rather than the blends of polyester and polycarbonate homopolymers.

In previous studies, it was discovered that varying molar ratios of base/TEB in the binary catalytic systems had a profound impact on the chemoselectivity of terpolymerization, leading to different sequences in the resultant copolymers.[43,47,49,53] For instance, block, tapered, and random copolymers were successfully synthesized via terpolymerization of CHO/PA/CO_2 with C_3N_3-Py-P_3/TEB ratios of 1/0.5, 1/1, and 1/2, respectively. However, the 1/2 ratio did not result in a truly random copolymer, as it was primarily composed of polycarbonate (PC/(PE + PC) > 85 mol %). In this study, we aimed to systematically investigate the influence of molar ratios of CTPB/TEB on chemoselectivity to achieve truly random copolymers through the terpolymerization of PO/PA/CO_2. Initially, we tested a CTPB/TEB ratio of 1/1, and a conversion of 98% PA was achieved within 3 h (Table 1 run 7). The proportions of polyester (PE) and polycarbonate (PC) in the resultant copolymer were 89 mol % and 11 mol %, respectively. Further increasing the amount of TEB (CTPB/TEB = 1/2), a conversion of 76% PA was achieved within 3 h, and the proportions of PE and PC were 87 mol % and 13 mol % (Table 1 run 8). When the time was extended to 4 h, PA reached a conversion of 88%, and the proportions of PE and PC were 77 mol % and 23 mol % (Figure S9; Table 1 run 9). Therefore, tapered poly(ester-carbonate) copolymers were obtained. With CTPB/TEB = 1/3, a conversion of 52% PA was achieved within 3 h. Based on the ^{1}H NMR of isolated copolymer, the sequence distributions contained 28 mol % ester−ester sequence (EE), 51 mol % ester-carbonate sequence (EC), and 21 mol % carbonate-carbonate sequence (CC), revealing a random copolymer was obtained (Table 1 run 10). When the time was extended to 4 h, PA reached a conversion of 65%, and the sequence distributions of EE, EC, and CC were 26 mol %, 50 mol %, and 24 mol % (Table 1 run 11; Figure S10 and S11), respectively, very close to the ratio of 25:50:25 for a truly random copolymer. The ^{1}H NMR spectrum of the random copolymer (Figure S10) exhibited two significant peaks a' and b' at 5.34 and 5.08 ppm and was distinguishing from that of block copolymer (Figure S7; Table 1 run 6). All these results indicated that the growth rates of polyester and polycarbonate were very close, and the truly random structure was obtained. Further increasing the amount of TEB (CTPB/TEB = 1/5) resulted in a copolymer with a lower PA conversion but a higher proportion of CC sequences (Table 1 run 13; Figure S12). According to previous study, the excess of Lewis acid could interact with carbonyl group and lead to an exothermic nucleophilic attack to CO_2, which accelerates the ROAC of epoxide with CO_2.[49] Therefore, well-defined block, tapered, or truly random poly(ester-*co*-carbonate) copolymers have been successfully synthesized by precisely adjusting the ratios of CTPB to TEB (Figure 3). The thermal properties of the copolymers were evaluated using differential scanning calorimetry (DSC), revealing a single T_g indicative of good compatibility between polyester and polycarbonate components (Figure S35a).

Synthesis of Poly(ester-carbonate) Copolymers via One-Pot Terpolymerization of CHO/PA/CO_2 by CTPB/TEB

To test the versatility of this CTPB/TEB binary catalyst and to verify the strategy of manipulating the sequences, another widely used epoxide CHO was also studied systematically, and the results are shown in Table 2. Since cyclic carbonate (cc) was not observed, the terpolymerizations of CHO/PA/CO_2 were carried out at 80 °C (Table 2), leading to the higher catalytic activity than that for terpolymerizations of PO/PA/CO_2 (Table 1). With CTPB/TEB = 1/0.5, PA was nearly fully consumed within 55 min, achieving a conversion of 99% (Table 2 run 3). The gradual decrease in peaks at 8.02 and 7.92 ppm, characteristic of the PA monomer, was evident, while the resonance at 5.14 ppm, indicative of the polyester, showed a corresponding increase (Figure S13). There was a notable absence of a peak around 4.64 ppm for polycarbonate initially. However, as the reaction time progressed from 55 to 80 min, a new signal emerged at 4.64 ppm, indicating the

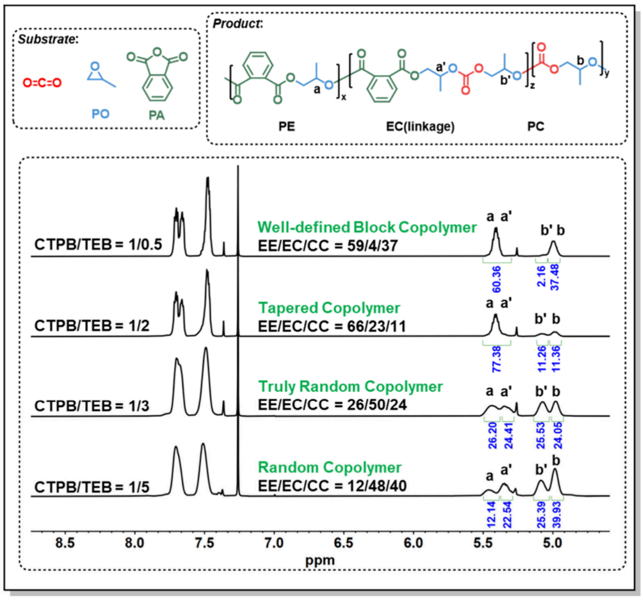


Figure 3. Stacked ^{1}H NMR spectra ($CDCl_3$) of poly(ester-*co*-carbonate) copolymers obtained from one-pot terpolymerizations of $PO/PA/CO_2$ with various CTPB/TEB ratios (Table 1 runs 6, 9, 11, and 13).

formation of polycyclohexene carbonate (PCHC) as CHO reacted with CO_2. Further extending the polymerization time, the signals for PCHC steadily increased, and the content of PC in copolymer reached 68 mol % within 80 min (Table 2 run 6). The structure of poly(CHO-*alt*-PA)-*b*-PCHC block copolymer was verified via ^{1}H, ^{13}C, and DOSY NMR analysis of isolated polymer (Figures S15–S17; Table 2 run 5). In the ^{1}H NMR spectrum (Figure S15), two minor signals, denoted as a' (4.99 ppm) and b' (4.78 ppm), were detected in proximity to the typical peaks of the polyester (5.14 ppm, a) and polycarbonate (4.64 ppm, b). These minor peaks (a' and b') were proposed to be junctions between the PE block and PC block segments, rather than indicative of a tapered structure.[49] The DOSY NMR analysis (Figure S17) revealed a single logarithm of the diffusion coefficient (log D) for the same sample (Table 2, run 5). Furthermore, the M_ns of the resulting copolymers by GPC increased with the prolongation of the polymerization time (Figure S14). Collectively, these findings authenticated the production of well-defined block poly(CHO-*alt*-PA)-*b*-PCHC copolymers, rather than a blend of polyester and polycarbonate homopolymers.

Similar to the terpolymerization of $PO/PA/CO_2$, increasing the amount of TEB resulted in the propensity toward ROAC of CHO/CO_2, producing tapered or random poly(CHO-*alt*-PA)-*co*-PCHC copolymers (Table 2 runs 7–17; Figures S18–S20). Particularly, with CTPB/TEB = 1/1.5, a conversion of 48% PA was achieved within 30 min, and the sequence distributions of EE, EC, and CC were 24 mol %, 50 mol %, and 26 mol % (Table 2 run 10), respectively, close to the theoretical ratio of 25:50:25 for a perfect random copolymer. When the time was extended to 45 min, PA reached a conversion of 66%, and the proportions of EE, EC, and CC were 24 mol %, 48 mol %, and 28 mol % (Table 2 run 11; Figure S19). The ^{1}H NMR spectrum of the random copolymer (Figure S19) exhibited two significant peaks a' (4.99 ppm) and b' (4.77 ppm) and was distinguishing from that of block copolymer (Figure S15; Table 2 run 5). With CTPB/TEB = 1/2 or 1/5, the random poly(CHO-*alt*-PA)-*co*-PCHC copolymers were also obtained but predominated by polycarbonate, of which contents in the products are over 80 mol % (Table 2 runs 14–17). These results indicate that the precise ratio of CTPB/TEB is crucial to synthesize copolymers with designed sequences and compositions. The thermal properties of the copolymers were evaluated using DSC, revealing a single T_g indicative of good compatibility between polyester and polycarbonate components (Figure S35b).

Table 2. One-Pot Terpolymerization of $CHO/PA/CO_2$ with CTPB/TEB[a]

				sequence distribution[b] (mol %)						
run	CTPB/TEB	t (min)	PA conv.[b] (%)	EE	EC	CC	polymer type	PC/(PE + PC)[b] (mol %)	$M_{n,GPC}$[c] (kDa)	$Đ$[c]
1	1/0.5	20	12	100	0	0	Polyester	0	n.d.[d]	n.d.[d]
2	1/0.5	35	57	100	0	0	Polyester	0	2.4	1.30
3	1/0.5	55	>99	100	0	0	Polyester	0	4.0	1.17
4	1/0.5	60	>99	81	9	10	Block	15	5.0	1.21
5	1/0.5	70	>99	42	6	52	Block	55	6.3	1.18
6	1/0.5	80	>99	29	6	65	Block	68	7.4	1.20
7	1/1	30	50	51	41	8	Tapered	25	2.1	1.21
8	1/1	50	77	47	42	11	Tapered	31	3.0	1.25
9	1/1	60	89	43	41	16	Tapered	35	3.3	1.20
10	1/1.5	30	48	24	50	26	Random	50	n.d.	n.d.
11	1/1.5	45	66	24	48	28	Random	50	2.5	1.27
12	1/1.5	55	81	19	45	36	Random	59	3.0	1.26
13	1/1.5	65	>99	17	39	44	Random	63	5.4	1.20
14	1/2	60	66	3	32	65	Random	81	4.4	1.46
15	1/2	90	>99	3	27	70	Random	84	11.7	1.17
16	1/5	90	76	2	28	70	Random	85	5.0	1.41
17	1/5	120	83	2	27	71	Random	85	7.4	1.32

[a] Conditions: [CHO]/[PA]/[BDM]/[CTPB] = 500/50/1/1, 0.014 mmol of CTPB, 7 mmol of CHO (0.71 mL), PA was 0.5 mol L^{-1} in THF, 1 MPa CO_2, 80 °C. [b] Determined by ^{1}H NMR; EE = ester–ester sequence, EC = ester-carbonate linkage sequence, and CC = carbonate-carbonate sequence. [c] Determined by GPC at 40 °C in THF relative to polystyrene standards. [d] Not determined.

Table 3. One-Pot Terpolymerization of EP/AH/CO_2 with CTPB/TEB[a]

run	EP	AH	T (°C)	CTPB/TEB	t (h)	AH conv.[b] (%)	PC/(PE + PC)[b] (mol %)	$M_{n,GPC}$[c] (kDa)	$Đ$[c]
1	PO	DGA	60	1/0.5	24	>99	0	2.6	2.38
2	PO	DGA	60	1/1	12	>99	45[d]	5.7	1.81
3	PO	DGA	60	1/2	4	>99	31	5.3	1.48
4	PO	DGA	60	1/3	2	99	0	3.1	1.77
5	PO	DGA	60	1/3	4	>99	46	5.8	1.51
6	PO	DGA	60	1/5	1	84	0	2.8	1.50
7	PO	DGA	60	1/5	4	>99	55	6.9	1.50
8	PO	SA	60	1/2	8	>99	0	1.6	2.66
9	PO	SA	60	1/3	8	>99	29	2.4	1.81
10	PO	SA	60	1/5	6	>99	26	2.3	1.68
11	CHO	DGA	80	1/2	1	89	0	n.d.[e]	n.d.[e]
12	CHO	DGA	80	1/2	2	>99	69	4.0	1.68
13	CHO	DGA	80	1/3	1	>99	70	4.2	1.54
14	CHO	DGA	80	1/5	1	>99	72	4.3	1.58

[a] Conditions: [EP]/[AH]/[BDM]/[CTPB] = 500/100/1/1, 0.014 mmol of CTPB, AH was 1 mol L^{-1} in THF, 1 MPa CO_2. [b] Determined by ^1H NMR.; PE = ester sequence, and PC = carbonate sequence. [c] Determined by GPC at 40 °C in THF relative to polystyrene standards. [d] Cyclic carbonate (cc) was also observed. [e] Not determined.

The Monomer Scope of Terpolymerization by CTPB/TEB Binary Catalyst

In the previous report, only the most commonly used anhydride, namely PA, was investigated for terpolymerization by C_3N_3-Py-P_3/TEB. To expand the applications of the CTPB/TEB catalytic system, we also attempted to prepare CO_2-based polymers using other anhydrides (AHs) including diglycolic anhydride (DGA), and succinic anhydride (SA), with PO or CHO in this study. The results are summarized in Table 3. The terpolymerizations under different polymerization conditions were monitored by NMR spectroscopy, and ^1H NMR spectra of the crudes are shown in Figures S21−S34, by which the conversions of AH and the products are readily recorded and analyzed. The terpolymerization of PO/DGA/CO_2 was first conducted with CTPB/TEB = 1/0.5 at 60 °C, similar to the terpolymerization of PO/PA/CO_2. However, after the PA was completely consumed, no reaction was observed between the PO and CO_2, with neither cyclic carbonate nor poly(propylene carbonate) (PPC) being detected (Table 3 run 1; Figure S21). Increasing the ratio of CTPB/TEB to 1/1 afforded poly(DGA-*alt*-PO)-*b*-PPC block copolymer, although cyclic carbonate (cc) was formed simultaneously (Table 3 run 2; Figure S22). To our delight, the formation of cc was successfully suppressed with further increasing the amount of TEB (CTPB/TEB = 1/2, 1/3, or 1/5), while the poly(DGA-*alt*-PO)-*b*-PPC block copolymer was still chemoselectively produced (Table 3 runs 3−7; Figures S23−S27). For example, with CTPB/TEB = 1/3, DGA was completely consumed to generate polyester block within 2 h without formation of polycarbonate (Table 3 run 4). It was clearly observed that the peak at 4.42 ppm that was typical for DGA monomer disappeared, while the characteristic resonance at 5.25 ppm for poly(DGA-*alt*-PO) polyester was observed (Figure S24). Meanwhile, no peak for PPC polycarbonate at around 5.00 ppm was observed. As time extended to 4 h (Table 3 run 5), a new signal appeared at 5.00 ppm (Figure S25), demonstrating that PO reacted with CO_2 to form PPC. In the terpolymerization of PO/SA/CO_2, block poly(SA-*alt*-PO)-*b*-PPC was obtained, as indicated by the characteristic resonances at 5.14 ppm for poly(SA-*alt*-PO) and 5.00 ppm for PPC (Figure S29). Block poly(DGA-*alt*-CHO)-*b*-PCHC was synthesized from one-pot terpolymerization of CHO/DGA/CO_2 with the ratios of CTPB/TEB in the range of 1/2 to 1/5 (Table 3, runs 11−14). The characteristic peaks at 4.89 ppm for poly(DGA-*alt*-CHO) and 4.63 ppm for PCHC (Figures S32−S34) confirmed the formation of block copolymers under different ratios of CTPB/TEB. These results revealed that both SA and DGA showed relatively lower reactivity as compared to PA, but the chemoselectivities for PO/DGA/CO_2, PO/SA/CO_2, and CHO/DGA/CO_2 terpolymerizations were higher than that in the presence of PA as monomer under otherwise identical conditions, especially with high ratio of CTPB/TEB. Thus, block copolymers were always produced despite of varying ratios of CTPB/TEB in the presence of DGA or SA as monomer (Table 3).

■ CONCLUSIONS

The binary system CTPB/TEB proved to be a highly effective metal-free catalyst for the chemoselective terpolymerization of epoxide/anhydride/CO_2. The molar ratios of CTPB/TEB played a crucial role in determining the chemoselectivity of the terpolymerization process and thus the sequence distribution in the resultant copolymers. With CTPB/TEB = 1/0.5, high chemoselectivity was achieved, and well-defined block copolymers were prepared from a mixture of PO, PA, and CO_2 through a one-pot method. With CTPB/TEB = 1/3, the ROAC of PO/PA and ROAC of PO/CO_2 took place simultaneously with compatible rates, generating truly random poly(ester-carbonate) copolymers (EE/EC/CC = 26/50/24). In the terpolymerization of CHO/PA/CO_2, well-defined poly(PA-*alt*-CHO)-*b*-PCHC was produced with CTPB/TEB = 1/0.5, while truly random copolymer (EE/EC/CC = 24/50/26) was obtained with CTPB/TEB = 1/1.5. The structures and properties of block and random copolymers were verified by ^1H NMR, ^{13}C NMR, DOSY, GPC, and DSC. However, in the cases of PO/DGA/CO_2, PO/SA/CO_2, and CHO/DGA/CO_2 terpolymerizations, only block copolymers were afforded despite the ratios of CTPB/TEB in the range of 1/2 to 1/5. In summary, CTPB/TEB was highly efficient to control chemoselective terpolymerization of epoxide/anhydride/CO_2, and a large family of poly(ester-carbonate) copolymers with diverse sequences and compositions were successfully synthesized.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/prechem.4c00062.

Experimental section, additional polymerization results, NMR spectra, GPC, MALDI-TOF MS, and DSC analyses of polymer materials (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (2021YFA1501600), the National Natural Science Foundation of China (22031005), and the Ministry of Education of the People's Republic of China.

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