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Title :

**Organobase-Catalyzed Ring-opening Copolymerization of Cyclic anhydrides and Oxetanes:
Establishment and Application in Block Copolymer Synthesis**

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ABSTRACT.

Polyesters are a prominent class of polymer materials. The ring-opening copolymerization (ROCOP) of cyclic anhydrides and cyclic ethers has attracted attention as a method for the precise synthesis of a variety of polyesters. However, epoxides have been the primary cyclic ether employed in this method, and precise polymerization with oxetane has been challenging. This paper accomplished organobase-catalyzed ROCOP of cyclic anhydrides and oxetanes for synthesizing polyesters. By applying *t*-BuP₂ as a catalyst for the ROCOP of phthalic anhydride (PA) and trimethylene oxide (TO), perfectly alternating P(PA-*alt*-TO) was obtained with predictive molecular weights ranging from 3,000 to 20,000 Da and low dispersities ($\bar{D} < 1.16$). A kinetic experiment on the ROCOP of PA and TO confirmed the controlled/living nature of the proposed ROCOP system. Furthermore, its remarkable tolerance for various functional groups facilitates the utilization of a wide range of monomers and initiators, resulting in polyesters with distinct glass transition temperatures (T_g , $-45.4\text{ }^{\circ}\text{C}$ to $60.8\text{ }^{\circ}\text{C}$). Moreover, this polymerization process can be seamlessly integrated with other ROCOP processes, such as the ring-opening polymerization of trimethylene carbonate, valerolactone, or L-lactide and the ROCOP of PA/epoxide; this enables the synthesis of polyester-based block copolymers in a one-pot/one-step manner, known as self-switchable polymerization. Consequently, this novel polymerization process expands the scope of the existing ROCOP approaches and paves the way to synthesizing diverse polyesters with tailored material properties.

Introduction

Polyesters are an important class of polymer materials that have applications in various forms such as fibers, elastomers, coatings, and plasticizers.¹ Owing to their diverse main- and side-chain structures, they exhibit versatile material properties. Given the hydrolyzable nature of ester functional groups, polyesters—particularly aliphatic polyesters—have garnered significant research interest as potential replacements for non-degradable polyolefin materials to address the pressing global issue of plastic waste.²⁻⁴

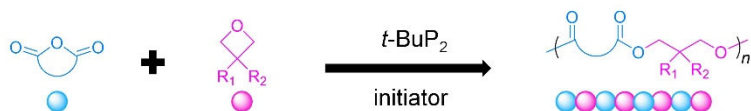
Polyesters are prepared primarily via two methods: polycondensation using diols and diacids and ring-opening polymerization (ROP) of cyclic esters.⁵⁻⁷ The ring-opening copolymerization (ROCOP) of cyclic anhydrides and cyclic ethers presents an alternative synthetic approach characterized by its chain-growth mechanism and wide tunability through potential combinations of various cyclic anhydrides and cyclic ethers.⁸ Since the pioneering work of Inoue *et al.* on living ROCOP of propylene oxide and phthalic anhydride (PA), this polymerization method has attracted substantial attention.⁹ Epoxides are the most commonly used cyclic ethers in ROCOP with cyclic anhydrides, resulting in polyesters with C2 linkers between the adjacent ester moieties.^{8,10,11} Reportedly, poly(propylene succinate), an aliphatic polyester with C3 linkers, shows increased biodegradability compared to poly(ethylene succinate), which has C2 linkers.^{12,13} Aside from the conventional synthetic pathway via polycondensation, the ROCOP of cyclic anhydrides and oxetanes, which are 4-membered ethers, is a suitable alternative approach to obtain such polyesters with C3 linkers. However, studies on this approach have been scarce, presumably owing to the lower reactivity of oxetanes compared to epoxides because of their lower ring strain and more complicated preparation method of oxetanes than epoxide so far.¹⁴⁻¹⁹ The first report on oxetane/cyclic anhydride ROCOP was by Endo *et al.* in 1999.¹⁵ They realized the ROCOP of trimethylene oxide (TO) and cyclic anhydrides by using titanium bisphenolate complexes as catalysts.

Although this is considered a pioneering achievement, the polyether structure due to the homopolymerization of TO was observed in the obtained copolymers. In 2002, Nishikubo *et al.* reported that nearly perfect alternating copolymers of oxetanes and cyclic anhydrides were obtained by utilizing quaternary onium salts as the catalyst and initiator; however, the catalytic reactivity was relatively low.¹⁶ Thereafter, research on the ROCOP of oxetanes and cyclic anhydrides remained relatively dormant for nearly two decades until recent breakthroughs. In 2021, Buchard *et al.* reported on the ROCOP of xylose-derived oxetane with cyclic anhydrides by using transition metal–salen complexes as catalysts.¹⁷ Subsequently, Williams *et al.* synthesized an intriguing ABB-type poly(ester-*alt*-ethers) structure by using the Zr(IV)-catalyzed ROCOP of oxetanes (B) and cyclic anhydrides (A).¹⁸ Our group realized a well-controlled ROCOP for oxetanes and cyclic anhydrides with perfectly alternating structures by using the simple and readily available cesium pivalate as the catalyst.¹⁹ Moreover, this method has been effectively applied to self-switchable polymerization by combining the ROCOP of epoxides and cyclic anhydrides. Thus, organocatalysts, including quaternary onium salts and alkaline metal carboxylates, can apparently facilitate the ROCOP of cyclic anhydrides and oxetanes to proceed in an alternative manner, despite their lower catalytic activity compared to transition metal complex catalysts. In light of our prior research wherein we used cesium pivalate to accomplish precise ROCOP of cyclic anhydrides and oxetanes, in this study, we aimed to explore other highly active organocatalysts.

In this study, we successfully established an organobase-catalyzed ROCOP of oxetanes and cyclic anhydrides, yielding polyesters with perfectly alternating structures, predictable molecular weights, and low dispersities (Figure 1A).²⁰ A broad range of initiators and monomers can be used to conveniently obtain various polyester structures. Furthermore, this method can be applied to self-switchable polymerization, enabling the synthesis

of polyester-based block copolymers in a one-pot/one-step process (Figure 1B).^{21,22} Our findings will potentially pave the way to efficient and controlled syntheses of complex polyester materials.

(A) ROCOP of cyclic anhydrides and oxetanes catalyzed by organobases



(B) Self-switchable polymerization

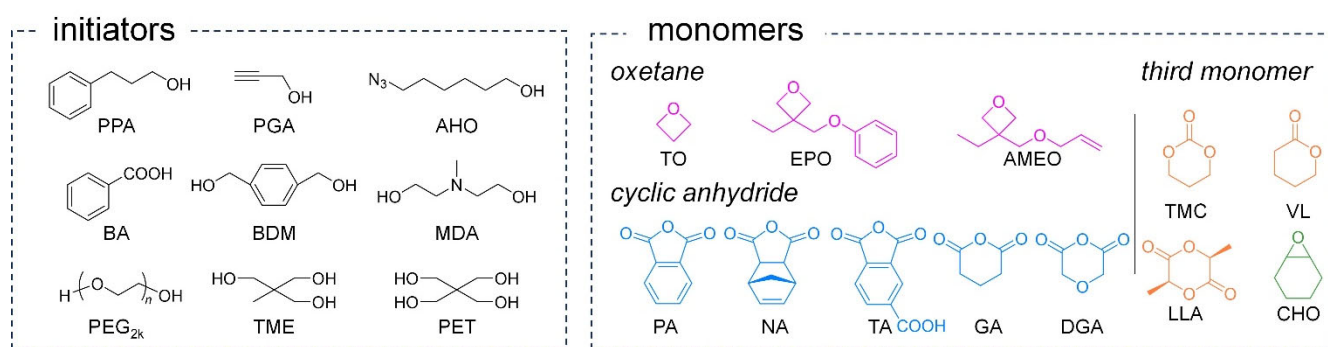
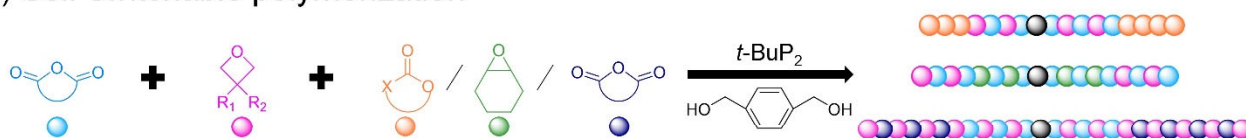


Figure 1. (A) Organobase-catalyzed ROCOP of cyclic anhydrides and oxetanes, and (B) its application in self-switchable polymerization.

Results and discussion

• Optimization of organobase catalysts

Scheme 1. ROCOP of PA and TO catalyzed by organobases

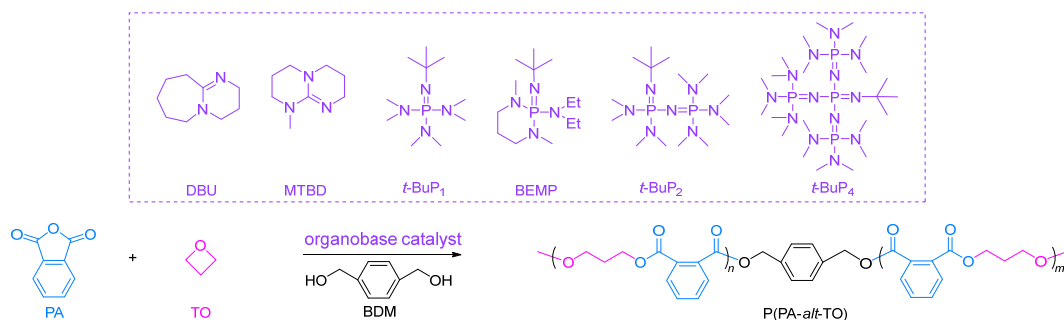


Table 1. ROCOP of PA and TO using various catalysts ^a

run	catalyst	time (h)	conv. PA ^b (%)	$M_{n,theo.}$ (kDa) ^c	$M_{n,NMR}$ (kDa) ^b	$M_{n,SEC}$ (kDa) ^d	$\bar{D}$ ^d
1	DBU	11	88	3.7	4.1	3.6	1.13
2	MTBD	8	99 ^e	4.2	4.1	2.8	1.09
3	<i>t</i> -BuP ₁	4	>99 ^e	4.3	3.8	2.8	1.09
4	BEMP	3	84	3.6	3.3	3.0	1.18
5	<i>t</i> -BuP ₂	3	81	3.5	3.0	3.1	1.15
6	<i>t</i> -BuP ₄	3	78	3.4	3.2	2.9	1.18
7	CsOPiv	20	94	4.0	4.5	3.0	1.14
8 ^f	<i>t</i> -BuP ₂	43	93	4.0	5.6	4.8	1.12
9 ^g	<i>t</i> -BuP ₂	9	>99	10.4	11.3	4.9	1.16
10 ^h	<i>t</i> -BuP ₂	14	98	20.2	20.6 ⁱ	7.3	1.13

^a To solvate the cyclic anhydrides, an excess amount of oxetanes was added. Polymerization conditions: bulk; temperature = 100 °C; atmosphere, Ar; initiator, BDM; [PA]₀/[TO]₀/[BDM]₀/[catalyst] = 20/100/1/1. ^b Determined by ¹H NMR spectroscopy in CDCl₃. ^c Calculated from [PA]₀/[BDM]₀ × conv._{PA}/100 × ((M.W. of PA) + (M.W. of TO)) + (M.W. of BDM). ^d Determined by SEC measurement of the polymer obtained in THF using a polystyrene standard. ^e The polymerizations were also conducted with ~70% conversion of PA. The unidentified subpeaks on MALDI-TOF MS spectra of the products were the same as the ones with almost full conversion of PA, although the relative intensities of the peaks are different (Figure S7–S12). ^f Polymerization was performed at 80 °C. ^g [PA]₀/[TO]₀/[BDM]₀/[*t*-BuP₂] = 50/200/1/1. ^h [PA]₀/[TO]₀/[BDM]₀/[*t*-BuP₂] = 100/400/1/1. ⁱ $M_{n,MALS}$ = 17.5 kDa (Figure S19).

The investigation of the ROCOP of cyclic anhydrides and oxetanes began with the optimization of organobase catalysts. PA and TO were selected as monomers and 1,4-benzenedimethanol (BDM) was used as the initiator (**Scheme 1**). Six representative organobase catalysts of various basicities were used. Their

pK_{BH}^+ values (in acetonitrile) range from 24.3 to 42.7.^{23,24} The polymerization was performed in bulk at a ratio of $[PA]_0/[TO]_0/[BDM]_0/[catalyst] = 20/100/1/1$ at 100 °C. When 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) ($pK_{BH}^+ = 24.3$) was employed as the catalyst, the conversion of PA reached 88% after 11 h, resulting in P(PA-*alt*-TO) with a low dispersity ($\bar{D} = 1.13$; run 1 in **Table 1**). Increasing the basicity of the catalyst by employing 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, $pK_{BH}^+ = 25.5$) reduced the polymerization time to 8 h while maintaining good control over dispersity ($\bar{D} = 1.09$; run 2 in **Table 1**). Phosphazene bases (PBs), which have higher basicities than MTBD, are known to effectively catalyze the ROCOP of cyclic anhydrides and epoxides.²⁵ Four types of PBs, *t*-BuP₁, 2-*t*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diaza phosphorine (BEMP), *t*-BuP₂, and *t*-BuP₄ ($pK_{BH}^+ = 26.9, 27.6, 33.5$, and 42.7; runs 3–6 in **Table 1**), were tested in the ROCOP of PA and TO. As a result, the polymerization rate further increased, and the obtained P(PA-*alt*-TO)s exhibited low dispersity ($\bar{D} = 1.09$ –1.18).

According to the aforescribed initial catalyst screening, the relationship between catalytic activity and basicity of the organobase catalysts was examined (**Figure 2**). The turnover frequency (TOF) of the polymerization increased with increasing organobase-catalyst basicity (**Table S1**), reaching a maximum of approximately 6 h⁻¹ after the pK_{BH}^+ reached 27.6 when using BEMP. In the ROCOP using BEMP, *t*-BuP₂, and *t*-BuP₄, because of the extremely strong basicity of the catalysts, the naked anionic species could be considered at the propagating chain end, and almost the same TOF values were obtained. Notably, the highest TOF obtained using the phosphazene base was approximately seven times higher than that obtained using cesium pivalate (CsOPiv; run 7 in **Table 1**), as reported in our previous study. Interestingly, when 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was used as the catalyst, its catalytic efficiency was significantly lower than that of MTBD despite their similar basicities (**Figures S1 and S2**). This can be explained by hydrogen

bonding between the TBD and carboxylate at the end of the growing chain. This results in excessive stabilization of the intermediate and slow reaction rates.

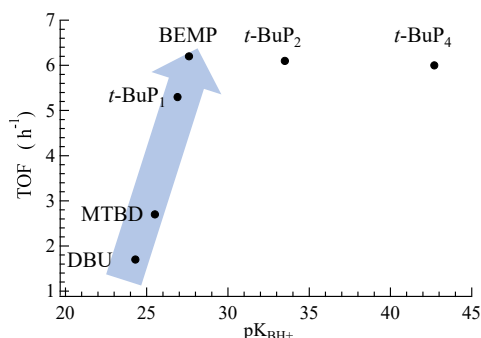


Figure 2. pK_{BH^+} (in acetonitrile) vs TOF for the ROCOP of PA and TO in the bulk at 100 °C.

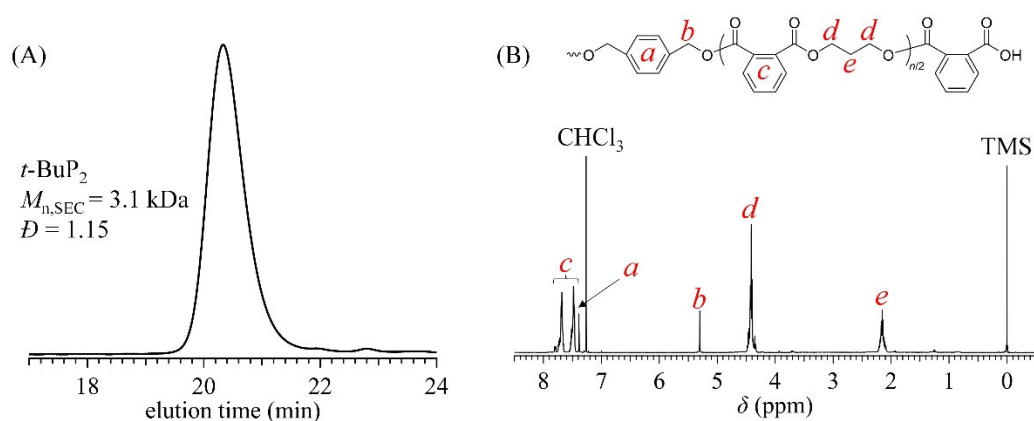


Figure 3. (A) SEC trace of P(PA-*alt*-TO) catalyzed by *t*-BuP₂ (run 5) (eluent, THF; flow rate, 1.0 mL min⁻¹; polystyrene standard). (B) ¹H NMR spectrum of P(PA-*alt*-TO) in CDCl₃ (400 MHz).

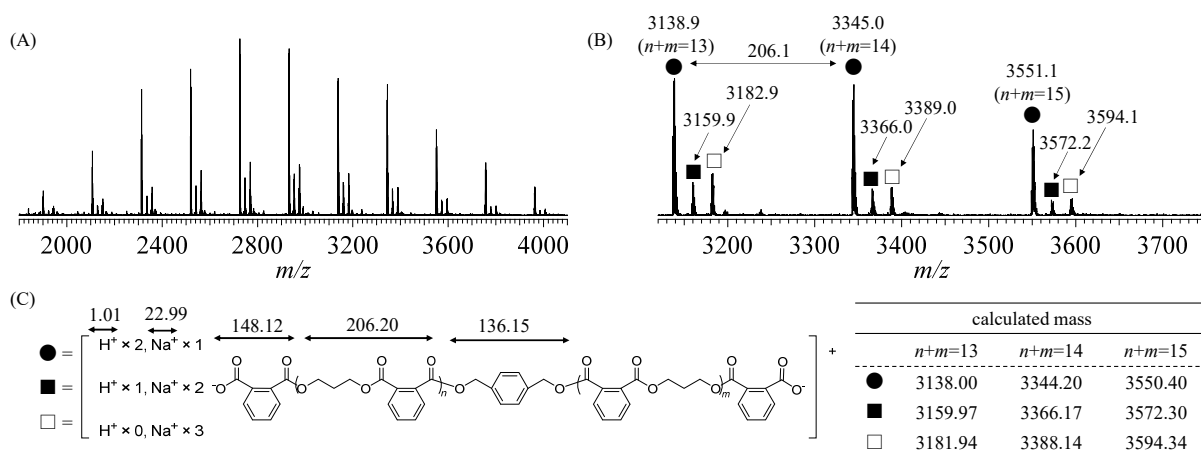


Figure 4. (A) MALDI-TOF mass spectrum of the obtained P(PA-*alt*-TO) using *t*-BuP₂ (run 5), (B) the expanded spectrum (ranging from 3,120 to 3,750), and (C) theoretical values.

Although the tested catalysts exhibited varied catalytic activities during the initial screening of organobase catalysts, satisfactory control over the molecular weight dispersity was achieved. Size exclusion

chromatography (SEC) analysis of the polymer products revealed a monomodal elution peak with low dispersity (**Figures 3A and S3**). The nuclear magnetic resonance (NMR)-based molecular weights ($M_{n,NMR}$) match the theoretical values ($M_{n,theo.}$) (runs 1–6 in **Table 1**). However, further characterization of the isolated P(PA-*alt*-TO)s via NMR and Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (MS) revealed distinct differences when different organobase catalysts were used (**Figures 3B, 4, and S4–S6**). When *t*-BuP₂ was used as the catalyst, the ¹H NMR spectrum of the obtained P(PA-*alt*-TO) exhibited signals corresponding to the repeating PA and TO monomer units, along with the BDM initiator, with only trace amounts of the remaining *t*-BuP₂ catalyst (**Figure 3B and Figure S21**). Notably, there was no signal indicating the presence of a polyether structure resulting from the homopolymerization of TO. The polymer structure was further confirmed by MALDI-TOF MS (**Figure 4**), wherein the major series of peaks corresponded to the sodium adduct of P(PA-*alt*-TO) containing BDM as the initiator and two PA units at both chain ends (**Figure S20**). And the transesterification byproducts were not observed. These results clearly demonstrate perfect alternation of the PA and TO units within the copolymers grown from the BDM initiator. In contrast, as indicated by NMR and MALDI-TOF-MS analyses, the P(PA-*alt*-TO) products obtained with the other organobase catalysts contained unidentified byproducts (**Figures S5 and S6**); the reason for these differences remains to be clarified. Consequently, *t*-BuP₂ was selected as the optimal catalyst for subsequent investigations.

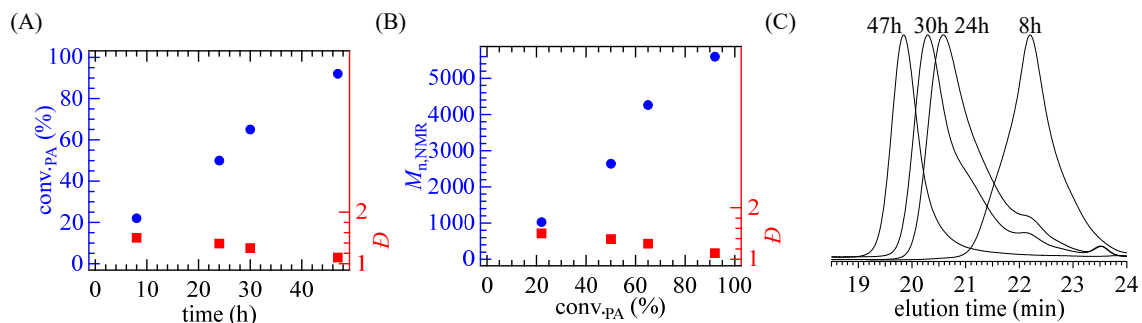
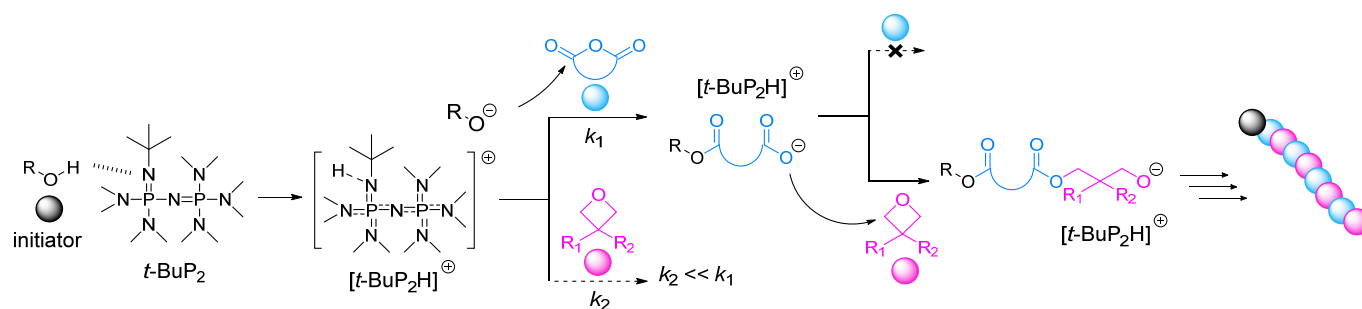


Figure 5. (A) Kinetic plots for the polymerization of PA and TO using $t\text{-BuP}_2$ at 80 °C with $[\text{PA}]_0/[\text{TO}]_0/[\text{BDM}]_0/[t\text{-BuP}_2] = 20/100/1/1$ (run 8), (B) dependence of $M_{n,NMR}$ (●) and D (■) on PA monomer conversion (conv.-PA) and (C) an overlay of the SEC traces.

Scheme 2. Proposed polymerization mechanism



Lowering the reaction temperature to 80 °C resulted in a decrease in the polymerization rate but yielded P(PA-*alt*-TO) with a low dispersity ($D = 1.12$; run 8 in **Table 1** and **Figure S13**). A kinetic experiment conducted under these conditions showed a linear increase in PA conversion with reaction time, indicating zero-order kinetics for PA in the ROCOP (**Figure 5A**). Therefore, the rate-determining step (RDS) of the ROCOP is not the ring-opening of PA but the ring-opening of TO. The molecular weight of P(PA-*alt*-TO) increased linearly with monomer conversion, demonstrating the well-controlled nature of the polymerization (**Figure 5B**). Similar results were observed for other catalysts (**Figure S14**). The polymerization mechanism is expected to be similar to the ROCOP of cyclic anhydrides and epoxides using PBs.²⁵ The reaction proceeds through successive reactions involving the nucleophilic attack of the terminal alkoxide on the cyclic anhydride and ring-opening of the oxetane by the terminal carboxylate anion (**Scheme 2**).

To confirm that the reaction between the terminal carboxylate and oxetane is an elementary step in the ROCOP of cyclic anhydride and oxetane, a model small-molecule reaction using benzoic acid and TO catalyzed by *t*-BuP₂ was conducted. ¹H and ¹³C NMR spectra confirmed the formation of the target structure, 3-hydroxypropyl benzoate, with no signals indicating the presence of poly(trimethylene oxide) (**Figures S15 and S16**).^{26,27} This provides conclusive evidence that the terminal carboxylic acid reacts with oxetane as an elementary reaction in the polymerization reaction.

Higher degrees of polymerization (DP) were used in subsequent experiments (runs 9 and 10 in **Table 1**). By increasing the initial monomer-to-initiator ratio, P(PA-*alt*-TO)s with *M*_{n,NMR} as high as 11.3 kDa and 20.6 kDa were successfully synthesized without compromising on the dispersity (**Figure S17–S19**).

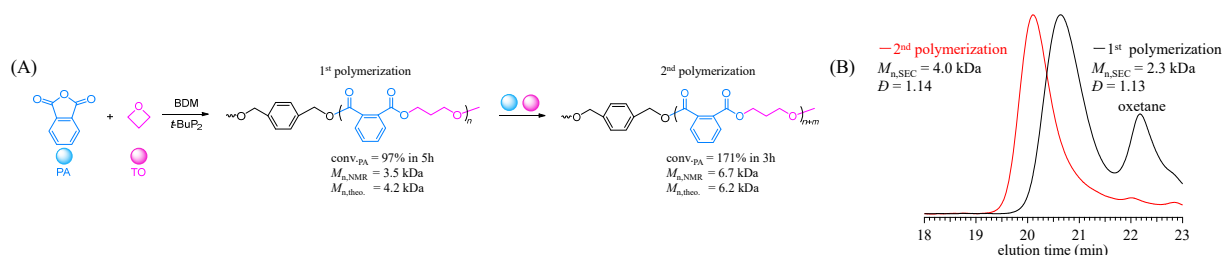


Figure 6. (A) Chain extension experiment for ROCOP of PA and TO to confirm the living nature. (B) SEC traces of the obtained P(PA-*alt*-TO) at the first and second stages of polymerization (black: first polymerization, red: second polymerization) (eluent, THF; flow rate, 1.0 mL min⁻¹; polystyrene standard).

The living polymerization nature of ROCOP was substantiated by sequential addition of monomers (**Figure 6**). Initially, polymerization was conducted at the ratio of [PA]₀/[TO]₀/[BDM]₀/[catalyst] = 20/100/1/1. After the conversion of PA was nearly complete, 20 equivalents of PA and 100 equivalents of TO were added. Polymerization restarted immediately from the terminus of P(PA-*alt*-TO), as evidenced by the continuous monomer conversion and shift in the SEC traces.

• Initiator scope

Scheme 3. ROCOP of PA and TO using various initiator

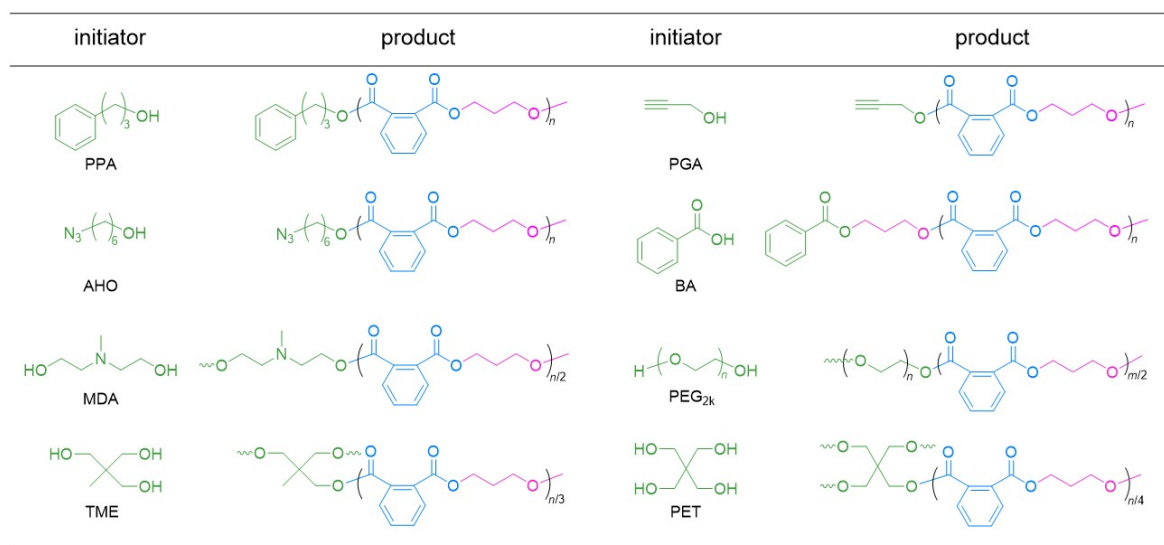


Table 2. ROCOP of PA and TO using *t*-BuP₂ as a catalyst with various initiators ^a

run	initiator	temp. (°C)	time (h)	conv. _{PA} ^b (%)	<i>M</i> _{n,theo.} (kDa) ^c	<i>M</i> _{n,NMR} (kDa) ^b	<i>M</i> _{n,SEC} (kDa) ^d	<i>Đ</i> ^d
1	PPA	80	45	>99	6.3	4.6	4.8	1.11
2	PGA	100	6	92	5.6	4.9	3.1	1.15
3	AHO	100	7	81	5.2	4.5	3.3	1.14
4	BA	100	13	87	5.5	5.1	4.6	1.12
5	MDA	80	13	81	5.1	— ^e	3.4	1.18
6	PEG _{2k}	100	7	78	6.8	5.6	4.1	1.24
7 ^f	TME	80	11	80	4.6	4.8	4.2	1.10
8	PET	80	12	78	5.0	3.9	3.2	1.18

^a Polymerization conditions: atmosphere, Ar; initiator, BDM; ([PA]₀/[TO]₀/[initiator]₀/[*t*-BuP₂]) = 30/120/1/1. ^b Determined by ¹H NMR spectroscopy in CDCl₃. ^c Calculated from [PA]₀/[initiator]₀ × conv._{PA}/100 × ((M.W. of PA) + (M.W. of TO)) + (M.W. of initiator). ^d Determined by SEC measurement of the polymer obtained in THF using a polystyrene standard. ^e Molecular weight cannot be calculated because the initiator signals overlap with the polymer signals. ^f [PA]₀/[TO]₀/[TME]₀/[*t*-BuP₂] = 27/107/1/0.9.

After optimizing the polymerization conditions, the initiator scope was investigated (**Scheme 3** and **Table 2**).

When monofunctional alcohols were used as initiators (runs 1–3 in **Table 2**), ROCOP proceeded smoothly, yielding P(PA-*alt*-TO)s in a well-controlled manner (**Figures S22–S33**). Notably, functional groups such as terminal alkynes and azido groups exhibited good tolerance, as confirmed by NMR and Fourier transform infrared spectroscopy (FT-IR) analyses (**Figures S27, S30 and S32**). These functional groups at the α-end of

P(PA-*alt*-TO) can be further utilized for chain-end modification via alkyne/azido click reactions.²⁸ Next, benzoic acid (BA) was tested as the initiator in the ROCOP of PA and TO (run 4 in **Table 2**). The ROCOP polymerization mechanism indicates the feasibility of the use of carboxylic acids as initiators (**Figure 6**). Although the polymerization rate was slightly lower than that obtained using alcohol initiators, the corresponding P(PA-*alt*-TO) was also produced in a well-controlled manner (run 4 vs. runs 2 and 3; **Figures S34–S36**). For diol initiators, apart from BDM utilized in the initial optimization, *N*-methyldiethanolamine (MDA) and polyethylene glycol (PEG) were examined as possible initiators. The resulting polymer products, amine-containing polyesters and amphiphilic polyester-*b*-PEG, show potential applicability as drug delivery carriers.^{29,30} When MDA was employed, the corresponding P(PA-*alt*-TO) was obtained with low dispersity ($\bar{D} = 1.18$; run 5 in **Table 2**, **Figures S37 and S38**). Because of the peak overlap between the initiator moiety and the polymer in the ¹H NMR spectrum, the polymer structure was confirmed using MALDI-TOF MS (**Figure S39**). When PEG_{2k} was used as the initiator (run 6 in **Table 2**), the SEC traces of the produced polymer clearly shifted to the high-molecular-weight region from the initiator while maintaining a low dispersity, indicating the growth of P(PA-*alt*-TO) from the PEG_{2k} macroinitiator and the formation of the PEG-*b*-P(PA-*alt*-TO) block copolymer (**Figure S40**). The formation of the block copolymer was also confirmed via ¹H NMR analysis (**Figure S41**). Subsequently, initiators with three and four hydroxyl groups were examined for the synthesis of three- and four-armed star polyesters, respectively. Aliphatic polyester stars are known for their potential application in biomedicine and nanotechnology.³¹ The ROCOP of cyclic anhydrides and oxetanes using a triol (trimethylolethane, TME) and a tetraol (pentaerythritol, PET) as initiators was investigated (runs 7 and 8 in **Table 2**). ¹H NMR measurements confirmed that polymerization progressed from all alcohol residues in the initiators, leading to the successful synthesis of the desired P(PA-*alt*-TO) (**Figures S42–S51**).

The results obtained from the initiator scope study demonstrated good functional group tolerance and versatility in the synthesis of polyesters with diverse structures. Notably, different reaction temperatures, both 80 °C and 100 °C, work fine for the polymerization using different initiators (**Table S2**).

• Monomer scope

Scheme 4. ROCOP of various anhydride and oxetane using *t*-BuP₂

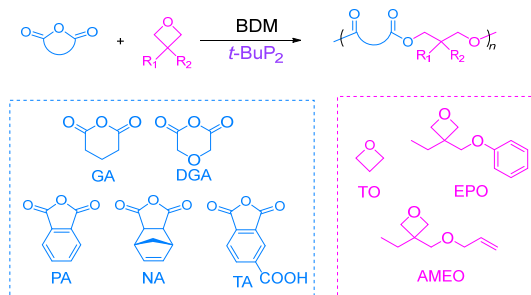


Table 3. ROCOP of various cyclic anhydrides and various oxetanes using *t*-BuP₂ ^a

run	cyclic anhydride	oxetane	temp. (°C)	time (h)	conv. ^b (%)	<i>M</i> _{n,theo.} ^c (kDa)	<i>M</i> _{n,NMR} ^b (kDa)	<i>M</i> _{n,SEC} ^d (kDa)	<i>D</i> ^d
1	PA	EPO	130	13	70	7.2	7.7	5.4	1.13
2	PA	AMEO	130	24	94	9.3	8.7	6.3	1.14
3	GA	TO	100	14	63	3.4	3.2	3.6	1.23
4	DGA	TO	100	7	>99	5.4	3.1	1.6	1.35
5	NA	TO	100	37	87	6.3	5.4	4.0	1.29
6 ^e	TA	EPO	130	6	>99	17.4	18.3	8.0	1.90

^a Polymerization conditions: atmosphere, Ar; initiator, BDM; ([cyclic anhydride]₀/[oxetane]₀/[BDM]₀/[*t*-BuP₂]) = 30/120/1/1. ^b Determined by ¹H NMR spectroscopy in CDCl₃. ^c Calculated from [cyclic anhydride]₀/[BDM]₀ × conv. /100 × ((M.W. of cyclic anhydride) + (M.W. of oxetane)) + (M.W. of BDM). ^d Determined by SEC measurement of the polymer obtained in THF using a polystyrene standard. ^e *M*_{n,MALS} = 24.7 kDa (Figure S71).

Following the initiator screening, the scope of the monomers was examined. In addition to the combination of PA and TO, six other monomer pairs derived from five cyclic anhydrides and three oxetanes were investigated with regard to the ROCOP using *t*-BuP₂ as the catalyst and BDM as the initiator (**Scheme 4** and **Table 3**). Initially, the oxetane component was modified to 3,3-disubstituted oxetanes, namely 3-ethyl-3-(phenoxymethyl)-oxetane (EPO) and 3-((allyloxy)methyl)-3-ethyloxetane (AMEO), instead of TO (runs 1 and 2 in **Table 3**). Substitutions at the 3-position led to decreased reactivity of oxetanes, necessitating the polymerization at 130 °C with extended reaction time. Nevertheless, the resulting polyesters exhibited a perfectly alternating structure with low *D*, and their molecular weight measured using NMR agreed with their theoretical values (**Figures S52–S57**). After checking for variations in the oxetanes, different cyclic anhydrides were examined. Glutaric anhydride (GA), diglycolic anhydride (DGA), and 5-norbornene-2,3-

dicarboxylic anhydride (NA) were used in the ROCOP with TO (runs 3–5 in **Table 3**). Polymerization was performed at 100 °C. The polymerization rate varied with the cyclic anhydride component; DGA reached full conversion within 7 h, whereas NA showed the slowest reactivity (87% conversion after 37 h). Despite their different reactivities, the corresponding polyesters, namely P(GA-*alt*-TO), P(DGA-*alt*-TO), and P(NA-*alt*-TO), were confirmed using ^1H NMR spectra and SEC measurements with relatively low dispersity ($\bar{D} = 1.23\text{--}1.35$) (**Figures S58–S66**). Epimerization of the chair centres of P(NA-*alt*-TO) was observed (**Figure S64**). The remaining olefin moieties on P(NA-*alt*-TO) can be utilized for post-polymerization modification via thiol–ene reactions.³² Trimellitic anhydride (TA), a cyclic anhydride bearing a carboxylic acid moiety, copolymerizes with epoxides to produce hyperbranched polyesters.³³ In this study, the ROCOP of TA and EPO was realized to synthesize the corresponding hyperbranched P(TA-*alt*-EPO) (run 6 in **Table 3**). ^1H NMR analysis of the obtained P(TA-*alt*-EPO) indicated a DP ratio of $DP_{\text{TA}}:DP_{\text{EPO}} = 1:2.09$. This value is in close agreement with the theoretical value for hyperbranched P(TA-*alt*-EPO) with all chain ends as EPO ($DP_{\text{TA}}:DP_{\text{EPO}} = 1:2$, **Figures S67–S69**). This suggests that the obtained P(TA-*alt*-EPO) possesses a hyperbranched structure, with most of the chain ends as hydroxyl groups from the EPO monomers. Furthermore, compared to P(PA-*alt*-EPO), P(TA-*alt*-EPO) showed much lower $M_{\text{n, SEC}}$ as compared to $M_{\text{n, NMR}}$ (run 1 vs. run 6 in **Table 3**, **Figure S70**). The SEC with a multiangle light scattering detector confirmed the absolute molecular weight ($M_{\text{n, MALS}}$) of 24.7 kDa for P(TA-*alt*-EPO), which is in fair agreement to $M_{\text{n, NMR}}$, but much larger than $M_{\text{n, SEC}}$, indicating the formation of a branched structure due to decreased hydrodynamic volume (**Figure S71**). The broad $\bar{D}$ is attributable to the increased number of growing chain ends during the formation of branched structures, which increased the structural inhomogeneity.

• Thermal analysis

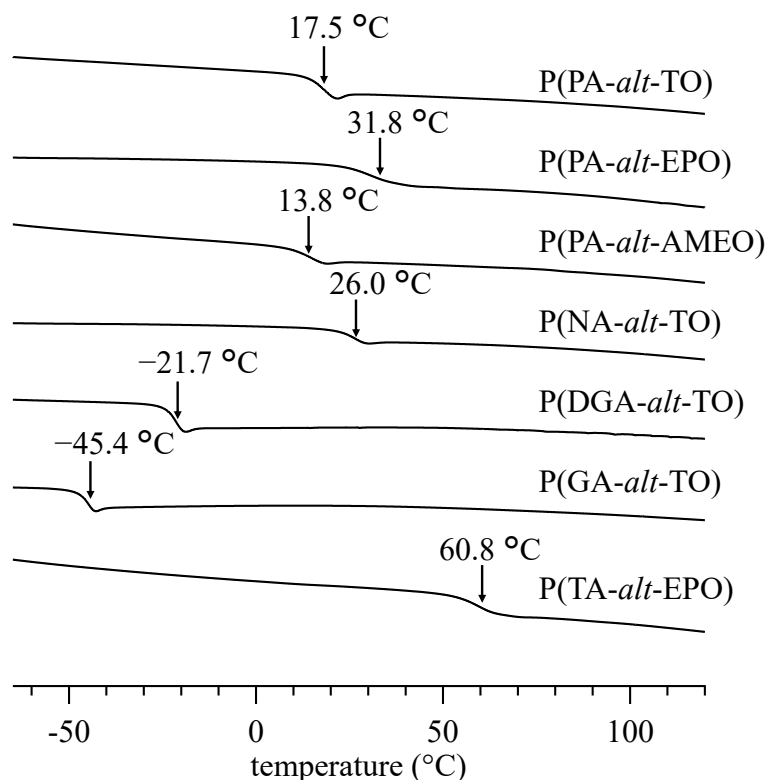


Figure 7. DSC curves of P(cyclic anhydride-*alt*-oxetane) during the second heating run (heating rate: 10 °C min⁻¹)

The thermal properties of the synthesized polyesters were analyzed using differential scanning calorimetry (DSC). Varying the combination of cyclic anhydride and oxetane monomers resulted in polyesters with a broad range of glass transition temperature (T_g)—from -45.4 °C to 60.8 °C (**Figure 7**). When PA or NA was employed in the ROCOP with oxetanes, the obtained polyesters showed T_g values in the proximity of the respective room temperatures: 17.5 °C for P(PA-*alt*-TO), 31.8 °C for P(PA-*alt*-EPO), 13.8 °C for P(PA-*alt*-AMEO), and 26.0 °C for P(NA-*alt*-TO). In contrast, aliphatic polyesters lacking rigid cyclic structures had much lower T_g values: -21.7 °C for P(DGA-*alt*-TO) and -45.4 °C for P(GA-*alt*-TO). The higher T_g observed in P(DGA-*alt*-TO) compared to P(GA-*alt*-TO) can be attributed to the presence of aliphatic ether moieties in P(DGA-*alt*-TO), which facilitate additional interactions between polymer chains. This phenomenon has been previously reported in polyesters synthesized via the ROCOP of cyclic anhydrides (DGA and GA) and epoxides.³⁴ The hyperbranched polyester P(TA-*alt*-EPO) exhibited a higher T_g of 60.8 °C. These findings

indicate that the polyesters synthesized using bicyclic anhydrides (PA) and tricyclic anhydrides (NA) generally show much higher T_g values than those synthesized using monocyclic anhydrides (DGA and GA). And the polymer topology also strongly affects the T_g (P(PA-*alt*-EPO) vs. P(TA-*alt*-EPO)). Melting and crystallization were not observed in the case of any of the polymers (**Figure S72**).³⁵

Changing the oxetane component from monocyclic to bicyclic or other rigid structures could be beneficial in further increasing the T_g of polyesters via cyclic anhydride/oxetane ROCOP.¹⁷ This trend aligns with that of the polyesters obtained via cyclic anhydride/epoxide ROCOP.¹⁰ However, in comparison to epoxides, the use of oxetanes in ROCOP with cyclic anhydrides introduces an additional sp^3 carbon in each repeating unit of the polymer main chain, thereby increasing the main chain flexibility and lowering the T_g value. For instance, the T_g of P(PA-*alt*-TO) ($T_g = 17.5\text{ }^\circ\text{C}$) is lower than that of poly(ethylene phthalate) ($T_g = 38.2\text{ }^\circ\text{C}$)³⁶ and P(PA-*alt*-PO) ($T_g = 63\text{ }^\circ\text{C}$).³⁷

• Synthesis of block copolymers via self-switchable polymerization

Scheme 5. Synthesis of block polyesters from monomer mixtures

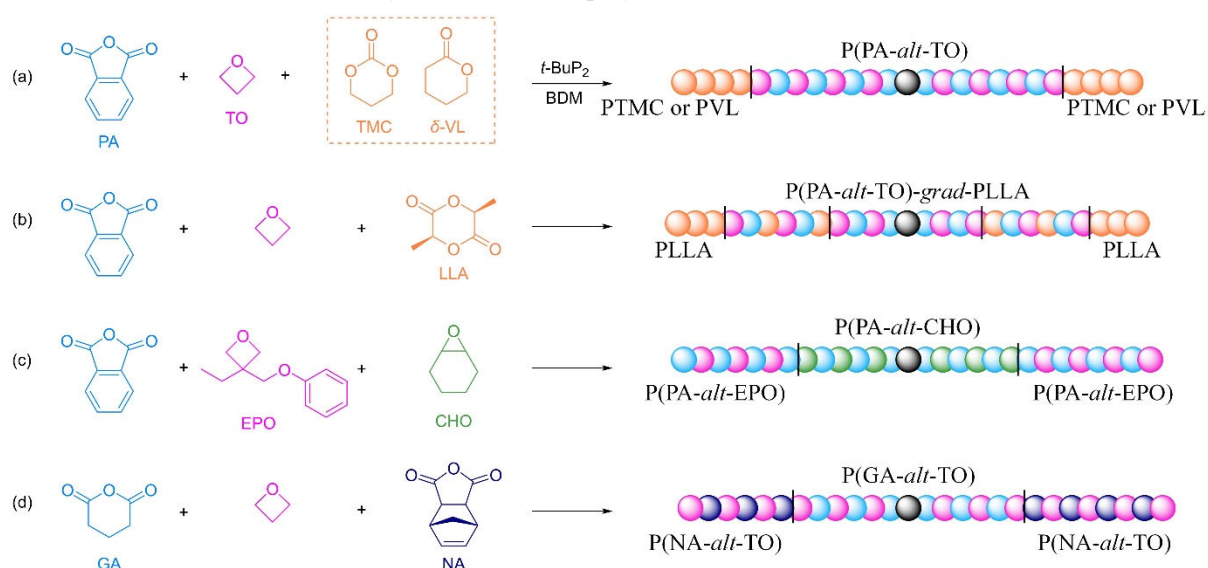


Table 4. Self-switchable polymerization catalyzed by $t\text{-BuP}_2$ ^a

run	monomers	$\frac{[\text{monomers}]_0}{[t\text{-BuP}_2]_0} / \frac{[\text{BDM}]_0}{[\text{BDM}]_0}$	time (h)	conv. ^c (%)	DP	$M_{n,\text{theo.}}^c$ (kDa)	$M_{n,\text{NMR}}^b$ (kDa)	$M_{n,\text{SEC}}^d$ (kDa)	$\bar{D}^d$
1	PA/TO/TMC	25/100/50/1/1	5	PA>99 TMC=35	PA=25 TMC=18	7.1	8.1	6.9	1.14
2	PA/TO/VL	25/27/100/1/1	75	PA>99 VL=23	PA=25 VL=23	7.6	6.6	4.5	1.28
3	PA/TO/LLA	25/100/25/1/1	9	PA>99 LLA = 90	PA=25 LLA=23	8.5	9.1	4.8	1.11
4 ^e	PA/EPO/CHO	50/100/25/1/1	11	CHO>99 EPO=23	CHO=25 EPO=23	14.2	10.8	9.4	1.07
5	GA/NA/TO	25/25/125/1/1	48	GA>99 NA=72	GA=25 NA=18	8.5	9.3	2.6	1.50

^a Polymerization conditions: atmosphere, Ar; temp., 100 °C; initiator, BDM. ^b Determined by ^1H NMR spectroscopy in CDCl_3 . ^c Calculated from monomer conversions determined by ^1H NMR spectroscopy. ^d Determined by SEC of the polymer obtained in THF using a polystyrene standard. ^e temp.=130 °C.

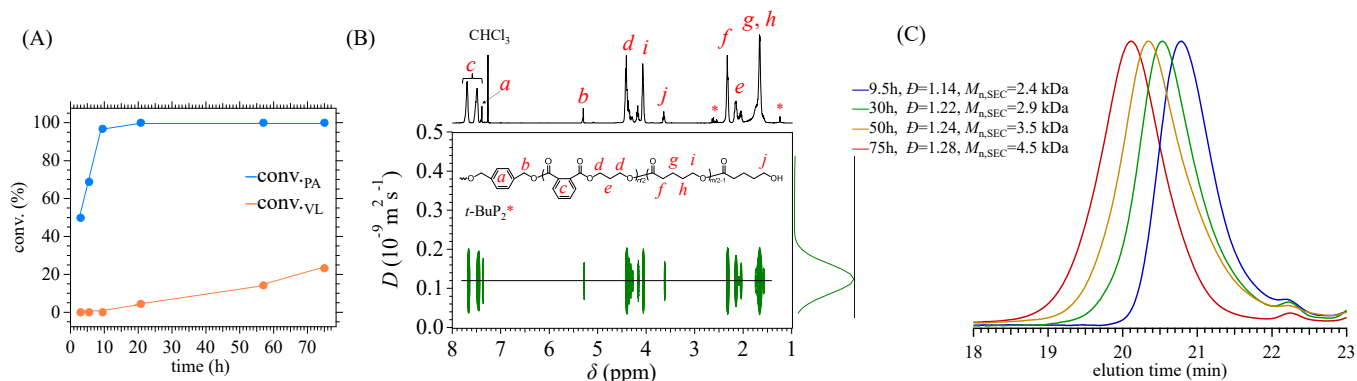


Figure 8. (A) The plots of monomer conversion versus time. The polymerization of PA, TO, and VL was performed at 100 °C. (B) DOSY spectrum in CDCl₃ and (C) SEC trace of P(PA-*alt*-TO)-*b*-PVL (eluent, THF; flow rate, 1.0 mL min⁻¹; polystyrene standard).

The synthesis of block copolymers using monomer mixtures in a one-pot/one-step manner, referred to as self-switchable polymerization, has garnered significant interest.^{21,22} This method entails connecting different catalytic cycles, such as the cyclic ester ROP and cyclic anhydride/epoxide ROCOP, to establish versatile polymerization systems. Given the successful establishment of the cyclic anhydride/oxetane ROCOP by using organobase catalysts, we investigated their application in self-switchable polymerization (**Scheme 5**).

Initially, we investigated the self-switchable polymerization integrating the ROCOP of PA and TO with the ROP of cyclic carbonates or cyclic esters (runs 1–3 in **Table 4**). When trimethylenecarbonate (TMC) was copolymerized together with PA and TO under the optimized condition, PA was consumed first, acting as a “switch” for subsequent rapid ROP of TMC after its full conversion in 4.5 h (run 1 in **Table 4**, **Figure S73**).

¹H NMR measurements showed that the signals were derived only from P(PA-*alt*-TO) and PTMC without a clear tapered region (**Figure S74**). Additionally, SEC measurements showed a shift of the elution peak toward higher molecular weights while maintaining low *D* (**Figure S75**). The aforementioned experimental observations confirm that the polymerization results in the block terpolymer PTMC-*b*-P(PA-*alt*-TO)-*b*-PTMC.

In the copolymerization of PA/TO/ δ -valerolactone (VL), PA/TO ROCOP occurred prior to the ROP of VL as in the case with TMC (run 2 in **Table 4**). When the conversion of PA reached 97% after 9.5 h, the ROP of VL

began (**Figure 8A**). Thus, a block-like copolymer with a narrow tapered region was obtained. After an additional 65.5 h (75 h in total), 23% of VL was converted. The formation of triblock copolymers, rather than a polymer blend, was confirmed by the single diffusion coefficient in diffusion-ordered NMR spectroscopy (DOSY) (**Figure 8B**). The monomodal SEC trace of the obtained copolymers clearly shifted to the high-molecular-weight region with D of 1.28 (**Figure 8C**). In contrast to the nearly perfect self-switchable reactivity when using TMC or VL, employing L-lactide (LLA) in the copolymerization with PA/TO resulted in a gradient copolymer (run 3 in **Table 4**). Although the PA/TO ROCOP proceeded faster, the ROP of LLA occurred simultaneously. When PA was fully converted, 50% of the LLA was polymerized (**Figure S76**). Subsequently, the ROP of LLA produced a PLLA block (**Figures S77 and S78**).

Additionally, self-switchable polymerizations involving two different ROCOP cycles were explored (runs 4 and 5 in **Table 4**). The copolymerization of PA, EPO, and cyclohexene oxide (CHO) resulted in sequential switching between cyclic anhydride/epoxide ROCOP and cyclic anhydride/oxetane ROCOP (run 4 in **Table 4**). Under 130 °C, the consumption of CHO reached 95% within 1 h, prior to EPO, thus resulting in a P(PA-*alt*-EPO)-*b*-P(PA-*alt*-CHO)-*b*-P(PA-*alt*-EPO) triblock terpolymer with a narrow tapered region (**Figures S79–S81**). Notably, *t*-BuP₂ exhibited higher reactivity than did the previously used CsOPiv catalyst without diminishing the efficient switching selectivity.¹⁹

Finally, the copolymerization of TO and two cyclic anhydrides, NA and GA, was performed (run 6 in **Table 4**). When GA reached full consumption after 26 h, the conversion of NA was only 6%. Upon extending the reaction for an additional 22 h (*i.e.*, 48 h in total), the conversion of NA reached 72% (**Figure S82**). The SEC traces gradually shifted to the high-molecular-weight region during polymerization while maintaining a monomodal distribution, although the elution peak gradually became slightly broader (**Figures S83 and S84**).

These results underscore the potential of the organobase-catalyzed cyclic anhydride/oxetane ROCOP in the design and synthesis of complex polymeric materials through self-switchable polymerization, paving the way for advanced applications in various fields.

CONCLUSION

This study demonstrated the effectiveness of organobases in catalyzing the ring-opening copolymerization (ROCOP) of oxetanes with cyclic anhydrides in a perfectly alternating fashion, leading to the synthesis of diverse polyesters. Among the tested organobases, *t*-BuP₂, the phosphazene base, exhibited superior catalytic activity and controllability. Notably, this catalytic system showed remarkable tolerance toward various functional groups and versatility in generating polyesters with diverse structures by manipulating the initiators and monomers. Importantly, our findings showcase the applicability of this approach to self-switchable polymerization, wherein it is seamlessly integrated with the ROP of cyclic esters and cyclic carbonates as well as different ROCOP processes involving epoxides and cyclic anhydrides. This opens new avenues for the synthesis of polyester-based polymers. Consequently, our synthetic methodology holds promise for advancing the development of novel biodegradable polyesters with tunable material properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedure; polymerization kinetic plots; NMR spectra, MALDI-TOF spectra, SEC traces, and DSC curves of the synthesized polymers.

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