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Smart Access to Sequentially and Architecturally Controlled Block Polymers via a Simple Catalytic Polymerization System

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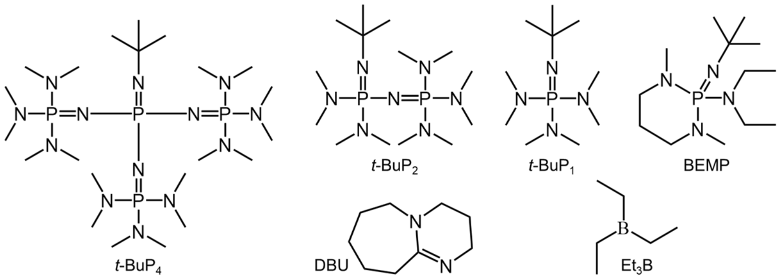
ABSTRACT: Self-switchable polymerization is an attractive strategy for precisely controlling the microstructures and monomer sequences of polymers. To date, catalysts for the polymerization are generally limited to metal complex catalysts and some organocatalysts. In this article, we report that simple, inexpensive, and environmentally benign alkali metal carboxylate catalysts smartly switch between the ring-opening alternating copolymerization of epoxides with cyclic anhydrides and the ring-opening polymerization of cyclic esters to create a single synthetic step and thus achieve sequence-controlled multiblock polyesters. This polymerization system shows extremely high effectiveness and versatility for different combinations of epoxides, cyclic anhydrides, cyclic esters, and initiators. As a result, various types of complex block copolymers, such as AB diblocks, BAB triblocks, star copolymers, hyperbranched copolymers, and CAB triblocks, can be simply prepared and postpolymerization modification can be performed. As a proof of concept, polyester-based elastomers and adhesives were successfully synthesized via one-step procedures by reasonably designing the monomer structures of triblock copolymers, showing great potential for industrial applications of polyesters.

Keywords: *block copolyesters; alkali metal carboxylate catalysts; ring-opening alternating copolymerization; ring-opening polymerization; switchable polymerization*

INTRODUCTION

Multiblock copolymers, combining two or more distinctly different block sequences, have found widespread uses in drug delivery, energy storage, lithography, and as self-healing materials because of unique properties and adjustable functionality that cannot be obtained from homopolymers or polymer blends.[1–4] The "self-switchable polymerization" is an attractive approach for synthesizing these types of polymers, because it allows the spontaneous and selective transformation of a monomer mixture into a sequence-controlled block copolymer,[5–11] thereby obviating complex procedures such as monomer addition, purification, and protection/deprotection reaction steps.[12,13] The realization of such a strategy requires a special catalyst that can smartly switch between different polymerization cycles. [5–11]

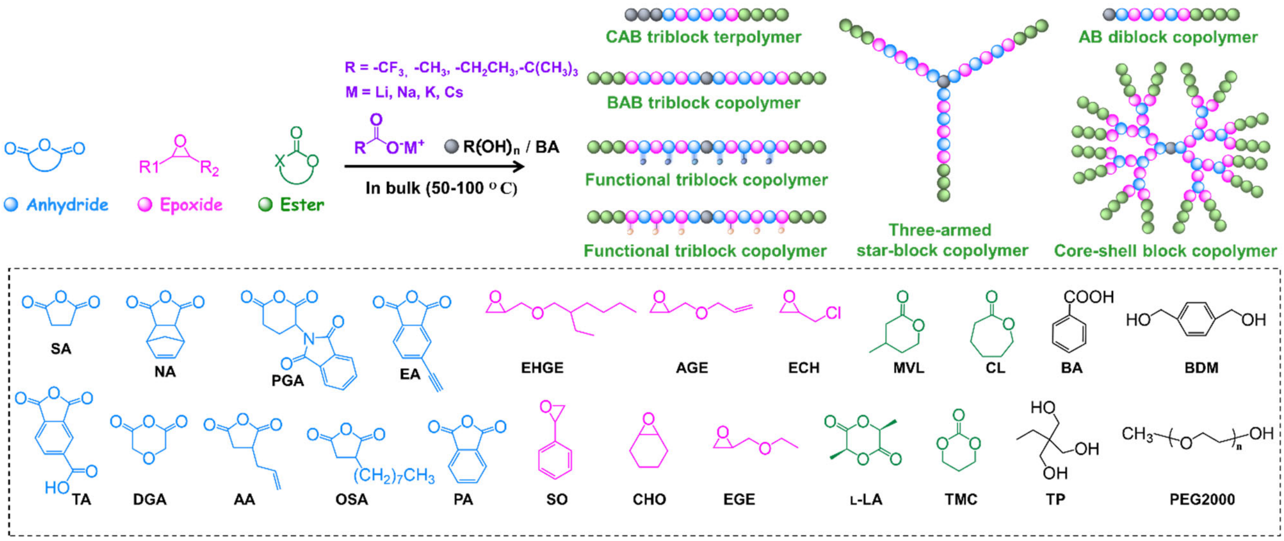
Scheme 1. The chemical structures of different organocatalysts.



In 2008, Coates et al. used a dizinc catalyst to spontaneously combine two ring-opening alternating copolymerization (ROAC) reactions for the one-step synthesis of $(AB)_n(CB)_m$ type block copolymers from mixtures of cyclic anhydrides (A), epoxides (B), and CO_2 (C).[14] In 2014, Williams and co-workers first proposed the "switch catalysis" concept that was subsequently proven to involve a single catalyst that switches it between at least two different mechanisms.[5,6,8–11] A series of switchable catalysts, including Zn-, Cr-, and Al-based catalysts, were developed by their team, and these catalysts were effective for the one-step synthesis of diverse block copolymers.[15–18] The self-switchable polymerization has been successfully applied to transition metal catalysts by other researchers.[19] Although the switchable catalysis leading activities remain with metal complex catalysts, the toxic metal residuals, to some extent, would limit their potential in food packing and biomedical devices. To address the concern of metal contaminants, organocatalysts have been developed in recent years and confirmed to show the potential to promote self-switchable polymerization. Strong phosphazene bases (e.g., t-BuP_4) can easily cause transesterification, etherification, and deprotonation.[20] Thus, relatively weak single and bicomponent catalysts were selected for the synthesis of different type block copolymers from mixtures of anhydrides and epoxides with or without cyclic esters via a one-step procedure (Scheme 1).[11,21–24] In particular, Li and Zhang reported the self-switchable catalysis by using t-BuP_1 and mixtures of anhydrides/epoxides/lactides to produce polyesters. Li also found that BEMP showed the same catalytic property as that of t-BuP_1.[11,21] However, N-heterocycles such as DBU showed significantly lower catalytic activity, and transesterification was also detected during the polymerization.[11] Organic Lewis pairs (t-BuP_2/Et_3B and t-BuP_1/Et_3B) were proven to spontaneously connect anhydrides/epoxides ROAC with ring-opening polymerizations (ROP) of epoxides to directly synthesize poly(ester-*b*-ether) block copolymers.[22,23] Although organocatalysts are simpler and more environmentally benign than transition metal complex catalysts, they tend to be less active even at a high temperature.[5,6,11,25] Furthermore, their strong basicity hinders the expansion of the synthetic scope for application and high production costs also limit their applicability for industrial multiblock copolyester synthesis.

To achieve a more feasible and versatile catalyst system, we recently focused on a series of alkali metal carboxylates, the most representative example being sodium acetate, which has been widely utilized as a food additive. From a practical point of view, alkali metal carboxylates are highly valuable catalysts for industrial polyester production because of their low cost, easy handling, low toxicity, and good stability. Besides, the acid/base characteristics of alkali metal carboxylates can be tuned by choosing appropriate carboxylate moieties and countercations. Such tunability provides a simple and effective strategy for controlled/living polymerization, and the great competence for the ROP of cyclic esters has been demonstrated in our previous works.[26,27] Although other small molecules, including the salts of inorganic and organic acids, bases, and amines, have been reported as catalysts or initiators for the ROAC of anhydrides and epoxides in the 1960s, the roles of these small molecules and the corresponding polymerization mechanisms are completely different from those in our catalytic system.[28,29] Very recently, alkali metal carboxylates have been used as initiators for anhydrides/epoxides ROAC, allowing the synthesis of polyesters with perfectly alternating structure and high molecular weight (>100 kDa), and two possible polymerization mechanisms (anionic polymerization and cooperative catalysis) were proposed.[30] However, the investigation about alkali metal carboxylate catalysts is still in the beginning state. Specifically, because alkali metal carboxylates were used as initiators, end group control is seriously limited, and the mechanism of anhydrides/epoxides ROAC in presence of alcohol initiators or carboxylic acid initiators was unable to be involved. So far, alkali metal carboxylates have been mainly used as catalysts for a single catalytic polymerization cycle such as ROAC of anhydrides/epoxides or ROP of

Scheme 2. Switchable polymerization of mixed anhydrides, epoxides, and cyclic esters with alkali metal carboxylates as catalysts and carboxylic acids/alcohols as initiators. The A, B, and C represent the alternating copolymer block, polyester block, and macro initiator, respectively.



esters but never used for the self-switchable polymerization, thus the switch catalysis properties of these catalysts are still unclear. To address these concerns, we developed a self-switchable polymerization system that bridges ROAC of anhydrides/epoxides and ROP of esters based on alkali metal carboxylate catalysts (Scheme 2) as a substitute for conventional procedures using transition metal complex catalysts and organocatalysts, and systematically studied the structure-activity relationships of these catalysts for such polymerization.[31–35] This self-switchable polymerization system (1) achieves green and highly controllable copolymerization using simple catalysts; (2) provides easy access to the synthesis of sequentially and architecturally controlled block polyesters; and (3) shows a great capability for expanding the synthetic scope to various functional monomers.[18,36] Further, we focused on the properties of the resultant copolymers and attempted to produce materials in a smart way for various applications such as elastomers and adhesives.

RESULTS AND DISCUSSION

ROAC by Alkali Metal Carboxylate Catalysts. First, we examined the ROAC of phthalic anhydride (PA) and ethyl glycidyl ether (EGE) in the bulk using cesium pivalate (t-BuCO$_2$Cs) as the catalyst and 1,4-benzenedimethanol (BDM) as the initiator at a [t-BuCO$_2$Cs]/[BDM]$_0$/[PA]$_0$/[EGE]$_0$ ratio of 1/2/50/250 and 100 °C (Table S1). Size-exclusion chromatography SEC and ^{1}H NMR analysis indicated that the product had a perfect alternating sequence distribution with a narrow polydispersity ($Đ = 1.06$), and the NMR-based molecular weight ($M_{\mathrm{n,NMR}}$ = 6.0 kDa) were similar to the theoretical value ($M_{\mathrm{n,th}}$ = 6.1 kDa) (entry 4 in Table S1, Figures S1 – S3). The ROAC of PA and EGE followed zero-order kinetics (Figure S4), and the $M_{\mathrm{n,NMR}}$ values of the resultant product (P(PA-*alt*-EGE)) showed a linear correlation with PA conversion (Figure S5). To confirm the living polymerization behavior of the catalytic system, 25 equiv of PA was introduced after PA was fully consumed (at 1.5 h). The addition of PA immediately restarted the propagation from the terminus of P(PA-*alt*-EGE), as evidenced by NMR spectroscopy (Figures S6 and S7). When the ROAC of PA and EGE was prolonged to 6 h, the conversion of EGE remained unchanged, even after the complete consumption of PA, indicating that the self-propagation of

EGE was well suppressed (Figure S8). The MALDI-TOF MS spectrum showed two major mass populations (Figure 1). The dominant mass population corresponded to P(PA-*alt*-EGE) initiated from

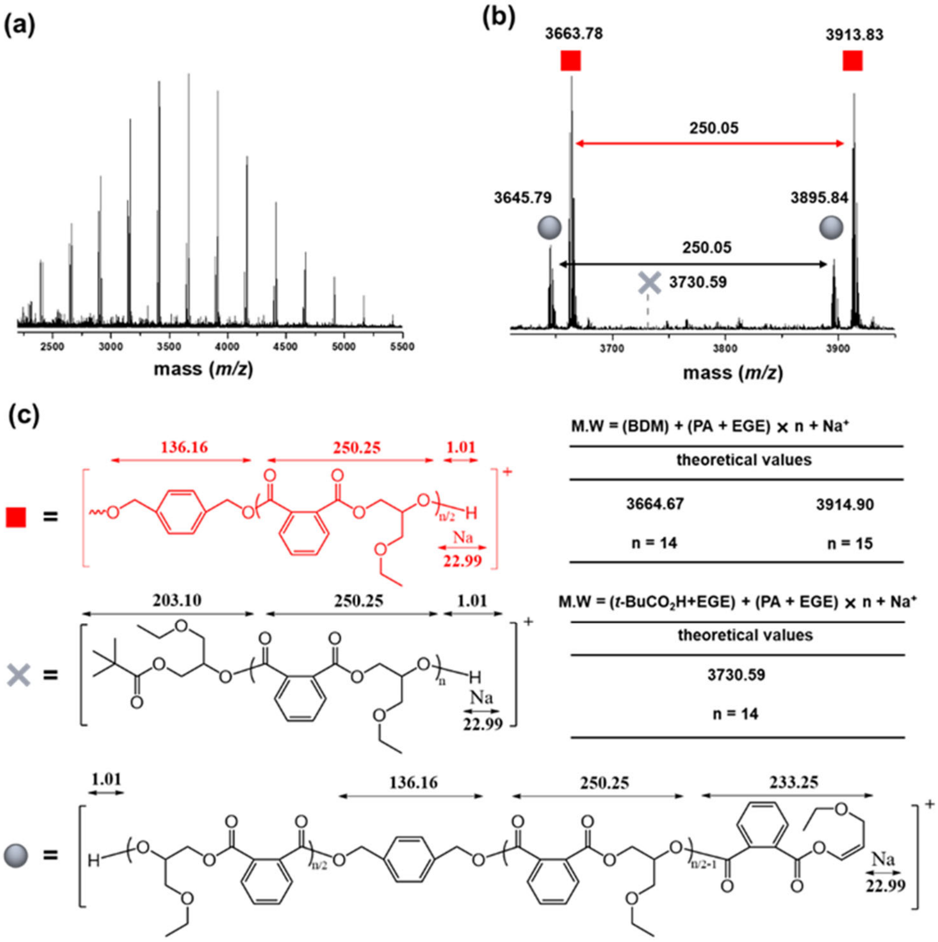


Figure 1. (a) MALDI TOF-MS spectrum of the P(PA-*alt*-EGE) from entry 1 in Table S2, (b) expanded spectrum in the *m/z* 3610–3950 range, and (c) expected structures and theoretical molecular weights of P(PA-*alt*-EGE).

BDM. In contrast, the minor mass population was due to P(PA-*alt*-EGE) with a double bond formed by the dehydration of one of the end groups. The ^{1}H NMR spectra of crude aliquots did not show the formation of such double bonds. Although the ^{1}H NMR spectra of crude aliquots provided an evidence that the double bonds were formed during the MALDI-TOF MS measurements,[37] it is also possible that these dehydration end groups are present in the crude samples but at too low a concentration to detect by NMR spectroscopy. Very recently, Li et al have reported that in the absence of alcohol initiators,

Table 1 Self-Switchable Polymerization of Anhydrides and Epoxides with Cyclic Esters Catalyzed by Cesium Pivalate. [a]

entry	monomers	initiator	[anhydride]$_0$/[epoxide]$_0$/[cyclic ester]$_0$/[I]$_0$/[cat.]$_0$	temp. [°C]	time [h]	TOF_{ROAC}	TOF_{ROP}	TOF_{ROAC}/TOF_{ROP}	conv. [b] [%] (anhydride)	conv.[b] [%] (cyclic ester)	$M_{n,th.}$ [c] [kDa]	$M_{n,NMR}$ [b] [kDa]	$M_{n,SEC}$ [d] [kDa]	$Đ$ [d]
1	PA/EGE/L-LA	BDM	50/250/100/2/1	50	92	0.75	3.00	0.25	>99	97	13.4	13.9	8.3	1.08
2	PA/SO/L-LA	BDM	50/250/100/2/1	50	112	1.22	1.11	1.10	>99	95	13.7	n.d.	4.5	1.32
3	PA/CHO/L-LA	BDM	50/250/100/2/1	50	70	1.12	3.20	0.35	>99	86	12.5	14.0	6.3	1.16
4	PA/AGE/L-LA	BDM	50/250/100/2/1	50	84	0.91	3.63	0.25	>99	99	13.8	15.4	5.4	1.12
5	PA/EGE/L-LA	BDM	50/250/100/2/1	100	3	37.20	93.00	0.40	>99	95	13.2	14.7	8.2	1.12
6	PA/EGE/L-LA	BA	50/250/100/2/1	100	4.8	23.98	90.68	0.26	>99	82	12.3	12.8	8.8	1.15
7	PA/EGE/L-LA	PEG	50/250/100/2/1	100	3	35.50	88.74	0.40	>99	84	14.4	14.3	9.5	1.32
8	PA/EGE/L-LA	TP	50/250/100/2/1	100	4	28.87	64.16	0.45	>99	90	12.9	12.2	6.5	1.25
9	PA/ECH/L-LA	BDM	50/250/100/2/1	100	1.5	52.53	218.86	0.24	>99	96	13.1	12.5	6.5	1.42
10	PA/EHGE/L-LA	BDM	150/750/434/2/1	100	30	n.d.	n.d.	n.d.	>99	81	50.5	n.d.	13.8	1.11
11	PA/EHGE/L-LA	BDM	120/600/520/2/1	100	34	n.d.	n.d.	n.d.	>99	80	50.0	n.d.	14.3	1.13
12	PA/EHGE/L-LA	BDM	90/450/606/2/1	100	26	n.d.	n.d.	n.d.	>99	55	52.3	n.d.	12.4	1.19
13	PA/EHGE/L-LA	BDM	60/300/694/2/1	100	38	n.d.	n.d.	n.d.	>99	84	52.1	n.d.	11.7	1.16
14	EA/EGE/L-LA	BDM	50/250/100/2/1	100	2.5	28.88	192.00	0.15	>99	92	12.9	13.2	8.2	1.19
15	AA/EGE/L-LA	BDM	50/250/100/2/1	100	2.7	18.8	62.67	0.30	>99	99	13.3	13.4	6.3	1.15
16[e]	AA/EGE/L-LA	BDM	50/250/100/2/1	100	2.0	n.d	n.d	n.d.	>99	98	13.4	11.4	5.6	1.58
17	PGA/EGE/L-LA	BDM	50/250/100/2/1	100	3.8	32.63	130.5	0.25	>99	98	16.2	n.d.	11.3	1.22
18	TA/EGE/L-LA	BDM	50/250/100/2/1	100	2.5	31.35	33.00	0.95	>99	90	14.0	13.8	6.9	1.36
19	SA/EGE/L-LA	BDM	50/250/100/2/1	50	329	0.17	3.40	0.05	>99	96	12.1	12.0	5.1	1.13
20	DGA/EGE/L-LA	BDM	50/250/100/2/1	50	284	0.20	4.10	0.05	>99	91	12.1	12.9	7.4	1.20
21	NA/EGE/L-LA	BDM	50/250/100/2/1	50	209	n.d.	n.d.	n.d.	>99	95	13.6	16.4	7.0	1.14
22	PA/EGE/TMC	BDM	50/250/100/2/1	50	43	1.38	31.36	0.04	>99	98	11.4	11.0	9.9	1.36
23	PA/BO/CL	BDM	50/250/100/2/1	50	94	1.61	0.92	1.75	>99	43	8.1	7.2	6.9	1.29
24	PA/BO/MVL	BDM	50/250/100/2/1	50	240	0.93	0.23	4.00	>99	35	7.6	6.8	5.7	1.08
25[f]	SA/EHGE/L-LA	BDM	174/536/346/2/1	100	54	n.d.	n.d.	n.d.	>99	93	48.3	45.0	11.9	1.51

[a] Polymerization conditions: in the bulk under an Ar atmosphere. [b] Determined by ^{1}H NMR analysis of the obtained polymer in $CDCl_3$. [c] Calculated using [anhydride]$_0$/[I]$_0$ × conv. × (M.W. of anhydride + M.W. of epoxide) + [cyclic ester]$_0$/[I]$_0$ × conv. × (M.W. of cyclic ester) + (M.W. of initiator). [d] Determined by SEC analysis of the obtained polymer in THF with a PSt standard. [e] Catalyst was *t*-BuP_1. [*f*] Catalyst was sodium acetate (CH_3COONa)

alkali metal carboxylates can act as initiators for ROAC of cyclic anhydrides/epoxides.[30] However, in our study, a mass population corresponding to P(PA-*alt*-EGE) initiated from cesium pivalate was not observed (Figure 1), confirming that cesium pivalate did not initiate the ROAC of PA/EGE during the copolymerization process. In the present catalysts/alcohol initiators coexisting system, the carboxylate could be more prone to activate initiators or OH terminated growing chain end via H-bonding rather than directly initiate the ring-opening of the activated epoxides via a nucleophilic attack. This renders the OH group sufficiently nucleophilic to undergo nucleophilic attack toward the activated monomer.[26,27,38,39] Other potential side reactions, such as the self-propagation of EGE and transesterification, were also successfully suppressed during ROAC, as evidenced by the absence of corresponding mass populations. These results revealed that the present catalytic system exhibited controlled/living behavior (Figures S6 and S7).

To gain further insight into the influence of the catalyst design on the ROAC of PA and EGE, we examined both pivalate and acetate with various countercations, including Li, Na, K, and Cs (Table S2). Increasing the catalyst cation size significantly enhanced the turnover frequency (TOF) from 14.9 h^{-1} (lithium acetate, $pK_b = 6.04$) to 44.6 h^{-1} (cesium acetate, $pK_b = 6.87$). A comparison of the sodium salts of acetate, propionate, pivalate, and trifluoroacetate (acetic acid, $pK_a = 4.76$; propionic acid, $pK_a = 4.87$; pivalic acid, $pK_a = 5.05$; trifluoroacetic acid, $pK_a = -0.26$) revealed that an electron-donating group on the alkyl moiety enhanced the catalytic activity. For example, the TOF value of sodium pivalate was 20.0 h^{-1}, whereas that of sodium acetate was 16.8 h^{-1} (Figure 2). This tendency is in agreement with previous results for the ROP of cyclic esters by alkali metal carboxylate catalysts.[26] It is worth emphasizing that sodium trifluoroacetate was a special case. The catalyst with the weakest electron donating alkyl substituent should show the lowest activity, but it presented the highest ROAC rate among these sodium salts (Time = 1 h, Conv. = 43.3 %, TOF = 21.7), which could be attributed to sodium trifluoroacetate having a high solubility in EGE than the other sodium salts (Figure S9).

According to the kinetic plots (Figure S10), the kinetics of PA insertion varied depending on the alkali metal carboxylate catalysts. The ROAC process followed zero-order kinetics for more active alkali metal carboxylate catalysts and first-order kinetics for less active ones. The molecular weight distribution of the resulting copolymers was maintained in a narrow range ($Đ$ = 1.06–1.28) and decreasing the initiator loading led to a higher $M_{n,SEC}$ of 37.1 kDa (entry 4 in Table S2, Figure S11). This result demonstrated that a high degree of control can be achieved using alkali metal carboxylate catalyzed systems. Moreover, the polymerization properties can be flexibly controlled by selecting an appropriate alkyl group and countercation for the catalyst. Among the various alkali metal carboxylates, cesium pivalate achieved both high polymerization rates and a high degree of control/selectivity. Therefore, cesium pivalate was used as a model catalyst for the subsequent selective multicomponent polymerization involving anhydrides, epoxides, and cyclic esters.

Polymerization of Anhydrides, Epoxides, and Cyclic Esters. To further investigate the potential of the alkali metal carboxylates for establishing a self-switchable polymerization system, we polymerized mixtures of PA, EGE, and l-lactide (L-LA) using cesium pivalate and BDM as the catalyst and initiator, respectively. The evolution of ^{1}H NMR spectra revealed that the reaction with the proposed catalytic system proceeded with high selectivity to form triblock copolyesters, namely, PLLA-*b*-P(PA-*alt*-EGE)-*b*-PLLA (Figures S12 and S13). In detail, the ROAC of PA and EGE occurred first, as evidenced by the decrease in ^{1}H NMR signals corresponding to PA and the appearance of ^{1}H NMR signals associated with P(PA-*alt*-EGE) at 7.8–7.4 (proton a), 5.4–5.2 (proton c), and 4.7–4.4 ppm (proton b). During this period, no signal appeared at 5.2–5.1 ppm (proton g) and the signal at 5.1–5.0 ppm (methine proton of L-LA) remained unchanged, indicating that L-LA remained intact without any PLLA formation. The ROP of L-LA only turned on after PA was fully consumed (Figure 3a). It is worth noting that the ROAC of PA and EGE proceeded first, even though this reaction was significantly less active than the ROP of L-LA (TOFROAC/TOFROP = 0.25, entry 1 in Table 1). The SEC profile of the resulting copolymers exhibited a narrow and unimodal distribution ($Đ$ =1.08, entry 1 in Table 1 and Figure S14) and the elution peak maximum continuously shifted toward shorter elution times (higher molecular weights) as polymerization progressed (Figure 3b), demonstrating that propagation from the mixtures of PA, EGE and L-LA was well controlled. These results confirmed that block copolyesters were formed by a one-step procedure in which the initial PA/EGE copolymerization reaction was followed by the ROP of L-LA, with propagation occurring from both termini of P(PA-*alt*-EGE), to finally form PLLA-*b*-P(PA-*alt*-EGE)-*b*-PLLA triblock copolymers.

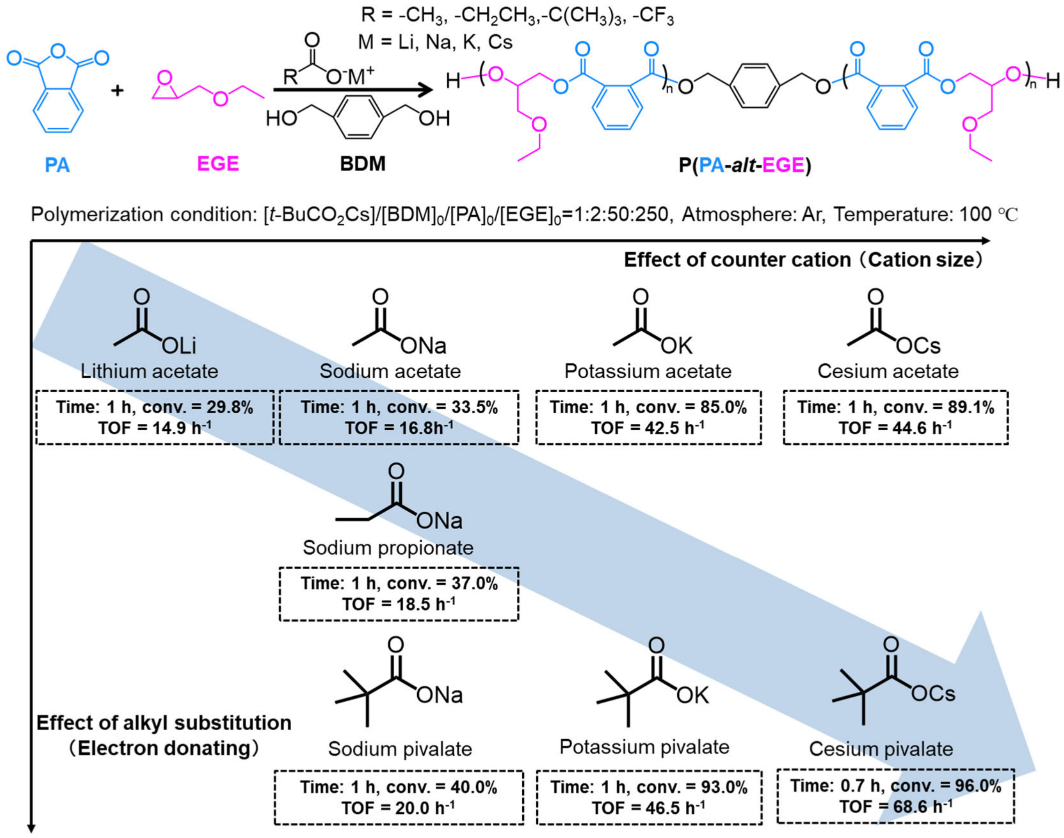


Figure 2. Catalytic performance of alkali metal carboxylates for the ROAC of PA and EGE.

The ^{13}C and 2D NMR spectra of the obtained triblock copolymer showed signals associated with both blocks (Figures S15–S17). In addition, the diffusion-ordered NMR (DOSY) spectrum gave only one diffusion coefficient for the observed signals of both P(PA-*alt*-EGE) and PLLA, providing solid evidence that these blocks are covalently linked (Figure 3c). In contrast, when two separately synthesized homopolymers were mixed, two different diffusion coefficients were observed for P(PA-*alt*-EGE) and PLLA (Figure S18). Moreover, the ^{1}H NMR spectra of the purified copolymer showed signals at 5.20–5.31 ppm owing to the junction between the P(PA-*alt*-EGE) and PLLA blocks (Figure S19), which further confirmed the formation of a BAB-type block polymer rather than a blend of unlinked P(PA-*alt*-EGE) and PLLA.

Mechanistic Studies. To reveal the copolymerization pathway and gain further mechanistic insights, cesium pivalate, 3-phenyl-1-propanol (PPA), PA, and L-LA were mixed in THF at a molar ratio of 1/2/3/12 and heated at 100 °C. After reacting for 3 min, PPA was completely consumed, accompanied by ~67% conversion of PA, whereas L-LA remained intact (Figure S20). These results indicated that PA had a much higher reactivity with alcohols than L-LA. We also mixed cesium pivalate, benzoic acid (BA), and L-LA in THF at a molar ratio of 1/10/10 and heated the mixture at 100 °C for 22 h. The absence of the ^{1}H NMR signal of PLLA indicated that the ROP of L-LA could not be initiated by carboxylates (Figure S21),[21,40] although the carboxylate was active enough to react with EGE (Figure S22). It can be reasonably deduced that the insertion of L-LA into the active chain end cannot occur in the presence of PA, even at very low [PA]/[L-LA] ratios; Thus, the ROP of L-LA can only start after PA is fully consumed. Cesium pivalate, PPA, EGE, and L-LA were mixed at a molar ratio of 1/2/250/100 and heated at 100 °C. After 35 min, PLLA with a narrow $Đ$ of 1.20 was obtained with ~93.5% L-LA conversion and no ROP of EGE occurred. When the reaction was prolonged to 19 h, EGE did not self-propagate (Figure S23). This result suggested that the self-propagation of EGE was well-suppressed throughout the entire reaction.

To further elucidate the catalysis mechanism, the fourier transform infrared spectroscopy (FT-IR) spectra of initiators (PPA and acetic acid), an anhydride (allylsuccinic anhydride; AA), and an epoxide (EGE) were collected in the presence and absence of cesium pivalate (Figure S24). The FT-IR spectrum of the mixture of PPA and cesium pivalate exhibited a slight blue shift in the absorption peak corresponding to the stretching vibration of the hydroxyl group, and the same phenomenon was observed for the mixture of acetic acid and cesium pivalate, indicating that cesium pivalate can activate the hydroxyl/carboxyl groups of propagating chain ends/initiators. In the presence of cesium pivalate, the absorption peaks corresponding to the C=O stretching vibration of AA and the C–O–C stretching vibration of EGE also showed a slight shift, implying that anhydrides and epoxides can be also activated by cesium pivalate. We can deduce that the smart catalysis involves a multiactivation mechanism, and the similar mechanism was reported in the ROP of L-LA via experimental and computational studies.[26,39]

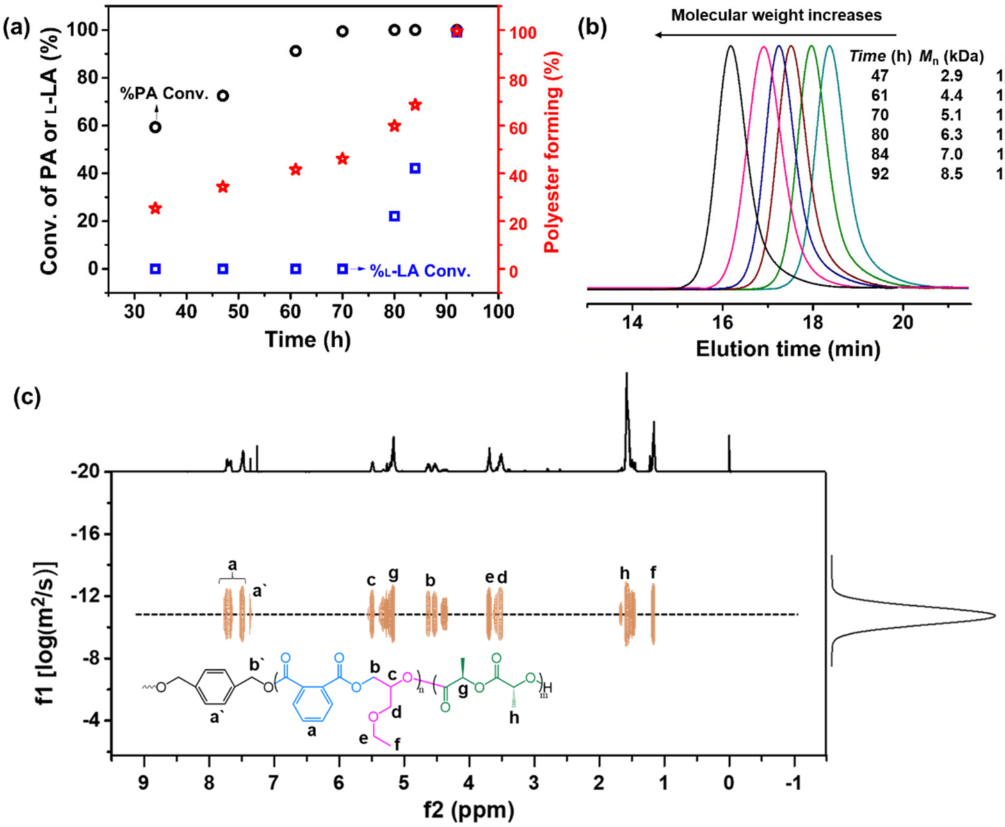


Figure 3. (a) Plots of monomer conversion versus time as monitored by ^{1}H NMR spectroscopy. (b) Evolution of SEC traces over time. (c) DOSY spectrum of resultant polymer. Polymerization conditions: in the bulk at 50 °C under an Ar atmosphere with a [PA]$_0$/[EGE]$_0$/[L-LA]$_0$/[BDM]$_0$/[t-BuCO$_2$Cs] feed ratio of 50/250/100/2/1 (entry 1 in Table 1).

Based on these experimental results, we can reasonably describe the proposed chemoselective mechanistic pathway for the polymerization of a monomer mixture (Scheme 3). First, the carbonyl group of the anhydride is activated by a cesium cation. Owing to their extremely high electrophilicity, the activated anhydride is prone to nucleophilic attack from the cesium pivalate activated hydroxyl group rather than the epoxide or cyclic ester. The resulting carboxylate species is active enough to react with the cesium cation activated epoxide, thus forming a copolymer with a perfect alternating chemical structure. When the anhydride is completely consumed, the termini of the alternating copolymer are occupied by hydroxyl groups that can persist and finally switch on the ROP of the cyclic ester in the smart system to form a multiblock copolymer.[20,41] During the self-switchable polymerization, the ring-opening step may follow two possible mechanisms including the monometallic pathway and bimetallic pathway.[26,39,42,43]

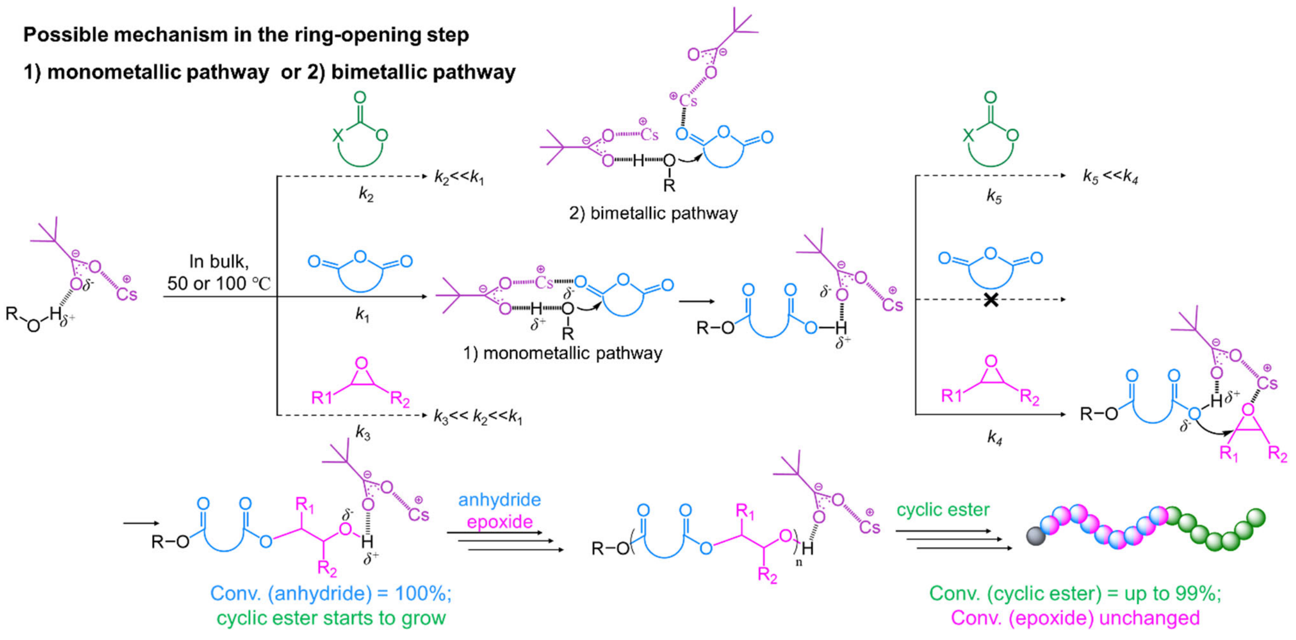
Expanding the Polymerization System. The established self-switchable polymerization system provides an extremely simple route to synthesize a wide variety of block copolymers. To further demonstrate the potential of this approach for the polymerization of a large library of structurally and functionally diverse monomers, a variety of anhydrides, epoxides, and cyclic esters were tested. Using PA and L-LA as models, the present catalysis was successfully applied to six epoxides (EGE, styrene oxide (SO), cyclohexene oxide (CHO), allyl glycidyl ether (AGE), 2-ethylhexyl glycidyl ether (EHGE), and epichlorohydrin (ECH)). The BAB triblock copolymers, where the A and B blocks were prepared by ROAC and ROP, respectively, obtained using PA/SO/L-LA showed relatively broad molecular weight distributions (entry 2 in Table 1, Figures S25–S29). Better control was achieved when using CHO, which gave a well-defined monomodal molecular weight distribution (entry 3 in Table 1, Figures S30–S34). The copolymerization of PA/AGE/L-LA also resulted in a high degree of control (entry 4 in Table 1, Figures S35–S39), and the obtained copolymers could be used for postpolymerization modification. Although these polymerization reactions showed very low rates at 50 °C, high efficiencies could be obtained by increasing the reaction temperature. For example, increasing the reaction temperature from 50 to 100 °C greatly shortened the reaction time from 94 to 3 h while maintaining a high degree of control/selectivity, as evidenced by the successful synthesis of a triblock copolymer with a narrow and monomodal molecular weight distribution ($Đ$ = 1.12, entry 5 in Table 1). The absence of side reactions during the polymerization of PA/ECH/L-LA revealed the effectiveness of the catalyst system for functional epoxides (entry 9 in Table 1, Figures S40–S44). EHGE could be used to prepare BAB-type block copolymers containing a middle block with a low glass transition temperature (T_g). The SEC traces of the resulting polymers, namely, PLLA-*b*-P(PA-*alt*-EHGE)-*b*-PLLA, showed narrow and monomodal molecular weight distributions ($Đ$ = 1.11–1.19) even when the block ratio (w/w) was varied (entries 10–13 in Table 1, Figures S45–S58).

Next, different cyclic anhydrides, including monocyclic (succinic anhydride (SA) and diglycolic anhydride (DGA)), dicyclic (PA), and tricyclic anhydrides (5-norbornene-endo-2,3-dicarboxylic anhydride (NA)) and their functional derivatives (4-ethynylphthalic anhydride (EA), AA, 2-phthalimidoglutaric anhydride (PGA), and trimellitic anhydride (TA)), were evaluated in the polymerization system using EGE and L-LA as models. For the commonly employed anhydrides (PA, SA, and DGA), the copolymerization reaction displayed good controllability and chemoselectivity ($Đ$ = 1.08–1.20, entries 1 and 19–20 in Table 1, Figures S13 and S59–S68), even though the reaction rate was obviously influenced by the anhydride structure. However, the catalysis using the three-component mixtures of NA/EGE/L-LA was lowly selective and the copolymer with an obvious tapered region was obtained, which is due to insufficient large reactivity difference between NA and L-LA (entries 21 in Table 1, Figures S69–S73)). EA, AA, and PGA have potential applicability for post-polymerization modification through reactions such as azido–alkyne click reactions, thiolene reactions, and deprotection to form amino groups. However, undesirable side reactions could easily occur at the unsaturated groups of these anhydrides, which is a known challenge in ROAC, and only a few catalysts successfully avoid side reactions.[44,45] Owing to its relatively weak basicity, *t*-BuP$_1$ is considered an ideal catalyst that provides a high degree of control for self-switchable polymerization with common reactive anhydrides. As shown in Table 1 (entry 16), although *t*-BuP$_1$ displayed high activity for the copolymerization of the AA/EGE/L-LA system, undesirable side reactions occurred, as evidenced by leading toward higher molecular weight region and a high $Đ$ of 1.58 (Figure S74). In contrast, the present catalytic system provided good polymerization control ($Đ$ < 1.23, entries 14, 15, and 17 in Table 1) with the functional anhydrides (EA, PGA, and AA) without any obvious side reactions (Figures S75–S90).

TA is of interest for the synthesis of hyperbranched copolymers because it includes an additional carboxylic acid group that can act as a propagating site for ROAC. TA conversion reached nearly 100% in the copolymerization of the TA/EGE/L-LA system, which produced a core–shell-type block copolymer consisting of a hyperbranched P(TA-*alt*-EGE) (degree of branching (DB) of ~0.70) core and a PLLA outer shell. The obtained copolymer had a unimodal and relatively narrow molecular weight distribution (*Đ* = 1.36, entry 18 in Table 1, Figures S91–S95). Thus, compared with conventional stepwise syntheses, the catalytic system provided an efficient and simple one-step procedure for the preparation of core–shell-type block copolymers.

We further explored the effect of the cesium pivalate catalyst on the regioselective alcoholysis of asymmetric anhydrides. The reaction of AA with excessive *n*-butanol in THF at 100 °C in the presence of cesium pivalate was completed in 1 h to produce monoesters a and b in a ratio of 51:49 (Figure 4 and S96), demonstrating no regioselectivity for the ring-opening of asymmetric anhydrides. This result implies that no regioregularity of the anhydride side chain exists in the alternating copolymers obtained from EA, AA, PGA, and TA.

Scheme 3. Proposed mechanism of the self-switchable polymerization from a mixture of anhydrides, epoxides, and cyclic esters with cesium pivalate as the catalyst and alcohol as the initiator.



Subsequently, we investigated the polymerization of PA, EGE, or 1,2-butylene oxide (BO) with trimethylene carbonate (TMC) or various cyclic esters, such as *ε*-caprolactone (CL) and *β*-methyl-*δ*-valerolactone (MVL), in the presence of BDM as the initiator. All the polymerization reactions provided the desired triblock copolymers well-controlled, monomodal molecular weight distributions (*Đ* = 1.08–

1.36, entries 22–24 in Table 1, Figures S97–S111). It is worth emphasizing that the ROACs of anhydrides and epoxides were more favorable than the ROP of cyclic esters, both kinetically and thermodynamically. This behavior is consistent with the theoretical calculations reported by Williams and co-workers, who proposed that chemoselectivity in the salcyCrCl/PPNCl catalytic system depended on large reactivity differences between the two polymerization cycles.[6,15] In the polymerization process, the TOF of ROP was much higher than that of ROAC in the PA/EGE/TMC system ($TOF_{ROAC}/TOF_{ROP} = 0.04$, entry 22 in Table 1), whereas the opposite result was observed in the PA/BO/MVL system ($TOF_{ROAC}/TOF_{ROP} = 4$, entry 23 in Table 1). Actually, insertion of anhydrides is rapid and the insertion order between anhydrides and cyclic esters depends on the established reactivity trend of anhydride >> cyclic ester, which is the product-determining step, whereas insertion of epoxides is slow and thereby considered as the rate-determining step for ROAC. Therefore, the chemoselectivity mainly depends on the reactivity difference between anhydride and cyclic ester rather than the values of TOF_{ROAC}/TOF_{ROP}. A similar polymerization mechanism in the mixture system of DGA/CO_2/epoxides was also reported by Geoffrey W. Coates.[10]

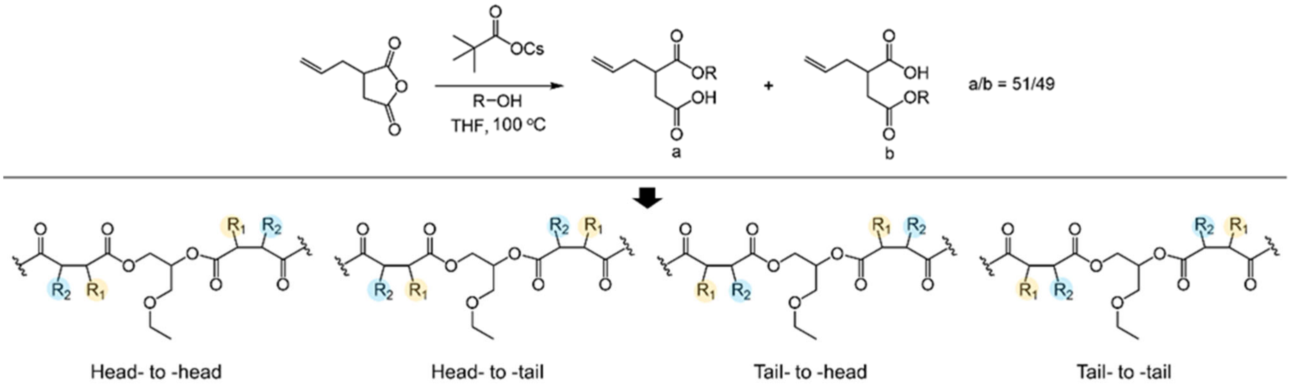


Figure 4. Regioselectivity in the alcoholysis of AA in the presence of cesium pivalate.

A series of initiators, including BA, BDM, poly(ethylene glycol) monomethyl ether (PEG), and trimethylolpropane (TP), were studied in the polymerization system. Good control was achieved with BA, and the resultant diblock copolymer displayed a narrow and monomodal molecular weight distribution (*Đ* =1.15, entry 6 in Table 1, Figures S112–S115). A CAB-type triblock terpolymer was achieved using

PEG (M_n = 2000, PEG2000), where the C, A, and B blocks were PEG, P(PA-*alt*-EGE), and PLLA, respectively (entry 7 in Table, Figures S116–S120). A three-armed star-block copolymer was successfully obtained when TP was employed as the initiator (entry 8 in Table, Figures S121–S125). These results show the advantages of the proposed simple one-step procedure for synthesizing polyester copolymers with diverse topologies, as shown in Scheme 2.

Design of All-Polyester Elastomers and Adhesives. Based on these advantages, we used the one-step procedure to synthesize a series of new BAB-type triblock copolymers with a "soft" A block and a "hard" B block using mixtures of SA or *n*-octylsuccinic anhydride (OSA), EHGE, and L-LA (entry 25 in Table 1, Table S3) with the aim of creating all-polyester elastomers and adhesives. For PLLA-*b*-P(SA-*alt*-EHGE)-*b*-PLLA with a 50:50 block ratio (w/w), only one glass transition temperature (T_g = −10 °C, Figure S126) was observed, which was located between $T_{g,\mathrm{P(SA}\text{-}alt\text{-}\mathrm{EHGE)}}$ (−48 °C, Figure S127) and $T_{g,\mathrm{PLLA}}$ (47 °C, Figure S128). This observation indicated the absence of microphase separation, which could be because the polarity difference between the hard and soft blocks was too small. Fortunately, the polarity of the blocks could be tuned by choosing appropriate monomers. SA was replaced with OSA to decrease the polarity of the soft block. The obtained large polarity difference between the hard block (PLLA) and soft block (P(OSA-*alt*-EHGE)) allowed microphase separation, which resulted in two T_g values ($T_{g,\mathrm{P(OSA}\text{-}alt\text{-}\mathrm{EHGE)\ block}} \cong -41$ °C, $T_{g,\mathrm{PLLA\ block}} \cong 26$ °C, Figure S129) at temperatures comparable to those observed for the corresponding homopolymers ($T_{g,\mathrm{P(OSA}\text{-}alt\text{-}\mathrm{EHGE)}} \cong -58$ °C, Figure S130; $T_{g,\mathrm{PLLA}} \cong 47$ °C, Figure S128b).[46,47] For PLLA-*b*-P(OSA-*alt*-EHGE)-*b*-PLLA with a 50:50 block ratio (w/w) (BAB-LLA-50), a melting peak was also observed at 160 °C, revealing the crystallization ability of the PLLA block. The upper T_g disappeared in the DSC thermograms of samples with a lower PLLA content (BAB-LLA-40) could be attributed to the reduced concentration of hard blocks (Figure S131).[48]

PLLA-*b*-P(SA-*alt*-EHGE)-*b*-PLLA with a 50:50 block ratio (w/w) showed a very high elongation at break (Figure S132) but very low elasticity owing to the absence of microphase separation between the hard and soft blocks. Such materials could potentially be used for adhesives. PLLA-*b*-P(OSA-*alt*-EHGE)-

b-PLLA with a 50:50 block ratio (w/w) exhibited elastomeric behavior without an obvious yield point and recovered its original shape once the stress was removed (Figure 5 and S133). Although this material showed a relatively small elongation at break (~220%), this could be improved by increasing the total molecular weight.[25] When the content of PLLA was decreased (BAB-LLA-40), a viscous and sticky material was obtained (Figure S134), showing potential for adhesive applications. The one-step synthesis of triblock copolymers for realistic applications remains a huge challenge, especially for elastomers.[49] The proposed self-switchable polymerization system shows considerable potential for the synthesis of elastomers and provides a simple method for creating new materials for other applications.

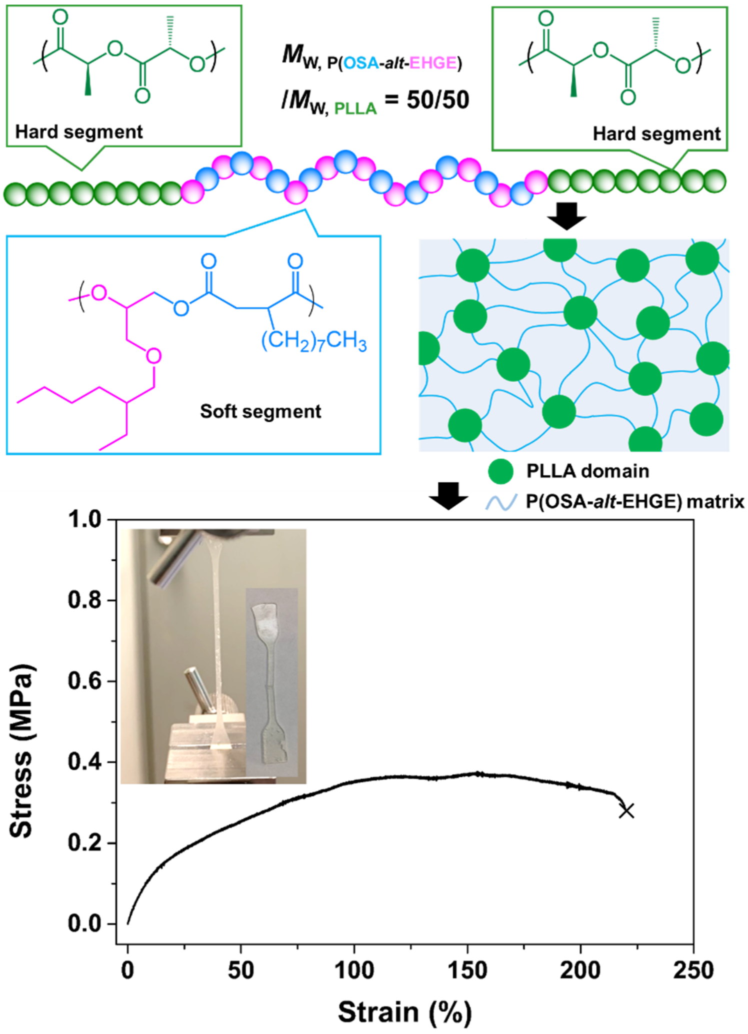


Figure 5. Structure–property relationship for PLLA-*b*-P(OSA-*alt*-EHGE)-*b*-PLLA with a 50:50 block ratio (w/w).

CONCLUSION

In conclusion, the potential of alkali metal carboxylates as an environmentally benign, biocompatible, and cheap catalyst system was revealed for the synthesis of sequentially and architecturally controlled block polyesters from monomer mixtures. This self-switchable polymerization system spontaneously and tandemly combined the ROAC of epoxides and cyclic anhydrides with the ROP of cyclic esters. Moreover, the displayed smart features, including rapidity, living nature, and perfect chemoselectivity, were similar to those in natural systems. Compared with conventional transition metal complex catalysts and organocatalysts, the alkali metal carboxylate catalysts provided unprecedented tunable basicity. As a result, this catalyst system was applicable to a wider range of monomers and allowed the preparation of well-defined sequence-controlled copolymers. A notable advantage of the present system is its applicability to the simple synthesis of complex, diverse, and functional multiblock copolymers for high-value emerging applications such as drug delivery, nanostructured materials, energy storage, and self-healing materials. Ongoing studies are aimed at synthesizing multiblock polyesters with up to 11 blocks in a one-step procedure using a smart polymerization system that links five catalytic cycles.

ASSOCIATED CONTENT

Supporting Information.

This information is available free of charge on the ACS Publications website.

Experimental section, alternating copolymerization of EGE and PA, terpolymerization of various mixtures, and properties of triblock copolymers.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Sanchez, C., Arribart, H., Guille, M. M. G. J. N. m., Biomimetism and bioinspiration as tools for the design of innovative materials and systems. *Nature materials* **2005**, *4*, 277-2882.

2. Lutz, J.-F., Ouchi, M., Liu, D. R., Sawamoto, M. J. S., Sequence-controlled polymers. *Science* **2013**, 341 (6146).

3. Engelis, N. G., Anastasaki, A., Nurumbetov, G., Truong, N. P., Nikolaou, V., Shegiwal, A., Whittaker, M. R., Davis, T. P., Haddleton, D. M. J. N. c., Sequence-controlled methacrylic multiblock copolymers via sulfur-free RAFT emulsion polymerization. *Nature chemistry* **2017**, *9*, 171-178.

4. Polymeropoulos, G., Zapsas, G., Ntetsikas, K., Bilalis, P., Gnanou, Y., Hadjichristidis, N. J. M., 50th

Anniversary perspective: polymers with complex architectures. *Macromolecules* **2017**, *50*, 1253-1290.

5. Romain, C., Williams, C. K. Chemoselective Polymerization Control: From Mixed-Monomer Feedstock to Copolymers. *Angewandte Chemie International Edition* **2014**, *126*, 1633-1636.

6. Romain, C., Zhu, Y., Dingwall, P., Paul, S., Rzepa, H. S., Buchard, A., Williams, C. K. Chemoselective polymerizations from mixtures of epoxide, lactone, anhydride, and carbon dioxide. *Journal of the American Chemical Society* **2016**, *138*, 4120–4131.

7. Paul, S., Romain, C., Shaw, J., Williams, C. K., Sequence selective polymerization catalysis: a new route to ABA block copoly (ester-*b*-carbonate-*b*-ester). *Macromolecules* **2015**, *48*, 6047-6056.

8. Zhu, Y., Romain, C., Williams, C. K. Selective polymerization catalysis: controlling the metal chain end group to prepare block copolyesters. *Journal of the American Chemical Society* **2015**, *137*, 12179-12182.

9. Kernbichl, S., Reiter, M., Adams, F., Vagin, S., Rieger, B., CO_2-controlled one-pot synthesis of AB, ABA block, and statistical terpolymers from *β*-butyrolactone, epoxides, and CO_2. *Journal of the American Chemical Society* **2017**, *139*, 6787-6790.

10. Chen, T. T., Zhu, Y., Williams, C. K., Pentablock copolymer from tetracomponent monomer mixture using a switchable dizinc catalyst. *Macromolecules* **2018**, *51*, 5346-5351.

11. Ji, H.-Y., Wang, B., Pan, L., Li, Y.-S. One-step access to sequence-controlled block copolymers by self-switchable organocatalytic multicomponent polymerization. *Angewandte Chemie International Edition* **2018**, *57*, 16888–16892.

12. Hsu, L. C., Isono, T., Lin, Y. C., Kobayashi, S., Chiang, Y. C., Jiang, D. H., Hung, C. C., Ercan, E., Yang, W. C., Hsieh, H. C., Tajima, K., Satoch, T., Chen, W. C., Stretchable OFET Memories: Tuning the Morphology and the Charge-Trapping Ability of Conjugated Block Copolymers through Soft Segment Branching. *ACS Applied Materials & Interfaces* **2021** *13*, 2932-2943.

13. Liu, S., Bai, T., Ni, K., Chen, Y., Zhao, J., Ling, J., Ye, X., Zhang, G. Biased lewis pairs: a general catalytic approach to ether-ester block copolymers with unlimited ordering of sequences. *Angewandte Chemie International Edition* **2019**, *58*, 15478–15487.

14. Jeske, R. Q., Rowley, J. M., Coates, G. W. Pre-rate-determining selectivity in the terpolymerization of epoxides, cyclic anhydrides, and CO_2: a one-step route to diblock copolymers. *Angewandte Chemie International Edition* **2008**, *47*, 6041-6044.

15. Stößer, T., Williams, C. K. Selective polymerization catalysis from monomer mixtures: using a commercial Cr-salen catalyst to access ABA block polyesters. *Angewandte Chemie International Edition* **2018**, *57*, 6337–6341.

16. Stößer, T., Chen, T. T. D., Zhu, Y., Williams, C. K., ‘Switch’catalysis: from monomer mixtures to sequence-controlled block copolymers. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2018**, *376*, 20170066.

17. Stößer, T., Mulryan, D., Williams, C. K. Switch catalysis to deliver multi-block polyesters from mixtures of propene oxide, lactide, and phthalic anhydride. *Angewandte Chemie International Edition* **2018**, *57*, 16893–16897.

18. Stößer, T., Sulley, G. S., Gregory, G. L., Williams, C. K. Easy access to oxygenated block polymers via switchable catalysis. *Nature Communications* **2019**, *10*, 2668.

19. Hu, C., Duan, R., Yang, S., Pang, X., & Chen, X., CO_2 controlled catalysis: switchable homopolymerization and copolymerization. *Macromolecules* **2018**, *51*, 4699-4704.

20. Li, H., Zhao, J., & Zhang, G., Self-buffering organocatalysis tailoring alternating polyester. *ACS Macro Letters* **2017**, *6*, 1094-1098.

21. Li, H., Luo, H., Zhao, J., Zhang, G. Sequence-selective terpolymerization from monomer mixtures using a simple organocatalyst. *ACS Macro Letters* **2018**, *7*, 1420–1425.

22. Li, H., He, G., Chen, Y., Zhao, J., Zhang, G. One-step approach to polyester–polyether block copolymers using highly tunable bicomponent catalyst. *ACS Macro Letters* **2019**, *8*, 973–978.

23. Ji, H.-Y., Song, D.-P., Wang, B., Pan, L., Li, Y.-S. Organic lewis pairs for selective copolymerization of epoxides with anhydrides to access sequence-controlled block copolymers. *Green Chemistry* **2019**, *21*, 6123–6132.

24. Zhu, S., Zhao, Y., Ni, M., Xu, J., Zhou, X., Liao, Y., Wang, Y., Xie, X. One-step and metal-free synthesis of triblock quaterpolymers by concurrent and switchable polymerization. *ACS Macro Letters* **2020**, *9*, 204–209.

25. Sulley, G. S., Gregory, G. L., Chen, T. T. D., Peña Carrodeguas, L.; Trott, G.; Santmarti, A.; Lee, K.-Y.; Terrill, N. J.; Williams, C. K., Switchable catalysis improves the properties of CO_2-derived polymers: poly(cyclohexene carbonate-b-ε-decalactone-b-cyclohexene carbonate) adhesives, elastomers, and toughened plastics. *Journal of the American Chemical Society* **2020**, *142*, 4367–4378.

26. Saito, T., Aizawa, Y., Yamamoto, T., Tajima, K., Isono, T., Satoh, T. Alkali metal carboxylate as an efficient and simple catalyst for ring-opening polymerization of cyclic esters. *Macromolecules* **2018**, *51*, 689–696.

27. Takojima, K., Saito, T., Vevert, C., Ladelta, V., Bilalis, P., Watanabe, J., Hatanaka, S., Konno, T., Yamamoto, T., Tajima, K., Hadjichristidis, N., Isono, T., Satoh, T. Facile synthesis of poly (trimethylene carbonate) by alkali metal carboxylate-catalyzed ring-opening polymerization. *Polymer Journal* **2020**, *52*, 103–110.

28. Von Schwenk, E., Gulbins, K., Roth, M., Benzing, G., Maysenhölder, R., Hamann, K. Synthese von polyestern aus dicarbonsäureanhydriden und epoxyden oder cyclischen carbonaten von diolen. *Macromolecular Chemistry and Physics* **1962**, *51*, 53–69.

29. Hilt, V. A., Reichert, K. H., Hamann, K. Synthese von polyestern durch copolymerisation von dicarbonsäreanhydriden und ringäthern. *Macromolecular Chemistry and Physics* **1967**, *101*, 246–270.

30 Chen, C. M., Xu, X., Ji, H. Y., Wang, B., Pan, L., Luo, Y., & Li, Y. S. Alkali Metal Carboxylates: Simple and Versatile Initiators for Ring-Opening Alternating Copolymerization of Cyclic Anhydrides/Epoxides. *Macromolecules* **2021**, *54*, 713–724.

31. Longo, J. M., Sanford, M. J., Coates, G. W. Ring-opening copolymerization of epoxides and cyclic anhydrides with discrete metal complexes: structure–property relationships. *Chemical Reviews* **2016**, *116*, 15167–15197.

32. Zhang, D., Boopathi, S. K., Hadjichristidis, N., Gnanou, Y., Feng, X. Metal-free alternating copolymerization of CO_2 with epoxides: fulfilling "green" synthesis and activity. *Journal of the American Chemical Society* **2016**, *138*, 11117–11120.

33. Fieser, M. E., Sanford, M. J., Mitchell, L. A., Dunbar, C. R., Mandal, M., Van Zee, N. J., Urness, D. M., Cramer, C. J., Coates, G. W., Tolman, W. B. Mechanistic insights into the alternating copolymerization of epoxides and cyclic anhydrides using a (Salph) AlCl and iminium salt catalytic system. *Journal of the American Chemical Society* **2017**, *139*, 15222–15231.

34. Wan, Z.-Q., Longo, J. M., Liang, L.-X., Chen, H.-Y., Hou, G.-J., Yang, S., Zhang, W.-P., Coates, G. W., Lu, X.-B. Comprehensive understanding of polyester stereocomplexation. *Journal of the American Chemical Society* **2019**, *141*, 14780–14787.

35. Abel, B. A., Lidston, C. A., Coates, G. W. Mechanism-inspired design of bifunctional catalysts for the alternating ring-opening copolymerization of epoxides and cyclic anhydrides. *Journal of the American Chemical Society* **2019**, *141*, 12760–12769.

36. Chen, T. T., Carrodeguas, L. P., Sulley, G. S., Gregory, G. L., & Williams, C. K. (2020). Bio-based and Degradable Block Polyester Pressure-Sensitive Adhesives. *Angewandte Chemie International Edition* **2020**, *59*, 23450 – 23455

37. Li, H., Zhao, J., Zhang, G. Self-buffering organocatalysis tailoring alternating polyester. *ACS Macro Letters* **2017**, *6*, 1094–1098.

38. Makiguchi, K., Yamanaka, T., Kakuchi, T., Terada, M., & Satoh, T., Binaphthol-derived phosphoric acids as efficient chiral organocatalysts for the enantiomer-selective polymerization of rac-lactide. *Chemical Communications* **2014**, *50*, 2883-2885.

39. Ozen, C., Satoh, T., Maeda, S. A theoretical study on the alkali metal carboxylate–promoted ʟ–Lactide polymerization. *Journal of Computational Chemistry* **2020**, *41*, 2197–2202.

40. Kernbichl, S., Reiter, M., Mock, J., & Rieger, B. Terpolymerization of β-Butyrolactone, Epoxides, and CO_2: Chemoselective CO_2-Switch and Its Impact on Kinetics and Material Properties. *Macromolecules* **2019**, *52*, 8476-8483.

41. Li, H., Luo, H., Zhao, J., Zhang, G. Well-defined and structurally diverse aromatic alternating polyesters synthesized by simple phosphazene catalysis. *Macromolecules* **2018**, *51*, 2247–2257.

42. Liu, J., Bao, Y. Y., Liu, Y., Ren, W. M., & Lu, X. B., Binuclear chromium–salan complex catalyzed alternating copolymerization of epoxides and cyclic anhydrides. *Polymer Chemistry* **2013**, *4*, 1439-1444.

43. Ohkawara, T., Suzuki, K., Nakano, K., Mori, S., & Nozaki, K., Facile estimation of catalytic activity and selectivities in copolymerization of propylene oxide with carbon dioxide mediated by metal complexes with planar tetradentate ligand. *Journal of the American Chemical Society* 2014, *136*, 10728-10735.

44. Nejad, E. H., Paoniasari, A., Koning, C. E., Duchateau, R. Semi-aromatic polyesters by alternating ring-opening copolymerisation of styrene oxide and anhydrides. *Polymer Chemistry* **2012**, *3*, 1308–1313.

45. Wilson, J. A., Luong, D., Kleinfehn, A. P., Sallam, S., Wesdemiotis, C., Becker, M. L. Magnesium catalyzed polymerization of end functionalized poly (propylene maleate) and poly (propylene fumarate) for 3D printing of bioactive scaffolds. *Journal of the American Chemical Society* **2018**, *140*, 277–284.

46. Watanabe, K., Katsuhara, S., Mamiya, H., Yamamoto, T., Tajima, K., Isono, T., Satoh, T. Downsizing feature of microphase-separated structures via intramolecular crosslinking of block copolymers. *Chemical Science* **2019**, *10*, 3330–3339.

47. Isono, T., Nakahira, S., Hsieh, H.-C., Katsuhara, S., Mamiya, H., Yamamoto, T., Chen, W.-C., Borsali, R., Tajima, K., Satoh, T. Carbohydrates as Hard Segments for Sustainable Elastomers: Carbohydrates Direct the Self-Assembly and Mechanical Properties of Fully Bio-Based Block Copolymers. *Macromolecules* **2020**, *53*, 5408–5417.

48. Kember, M. R., Copley, J., Buchard, A., Williams, C. K. Triblock copolymers from lactide and telechelic poly (cyclohexene carbonate). *Polymer Chemistry* **2012**, *3*, 1196–1201.

49. Paul, S., Romain, C., Shaw, J., Williams, C. K. Sequence selective polymerization catalysis: a new route to ABA block copoly (ester-*b*-carbonate-*b*-ester). *Macromolecules* **2015**, *48*, 6047–6056.

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