

Article

An Investigation of the Organoborane/Lewis Base Pairs on the Copolymerization of Propylene Oxide with Succinic Anhydride

Lan-Fang Hu, Dan-Jing Chen, Jia-Liang Yang and Xing-Hong Zhang * 

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China; 11529021@zju.edu.cn (L.-F.H.); 3160103167@zju.edu.cn (D.-J.C.); 11529008@zju.edu.cn (J.-L.Y.)

* Correspondence: xhzhang@zju.edu.cn; Tel.: +86-571-8795-5732

Received: 7 December 2019; Accepted: 27 December 2019; Published: 8 January 2020



Abstract: The copolymerization of biorenewable succinic anhydride (SA) with propylene oxide (PO) is a promising way to synthesize biodegradable aliphatic polyesters. However, the catalytic systems for this reaction still deserve to be explored because the catalytic activity of the reported catalysts and the molecular weights of produced polyesters are unsatisfied. Herein, we investigate the copolymerization of SA with PO catalyzed by the organoborane/base pairs. The types of Lewis bases, organoboranes, and their loadings all have a large impact on the activity and selectivity of the copolymerization. High ester content of >99% was achieved when performed the PO/SA copolymerization using triethyl borane (TEB)/phosphazene base P1-*t*-Bu (*t*-BuP₁) pair with a molar ratio of 1/1 at 30–80 °C. Using TEB/*t*-BuP₁ pair with the molar ratio of 4/1 at 80 °C, the turnover of frequency (TOF) was up to 128 h⁻¹ and clearly higher than the known TOF values (0.5–34 h⁻¹) of the PO/SA copolymerization by previously reported catalysts. The number-average molecular weights (M_n s) of the resultant polyesters reached up to 20.4 kg/mol when copolymerization was carried out using TEB/*t*-BuP₁ (1/1, in molar ratio) at 30 °C.

Keywords: succinic anhydride; propylene oxide; aliphatic polyester; organoborane; Lewis base

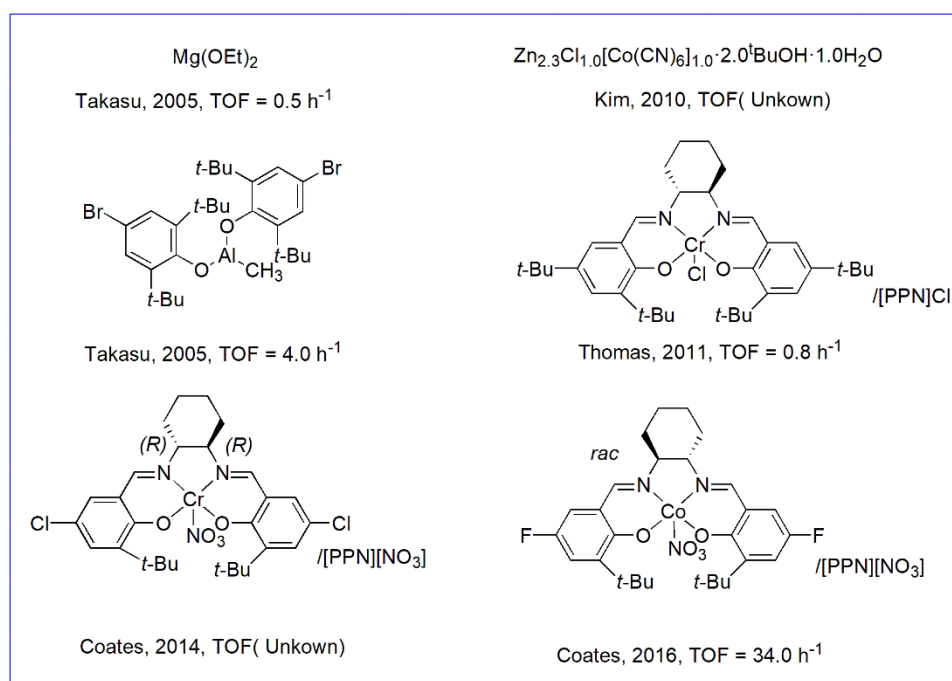
1. Introduction

Plastic litter, usually made by petroleum-based feedstocks, is an ever-increasing global issue and one of the environmental challenges. Conventional petroleum-based plastic waste is recognized to biodegrade very slowly. Scientists found that plastic waste can break down into ever smaller pieces, become tiny enough to waft in the air and flow in the water and accumulate in organisms or human beings [1,2]. Therefore, it is of great importance to prepare biodegradable materials to replace those plastics.

Aliphatic polyesters are a class of technologically important alternatives to conventional petroleum-based materials because of their biodegradable and the use of renewable resources as feedstock materials [3–5]. For example, poly(alkylene succinate)s including poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS) are some of the most important biodegradable polyesters and could be produced by polycondensation of biorenewable resources succinic acid with glycol, butanediol [6,7]. However, the polycondensation method is often energy-intensive and requires removal of small molecules under highly reduced pressure.

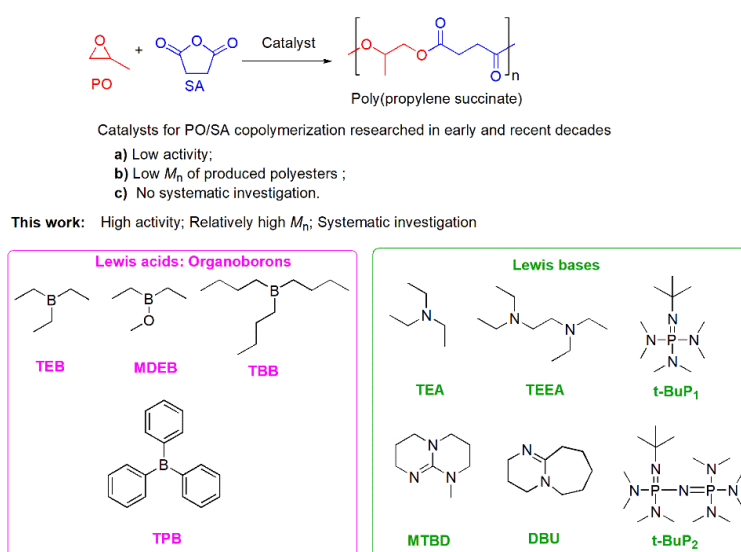
It is of great interest to synthesize polyesters from the copolymerization of epoxides with cyclic anhydrides [8–10], because a variety of epoxides and cyclic anhydrides are commercially available and polyesters with various structures can be prepared under mild conditions. Especially, the monomers from

renewable resources are intriguing from the environmental viewpoint [11–16]. Among various anhydrides studied for the production of polyesters, succinic anhydride (SA) is a kind of promising building block since it is commercially available from renewable resources [6,14,17]. For the copolymerization with epoxide, SA is generally less reactive than other anhydrides, such as maleic anhydride, phthalic anhydride etc., and M_n s of the SA/epoxide copolymers are relatively low (the reported maximum M_n : 9.2 kg/mol [18]) because of the formation of cyclic polymer chains, transesterification of polymer chains or the chain transfer reaction in these systems [19,20]. Therefore, it remains a challenge to develop catalysts with high activity and selectivity for synthesizing high molecular weight SA/epoxide copolymers. Several catalysts such as zinc [19], aluminum [20], chromium [14], cobalt [18,21], and magnesium [20] complexes have been reported to produce alternating propylene oxide (PO)/SA copolymer (Scheme 1). However, the (salen) Co complex showed a maximum turnover of frequency (TOF) of 34 h^{-1} in all the reported catalysts for PO/SA copolymerization [21]. In addition, the metallic residues in polyesters may restrain their application in high-value and sensitive domains, such as biomedical and personal beauty care applications, microelectronic devices, or food packaging.



Scheme 1. Several catalysts reported for the copolymerization of succinic anhydride (SA) with propylene oxide (PO).

Recently, there has been rapidly growing interest in implementing epoxide-based alternating copolymerization using metal-free catalysts [22–32]. The competence and potential of organocatalysts have been fully verified by the achievements of strictly alternating sequence distribution and high activity. In this work, aiming at efficiently catalyzing the copolymerization of SA with PO that is still rarely investigated, we studied the effect of the structure of organoboranes (OBs) as the Lewis acid (LA), the basicity of Lewis bases (LBs), the LA/LB molar ratios on the activity and selectivity of the copolymerization of SA with PO. We propose a simple organocatalyst system with high catalytic activity (Scheme 2).



Scheme 2. Different catalytic systems for PO/SA copolymerization.

2. Results

In early years, metal-free initiators, especially the tertiary amines, were used to catalyze the epoxide/anhydride copolymerization [33]. The PO/SA copolymerization was carried out in the presence of triethylamine (TEA) alone (entry 1, Table 1), the result showed a low activity with a TOF of 1 h^{-1} that is similar to the previously reported system [14,20]. Additionally, the ester content of the resultant polyester calculated from the $^1\text{H NMR}$ spectrum is 86% (Figure 1(1)). We then used triethyl borane (TEB) paired with TEA for the copolymerization (entry 2, Table 1), and the $^1\text{H NMR}$ spectrum showed that high alternating degree (i.e., ester content: 95%) was achieved (Figure 1(2)). This result is well consistent with the copolymerization of PO/SA by TEB/quaternary onium salt pair (SA conversion: 79%, 45 °C, 10 h) [27]. It was proposed that TEB protected the growing anion to form a tetracoordinate bond-carboxylate (or alkoxide) anion that accelerated the copolymerization [23,27,30]. The matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrum of the SA/PO copolymer catalyzed by the TEB/TEA pair revealed the $-\text{N}(\text{CH}_2\text{CH}_3)_3^+$, $-\text{OH}$ terminated copolymer as the major distribution, suggesting that no significant transesterification took place under these conditions (Figure 2). And similar results were also reported by Li et al [34]. They observed DMAP^+ , OH -capped polyester chains from MALDI-TOF MS. In addition, inspired by the TEB/double-site base pairs for highly active and living synthesis of carbonyl sulfide (COS)/epoxide copolymers [35], N,N,N',N' -tetraethylethylenediamine (TEEA) was solely employed to catalyze the PO/SA copolymerization (entry 3, Table 1). The SA conversion was up to 62% within 48 h, and the resultant copolymer had the ester content of 93% that was higher than that of polyester produced by TEA alone (86%, Figure 1(3,4)).

Table 1. SA/PO copolymerization catalyzed by LA/LB pairs ¹.

Entry	LA	LB	Time (h)	SA Conv. (%) ²	Ester (%) ²	TOF (h^{-1}) ³	M_n (kg/mol) ⁴	D^4
1		TEA	48	55	86	1	3.5	1.20
2	TEB	TEA	10	74	95	7	5.1	1.10
3		TEEA	48	62	93	1	3.0	1.22
4	TEB	TEEA	10	>99	97	10	6.4	1.15
5	TBB	TEEA	10	70	88	7	4.1	1.06
6	TPB	TEEA	10	48	85	5	3.3	1.12
7	MDEB	TEEA	10	92	94	9	5.0	1.11

¹ Reactions were run at 60 °C in neat PO (4 mmol), $[\text{PO}]/[\text{SA}]/[\text{OB}]/[\text{LB}] = 400/100/1/1$. ² SA conversion and Ester were determined by $^1\text{H NMR}$ spectroscopy of crude reaction mixture. ³ TOF = Turnover frequency, mol SA consumed \cdot mol $\text{LB}^{-1} \text{ h}^{-1}$. ⁴ Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

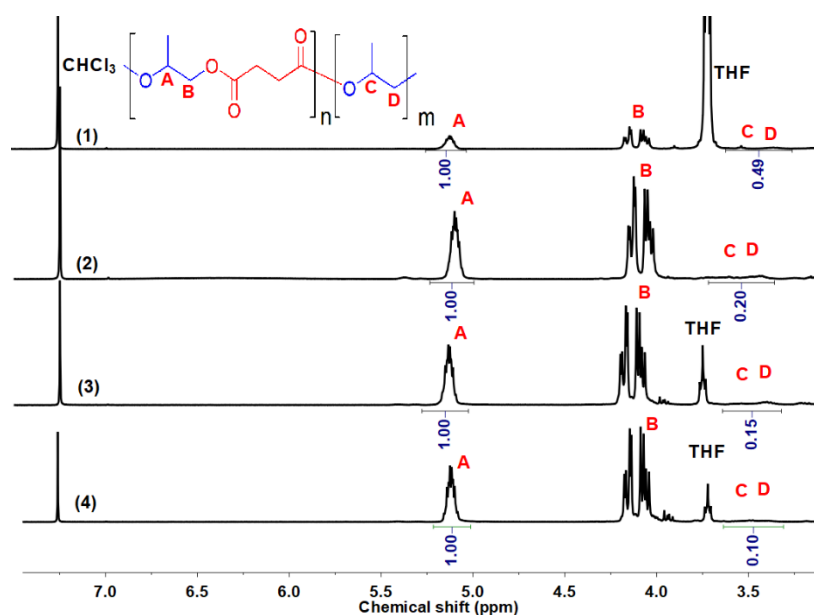


Figure 1. ^1H NMR spectra of crude products at different catalyst systems: (1) trimethylamine (TEA) (entry 1, Table 1); (2) tetraethylethylenediamine (TEEA) (entry 3, Table 1); (3) triethyl borane (TEB)/TEA (entry 2, Table 1); (4) TEB/TEEA (entry 4, Table 1).

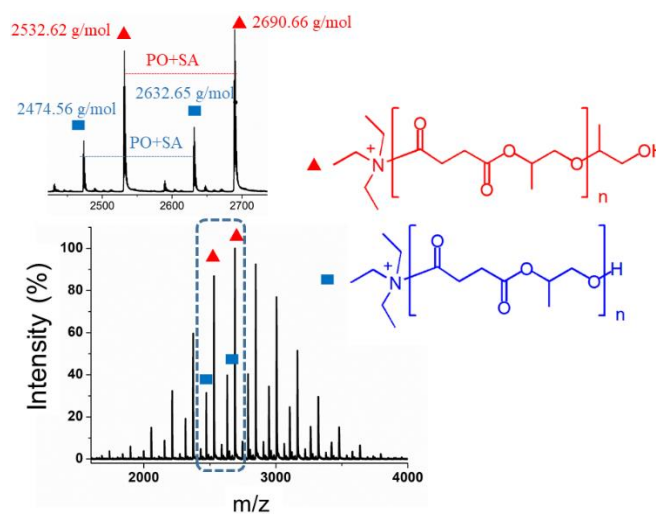


Figure 2. MALDI-TOF-MS spectrum of poly(propylene succinate) produced using TEB/TEA (entry 2, Table 1).

In order to evaluate the relationship of catalytic performance with the structure of the LA/LB pairs, we then studied the effect of the OB/TEEA pairs on the PO/SA copolymerization. The catalysis of the combination of TEEA with OBs (including TPB, TBB, and MDEB, Scheme 2) for the PO/SA copolymerization was investigated, as summarized in Table 1 (entries 4–7). Thereof, TEB/TEEA (1/1) pair led to >99% conversion of SA, and showed higher activity (TOF: 10 h^{-1}) and higher selectivity (ester% = 97%) than other OBs companied with 1 equiv TEEA. TOFs of the TEB/TEEA, MDEB/TEEA, TBB/TEEA, TPB/TEEA pairs were 10, 9, 7, and 5 h^{-1} , respectively. Correspondingly, the ester contents of the resultant poly(propylene succinate)s were 97%, 94%, 88%, and 85%, respectively. Both activity and selectivity decreased with the order of the steric hindrance of TPB < TBB < MDEB < TEB, while increased with the order of the acidity of TEB > MDEB > TBB > TPB [36,37].

In an attempt to shed light on the effect of LBs on the activity and selectivity for the PO/SA copolymerization, the LBs, *t*-BuP₁, *t*-BuP₂, DBU, and MTBD were tested, as summarized in Table 2.

The LBs were chosen to span a range of basicity (the pKa values of their conjugate acid LB-H⁺ listed are reported in MeCN, THF, DMSO, or H₂O, see Table S1 in the Supporting Information)[38,39]: TEEA (pKa^{cal} = 9.03) < TEA (pKa^{cal} = 10.62, pKa^{MeCN} = 18.7) < DBU (pKa^{MeCN} = 24.3) < MTBD (pKa^{MeCN} = 25.4) < *t*-BuP₁ (pKa^{MeCN} = 26.9) < *t*-BuP₂ (pKa^{MeCN} = 33.5). TEA, DBU, *t*-BuP₁ have been previously reported to copolymerize epoxides and anhydrides, but showed low activities [26,28,40]. The equimolar combination of these LBs (TEA, TEEA, *t*-BuP₂, DBU) with TEB exhibited improved activity towards the PO/SA copolymerization, and the ester contents of the resultant poly(propylene succinate)s were ≥93%. TOFs of these TEB/LB pairs increased with basicity of the bases in the following order: TEA (7 h⁻¹) < DBU (9 h⁻¹) < MTBD (11 h⁻¹) < *t*-BuP₁ (15 h⁻¹) < *t*-BuP₂ (20 h⁻¹). However, the situation is different for TEB/TEEA pair, the TOF (10 h⁻¹) of TEB/TEEA pair was slightly higher than that of TEB/TEA pair. This is because TEEA is a double-site initiator, which is more efficient to initiate the copolymerization than TEA, although the detail mechanism is still undisclosed [34].

Table 2. SA/PO copolymerization catalyzed by various LBs with TEB¹.

Entry	LB	[PO]:[SA]: [TEB]:[LB]	Time (h)	SA Conv. (%) ²	Ester (%) ²	TOF (h ⁻¹) ³	M _n (kg/mol) ⁴	D ⁴
1	<i>t</i> -BuP ₁	400:100:1:1	5	73	>99	15	6.0	1.10
2	<i>t</i> -BuP ₂	400:100:1:1	5	98	99	20	8.3	1.30
3	DBU	400:100:1:1	5	45	93	9	3.6	1.14
4	MTBD	400:100:1:1	5	57	98	11	4.2	1.13
5 ⁵	<i>t</i> -BuP ₁	400:100:4:1	0.5	64	96	128	1.7	1.24
6 ⁶	<i>t</i> -BuP ₁	400:200:1:1	84	98	>99	1	20.4	1.42

¹ Reactions were run at 60 °C in neat PO (4 mmol). ² SA conversion and Ester was determined by ¹H NMR spectroscopy of crude reaction mixture, ³ TOF = Turnover frequency, mol SA consumed·mol LB⁻¹·h⁻¹. ⁴ Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. ⁵ 80 °C. ⁶ 30 °C.

The TEB/*t*-BuP₂(*t*-BuP₁) pairs performed well for the PO/SA copolymerization, and exhibited TOFs of 15–20 h⁻¹ (entries 1,2 in Table 2), affording poly(propylene succinate)s with ester content of more than 99%, as shown in Figure 3. The proton resonance of the CH(A) next to the oxygen atom was observed at 5.12 ppm, with the proton signal of the CH₂(B) groups from PO found in the range 4.08–4.14 ppm. The signal of CH₃(C) was observed at 1.21 ppm and the signal of CH₂(D) from SA was observed at 2.60 ppm. No signals of polyether linkages were observed at 3.5–3.8 ppm, which verified the fully alternating structure of poly(propylene succinate). All poly(propylene succinate)s synthesized using various bases in Table 2 have high ester contents of 93% to >99% when the TEB/LB molar ratio was 1/1. It seems that the ester selectivity was less correlated with the basicity of LB. It is reasonable that the production of ether linkage was caused by consecutive attacking to PO which could be mainly inhibited by TEB-masked growing anions [27,32].

The LA/LB feeding ratio greatly affected the activity and selectivity of the PO/SA copolymerization. With the increase of TEB/LB molar ratios, the activity improved but selectivity decreased (entries 2, 4, Table 1, entries 1–4, Table 2 and Table S2). For example, when the molar ratio of the TEB/*t*-BuP₁ pair increased from 1/1 to 4/1 at 60 °C, TOF increased from 15 to 59 h⁻¹, and the ester contents was 95%. For the TEB/DBU pair-catalyzed PO/SA copolymerization, when the TEB/DBU molar ratio increased from 1/1 to 4/1, TOF values increased from 9 to 33 h⁻¹, however, the ester content of the resultant poly(propylene succinate)s sharply decreased from 93% to 37%.

We next investigated the effect of temperature on PO/SA copolymerization catalyzed by the TEB/*t*-BuP₁ pair at a wide temperature range from 0 to 80 °C (entries 1, 5, Table 2 and Table S3). As shown in Figure 4, TOFs of the copolymerizations increased significantly with the temperature, and the turning point was about 30–40 °C. Notably, the TOF value was up to 128 h⁻¹ at 80 °C in the presence of TEB/*t*-BuP₁ pair with the molar ratio of 4/1 (entry 2, Table 2) [21], which is higher than all previously reported TOFs (0.5–34 h⁻¹) for the PO/SA copolymerization (Scheme 1) [27]. Moreover, we observed that increasing the reaction temperatures from 30 to 80 °C, the ester contents of all the resultant

copolymers were more than 99% when the molar ratio of the TEB/*t*-BuP₁ pair was 1/1 (Figure 4A) and increased from 76% to 96% when the molar ratio of the TEB/*t*-BuP₁ pair was 4/1 (Figure 4B). It is reasonable that excess TEB could activate greater amounts of PO, and the TEB-activated PO was easily attacked by the growing species, leading to the formation of ether linkage (Figure 4B) [27,32]. In addition, M_n of the poly(propylene succinate) decreased with reaction temperatures increased, because of obvious chain transfer reaction at high reaction temperatures. We therefore performed the PO/SA copolymerization with the TEB/*t*-BuP₁ molar ratio of 1/1 at 30 °C with prolonged time (84 h, entry 2, Table 2), the conversion of SA was up to 98%, and M_n of the resultant poly(propylene succinate) was high (20.4 kg/mol) (Figure S2), which is close to the calculated value (31.0 kg/mol).

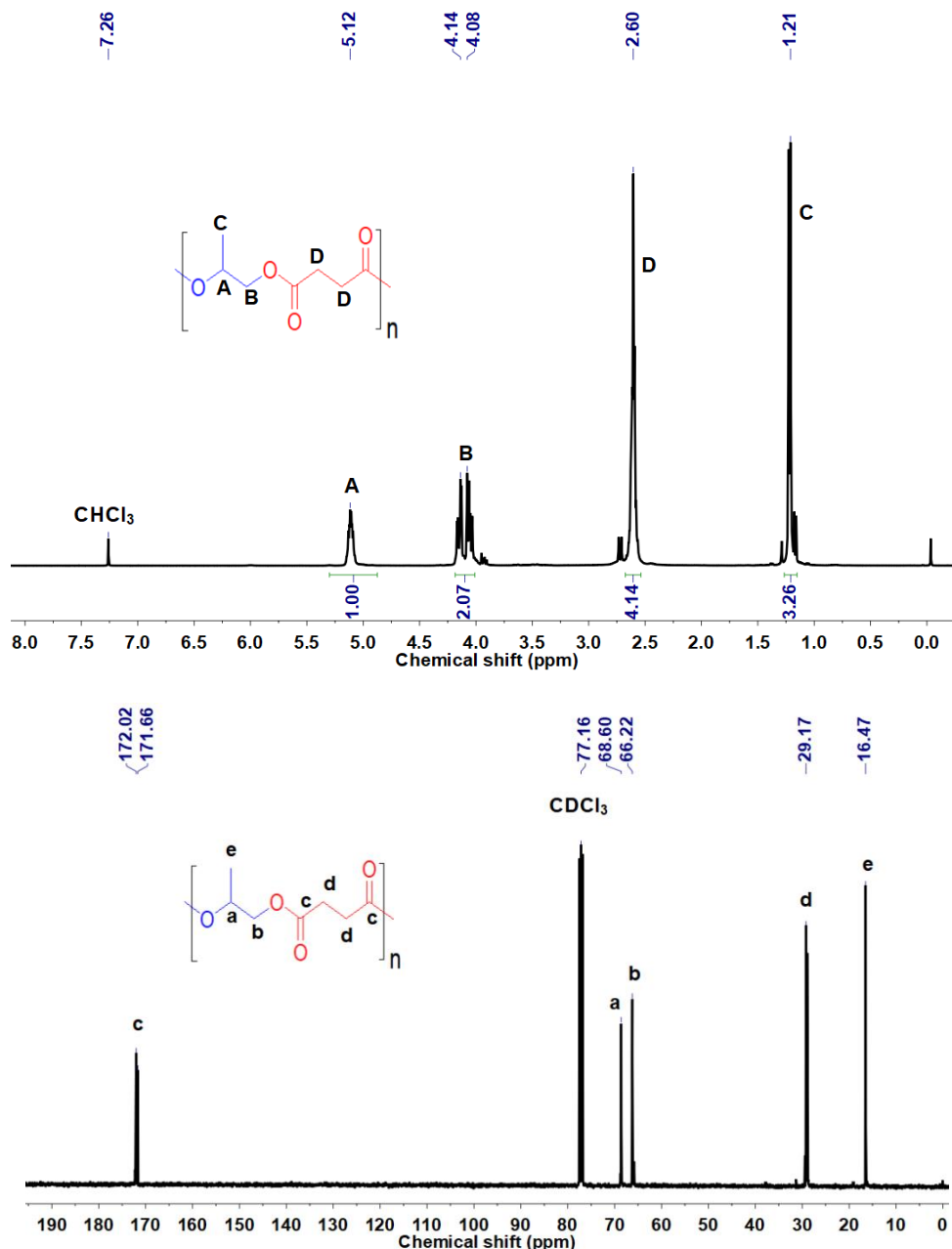


Figure 3. NMR spectra of purified poly(propylene succinate) in CDCl₃. Top: ¹H NMR spectrum. Bottom: ¹³C NMR spectrum (entry 1, Table 2).

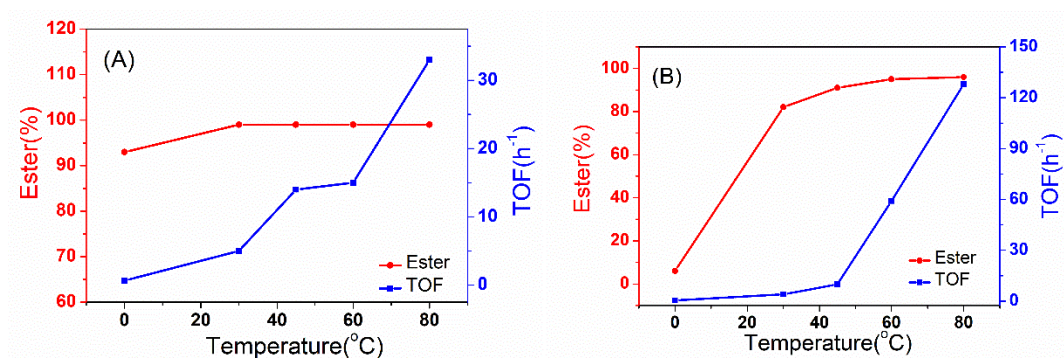
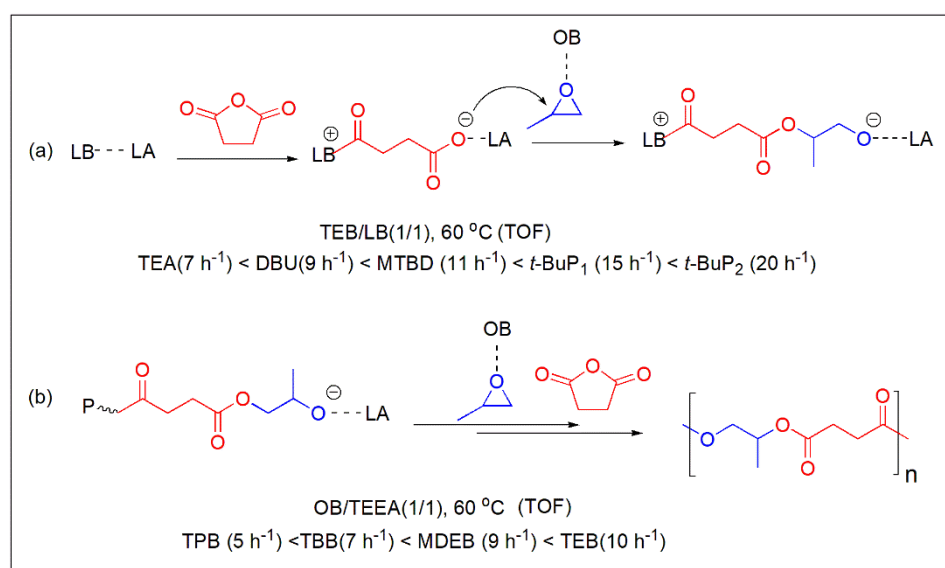


Figure 4. The effect of temperature on turnover of frequency (TOF) values and ester content of the SA/PO copolymerization catalyzed by TEB/*t*-BuP₁ pairs with the molar ratio of (A) 1/1; (B) 4/1.

The catalytic mechanism of the LA/LB pair for the copolymerization of epoxide and anhydride has been investigated [26,27,41,42]. For the PO/SA copolymerization, the LB/OB pair firstly reacts with SA, which was determined by MALDI-TOF-MS spectrum (Figure 2). Then the adduct of SA with LA/LB pair generates the zwitterion, which attacks PO for forming growing species (Scheme 3a). For a given OB, the stronger LB was, the faster the initiation step was reached, which results in a higher activity of the PO/SA copolymerization. As our previous reports [27,32], OB could coordinate with the growing carboxylate (or alkoxide) anions when LA/LB molar ratio was 1/1. When excess OB used, OB not only coordinates with the growing carboxylate (or alkoxide) anions for stabilizing them, but also activates PO (Scheme 3b). Therefore, excess OB addition often leads to the contaminant ether linkage and high activity. For a given LB, OB with high acidity and less steric hindrance leads to the higher activity.



Scheme 3. Proposed copolymerization mechanism using the LA/LB pair: (a) initiation; (b) propagation.

3. Materials and Methods

3.1. Materials

Unless otherwise specified, synthesis operation was carried out on a double-manifold Schlenk vacuum line under nitrogen atmosphere or in a nitrogen-filled glove box. Following purification, materials were stored in a nitrogen-filled glovebox prior to use unless otherwise specified. Triethyl borane (TEB) in THF (1.0 M), triphenylboron (TPB, 0.25 M in THF), Tributylborane (TBB, 1.0 M in THF), diethylmethoxyborane (DEMB) were purchased from Sigma-Aldrich (Shanghai, China) and used without further purifications. 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) was purified by

distillation after stirring with calcium hydride for 3 days. 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), phosphazene base P1-*t*-Bu (*t*-BuP₁; Sigma-Aldrich, 97%), Phosphazene base P2-*t*-Bu (*t*-BuP₂, 2.0 M in THF) were used as received. Triethylamine (TEA) and tetraethylethylenediamine (TEEA) were purchased from Sigma-Aldrich and purified by distillation after stirring with calcium hydride for 3 days. Propylene oxide (PO) was purified by distillation after stirring with calcium hydride for 3 days. Succinic anhydride (SA) was purchased from Aladdin (Shanghai, China) and purified by sublimation.

3.2. Copolymerization of SA with PO, Experimental Details

A 10-mL vial with magnetic stirrer was dried in an oven at 110 °C overnight, then immediately placed into the glovebox chamber. After keeping under vacuum for 2–3 h, the reaction vessel was moved into the glovebox with nitrogen atmosphere. The copolymerization of SA with PO described below is taken from entry 1 in Table 1 as the example. SA (100 mg, 1 mmol) was firstly added into the reactor. Then, PO (0.28 mL, 4 mmol) was added into the vessel after the introduction of the set amount of TEB (10 µL, 0.01 mmol) and TEA (1.9 µL, 0.01 mmol). The vial was sealed with a Teflon lined cap, taken out from the glovebox, and placed in an oil bath. The copolymerization was carried out at 60 °C for 10 h. The reactor was then cooled in ice-water bath, and an aliquot was taken from the crude product for the determination of the ratio of ester/ether linkages by ¹H NMR spectrum. The collected product was dissolved with dichloromethane and then precipitated in alcohol. The product was collected by centrifugation and dried in vacuum at 40 °C overnight.

3.3. Characterization

All ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE DMX 400 MHz instrument (Bruker, MA, USA) in CDCl₃. Chemical shift values were referenced to CHCl₃ at 7.26 ppm for ¹H NMR and 77.16 ppm for ¹³C NMR. Molecular weights and molecular weight distributions of the resultant copolymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories, CA, USA) equipped with an HP 1100 pump (Agilent Technologies, CA, USA). The GPC columns were eluted with THF with 1.0 mL/min at 40 °C. The sample concentration was 0.4 wt%, and the injection volume was 50 µL. Calibration was performed using monodisperse polystyrene standards covering the molecular weight range from 500 to 5,000,000 Da.

4. Conclusions

In summary, the LA/LB pair is a broad class of active and selective catalysts for the PO/SA copolymerization, which is a biorenewable route to biodegradable polyesters. This work comprehensively disclosed the effect of the structure of the LA/LB pair on the PO/SA copolymerization. The fully alternating copolymers were synthesized in a metal-free catalytic way. The highest activity (TOF: 128 h⁻¹) was achieved when the TEB/*t*-BuP₁ (4/1 in molar ratio) pair was used at 80 °C. *M*_n of the resultant poly(propylene succinate) reached up to 20.4 kg/mol using TEB/*t*-BuP₁ (PO/SA/TEB/*t*-BuP₁ = 400/200/1/1) at 30 °C. This work demonstrated that the organocatalyst is a powerful tool to catalyze the copolymerization of PO with SA. The development of highly active and selective catalysts for synthesizing a high molecular weight copolymer is ongoing in our lab.

Supplementary Materials: The following are available online. Figure S1. Selected GPC curves of poly(propylene succinate)s; Figure S2. GPC curve of the poly(propylene succinate) of entry 6 in Table 2; Table S1 pK_a values of LBs from the Literature; Table S2. SA/PO copolymerization catalyzed by various LBs with TEB; Table S3. SA/PO copolymerization catalyzed by TEB/*t*-BuP₁ pair at different temperature.

Author Contributions: L.-F.H. and X.-H.Z. designed the experiments; L.-F.H. performed the copolymerization experiments; D.-J.C. and J.-L.Y. participated in the discussion and purified and characterized all the materials; L.-F.H. and X.-H.Z. wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Science Foundation of the People's Republic of China (no. 21774108) and the financial support of the Distinguished Young Investigator Fund of Zhejiang Province (LR16B040001).

Acknowledgments: In this section you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cox, K.D.; Covernton, G.A.; Davies, H.L.; Dower, J.F.; Juanes, F.; Dudas, S.E. Human Consumption of Microplastics. *Environ. Sci. Technol.* **2019**, *53*, 7068–7074. [[CrossRef](#)]
2. Allen, S.; Allen, D.; Phoenix, V.R.; Le Roux, G.; Jiménez, P.D.; Simonneau, A.; Binet, S.; Galop, D. Atmospheric transport and deposition of microplastics in a remote mountain catchment. *Nat. Geosci.* **2019**, *12*, 339–344. [[CrossRef](#)]
3. Hillmyer, M.A.; Tolman, W.B. Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–2396. [[CrossRef](#)] [[PubMed](#)]
4. Hong, M.; Chen, E.Y. Towards Truly Sustainable Polymers: A Metal-Free Recyclable Polyester from Biorenewable Non-Strained γ -Butyrolactone. *Angew. Chem. Int. Ed.* **2016**, *55*, 4188–4193. [[CrossRef](#)] [[PubMed](#)]
5. Liu, X.; Hong, M.; Falivene, L.; Cavallo, L.; Chen, E.Y.-X. Closed-Loop Polymer Upcycling by Installing Property-Enhancing Comonomer Sequences and Recyclability. *Macromolecules* **2019**, *52*, 4570–4578. [[CrossRef](#)]
6. Bechthold, I.; Bretz, K.; Kabasci, S.; Kopitzky, R.; Springer, A. Succinic Acid: A New Platform Chemical for Biobased Polymers from Renewable Resources. *Chem. Eng. Technol.* **2008**, *31*, 647–654. [[CrossRef](#)]
7. Bikiaris, D.N.; Achilias, D.S. Synthesis of Poly(Alkylene Succinate) Biodegradable Polyesters I. Mathematical Modelling of the Esterification Reaction. *Polymer* **2006**, *47*, 4851–4860. [[CrossRef](#)]
8. Paul, S.; Zhu, Y.; Saini, P.K.; Williams, C.K.; Romain, C.; Brooks, R. Ring-opening copolymerization (ROCOP): Synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* **2015**, *51*, 6459–6479. [[CrossRef](#)]
9. Longo, J.M.; Sanford, M.J.; Coates, G.W. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure–Property Relationships. *Chem. Rev.* **2016**, *116*, 15167–15197. [[CrossRef](#)]
10. Lanfang, H.; Zhang, X. Recent Progress in the Copolymerization of Cyclic Ethers and Cyclic Anhydrides Via Organocatalysts. *J. Funct. Polym.* **2019**, *32*, 259–270.
11. Van Zee, N.J.; Coates, G.W. Alternating Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures. *Angew. Chem. Int. Ed.* **2015**, *54*, 2665–2668. [[CrossRef](#)]
12. Sanford, M.J.; Carrodegua, L.P.; Van Zee, N.J.; Kleij, A.W.; Coates, G.W. Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures. *Macromolecules* **2016**, *49*, 6394–6400. [[CrossRef](#)]
13. Carrodegua, L.P.; Martín, C.; Kleij, A.W. Semiaromatic Polyesters Derived from Renewable Terpene Oxides with High Glass Transitions. *Macromolecules* **2017**, *50*, 5337–5345. [[CrossRef](#)]
14. Robert, C.; De Montigny, F.; Thomas, C.M. Tandem synthesis of alternating polyesters from renewable resources. *Nat. Commun.* **2011**. [[CrossRef](#)] [[PubMed](#)]
15. Winkler, M.; Romain, C.; Meier, M.A.R.; Williams, C.K. Renewable polycarbonates and polyesters from 1,4-cyclohexadiene. *Green Chem.* **2015**, *17*, 300–306. [[CrossRef](#)]
16. Zhu, Y.; Romain, C.; Williams, C.K. Sustainable polymers from renewable resources. *Nature* **2016**, *540*, 354–362. [[CrossRef](#)] [[PubMed](#)]
17. Zeikus, J.G.; Jain, M.K.; Elankovan, P. Biotechnology of succinic acid production and markets for derived industrial products. *Appl. Microbiol. Biotechnol.* **1999**, *51*, 545–552. [[CrossRef](#)]
18. Longo, J.M.; DiCiccio, A.M.; Coates, G.W. Poly(propylene succinate): A New Polymer Stereocomplex. *J. Am. Chem. Soc.* **2014**, *136*, 15897–15900. [[CrossRef](#)]
19. Suh, H.S.; Ha, J.Y.; Yoon, J.H.; Ha, C.-S.; Suh, H.; Kim, I. Polyester polyol synthesis by alternating copolymerization of propylene oxide with cyclic acid anhydrides by using double metal cyanide catalyst. *React. Funct. Polym.* **2010**, *70*, 288–293. [[CrossRef](#)]

20. Takasu, A.; Bando, T.; Morimoto, Y.; Shibata, Y.; Hirabayashi, T. Asymmetric Epoxidation of α -Olefins Having Neighboring Sugar Chiral Templates and Alternating Copolymerization with Dicarboxylic Anhydrides. *Biomacromolecules* **2005**, *6*, 1707–1712. [[CrossRef](#)]
21. DiCiccio, A.M.; Longo, J.M.; Rodríguez-Calero, G.G.; Coates, G.W. Development of Highly Active and Regioselective Catalysts for the Copolymerization of Epoxides with Cyclic Anhydrides: An Unanticipated Effect of Electronic Variation. *J. Am. Chem. Soc.* **2016**, *138*, 7107–7113. [[CrossRef](#)] [[PubMed](#)]
22. Zhang, D.; Boopathi, S.K.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. Metal-Free Alternating Copolymerization of CO₂ with Epoxides: Fulfilling “Green” Synthesis and Activity. *J. Am. Chem. Soc.* **2016**, *138*, 11117–11120. [[CrossRef](#)] [[PubMed](#)]
23. Yang, J.-L.; Wu, H.-L.; Li, Y.; Zhang, X.-H.; Darensbourg, D.J. Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides by Metal-Free Lewis Pairs. *Angew. Chem.* **2017**, *129*, 5868–5873. [[CrossRef](#)]
24. Zhang, C.-J.; Wu, H.-L.; Li, Y.; Yang, J.-L.; Zhang, X.-H. Precise synthesis of sulfur-containing polymers via cooperative dual organocatalysts with high activity. *Nat. Commun.* **2018**. [[CrossRef](#)]
25. Lin, B.; Waymouth, R.M. Urea Anions: Simple, Fast, and Selective Catalysts for Ring-Opening Polymerizations. *J. Am. Chem. Soc.* **2017**, *139*, 1645–1652. [[CrossRef](#)]
26. Li, H.; Zhao, J.; Zhang, G. Self-Buffering Organocatalysis Tailoring Alternating Polyester. *ACS Macro Lett.* **2017**, *6*, 1094–1098. [[CrossRef](#)]
27. Hu, L.-F.; Zhang, C.-J.; Wu, H.-L.; Yang, J.-L.; Liu, B.; Duan, H.-Y.; Zhang, X.-H. Highly Active Organic Lewis Pairs for the Copolymerization of Epoxides with Cyclic Anhydrides: Metal-Free Access to Well-Defined Aliphatic Polyesters. *Macromolecules* **2018**, *51*, 3126–3134. [[CrossRef](#)]
28. Hošťálek, Z.; Trhliková, O.; Walterová, Z.; Martínez, T.; Peruch, F.; Cramail, H.; Merna, J. Alternating copolymerization of epoxides with anhydrides initiated by organic bases. *Eur. Polym. J.* **2017**, *88*, 433–447. [[CrossRef](#)]
29. Lin, L.; Liang, J.; Xu, Y.; Wang, S.; Xiao, M.; Sun, L.; Meng, Y. Fully alternating sustainable polyesters from epoxides and cyclic anhydrides: Economical and metal-free dual catalysis. *Green Chem.* **2019**, *21*, 2469–2477. [[CrossRef](#)]
30. Kummari, A.; Pappuru, S.; Chakraborty, D.; Kanji, A. Fully alternating and regioselective ring-opening copolymerization of phthalic anhydride with epoxides using highly active metal-free Lewis pairs as a catalyst. *Polym. Chem.* **2018**, *9*, 4052–4062. [[CrossRef](#)]
31. Ji, H.-Y.; Chen, X.-L.; Wang, B.; Pan, L.; Li, Y.-S. Metal-free, regioselective and stereoregular alternating copolymerization of monosubstituted epoxides and tricyclic anhydrides. *Green Chem.* **2018**, *20*, 3963–3973. [[CrossRef](#)]
32. Zhang, C.-J.; Zhang, X.-H. Organocatalytic polymerization. *Sci. China Ser. B Chem.* **2019**, *62*, 1087–1089. [[CrossRef](#)]
33. Luston, J.; Vass, F. Anionic Copolymerization of Cyclic Ethers with Cyclic Anhydrides. In *Anionic Polymerization; Advances in Polymer Science*; Springer: Berlin, Germany, 1984; Volume 56, pp. 91–133.
34. Ji, H.-Y.; Wang, B.; Pan, L.; Li, Y.-S. Lewis Pairs for Ring-Opening Alternating Copolymerization of Cyclic Anhydrides and Epoxides. *Green Chem.* **2018**, *20*, 641–648. [[CrossRef](#)]
35. Yang, J.-L.; Wang, H.-L.; Hu, L.-F.; Hong, X.; Zhang, X.-H. A double-site Lewis pair for highly active and living synthesis of sulfur-containing polymers. *Polym. Chem.* **2019**, *10*, 6555–6560. [[CrossRef](#)]
36. Sivaev, I.B.; Bregadze, V.I. Lewis acidity of boron compounds. *Coord. Chem. Rev.* **2014**, *270*, 75–88. [[CrossRef](#)]
37. Jiang, Y.; Hess, J.; Fox, T.; Berke, H. Rhenium Hydride/Boron Lewis Acid Cocatalysis of Alkene Hydrogenations: Activities Comparable to Those of Precious Metal Systems. *J. Am. Chem. Soc.* **2010**, *132*, 18233–18247. [[CrossRef](#)]
38. Lin, B.; Waymouth, R.M. Organic Ring-Opening Polymerization Catalysts: Reactivity Control by Balancing Acidity. *Macromolecules* **2018**, *51*, 2932–2938. [[CrossRef](#)]
39. Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; et al. Extremely Strong, Uncharged Auxiliary Bases; Monomeric and Polymer-Supported Polyaminophosphazenes (P2–P5). *Liebigs Annalen* **1996**, *1996*, 1055–1081. [[CrossRef](#)]
40. Han, B.; Zhang, L.; Liu, B.; Dong, X.; Kim, I.; Duan, Z.; Theato, P. Controllable Synthesis of Stereoregular Polyesters by Organocatalytic Alternating Copolymerizations of Cyclohexene Oxide and Norbornene Anhydrides. *Macromolecules* **2015**, *48*, 3431–3437. [[CrossRef](#)]

41. 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 Lett.* **2019**, *8*, 973–978. [[CrossRef](#)]
42. Ji, H.-Y.; Wang, B.; Pan, L.; Li, Y.-S. One-Step Access to Sequence-Controlled Block Copolymers by Self-Switchable Organocatalytic Multicomponent Polymerization. *Angew. Chem. Int. Ed.* **2018**, *57*, 16888–16892. [[CrossRef](#)] [[PubMed](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).