CO₂ Deprotection-Mediated Switchable Polymerization for Precise Construction of Block Copolymers

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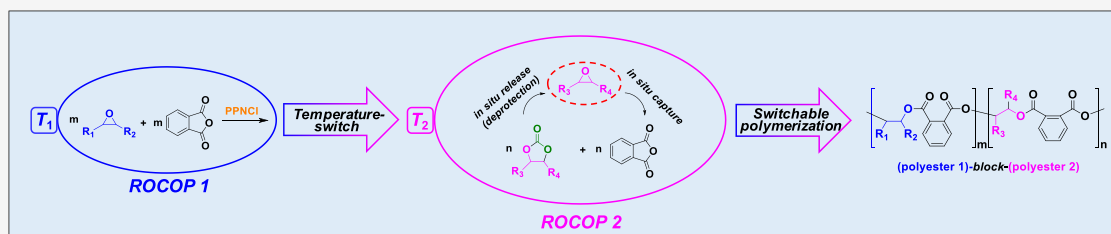
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ABSTRACT: A significant challenge in block copolymers (BCP) synthesis is to precisely control the block sequence and customize the composition and structure of target products from monomer mixtures. Herein, we reported a facile temperature-programmed switchable strategy based on deprotection chemistry of CO_2, enabling precise construction of BCPs. The proposed pattern was achieved via temperature-triggered switchable terpolymerization of epoxides/five-membered cyclic carbonates/cyclic anhydrides based on the protection and deprotection chemistry of CO_2. The chemoprotection of epoxides into cyclic carbonates and subsequent deprotection of cyclic carbonates into epoxides played a crucial role in the whole process. On the one hand, the low ring tension of five-membered cyclic carbonates resulted in vast temperature gaps between the copolymerization of epoxides/cyclic anhydrides and cyclic carbonates/cyclic anhydrides. Consequently, a facile control over the temperature-programmed parameter could direct the copolymerization cycles from epoxides/cyclic anhydrides (giving the first block at 110 °C) to cyclic carbonates/cyclic anhydrides (yielding the second block at 180 °C), thus ensuring precise fabrication of BCPs. Moreover, this protocol was significantly effective in extending the diversity of structures and properties of blocky polyesters by selecting distinct epoxide/cyclic carbonate combinations on demand.

INTRODUCTION

Block copolymers (BCPs), constructed by linking discrete homopolymer segments into block architectures,[1] represent an important class of hybrid macromolecules in polymer science. Benefiting from the tunable physicochemical properties, BCPs have found widespread applications in thermoplastic elastomers,[2−4] phase compatibilizers,[5,6] polymer electrolytes,[7,8] biomedical fields,[9,10] and so forth. Over the past decades, tremendous progress has been achieved toward BCP construction based on various living/controlled polymerization mechanisms and synthetic methodologies.[11−27] Most commonly, the sequential monomer addition or the use of a premade macroinitiator[28−31] manifested as a vigorous approach and has been applied with success to a wide array of BCPs [Figure 1A(a)]. However, this method involves a somewhat tedious polymerization process since it requires strict stepwise addition of different monomers. Postpolymerization modification and coupling reactions[32−38] also contribute a lot to BCP production, while labor-intensive purification treatments of the prepolymers restrict its further applications. Intelligent polymerization routes appear to provide viable and advantageous alternatives to avert the aforementioned limitations.[39] In particular, the recently emerged switchable

or chemoselective catalysis exhibits fairly decent performance, for it allows the economic and efficient synthesis of sequence-controlled BCPs from monomer mixtures.[40]

Switchable catalysis refers to a unique process, in which polymerization reactions could be directed to different cycles in response to the mechanistic switch [Figure 1A(b)].[41] By the combination of ring-opening polymerization (ROP) and ring-opening copolymerization (ROCOP) of cyclic monomers, switchable catalysis has gained strong momentum in the domain of BCP preparation. Initially, these switch mechanisms fundamentally originate from the high chemoselectivity for one specific monomer in one-pot mixtures, that is, kinetic control or self-switch. For example, using a highly active β-diiminate ZnOAc complex, Coates and co-workers[42] pioneered self-switchable polymerization from epoxides/cyclic anhydrides/CO_2 mixtures to yield diblock copoly(ester carbonates) based
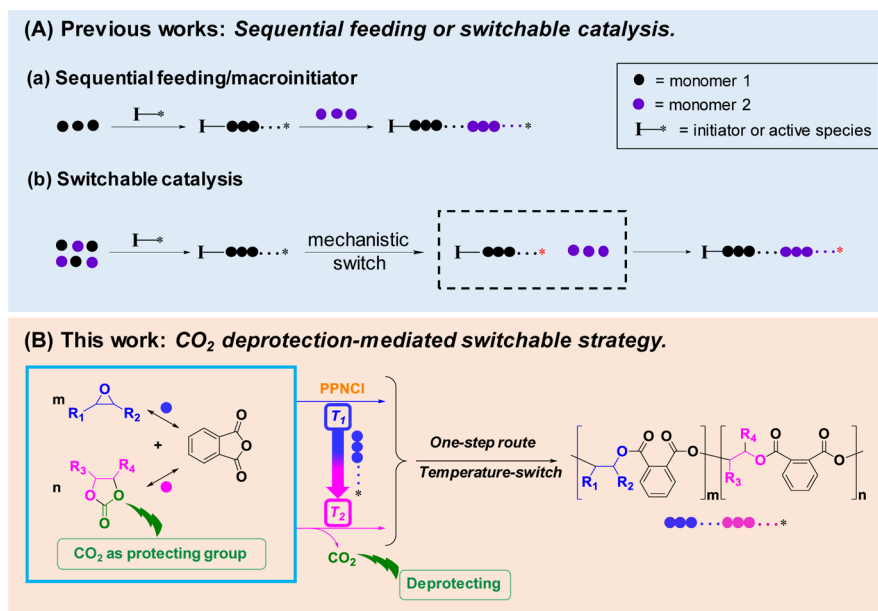
Figure 1. Schematic illustration of the methods for BCP construction. (A) Sequential feeding route and switchable catalysis in previous works. (B) CO_2 deprotection-mediated switchable strategy in this work.

on the much faster insertion of cyclic anhydride to zinc alkoxide intermediate than the insertion of CO_2. Subsequently, Williams and co-workers[43] demonstrated a dizinc complex-catalyzed selective polymerization from lactone/epoxide/anhydride mixtures, whereby the Zn−O active center preferred epoxide/anhydride ROCOP to lactone ROP. The groups of Darensbourg,[44] Nozaki,[45] Rieger,[46] Li,[47−49] Lu,[50] and Wang[51] et al. also delivered excellent reports on enriching the self-switchable catalysis strategies. These remarkable studies have opened avenues toward switchable catalytic polymerization to prepare BCPs in an efficient way. However, it must be noteworthy that there must exist enough kinetic gap in monomer mixtures for self-switchable approaches,[40,52] thereby strictly limiting the scope of available substrates and polymer structures. Gratifyingly, stimuli-triggered switchable catalysis guided another innovative route to diversifying the monomer candidates and BCP structures. In a general process of this method, a mechanistic switch can be modulated by external fields[39] such as redox, electrochemical, or photochemical stimuli, thus leading to wider monomer applicability. For instance, Diaconescu and co-workers[53] employed a redox-switchable titanium catalyst to direct the synthesis of block polyesters from L-lactide (L-LA)/ε-caprolactone mixtures by in situ switching the catalyst from reduced to oxidized form toggled by redox agents. Byers and co-workers[54] reported an electrochemically switchable ROP of L-LA and cyclohexene oxide (CHO) to prepare poly(LA-b-CHO) BCPs, in which electrochemistry-mediated in situ transformation between formally iron(II) and iron(III) oxidation states of a bis-(imino)pyridine iron alkoxide complex explained its intriguing selectivity. Wang and co-workers[55] developed an oxygen-triggered switchable polymerization of vinyl monomers/CO_2/epoxides for the synthesis of copoly(olefin carbonates) based on the Co−C to Co−O bond transition in a (Salen)Co system. Stimuli-triggered switchable catalysis has been exactly demonstrated to be a productive method for multifarious BCP outputs from monomer mixtures.[41,56,57] However, additional implementation of external stimuli also makes this method

experimentally challenging. Accordingly, developing convenient and efficient switchable strategies for extensive BCP construction continues to be an appealing target.

To make progress in this direction, herein, a straightforward temperature-programmed switchable strategy based on the deprotection chemistry of CO_2, for the first time, is proposed to produce polyester-based BCPs from epoxide/carbonate/anhydride mixtures by organocatalysis (Figure 1B). As a proof-of-concept, for the representative CHO/propylene carbonate [PC, CO_2-protected propylene oxide (PO)]/phthalic anhydride (PA) system, poly(CHO-alt-PA)-b-poly(PO-alt-PA) BCPs can be facilely obtained by regulation of reaction temperature under the catalysis of a commercial organocatalyst bis(triphenylphosphine)iminium chloride (PPNCl). The key prime of this strategy lies in the initial CO_2 chemoprotection of reactive PO into temporarily inert PC, thereby leading to the exclusive formation of a poly(CHO-alt-PA) block at 110 °C from CHO/PC/PA mixtures. Interestingly, PO could be in situ released from PC after a handy thermal stimulus and immediately captured by PA to give poly(PO-alt-PA).[58] Therefore, after CHO was entirely consumed, a facile programmed switch of the reaction temperature from 110 to 180 °C enabled the fast and quantitative formation of diblock copolymers through the CO_2-deprotection chemistry of PC (release of PO). Moreover, the proportions and thermal properties of resultant BCPs could be well-regulated by accessible control over reaction time or initial feed ratios. Further universality investigations demonstrated that the backbone structures of diblock copolymers could be well-designed via the CO_2 deprotection-mediated switchable polymerization of various epoxide/cyclic carbonate/cyclic anhydride sets, thus offering a novel and practical synthetic methodology for BCP production.

■ RESULTS AND DISCUSSION

To demonstrate the feasibility of the CO_2 deprotection-mediated switchable strategy, an apparent kinetics study based on PPNCl-catalyzed ring-opening alternating copolymeriza-
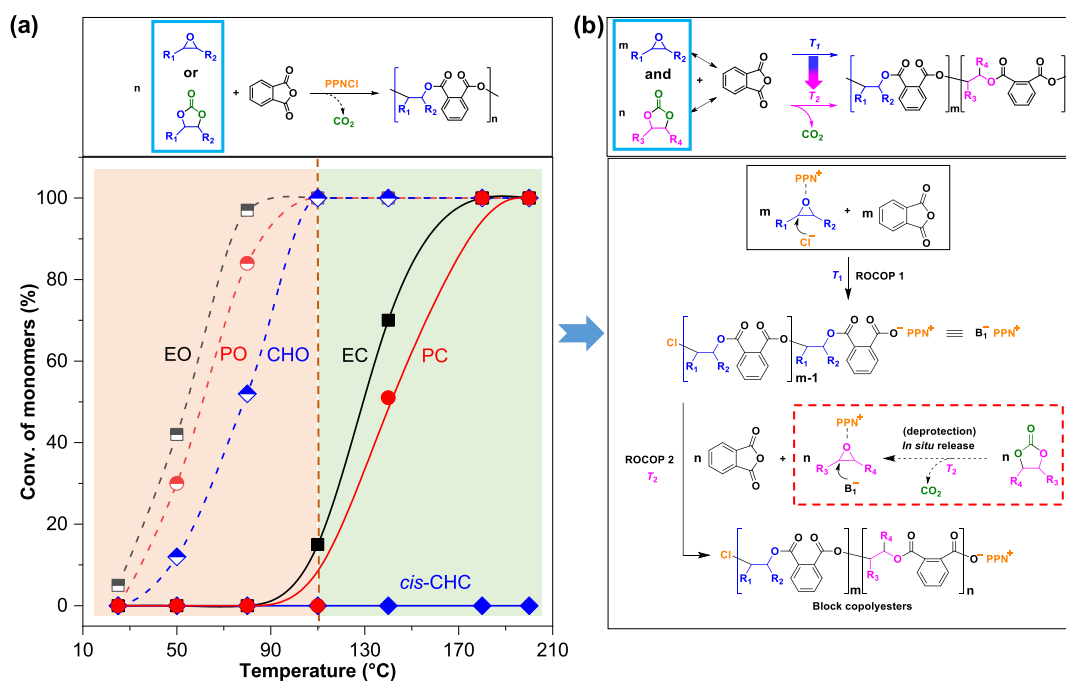
Figure 2. Outline of the proposed strategy to produce block polyesters. (a) Apparent reaction kinetics of various epoxide sources in the copolymerization with PA at different temperatures catalyzed by PPNCl. (b) Description of the general mechanism of CO_2 deprotection-mediated switchable terpolymerization for block polyester production.

Table 1. CO_2 Deprotection-Mediated Switchable Terpolymerization of CHO/PC/PA Catalyzed by PPNCl[a]
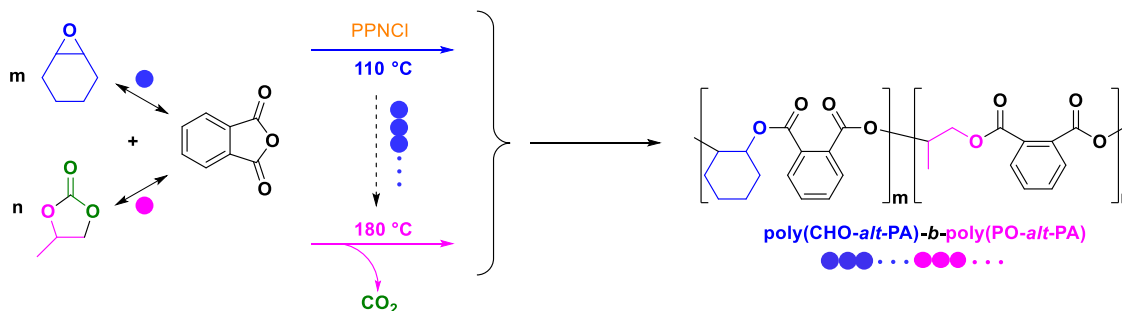
entry	temp (°C)	time (h)	conv. of CHO[b] (%)	conv. of PC[b] (%)	conv. of PA[b] (%)	m/n[c]	$M_{n,GPC}$[d] (kg mol^{-1})	$M_{n,theo}$[e] (kg mol^{-1})	Đ[d]
1	110	12	>99	0	54	1/0	9.7	49.2	1.28
2[f]	110 + 180	12 + 0	>99	19	60	1/0.19	10.2	11.2	1.35
3	110 + 180	12 + 0.10	>99	28	63	1/0.27	11.1	12.0	1.36
4	110 + 180	12 + 0.25	>99	44	74	1/0.47	13.2	13.3	1.39
5	110 + 180	12 + 0.5	>99	69	84	1/0.77	16.4	15.3	1.38
6	110 + 180	12 + 0.75	>99	91	97	1/0.96	17.5	17.1	1.45
7	110 + 180	12 + 1	>99	96	98	1/1	17.9	17.5	1.49
8	110 + 180	12 + 3	>99	>99	>99	1/1	18.2	17.8	1.59

[a]Conditions: [CHO]/[PC][PA]/[PPNCl] = 200/200/400/1, with 10 mmol PA, in bulk; the polymerization was first performed at 110 °C for 12 h in a predried 10 mL autoclave and then directly heated to 180 °C for a desired time. [b]Calculated by ^{1}H NMR of crude products. [c]Calculated by ^{1}H NMR of purified polymers on the basis of integral ratios of (CHO-*alt*-PA)/(PO-*alt*-PA) at 5.0−5.2 ppm and 4.2−4.5 ppm, respectively. [d]Determined by GPC in CH_2Cl_2 at 35 °C relative to polystyrene standard. [e]$M_{n,theo}$ was calibrated according to the equation $M_{n,theo} = M_{n,1} \times (1 + n_{0,PC}/n_{0,CHO} \times conv._{PC}/conv._{CHO} \times M_{PO-alt-PA}/M_{CHO-alt-PA})$; $M_{n,1}$ represents the MW of the first block determined by GPC. [f]The polymerization was quenched immediately once the temperature arrived at 180 °C in 20 min.

tion[59] (ROAC) of the representative epoxides [ethylene oxide (EO), PO, and CHO] or corresponding cyclic carbonates [ethylene carbonate (EC), PC, and *cis*-cyclohexene carbonate, *cis*-CHC) with PA was carried out (Table S1). Preliminary results demonstrated that the involved epoxides and cyclic carbonates shared the same polyester structures but with quite different reactivity in the copolymerization with PA (Figures

S1−S16). Notably, owing to the low tension of the five-membered rings, cyclic carbonates require a high temperature for in situ release of corresponding epoxides, thus naturally providing a gap toward conventional epoxides/PA copolymerizations (Figure 2a). As an illustrative example, at 110 °C, the PO/PA copolymerization displayed almost complete monomer conversion in 12 h (entry 7, Table S1), while PC
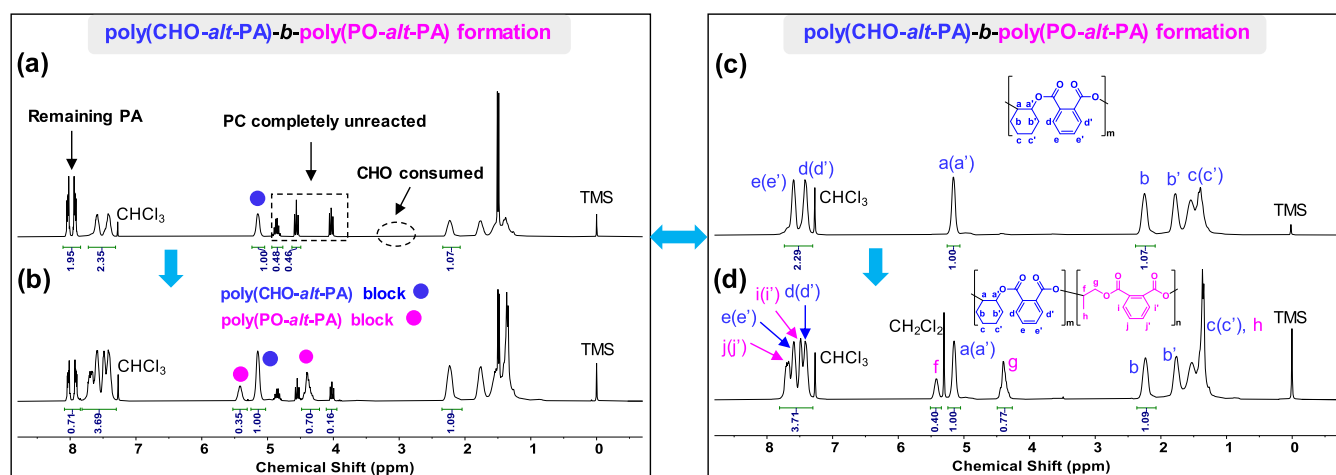
Figure 3. ^{1}H NMR spectra of products produced by CO_2 deprotection-mediated switchable terpolymerization of CHO/PC/PA. (a) 110 °C for 12 h (entry 1, Table 1). (b) 110 °C for 12 h and subsequent 180 °C for 0.75 h (entry 6, Table 1). (c) Purified poly(CHO-*alt*-PA) after stage I. (d) Purified poly(CHO-*alt*-PA)-*b*-poly(PO-*alt*-PA) after stage II.
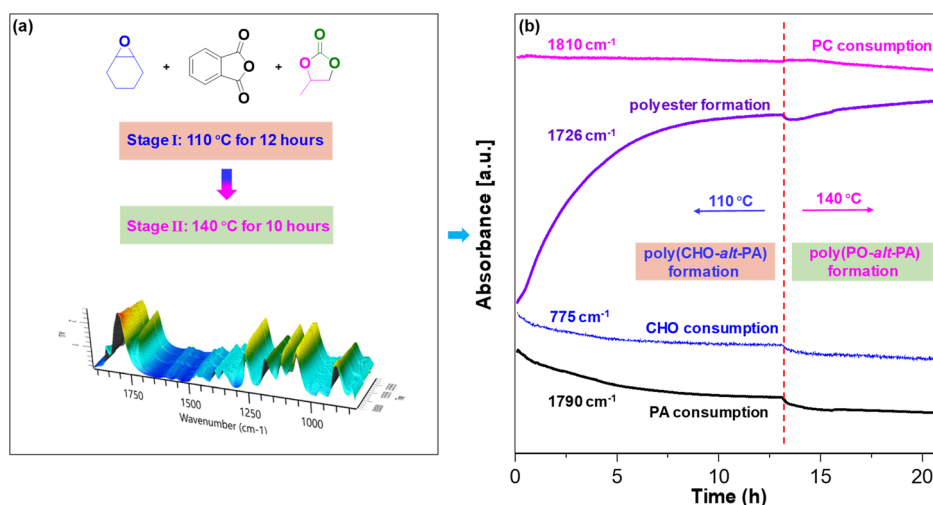

Figure 4. In situ ATR-IR analysis of the CHO/PC/PA copolymerization process through CO_2 deprotection-mediated switchable approach. (a) Three-dimensional stack plot of in situ ATR-IR. (b) In situ ATR-IR monitoring the consumption of CHO/PA at 110 °C for 12 h [stage I, poly(CHO-*alt*-PA) formation] and the consumption of PC/PA at 140 °C for 10 h [stage II, poly(CHO-*alt*-PA) formation]. Note: considering the upper-temperature limit of the instrument, the second copolymerization of PC/PA was carried out at 140 °C rather than 180 °C.

remained unreacted in this case (entries 15 and 16, Table S1). With an increase in temperature to above 140 °C, the PC/PA copolymerization proceeded smoothly to afford PO/PA alternating copolymers based on the mechanism of in situ release of CO_2 and PO (entries 17 and 18, Table S1). Accordingly, we could draw a preliminary conclusion that cyclic carbonates (such as EC and PC) could act as epoxide precursors to release epoxides on demand upon thermal stimulus for the potential synthesis of tailor-made BCPs.

On the basis of the foregoing findings, we tentatively proposed a temperature-programmed one-pot, one-step strategy for the synthesis of BCPs from epoxide/cyclic carbonate/cyclic anhydride mixtures (Figure 2b). When performed at the relative low temperature T_1, the PPNCl-catalyzed ring-opening copolymerization (ROCOP 1) of epoxide/PA exclusively gave the propagating block 1 (B_1^-). After the consumption of epoxide, elevating the temperature to T_2 would trigger the deprotection of cyclic carbonate into epoxide accompanied by decarboxylation, which was carefully discussed in our recent work[58] and other important

literature.[60] Then, B_1^- initiated ROCOP 2 of in situ released epoxide/PA proceeded to form the second block.

To guide the practical preparation of well-defined polyester-*b*-polyester BCPs through the above-mentioned strategy, a detailed investigation of the terpolymerization of CHO/PC/PA (molar ratio = 200/200/400/1) was conducted in priority. As shown in entry 1, Table 1 and Figure 3a,c, CHO was completely converted into alternating poly(CHO-*alt*-PA) with equimolar PA at 110 °C for 12 h (the first stage) without the participation of PC (Table S2 and Figures S17 and S18). Notably, the obtained M_n (9.7 kg mol^{-1}) was significantly lower than that of the theoretical value ($M_{n,theo}$ = 49.2 kg mol^{-1}), indicating the potential occurrence of chain transfer reactions derived from adventitious water or acids. Actually, this phenomenon was beneficial for the chain fidelity of subsequent PC/PA copolymer block by excluding these impurities. Upon elevating the temperature to 180 °C, an obvious increase of pressure from the autoclave gauge was observed, suggesting the proceeding of PC/PA copolymerization caused by PC decarboxylation (entries 2−8, Table 1). The

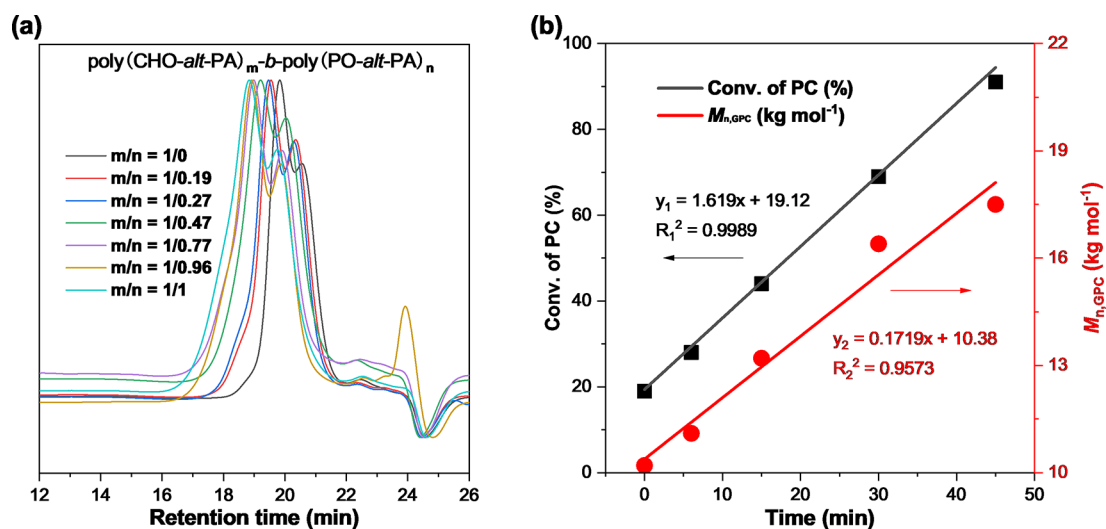**Figure 5.** GPC analysis of the resultant block polyesters. (a) GPC traces. (b) Determined MW and PC conversion versus reaction time at stage II.

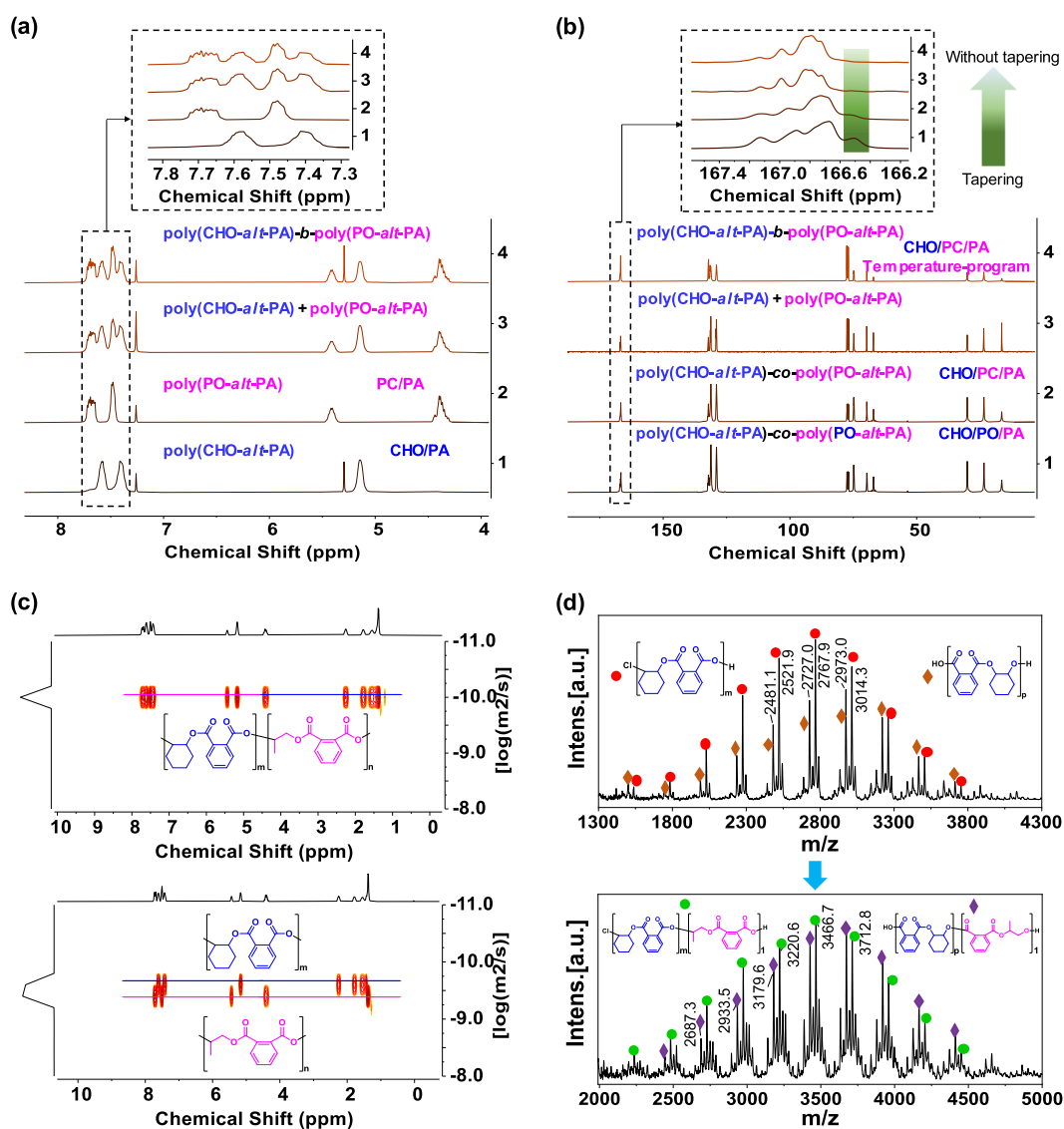**Figure 6.** Structural characterization of block polyesters produced by CO_2 deprotection-mediated switchable terpolymerization of CHO/PC/PA. (a) ^1H NMR spectra. (b) ^{13}C NMR spectra. (c) ^1H DOSY NMR spectra. (d) MALDI-TOF MS spectra.
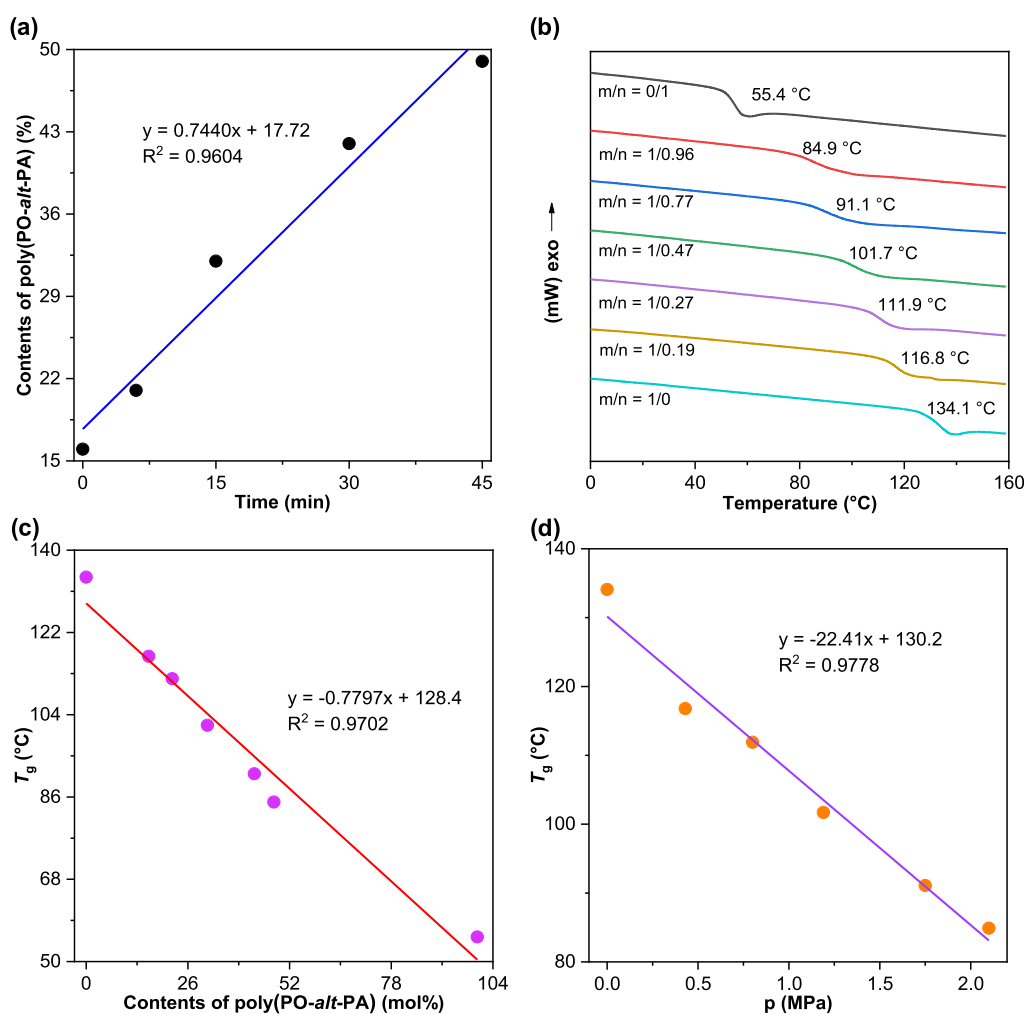
Figure 7. Control over the compositions and thermal properties of the copolymers via reaction time variations with $[CHO]/[PC]/[PA]/[PPNCl]$ = 200/200/400/1. (a) Plot of the contents of poly(PO-*alt*-PA) block versus reaction time. (b) DSC curves of copolymers with various contents of poly(PO-*alt*-PA) block. (c) Plot of T_g versus the contents of poly(PO-*alt*-PA) block. (d) Plot of T_g versus the generated CO_2 pressure. Note: *m/n* in Figure 7b corresponds to the molar ratio of poly(CHO-*alt*-PA)/poly(PO-*alt*-PA).

^{1}H NMR results confirmed the successful formation of the second block poly(PO-*alt*-PA) owing to the in situ capture of PO by PA (Figures 3b,d and S19). More importantly, the M_n of the diblock copolymers agreed well with the theoretical value, indicating good controllability. To further demonstrate the superiority of the strategy, control experiments for the terpolymerization of CHO/PO/PA at 50−110 °C and CHO/PC/PA directly at 140−180 °C (Table S3 and Figures S20−S28) resulted in random copolymers with tapering structures (Figure S27). These results exactly revealed the peculiarity of the proposed CO_2 deprotection-mediated switchable strategy for precise fabrication of block polyesters from (co)monomer mixtures.

To provide clear evidence supporting the definite pathways of BCP formation, the whole terpolymerization was monitored by in situ attenuated total reflectance infrared spectroscopy (in situ ATR-IR) analysis (Figure 4). The gradually decreased PA resonance at 1790 cm^{-1}, the newly emerging polyester poly(CHO-*alt*-PA) signal at 1726 cm^{-1}, as well as the unchanged PC signal (1810 cm^{-1}) demonstrated the exclusive ROAC of CHO/PA. Upon temperature-programming to 140 °C, the PC resonance (1810 cm^{-1}) began to drop and the polyester resonance continued to enhance, which suggested

the formation of a second poly(PO-*alt*-PA) block from PC/PA accompanied by a gradual pressure generation through PC decarboxylation.

Analysis of the resultant polymers by gel permeation chromatography (GPC) should be taken into account for its significance to comprehend the BCP formation intuitively.[41] Though displaying bimodal distributions of the first block, the GPC curves shifted to the higher-molecular-weight (MW) region after subsequent polymerization of PC/PA while maintaining consistent MW distribution (Figure 5a), again excluding the effect of chain transfer on the second stage. Furthermore, both MW (M_n) and PC conversion exhibited linear relationships with the reaction time for stage II at 180 °C, which indicated the controlled propagation of the second block (Figure 5b). Considering the consumption of adventitious impurities in stage I, the theoretical MW ($M_{n,theo}$) was reasonably calibrated (see Figure S29) according to the equation $M_{n,theo} = M_{n,1} \times (1 + n_{0,PC}/n_{0,CHO} \times \text{conv.}_{PC}/\text{conv.}_{CHO} \times M_{PO\text{-}alt\text{-}PA}/M_{CHO\text{-}alt\text{-}PA})$, where $M_{n,1}$ represents the experimental MWs of the first block determined by GPC, $M_{PO\text{-}alt\text{-}PA}$ = 206.2 g mol^{-1}, and $M_{CHO\text{-}alt\text{-}PA}$ = 246.2 g mol^{-1}. All of the above results demonstrated that CO_2 deprotection-mediated switchable terpolymerization of CHO/PC/PA was
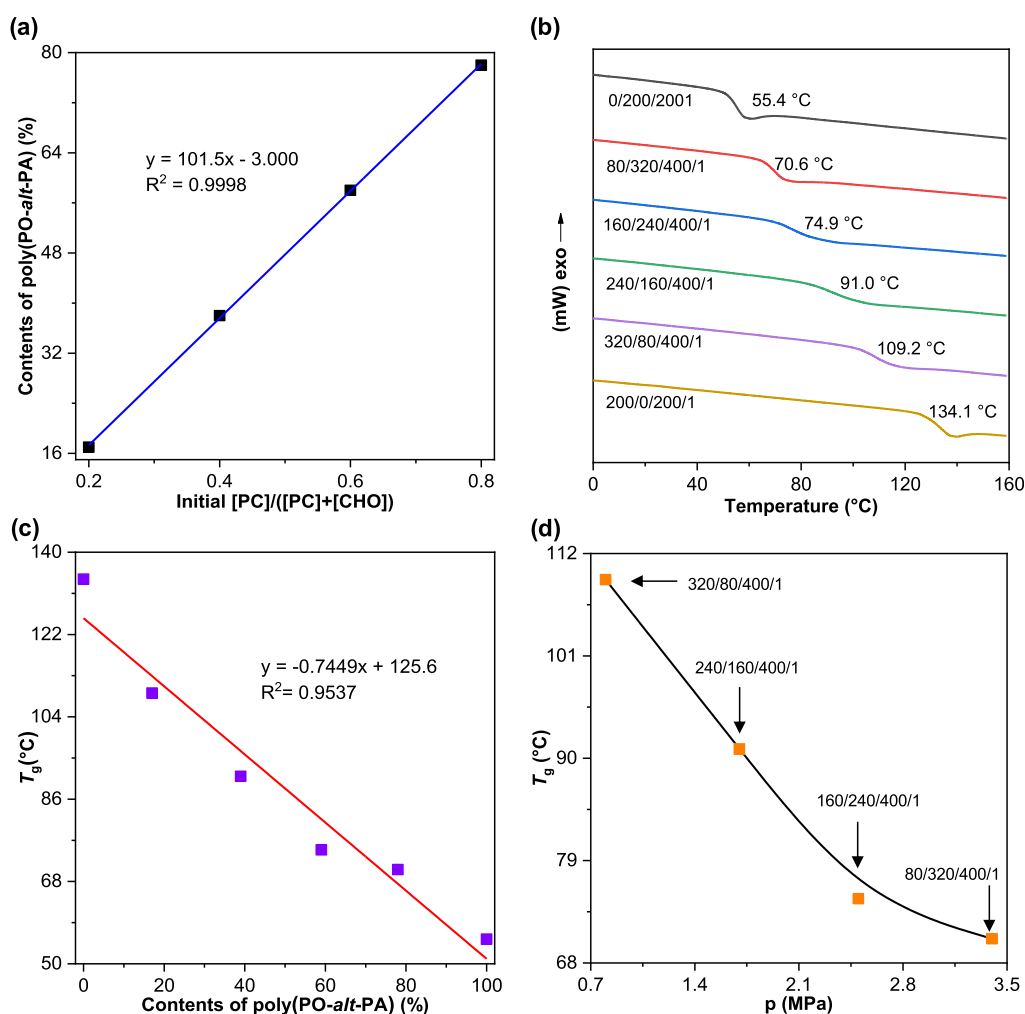
Figure 8. Control over the compositions and thermal properties of the poly(CHO-*alt*-PA)-*b*-poly(PO-*alt*-PA) diblock copolymers via initial feed ratio variations. (a) Plot of the contents of poly(PO-*alt*-PA) block versus initial molar ratios of [PC]/([PC] + [CHO]). (b) DSC curves of copolymers with various contents of poly(PO-*alt*-PA) block. (c) Plot of T_g versus the contents of poly(PO-*alt*-PA) block. (d) Plot of T_g versus the generated CO_2 pressure. Note: the ratios in Figure 8b,d correspond to [CHO]/[PC]/[PA]/[PPNCl].

an efficient and well-controlled approach to prepare block polyesters.

To further confirm the AB diblock polyester structure, we performed rigorous examinations of the aliquots by a combination of ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, ^{1}H diffusion-ordered spectroscopy NMR (^{1}H DOSY NMR), and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). As shown in the ^{1}H NMR spectra (Figure 6a), poly(CHO-*alt*-PA)-*b*-poly(PO-*alt*-PA) (entry 6, Table 1) exhibited typical proton signals corresponding to the respective blocks (entries 11, 18, Table S1). Furthermore, it was quite clear that the contour shape of characteristic peaks (especially in 7.3−7.8 ppm) for poly(CHO-*alt*-PA)-*b*-poly(CHO-*alt*-PA) was exactly the stacking of the two blocks without any interference, similar to the blends of two blocks, demonstrating the formation of diblock copolymers. In contrast, the random terpolymers of CHO/PO/PA displayed significant signal merging in the 7.3−7.8 ppm region (Figure S27). Similarly, ^{13}C NMR spectra (166.6−167.2 ppm, carbonyl carbon) further indicated the formation of a diblock structure from the well-separated carbon signals, which is distinct from the random copolymers (Figure 6b). Moreover, the nonexistence of the tapering structure

(continuous PO-PA-CHO) signal at 166.4−166.6 ppm suggested a negligible transesterification side reaction. Additionally, the ^{1}H DOSY NMR spectrum of poly(CHO-*alt*-PA)-*b*-poly(PO-*alt*-PA) only displayed a single diffusion coefficient for the observed signals, while there were two different diffusion coefficients for a blend of poly(CHO-*alt*-PA) and poly(PO-*alt*-PA), thus confirming the presence of only one polymer species for the former (Figure 6c). The resultant polymers were also analyzed by employing MALDI-TOF MS technology, which was helpful to identify the end groups and repeating units. The spectrum of initial block poly(CHO-*alt*-PA) revealed the coexistence of the −Cl chain end and the −OH chain end (top of Figure 6d), which were fairly regarded to come from PPNCl- and H_2O-initiated polymerization, respectively. This result also gave specific explanations for the bimodal distributions, as already noted in the section on GPC analysis. Satisfactorily, relatively exclusive synthesis of hydroxyl-terminated BCPs could be achieved by applying phosphazene base (^{t}Bu-P$_4$)/1,4-benzenedimethanol as the catalyst or using terephthalic acid as the chain transfer agent, as demonstrated by GPC and MALDI-TOF MS analyses (Figures S30 and S31). Turning up the temperature "switch" to a higher level naturally triggered the successive insertion of (PO-*alt*-PA)

Scheme 1. Libraries of Epoxides/Cyclic Carbonates/Cyclic Anhydrides for CO_2 Deprotection-Mediated Switchable Terpolymerization to Produce Block Polyesters
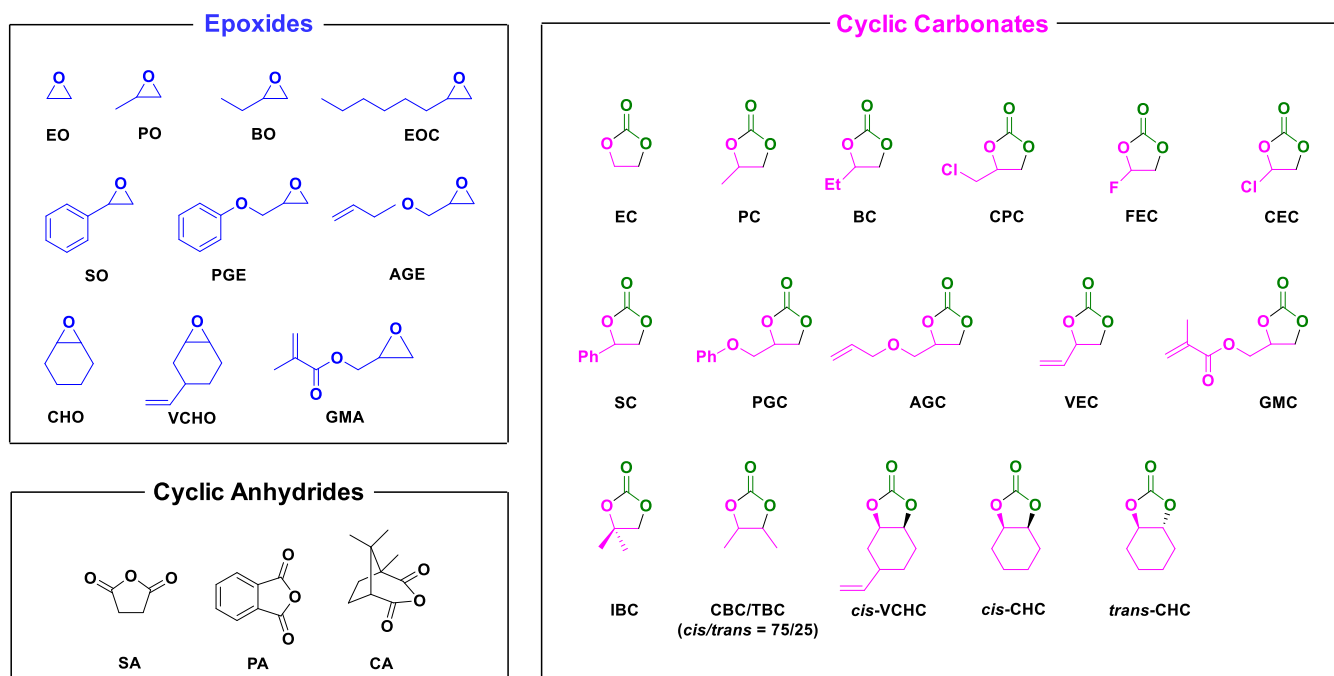

linkages (bottom of Figure 6d). Accordingly, well-defined diblock polyesters could be obtained without detectable side reactions through CO_2 deprotection-mediated switchable terpolymerization of CHO/PC/PA.

With an aim of screening out the optimal conditions, terpolymerizations were also conducted under different atmospheres and with different feed ratios. Generally, the M_n of targeted polymers showed a sharp increase when raising the feed ratios (Table S4, Figures S32, and S33), while there were a handful of differences in the compositions of the products (Figures S34 and S35). For example, with the initial feed ratio of [CHO]/[PC][PA]/[PPNCl] = 500/500/1000/1, the formation of ether linkages owing to CHO homopolymerization was observed (entries 5, 6, Table S4 and Figure S35). Besides, excessive PC was unfavorable despite its acceleration of polymerization, for an evident reduction in MW (from 17.5 to 13.6 kg mol^{-1}) was discovered and the remaining PC would cause "auxiliary waste" (entries 4, 8, Table S4). Accordingly, in order to acquire pure block structures, the subsequent polymerizations were conducted with equimolar mixtures of CHO/PC/PA and 0.25 mol % PPNCl loading.

To realize the precise control over the compositions of the BCPs (such as relative contents of each unit) and probe their influence on the thermal properties, we turned to prepare a range of poly(CHO-*alt*-PA)-*b*-poly(PO-*alt*-PA) through accessible variations of reaction time of the second stage. As illustrated in Figure 7a, relative contents of the second block poly(PO-*alt*-PA) presented an approximatively linear increase versus reaction time with the initial feed ratio of 200/200/400/1 (Table 1), indicating the quantitative growth. This behavior should be attributed to the controllable reaction kinetics of PC/PA ROAC as previously reported.[58] Preliminary assessments of the obtained BCPs' thermal properties showed that only a single glass transition temperature (T_g) existed on the differential scanning calorimeter (DSC) curves for all polymers (Figure 7b), while a blend of their homopolymers

displayed two identical T_g values ($T_{g,1}$ of 60.1 °C; $T_{g,2}$ of 137.8 °C) to their discrete blocks (Figure S36). These results possibly implied the inapparent microphase separation of the BCPs' two segments for their compatible structures[61] and provided another supplementary proof for the exclusive formation of BCPs. Notably, the T_g could be tunable spanning from 55.4 to 134.1 °C and exhibited a linear relationship with the poly(PO-*alt*-PA) contents (Figure 7c). Considering that CO_2 was promptly released during PC/PA ROAC, the generated pressure could serve as a visualized parameter to monitor the degree of polymerization, the compositions, and even the properties of BCPs (Table S5). As shown in Figure 7d, T_g displayed an almost linear correlation with the CO_2 pressure, thereby providing a reliable and practical protocol to direct the on-demand BCP synthesis. Additionally, thermogravimetric analysis revealed that the initial thermal decomposition temperatures ($T_{d,5\%}$) of all obtained polyesters including homopolymers, BCPs, and random copolymers were stable at 300−320 °C with small fluctuations (Figure S37), and there was a slight increase in $T_{d,5\%}$ with more poly(PO-*alt*-PA) block incorporating into BCPs (Figure S38).

Another route to manage the contents of each block to a greater extent relied on adjusting the feed ratio of [CHO]/[PC]. For this purpose, we carried out the terpolymerizations with the feed ratio of [CHO]/[PC]/[PA]/[PPNCl] varying from 320/80/400/1 to 80/320/400/1 (Tables S6 and S7). First, to prevent the probable chain scrambling if CHO/PC coexisted at 180 °C, complete consumption of CHO at 110 °C was essential to assure the entire formation of the first block poly(CHO-*alt*-PA) by selecting an appropriate reaction time (Table S6). More than 96% of CHO was found to be integrated into the first block poly(CHO-*alt*-PA) after 12 h for all experimental groups. Through raising the temperature to 180 °C, a rapid PC/PA copolymerization (within 1 h) was observed, thus constituting the second block with specified compositions (Table S7 and Figures S39−S43). It was

Table 2. CO₂ Deprotection-Mediated Switchable Terpolymerization of Epoxides/PC/PA by Changing the Epoxides[a]
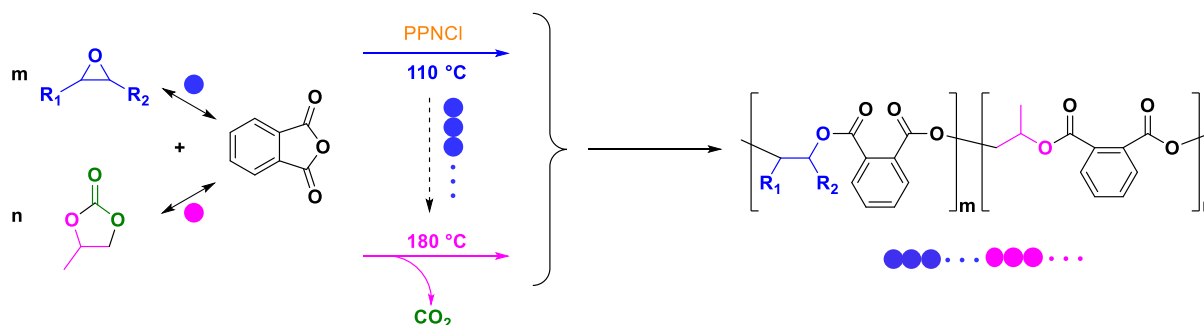
entry	(co)monomers	temp (°C)	time (h)	conv. of epoxides[b] (%)	conv. of PC[b] (%)	conv. of PA[b] (%)	m/n[c]	$M_{n,GPC}$[d] (kg mol^{-1})	$M_{n,theo}$[e] (kg mol^{-1})	$Đ$[d]
1	EO/PC/PA	80	20	94	0	48	1/0	9.4	36.1	1.36
2	EO/PC/PA	80 + 180	20 + 0.75	>99	48	77	1/0.44	15.6	14.6	1.36
3	AGE/PC/PA	110	8	94	0	51	1/0	10.5	49.3	1.20
4	AGE/PC/PA	110 + 180	8 + 0.75	>99	49	75	1/0.46	17.6	14.8	1.36
5	BO/PC/PA	110	8	>99	0	53	1/0	12.4	44.0	1.18
6	BO/PC/PA	110 + 180	8 + 0.75	>99	52	76	1/0.43	22.9	18.4	1.31
7	EOC/PC/PA	110	8	92	0	46	1/0	16.0	50.8	1.20
8	EOC/PC/PA	110 + 180	8 + 0.75	>99	72	86	1/0.72	34.1	25.3	1.48
9	VCHO/PC/PA	110	8	>99	0	49	1/0	18.3	54.5	1.22
10	VCHO/PC/PA	110 + 180	8 + 0.75	>99	65	82	1/0.77	37.5	27.3	1.72
11	PGE/PC/PA	110	12	>99	0	54	1/0	15.8	59.7	1.28
12	PGE/PC/PA	110 + 180	12 + 0.75	>99	87	94	1/0.80	37.5	25.3	1.50

[a]Conditions: [epoxides]/[PC][PA]/[PPNCl] = 200/200/400/1, with 10 mmol PA, in bulk; the polymerization was first performed at 110 °C for sufficient time in a predried 10 mL autoclave and then directly heated to 180 °C for a desired time. [b]Calculated by ¹H NMR of crude products. [c]Calculated by ¹H NMR of purified polymers on the basis of the internal ratios of respective characteristic peaks. [d]Determined by GPC in CH₂Cl₂ at 35 °C relative to polystyrene standard. [e]$M_{n,theo}$ was calibrated according to the equation $M_{n,theo} = M_{n,1} \times (1 + n_{0,PC}/n_{0,CHO} \times \mathrm{conv._{PC}}/\mathrm{conv._{CHO}} \times M_{PO\text{-}alt\text{-}PA}/M_{CHO\text{-}alt\text{-}PA})$; $M_{n,1}$ represents the MW of the first block determined by GPC.

noteworthy that the linear relationship of block constitution between experimental and theoretical values demonstrated good control of diblock copolymer architecture through monomer ratios (Figure 8a). Especially for [CHO]/[PC]/[PA]/[PPNCl] of 80/320/400/1, custom-tailored BCPs with a wide architecture control could be achieved via careful regulation of the length of second block (Table S8 and Figures S44–S46). DSC results of the samples with various initial feed ratios also gave a single T_g (Figure 8b), similar to those obtained through reaction time variations (Figure 7b). Likewise, the T_g of these samples matched well with the compositions of polymers and the released CO₂ pressure (Figure 8c,d and Table S9). Accordingly, BCPs with customized compositions and properties could be synthesized through facile control over initial feedings, the reaction time, as well as the smart "temperature parameter."

To demonstrate the generality of the proposed strategy of CO₂ deprotection-mediated switchable terpolymerization, different sets of epoxides/cyclic carbonates/cyclic anhydrides were explored. Considering the ready availability of epoxide comonomers and their satisfactory reactivity in the PPNCl-catalyzed copolymerization with PA (Table S10 and Figures S47–S60), initial efforts were directed to varying the epoxide types for the terpolymerization (the upper left of Scheme 1) to give various first blocks. As displayed in Table 2, in the switchable terpolymerization of epoxides/PC/PA, extensive variations of epoxides afforded BCPs with a wide variety of first blocks. The well-defined ¹H NMR spectra and the matching of experimental M_n with the theoretical value demonstrated the precise and quantitative synthesis of BCPs not only for alkyl or

phenyl-substituted epoxide systems such as EO, 1,2-butylene oxide (BO), 1,2-epoxyoctane (EOC), and phenyl glycidyl ether (PGE), but also for double-bond functional epoxides such as allyl glycidyl ether (AGE) and vinyl cyclohexene oxide (VCHO) (Figures S61–S72). Intriguingly, the present strategy showed high tolerance to the epoxides containing an unactivated double bond. For example, AGE-based temperature-programmed AGE/PC/PA terpolymerization produced poly(AGE-alt-PA)-b-poly(PO-alt-PA) with a relatively narrow Đ of 1.36 (entry 4, Table 2 and Figure S64), which indicated the negligible cross-linking and transesterification side reactions despite holding at 180 °C for 0.75 h. As a control, direct AGE/PA copolymerization (180 °C, 1 h) gave poly(AGE-alt-PA) with an extremely wide MW distribution (Đ = 5.50, entry 4, Table S10 and Figure S52). This result implied a possible protection of double bond by the poly(AGE-alt-PA) copolymer backbone compared with the AGE monomer. However, it should be stated that even using the present strategy, glycidyl methacrylate with the activated double bond could not achieve well-defined BCPs owing to the gelatinization via free radical cross-linking reactions.

Another route to diversifying the BCPs was expected to change the structures of cyclic carbonates (the right of Scheme 1). According to previous report,[62] cyclic carbonates with different structures can be synthesized nearly quantitatively through the epoxides/CO₂ cycloaddition reaction using commercial tetrabutylammonium bromide as the catalyst (Figures S73–S83). The detailed evaluation of the cyclic carbonates/PA copolymerization results indicated that the cyclic carbonate reactivity was remarkably associated with the

Table 3. CO$_2$ Deprotection-Mediated Switchable Terpolymerization of Epoxides/Cyclic Carbonates/PA by Simultaneous Changing Epoxides and Cyclic Carbonates[a]
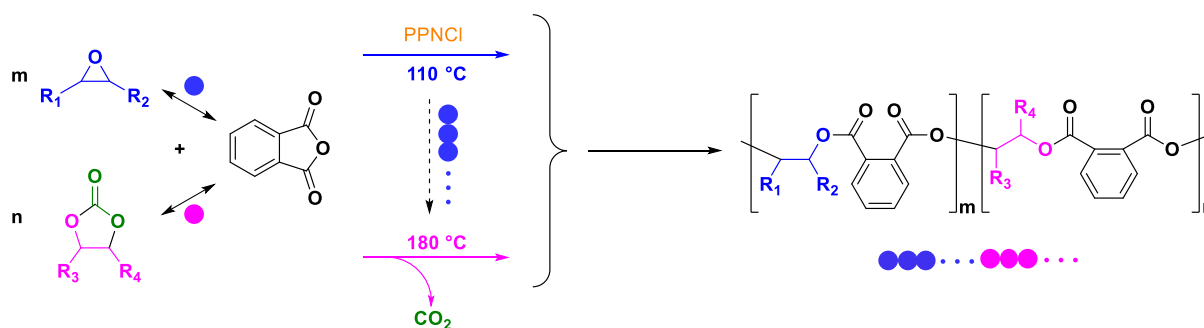
entry	(co)monomers	temp (°C)	time (h)	conv. of epoxides[b] (%)	conv. of carbonates[b] (%)	conv. of PA[b] (%)	m/n[c]	$M_{n,GPC}$[d] (kg mol⁻¹)	$M_{n,theo}$[e] (kg mol⁻¹)	Đ[d]
1	PO/AGC/PA	110	8	>99	0	51	1/0.02	13.6	41.2	1.26
2	PO/AGC/PA	110 + 180	8 + 0.50	>99	54	77	1/0.44	35.6	22.9	1.32
3	PO/SC/PA	110	8	>99	8	54	1/0.10	23.2	45.5	1.21
4	PO/SC/PA	110 + 180	8 + 0.17	>99	83	92	1/0.88	46.3	43.7	1.23
5	PO/PGC/PA	110	8	>99	0	55	1/0.08	17.5	41.2	1.23
6	PO/PGC/PA	110 + 180	8 + 0.17	>99	50	75	1/0.55	33.0	30.2	1.23
7	AGE/SC/PA	110	10	95	0	48	1/0	11.1	49.8	1.24
8	AGE/SC/PA	110 + 180	10 + 0.17	>99	52	77	1/0.56	19.4	17.3	1.32
9	AGE/PGC/PA	110	10	93	0	50	1/0.06	9.1	48.8	1.34
10	AGE/PGC/PA	110 + 180	10 + 0.17	>99	42	72	1/0.41	15.1	13.8	1.27
11	PGE/SC/PA	110	10	>99	0	50	1/0	17.5	59.7	1.29
12	PGE/SC/PA	110 + 180	10 + 0.08	>99	56	78	1/0.60	34.0	26.3	1.34
13	PGE/AGC/PA	110	10	92	0	50	1/0	13.0	54.9	1.34
14	PGE/AGC/PA	110 + 180	10 + 0.50	>99	41	74	1/0.34	32.3	18.1	1.42

[a]Conditions: [epoxides]/[cyclic carbonates][cyclic anhydrides]/[PPNCl] = 200/200/400/1, with 10 mmol PA, in bulk; the polymerization was first performed at 110 °C for sufficient time in a predried 10 mL autoclave and then directly heated to 180 °C for a desired time. [b]Calculated by ¹H NMR of crude products. [c]Calculated by ¹H NMR of purified polymers on the basis of the internal ratios of respective characteristic peaks. [d]Determined by GPC in CH$_2$Cl$_2$ at 35 °C relative to polystyrene standard. [e]$M_{n,theo}$ was calibrated according to the equation $M_{n,theo} = M_{n,1} \times (1 + n_{0,PC}/n_{0,CHO} \times conv._{PC}/conv._{CHO} \times M_{PO\text{-}alt\text{-}PA}/M_{CHO\text{-}alt\text{-}PA})$; $M_{n,1}$ represents the MW of the first block determined by GPC.

steric and electronic effect on the five-membered rings, displaying an order of nonsubstituted > monosubstituted > disubstituted (unreacted) (Table S11 and Figures S84−S93). Notably, the resulting cyclic carbonates/PA copolymers featured strictly a corresponding epoxide/PA alternating structure,[63] again demonstrating the advantage of "CO$_2$ protection-deprotection" approach.

To further demonstrate the universality of the present strategy, CO$_2$ deprotection-mediated switchable terpolymerizations involving simultaneous variations of epoxides/cyclic carbonates were conducted. As shown in Table 3 and Figures S94−S104, well-defined BCPs with distinct blocks derived from various epoxides and cyclic carbonates were synthesized, allowing the designed outputs of BCPs. It was remarkable that the synthesis sequences of the two blocks could be reversed through regulating the monomer feeding order. For example, to obtain the targeted BCPs, poly(AGE-alt-PA)-b-poly(PO-alt-PA), the synthetic way of AGE/PA/PC terpolymerization (Figure S63) was identical to that of PO/PA/AGC (AGE-based cyclic carbonate) by ingeniously regulating epoxide and cyclic carbonate types (entry 2, Table 3 and Figure S94). This finding not only expanded the synthetic methods for the desired BCPs but also provided an alternative way when one of the polymerization systems was out of operation. For instance, in the terpolymerization of styrene oxide (SO)/PC/PA, the in situ formed first block poly(SO-alt-PA) could not initiate the copolymerization of PC/PA (Figures S95 and S96), which was

presumably attributed to the influence of phenylacetaldehyde formed by the isomerization of SO (Figure S97).[64] By comparison, the terpolymerization of PO/PA/styrene carbonate based on CO$_2$ deprotection strategy afforded well-defined diblock poly(PO-alt-PA)-b-poly(SO-alt-PA) with high MWs and narrow distribution (M_n = 46.3 kg mol⁻¹, Đ = 1.23) (entry 4, Table 3, Figures S98, and S104). Also, the EO/PC/PA terpolymerization system (entry 2, Table 2) could serve as an alternative for PO/EC/PA group, principally because EC was extremely active in EC/PA copolymerization, giving an undesired random or tapered backbone structure (entries 1−3, Table S12 and Figure S105). Attempts to change cyclic anhydrides (the lower left of Scheme 1) were also made, yet it encountered problems including either a certain degree of tapered area for active camphoric anhydride (CA) or the sluggish process for the weakly active succinic anhydride (Table S12 and Figures S105−S114).

On the basis of above-mentioned results, it was concluded that all participating comonomers, including epoxides, cyclic carbonates and cyclic anhydrides, were of great relevance to the precise and quantitative BCP construction by employing the CO$_2$ deprotection-mediated switchable strategy. Besides cyclic anhydrides, the structures of cyclic carbonates played decisive roles in maximum customization of the BCPs' composition and structure (Scheme 2). Cyclic carbonates without substituent such as EC normally gave an unwanted tapering BCP structure owing to the high activity, while

Scheme 2. Diagram Illustrating the Selective Principle of Cyclic Carbonates to Produce BCPs Through CO₂ Deprotection-Mediated Switchable Terpolymerization of Epoxides/Cyclic Carbonates/PA[a]
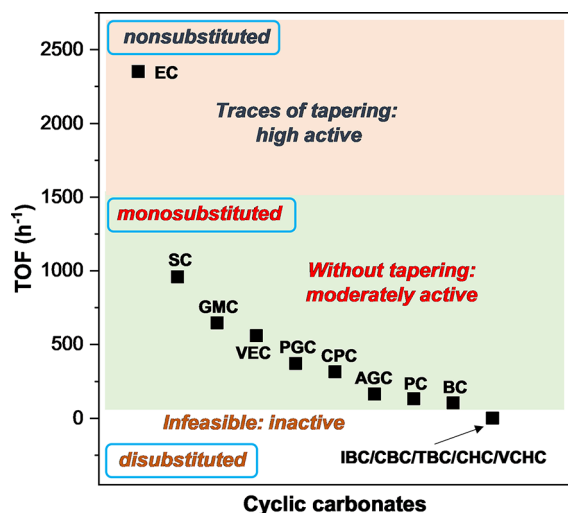
[a]Note: TOF refers to the turnover frequency of cyclic carbonates to alternating polyesters based on PPNCl in the copolymerization with PA, calculated from normalized integrals in the ^1H NMR spectra.

disubstituted cyclic carbonates were inapplicable to this system because of their deficient reactivity in the release of epoxides and subsequent copolymerization of epoxides/cyclic anhydrides, despite with more active CA or at higher temperature (Table S13 and Figures S115−S121). As moderately active cyclic carbonates, monosubstituted candidates not only proved the conceptual and practical feasibility of our proposed BCP construction in a controlled manner but also provided fruitful BCP production for their structural diversity.

CONCLUSIONS

In summary, we have reported a novel strategy of CO₂ deprotection-mediated switchable terpolymerization of epoxides/cyclic carbonates/cyclic anhydrides, allowing the precise and on-demand construction of block polyesters from monomer mixtures. The key premises of this strategy lied in the discovery that enormous temperature gaps existed between the epoxides and cyclic carbonates (i.e., CO₂-protected epoxides) in the copolymerization with cyclic anhydrides. Therefore, reaction temperature could operate as an "intelligent switch" to direct the copolymerization cycles to transform from epoxides/cyclic anhydrides ROAC at low temperature into cyclic carbonates/cyclic anhydrides ROAC at high temperature, affording block polyesters after one-shot feeding. Tapered microstructures were avoided due to the suppression of transesterification reactions, demonstrating the accurate fabrication of BCPs. Notably, the reaction progress, the compositions, and even the properties of BCPs could be closely in situ monitored by a pressure gauge. Therefore, CO₂ deprotection-mediated switchable approach not only provided a creative route to customized BCP fabrication but also opened avenues toward brand-new methodology programming preparation processes, product compositions, and properties for precise chemical synthesis in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c01812.

Details on materials and methods, experimental procedures, and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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