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Hydrogen Bonding-Driven Ring-Opening Polymerization of β-Lactones to Polyhydroxyalkanoates Using Aminocyclopropenium Carboxylates

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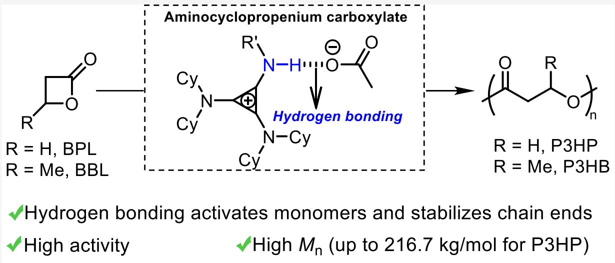
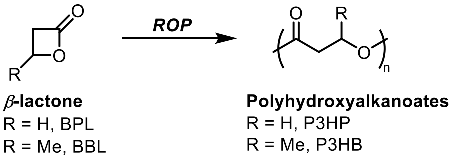


ABSTRACT: Although the chemical synthesis of polyhydroxyalkanoates by ring-opening polymerization (ROP) of four-membered β-lactones has attracted wide interest for sustainable materials, research on polyhydroxyalkanoates by organocatalysis remains rare and challenging. In particular, high activity of organic initiators/catalysts is always accompanied by acidic abstraction, resulting in low molecular weights and broad distribution. Herein, we report hydrogen bonding-driven ROP of β-butyrolactone and β-propiolactone by a series of aminocyclopropenium catalysts featuring tunable hydrogen bond donors for the preparation of poly(3-hydroxybutyrate) (P3HB) and poly(3-hydroxypropionate) (P3HP), respectively. The optimal catalyst achieved the desired reactivities and high molecular weights (up to 216.7 kg/mol for P3HP). Mechanism studies, ^{1}H NMR titrations, and *in situ* FTIR proved that hydrogen bonding prompted fast polymerization via activation of monomers. In propagation, hydrogen bonding between the N−H moiety and carboxylate stabilized active chain ends, limiting elimination/transesterification. The hydrogen bond donor aminocyclopropenium catalysts extend organocatalyzed polymerization of β-lactones to produce polyhydroxyalkanoates with high molecular weights.

■ INTRODUCTION

Polyhydroxyalkanoates (PHAs), a class of biodegradable and biocompatible polymers, are being pursued to reduce the accumulation of plastic waste in landfills and oceans.[1−6] Poly(3-hydroxybutyrate) (P3HB) and poly(3-hydroxypropionate) (P3HP), which could be prepared via ring-opening polymerization (ROP) of β-butyrolactone (BBL) and β-propiolactone (BPL), respectively (Scheme 1), are two classical representatives.[7,8] Natural P3HB with perfect isotacticity enables materials with high melting-transition temperature (up to ∼180 °C), good ultimate tensile strength, and excellent barrier to oxygen and moisture,[9,10] which is advantageous for replacing conventional polypropylene in packaging, tissue engineering, and drug delivery.[11] P3HP with repeating methylene units in the main chain, which shares a similar structure with polyethylene, is flexible and ductile,[12] showing great potential in plastic films.

Scheme 1. ROP of BPL and BBL to Produce PHAs



In terms of raw materials, BBL and BPL can be prepared by carbonylation of commercially available propylene oxide[13,14] or oxirane[15] respectively, which will be a solid economic driver for P3HB and P3HP production due to its low feedstock cost. In addition, the four-membered BBL and BPL possess higher ring strain and undergo faster polymerization than larger-ring lactones, thereby accelerating the enthalpy-driven polymerization rate.[16]

From the point of view of catalysts, the research on ROP of BBL and BPL by organocatalysis for the production of PHAs with high molecular weights remains rare compared to the vastly studied metal-based catalysts/initiators.[17−29] So far, N-heterocyclic carbenes and their precursors,[30−34] organic bases,[35,36] trifluoromethanesulfonic acids,[37−40] and quaternary ammonium/phosphonium salts with carboxylate anions[15,41−43] have been exploited for ROP of BBL or BPL. Cationic ROP catalyzed by acids is typically characterized by low activity and molecular weights of the resulting polymers, which appear to be less advantageous. Despite their strong nucleophilic properties, such as NHCs and organic superbases, which

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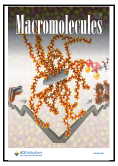

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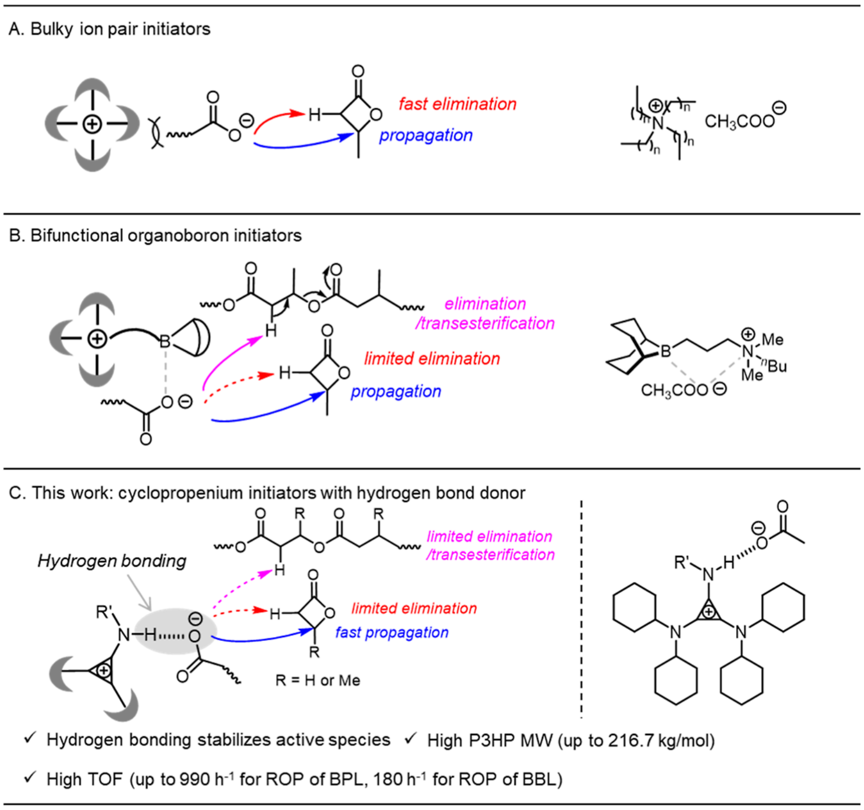
Scheme 2. Previously Representative Metal-Free Carboxylate Catalysts/Initiators and This Work; (A) Use of Bulky Ion Pair Initiators Resulted in High Activity, But Also Permitted Rapid Elimination, Which Ultimately Led to a Loss of Controllability; (B) Bifunctional Organoboron Catalysts Facilitated Living/Controlled Polymerization, Yet Promoted Elimination/Transesterification at the Main Chain at High Monomer Conversions; (C) This Study Presents the Utilization of Aminocyclopropenium Carboxylates with the N−H Hydrogen Bond Donor as Catalysts for ROP of BBL and BPL[a]



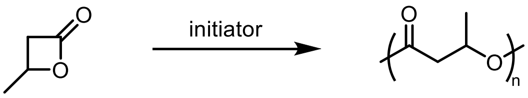
[a] Hydrogen bond was formed between the N−H moiety in the cation and the carboxylate chain end, which restrained elimination and transesterification reactions.

promote accelerated polymerization, their high basicity also leads to the elimination of monomers through α-H abstraction reactions (Scheme S1). This results in the formation of low molecular weight polymers. Conversely, weak nucleophiles, such as ammonium/phosphonium salts with carboxylate anions, have emerged as promising agents for ROP of BBL and BPL. Nonetheless, PHAs by organocatalysis still suffer from either low number-average molecular weight (M_n) or broad molar mass distribution (Đ), which makes it challenging to synthesize PHA by organocatalysis.

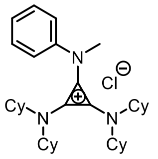
Bulky ion pair initiators with carboxylate anions, typically tetraalkylammonium carboxylate,[15,42] were designed via increasing steric hindrance of the cation to reduce electrostatic attraction between the cation and the active carboxylate anion. This results in an increase in the activity of the carboxylate anion, which, in turn, leads to a fast polymerization of BBL (Scheme 2A). Nevertheless, the elimination at high temperature, that is, the abstraction of a proton in BBL, can also be accelerated, resulting in transfer to the monomer and reduction in M_ns. The occurrence of these side reactions can be mitigated through the introduction of noncovalent interaction, as exemplified by bifunctional organoboron catalysts reported by our group (Scheme 2B).[41] The activation of the monomer and stabilization of the growing chain end by the boron center enabled the ROP of BBL by organoboron catalysts to proceed in a fast and living/controlled manner. However, the oxygen of the carbonyl in the polymer chain coordinated competitively with the organoboron center, which synchronously prompted ring opening of BBL and abstraction of the proton in the polymer main chain at late-stage polymerization, resulting in decreased M_ns at high conversions. These studies underscore the necessity of selectively stabilizing the carboxylate chain end rather than the monomer and polymer chain through noncovalent interaction.

In this context, hydrogen bonding can be viewed as an alternative due to its ability to facilitate anion bonding.[44,45] Aminocyclopropenium ions have been identified as effective organocatalysts for organic transformation[46−48] and polymerization.[48−51] For example, a bifunctional aminocyclopropenium aluminum complex was reported to prompt the copolymerization of epoxides and cyclic anhydrides with excellent activity and inhibit transesterification and epimerization side reactions.[49,51] The ion pair strain[52,53] exhibited by aminocyclopropenium ion pairs offers significant potential for enhancing anion reactivity, while the hydrogen bonding has the potential to stabilize active chain end and limit side reactions, which greatly raises our interest. Herein, a series of aminocyclopropenium carboxylates with a hydrogen bond donor were prepared and evaluated as catalysts for ROP of BBL and BPL (Scheme 2C). Hydrogen bonding prompted fast and controlled polymerization, producing PHAs with high molecular weights, especially for BPL (up to 216.7 kg/mol).

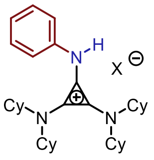
Table 1. Results of ROP of BBL by Aminocyclopropenium Catalysts[a]



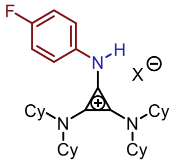
BBL **P3HB**



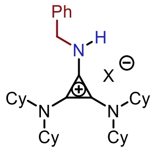
1-Cl



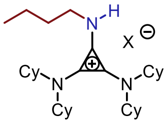
2-Cl X = Cl
2-ace X = CH_3COO
2-piv X = ^tBuCOO
2-cro X = $CH_3CH{=}CHCOO$



3-Cl X = Cl
3-ace X = CH_3COO



4-Cl X = Cl
4-ace X = CH_3COO



5-Cl X = Cl
5-ace X = CH_3COO

entry	initiator	cat/M	T/°C	t/h	conv.[b]/%	TOF[c]/h^{-1}	$M_{n,theo}$[d]/kg·mol^{-1}	$M_{n,SEC}$[e]/kg·mol^{-1}	Đ[e]
1	**1-Cl**	1/200	100	1	41	80	7.1	1.9	1.20
2	**2-Cl**	1/200	100	1	69	140	11.8	2.9	1.15
3	**2-ace**	1/500	100	2	74	180	31.8	13.3	1.27
4	**2-piv**	1/500	100	2	68	170	29.2	10.8	1.29
5	**2-cro**	1/500	100	2	89	220	38.3	7.2	1.48
6	**3-Cl**	1/200	100	1	85	170	14.6	2.7	1.17
7	**4-Cl**	1/200	100	1	57	110	9.8	2.4	1.16
8	**5-Cl**	1/200	100	1	50	100	8.6	2.4	1.14
9	**3-ace**	1/500	100	2	95	240	40.8	13.2	1.33
10	**4-ace**	1/500	100	2	72	180	31.0	5.9	1.24
11	**5-ace**	1/500	100	2	69	170	29.7	9.9	1.34

[a] All polymerizations were performed in bulk. 500 mg of BBL was used. The reaction mixtures were cooled rapidly by liquid N_2, and then the solution of benzoic acid in chloroform was added to quench polymerizations. [b] Monomer conversions were determined by ^1H NMR spectra. Conversion$_{BBL}$ = $I_{5.24ppm}/(I_{5.24ppm} + I_{4.70ppm})$. [c] Turnover frequency (TOF) was calculated by the equation. TOF = [M] × conv. × $[cat]^{-1}$ × time^{-1}. [d] Theoretical molecular weights were calculated by the equation. $M_{n,theo} = M_{monomer} \times [M] \times [cat]^{-1} \times$ conv. [e] The M_n and Đ of P3HB were determined by gel permeation chromatography (GPC) calibrated with polystyrene standards in tetrahydrofuran (THF) at 35 °C.

RESULTS AND DISCUSSION

ROP of BBL by Aminocyclopropenium Catalysts and Hydrogen Bonding Investigation. Prior to investigating the polymerization of BBL by hydrogen bonding, a control catalyst **1-Cl**, which is devoid of a hydrogen bond donor, was employed for comparison at 100 °C, resulting in 41% BL conversion (TOF = 80 h^{-1}, Table 1, entry 1). The subsequent application of various aminocyclopropenium catalysts with N−H hydrogen bond donors resulted in a notable increase in TOF values (Table 1, entries 2 and 6−8). In particular, **2-Cl**, a hydrogen bond donor analogue to **1-Cl**, exhibited a TOF value of 140 h^{-1}, which was 1.75 times higher than that of **1-Cl** (Table 1, entry 2). This result clearly demonstrates the significant enhancement of activity by the introduction of hydrogen bonding. However, the M_n of the obtained P3HB by **2-ace** was only 2.9 kg/mol, which is probably due to the chloride's role as a good leaving group, resulting in decreased M_ns.

Subsequently, anion screening was conducted based on **2-Cl** to improve molecular weights. The corresponding acetate (**2-ace**), pivalate (**2-piv**), and crotonate (**2-cro**) catalysts were prepared through simple ion exchange. ROP experiments were carried out at a feed ratio of 500/1 (Table 1, entries 3−5). The acetate anion (**2-ace**), which was identified as the optimal anion, exhibited a higher TOF value than the pivalate anion (**2-piv**), with a value of 180 h^{-1} compared to 170 h^{-1}, respectively. The acetate anions with varying structures not only accelerated the polymerization process but also yielded P3HB with higher M_ns (>7.0 kg/mol), which is significantly higher than the M_ns of polymers produced by chloride (M_ns < 3.0 kg/mol). Additionally, the acetate anion yielded P3HB with the highest molecular weight observed in this study of 13.3 kg·mol^{-1}. Although the highest TOF value (220 h^{-1}) was achieved by the crotonate catalyst **2-cro**, the lowest molecular weight (7.2 kg·mol^{-1}) and the broadest Đ (1.48) were observed (Table 1, entry 5).

The influence of electronic effects was assessed by modifying the substituents at the N-position of **2-Cl** (Table 1, entries 6−8). The results revealed that electron-withdrawing groups enhanced the catalyst activity. The highest TOF (170 h^{-1}) was achieved with **3-Cl** in conjunction with an electron-withdrawing 4-fluorophenyl substituent. The replacement of 4-fluorophenyl with benzyl and electron-donating *n*-butyl resulted in a notable reduction in activity, with TOF values of 110 h^{-1} (for **4-Cl**) and 100 h^{-1} (for **5-Cl**). This tendency was also observed when the chloride anions of **2-Cl**, **3-Cl**, **4-Cl**, and **5-Cl** were replaced by acetate anions (Table 1, entries 3 and 9−11). **3-ace** with the strongest hydrogen bond strength displayed the highest TOF value (240 h^{-1}). The TOF values decreased gradually to 170 h^{-1} as the substituents turned to electron-donating groups.

As is well established in the literature, hydrogen bond strength is strongly correlated with the electronic effect of substituents and can be evaluated by chemical shifts.[54−56] This prompted us to investigate the impact of hydrogen bond strength on the catalyst activity through the analysis of ^1H

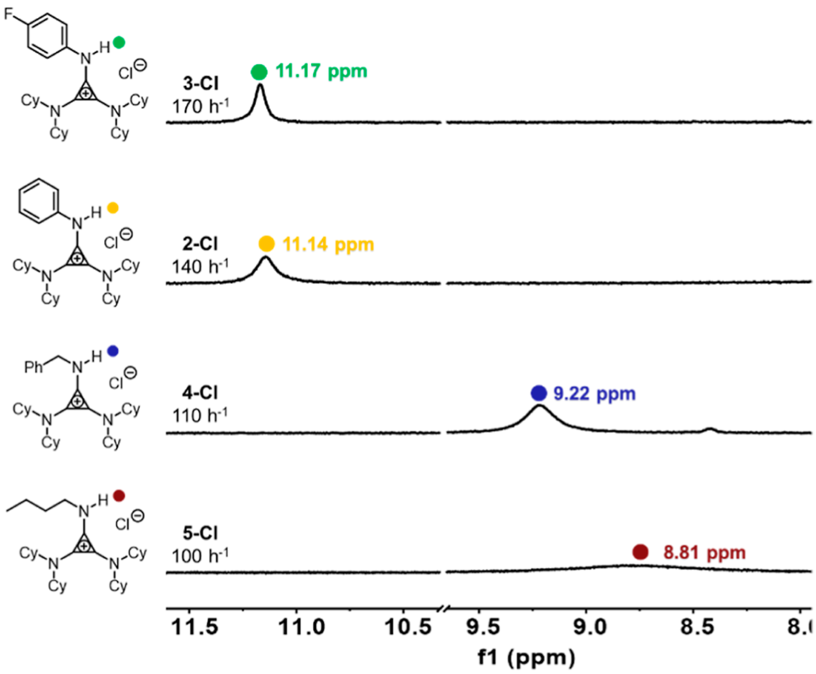


Figure 1. N−H chemical shifts of aminocyclopropenium catalysts **3-Cl**, **2-Cl**, **4-Cl**, and **5-Cl** along with their TOF values for ROP of BBL.

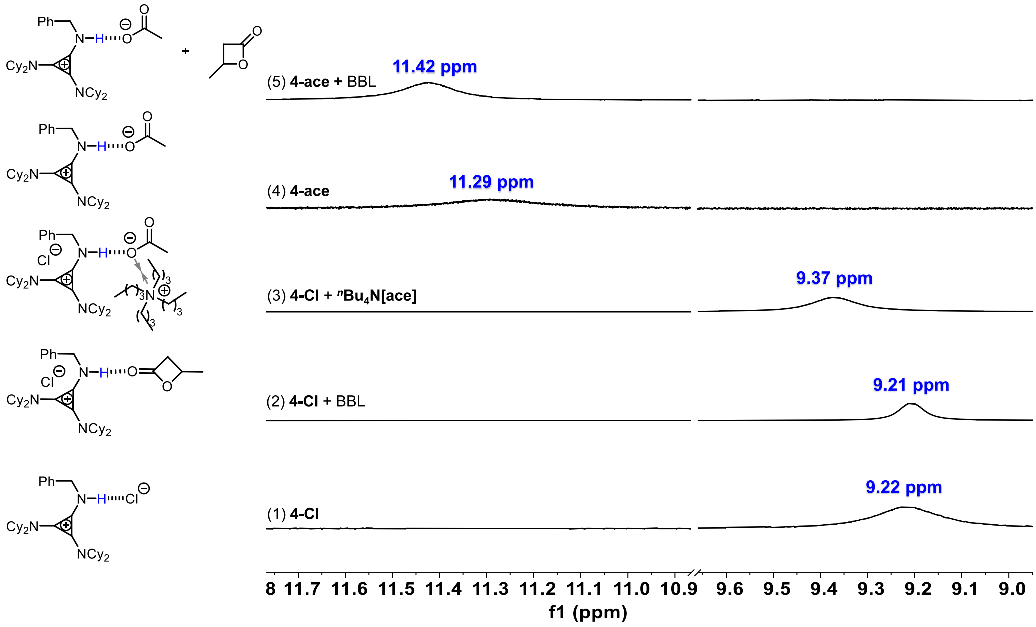
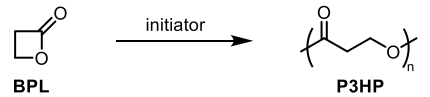


Figure 2. N−H chemical shifts of aminocyclopropenium catalysts in $CDCl_3$ (0.5 mL): (1) **4-Cl** with Cl^- as anion; (2) mixture of **4-Cl** (10 mg, 1.0 equiv) and BBL (1.7 mg, 1.0 equiv); (3) mixture of **4-Cl** (10 mg, 1.0 equiv) and tertrabutylammonium acetate (6.0 mg, 1.0 equiv); and (4) **4-ace** with CH_3COO^- as anion. Full spectra are provided in Figure S23 in the Supporting Information; and (5) mixture of aminocyclopropenium **4-ace** with CH_3COO^- as the anion (10 mg, 1.0 equiv) and BBL (1.5 mg, 1.0 equiv).

NMR spectra. The chemical shifts of N−H in aminocyclopropenium chlorides are illustrated in Figure 1. A distinct single peak was observed at 11.17 ppm in the ^{1}H NMR spectrum of **3-Cl**. Upon replacing the 4-fluorophenyl substituent with a phenyl, benzyl, or *n*-butyl groups at the N-position, the chemical shifts of N−H decreased to 11.14, 9.22, and 8.81 ppm, respectively. This notable upshift indicated a diminished capacity of the aminocyclopropenium cation to form hydrogen bonds, which corroborated the observed decline in TOF values from 170 h^{-1} for **3-Cl** to 100 h^{-1} for **5-Cl**.

^{1}H NMR titration experiments demonstrated that the N−H moiety in the aminocyclopropenium cation can form hydrogen bonding with both BBL and active chain ends (Figures 2 and S25). Aminocyclopropenium chloride **4-Cl** was selected as the model catalyst due to the distinct N−H peak and the moderate hydrogen bond strength. Upon the addition of BBL (1.0 equiv of **4-Cl**) to the solution of **4-Cl**, the chemical shift of N−H exhibited a slight upfield shift to 9.21 ppm (compared to 9.22 ppm for **4-Cl**), indicating the formation of a weak hydrogen bond between the N−H and the oxygen of the carbonyl in BBL, which resulted in a shielding effect. The downfield

Table 2. ROP of BPL by an Aminocyclopropenium Catalyst[a]



entry	cat/M	T/°C	t/h	conv.[b]/%	TOF[c]/h^{-1}	$M_{n,theo}$[d]/kg·mol^{-1}	$M_{n,SEC}$[e]/kg·mol^{-1}	Đ[e]
1	1/500	25	1	21	110	7.6		
2	1/500	25	1	47	240	16.9		
3	1/500	25	0.5	>99	990	36.0	65.5	1.18
4	1/1000	25	1	>99	990	72.0	95.7	1.27
5	1/2000	25	3	89	590	128.2	155.7	1.23
6	1/4000	25	8	88	440	253.4	216.7	1.27
7[f]	1/2000	25	3	71	470	102.2	115.2	1.19
8	1/2000	40	1.5	91	1210	131.0	48.1	2.16

[a] All polymerizations were performed with **3-ace** as a catalyst except entries 1−2. **1-Cl** was employed for entry 1, and **2-Cl** was employed for entry 2. 500 mg of BPL was used. The solution of benzoic acid in chloroform was added to quench polymerization. [b] Monomer conversions were determined by ^{1}H NMR spectra. Conversion$_{BPL}$ = $I_{2.61ppm}/(I_{2.61ppm} + I_{3.49ppm})$. [c] Turnover frequency (TOF) was calculated by the equation. TOF = [M] × conv. × $[cat]^{-1}$ × $time^{-1}$. [d] Theoretical molecular weight was calculated by the equation. $M_{n,theo} = M_{monomer} \times [M] \times [cat]^{-1} \times$ conv. [e] The M_n and Đ of P3HB were determined by GPC calibrated with polystyrene standards in chloroform at 35 °C. [f] Dichloromethane (DCM) was used as optimal solvent and $[PL]_0$ = 8 M. Procedure of solvent screening can be found in the Supporting Information.

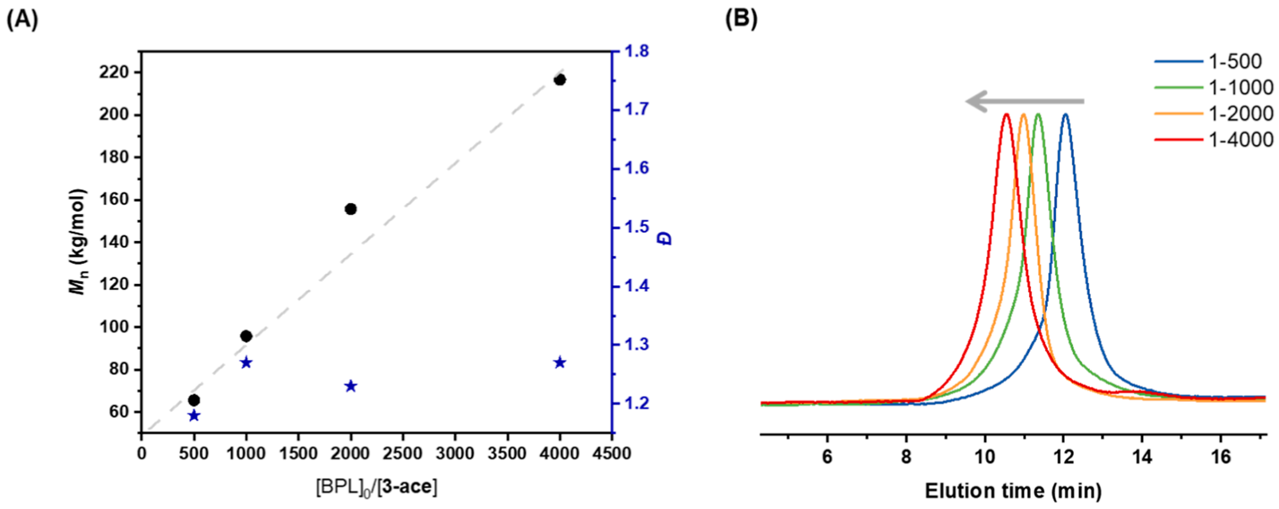


Figure 3. (A) Plots of M_n and Đ values of P3HP produced by an aminocyclopropenium catalyst **3-ace** at varied $[BPL]_0$/[**3-ace**] (Table 2, entries 3−6). (B) GPC curves for P3HP produced at different $[BPL]_0$/[**3-ace**] ratios (Table 2, entries 3−6).

chemical shift (9.37 ppm, N−H) was observed when an equivalent amount of *tert*-butylammonium acetate (**^{n}Bu$_4$N-[ace]**) was added to the solution of **4-Cl**. The formation of a hydrogen bond between the N−H and the acetate anion resulted in a deshielding effect and a reduction in electron density on the hydrogen atom. In light of the electrostatic attraction between the acetate anion and the tetrabutylammonium cation, the deshielding effect resulted in a 0.15 ppm downfield shift of the N−H signal. However, following the replacement of chloride with acetate to produce **4-ace**, a remarkable increase in the chemical shift (11.29 ppm, N−H in **4-ace**) was observed, indicating the formation of a more robust hydrogen bond. Given that the acetate anion is capable of imitating a growing chain end during polymerization, the observed downfield shift (1.92 ppm, N−H) indicated a tendency for a hydrogen bond to form between N−H and the growing carboxylate chain ends. When equivalent BBL was added into the solution of **4-ace**, the increasing amount of hydrogen bond acceptors caused a slight 0.13 ppm downshift of the N−H signal. The minor shift in spectra resulting from BBL addition suggests a weak hydrogen bonding interaction between BBL and the N−H moiety, which activates BBL and accelerates polymerization. This effect is more pronounced than that observed with catalysts devoid of hydrogen bond donors (80 vs 140 h^{-1}, Table 1, entry 1 vs 2). Conversely, the robust hydrogen bonding interaction between the carboxylate anions and the N−H moiety exhibited considerable potential to stabilize the growing chain ends during polymerization, thereby reducing side reactions and resulting in P3HB with higher molecular weights. In this context, **2-ace** and **3-ace**, which formed stronger hydrogen bonds with active chain ends, produced P3HB with higher M_ns (>13.0 kg/mol, Table 1, entries 3 and 9) than **4-ace** and **5-ace** (M_ns < 10.0 kg/mol, Table 1, entries 10−11).

ROP of BPL by an Aminocyclopropenium Catalyst. Hydrogen bonding was also found to promote the ROP of BPL significantly. The ROP of BPL initiated by **2-Cl** with an N−H hydrogen bond donor was processed with a TOF value of 240 h^{-1}, which is twice higher than the value observed for **1-Cl** (110 h^{-1}) (Table 2, entries 1−2). The huge difference in activity between **1-Cl** and **2-Cl** further validated that the weak

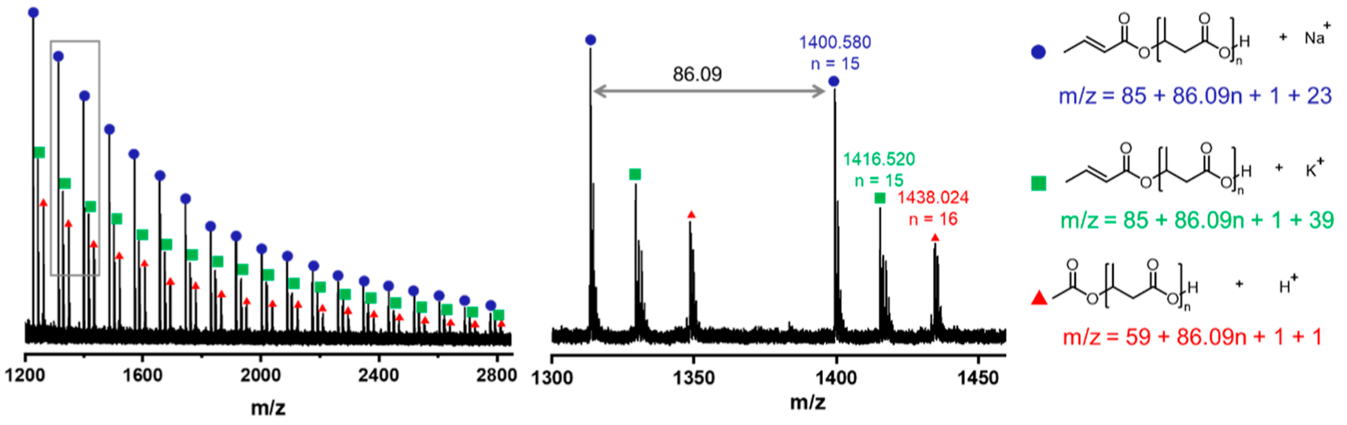


Figure 4. MALDI-TOF mass spectra of the P3HB synthesized by **2-ace**. Reaction conditions: BBL/**2-ace** = 200/1, 100 °C, 1 h.

hydrogen bonding activated the monomer and accelerated polymerization.

Based on the screening for ROP of BBL, the ROP of BPL by the aminocyclopropenium acetate **3-ace** resulted in >99% BPL conversion within 0.5 h at 25 °C and 500/1 feed ratio (Table 2, entry 3). The resulting P3HP, obtained through precipitation in methanol, exhibited a high molecular weight (65.5 kg·mol^{-1}) and narrow distribution (Đ = 1.18). The narrow distribution indicates a reduced occurrence of side reactions, which can be attributed to the robust hydrogen bonding between the N−H moiety in **3-ace** and the active carboxylate anions. An increase in the feed ratio from 1/500 to 1/1000, 1/2000, and 1/4000, accompanied by a prolongation of the reaction time, resulted in the production of corresponding P3HPs, whose M_ns exhibited a linear increase (Table 2, entries 3−6 and Figure 3A). The M_n was up to 216.7 kg·mol^{-1} at a feed ratio of 1/4000, and the Đ broadened but is still lower than 1.30 (Đ = 1.27), which exceeded the previously reported value. The GPC curves of produced P3HP showed four distinct unimodal peaks and demonstrated an increasing evolution of M_ns (Figure 3B). With the increasing feed ratio, the broadened Đ of polymers probably resulted from high viscosity of the reaction system at high monomer conversions and bulk conditions. The growing chain end was embedded in the high viscosity system, making it difficult for the N−H moiety in **3-ace** to form a hydrogen bond with growing chain ends. This issue could be addressed by utilizing dichloromethane as the solvent (see Supporting Information, Section Solvent Screening for ROP of BPL), and the resulting P3HP exhibited a high molecular weight (115.2 kg·mol^{-1}) and narrow dispersity (Đ = 1.19) (Table 2, entry 7). Further attempts to enhance the catalyst activity by increasing the reaction temperature to 40 °C resulted in a significant reduction in the M_n value (48.1 kg·mol^{-1}) and broad Đ (2.16) (Table 2, entry 8).

The DSC curves indicated that the obtained P3HP was semicrystalline, exhibiting a melting point (T_m) of 79 °C and a glass transition temperature (T_g) of −15 °C (Figure S31). These properties were attributed to the stacking of linear and repeating $-(CH_2)-$ units in the polymer chain. The decomposition temperature at 5% weight loss ($T_{d5\%}$) was determined to be 225 °C by TGA (Figure S32).

Side Reaction Investigations. The difference between theoretical molecular weights ($M_{n,theo}$) and molecular weights determined by SEC ($M_{n,SEC}$) manifested side reactions during the ROP of BBL and BPL at high temperatures. As illustrated in Figures 4 and S34, the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of P3HB offered valuable insights into side reactions. Three principal populations were discerned. The red population was identified as the acetate-initiated linear P3HB, characterized by the presence of acetate at one end and a carboxylate at the other end. This was expressed as $[C_2H_3O_2 + (C_4H_6O_2)_n + H + H^+]$, m/z = 59 + 86.09n + 1 + 1. The green cycles and blue squares represent the major population counterpart, wherein one end of the polymer chain is crotonate and the other end is carboxylate, despite the presence of different cations. That is, the attachment of Na$^+$ and K$^+$ was observed (expressed as $[C_4H_5O_2 + (C_4H_6O_2)_n + H + Na^+]$, m/z = 85 + 86.09n + 1 + 23 for blue cycles, $[C_4H_5O_2 + (C_4H_6O_2)_n + H + K^+]$, m/z = 85 + 86.09n + 1 + 39] for green squares). The ^{1}H NMR spectrum served to corroborate the generation of crotonate species, whose characteristic chemical shifts were observed at 6.93−7.00 and 5.83−5.97 ppm (Figure S26). Similar crotonate chain ends existed in P3HP produced at 40 °C, which is quite different from P3HP produced at 25 °C with an acetate chain end (Figure S41). Additionally, OH-initiated P3HB with about 6−7 BBL units was also found at 450 < m/z < 700 (Figure S34), which could be attributed to initiation by residue water in monomer. Therefore, it could be concluded that generation of crotonate species reduced M_ns of the obtained polymers, which were probably induced by high reaction temperatures because the ROP of BPL at room temperature showed no generation of crotonate species (Figure S41).

Lower temperatures were adopted for the ROP of BBL with **2-ace** as catalysts, as demonstrated in Table S1 (entries 1−3). A decrease in temperature from 100 to 80 °C led to an increase in the M_n of P3HB to 19.4 kg/mol, accompanied by 60% BBL conversion. A further decrease in temperature to 60 °C resulted in P3HB with 18.0 kg/mol, which is very close to the $M_{n,theo}$ value (19.4 kg/mol) at the cost of the catalyst activity. However, crotonate species were also identified in P3HB obtained at 80 and 60 °C (Figure S30), suggesting the continued occurrence of side reactions. At elevated temperatures, the weak interaction between hydrogen bond donors and acceptors was destroyed, leading to severe side reactions that were directly observable in the ^{1}H NMR spectra at these temperatures (see Figure S36). As the temperature was increased from 25 to 80 °C, the N−H in **2-Cl** exhibited a gradual upfield shift from 9.71 to 9.65 ppm, which was attributed to weakened hydrogen bonding interaction. The solvent with a hydrogen bond acceptor, for example, THF, was able to form the hydrogen bond competitively with N–H moiety in aminocyclopropenium catalysts and produced P3HB with lower molecular weights compared with toluene (Table S1, entries 4–5).

To monitor the generation of crotonate species at high temperature and exclude the negative impact of bulk viscosity on the signal, *in situ* FTIR experiments for ROP of BBL were conducted at 80 °C with the **2-ace** catalyst in toluene, as illustrated in Figure 5. The response at 1827 $\mathrm{cm^{-1}}$, which corresponds to the C═O bond in BBL, exhibited a decrease in intensity, while the response at 1741 $\mathrm{cm^{-1}}$, which corresponds to the C═O bond in P3HB, demonstrated an increase in intensity (Figure 5A,B). The response of the C═C bond in crotonate species was observed at 1655 $\mathrm{cm^{-1}}$, which increased during the initial 1 h and remained constant as the polymerization proceeded (Figure 5B,C). These findings suggest that crotonate species predominantly generated during the initial stages of polymerization and remained constant throughout the mid and late stages, which differs from our previous report using bifunctional organoboron catalysts (Scheme 2B).[41]

Mechanism Discussion. The plausible mechanism of aminocyclopropenium acetate-initiated ROP of β-lactones was proposed based on the above studies (Figure 6). At the initiation stage, the acetate anion has three possible pathways to attack β-lactones. One scenario involves attacking the β-C of β-lactones, which induces alkyl cleavage and produces carboxylate anions (Figure 6, **I**). The second way entails the attack on the carbonyl-C, which results in acyl cleavage and produces alkoxide anions. Quenching experiments with benzyl bromide revealed the existence of a carboxylate propagating chain end, confirming alkyl cleavage during ring opening of BBL and BPL (see Supporting Information, Section on Regioselectivity of Ring-Opening Polymerization). Moreover, *in situ* FTIR disclosed the immediate formation of crotonate species upon catalyst addition, which was attributed to acidic abstraction of the α-position proton by the acetate anion at high temperatures (Figure 6, **II**). Both acetate and crotonate anions initiated ROP of β-lactone by alkyl cleavage (Figure 6, **I** and **III**). Nevertheless, the two active species exhibited different initiation rates, i.e., $k_{\mathrm{i,acetate}}$ and $k_{\mathrm{i,crotonate}}$, considering that different TOF values (180 $\mathrm{h^{-1}}$ for acetate vs 220 $\mathrm{h^{-1}}$ for crotonate) were observed when acetate and crotonate anions were used to initiate polymerization under the same conditions (Table 1, entries 3 and 5). Acidic abstraction of BBL by the crotonate anion (Figure 6, **IV**) can be excluded because no *cis*- or *trans*-crotonic acid was found in the ^{1}H NMR spectrum (Figure S26).

After initiation, the formed carboxylate chain end went through three feasible pathways to the final acetate- or crotonate-terminated PHAs. Attack of β-C by the next monomer completed propagation (Figure 6, **V**). Protonic abstraction of another lactone led to termination of the active chain end, producing PHA and regenerating another active crotonate species to participate in a new initiation (Figure 6, **VI**). As the polymerization progressed to high conversion, proton abstraction from the polymer chain by the active carboxylate ends caused breakage of the polymer chain, generating PHA with a crotonate chain end and an active carboxylate end (Figure 6, **VII**).

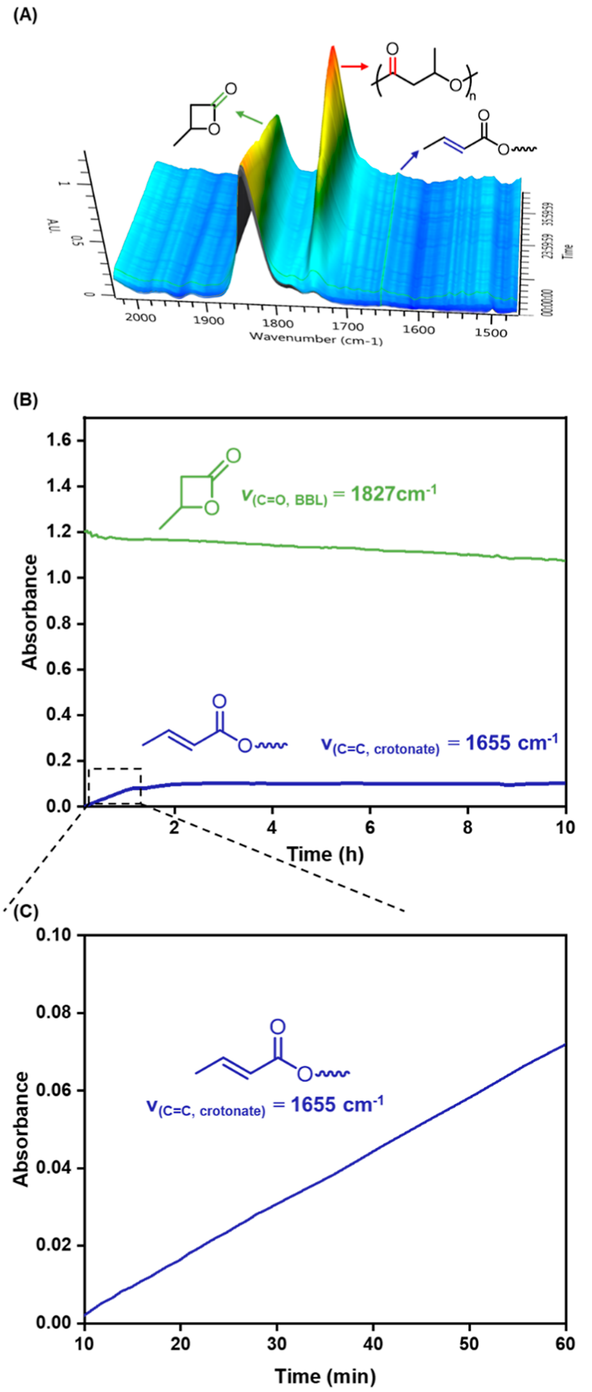


Figure 5. (A) Three-dimensional stack plot of the *in situ* FTIR spectra. (B) *In situ* FTIR profiles of ROP of BBL: BBL (1827 $\mathrm{cm^{-1}}$) and double bond of the crotonate end (1655 $\mathrm{cm^{-1}}$). (C) Double bond of the crotonate end (1655 $\mathrm{cm^{-1}}$) at the initial stage of polymerization (60 min). *In situ* FTIR spectroscopy studies were carried out in the presence of a **2-ace** catalyst (0.2 mol % loading) at 80 °C in toluene with [BBL] = 5.8 M. 90% conversion of BBL was achieved when the polymerization was stopped. The whole spectrum can be found in Supporting Information.

It is noteworthy that both chain initiation and propagation of ROP of β-lactones involve active anions via nucleophilic attacking β-C. The presence of a steric methyl group at the β-C in BBL has been observed to impede the activity of the carboxylate anions, thereby affecting the polymerization rate. This effect is evident in Tables 1 and 2, where BBL exhibits a significantly lower polymerization rate in the presence of a methyl group. Moreover, the effect of the steric methyl group

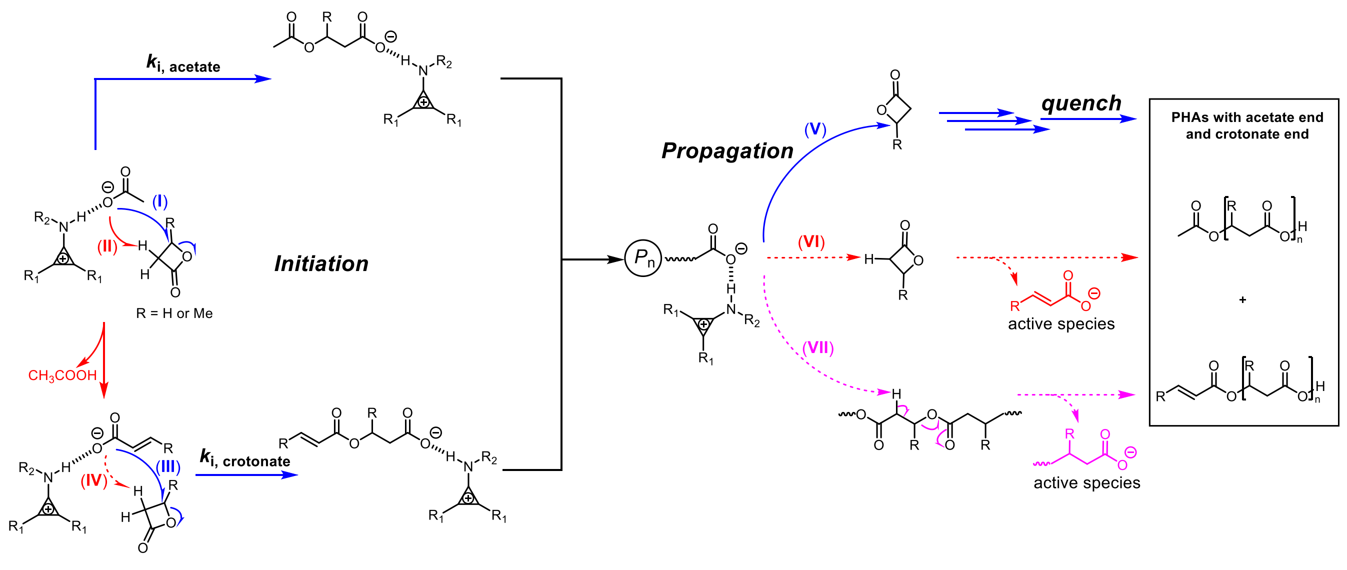


Figure 6. Proposed mechanism of initiation and propagation during polymerization of BBL and BPL initiated by aminocyclopropenium acetate.

on the ring stabilization contributed to the decreased inclination for ring-opening polymerization of BBL.[57,58]

The N−H moiety in aminocyclopropenium catalysts plays a crucial role in prompting polymerization. The weak hydrogen bond interaction between the N−H moiety and the carbonyl group of the β-lactones activated monomer resulted in faster polymerization compared with catalysts that lacked a hydrogen bond donor.

Furthermore, the presence of hydrogen bonds has been shown to impede the formation of crotonate species and subsequent side reactions, particularly at low temperatures. This effect is attributed to the formation of hydrogen bonds between the N−H moiety and the carboxylate growing chain ends. The P3HP produced by ROP of BPL at room temperature exhibited high molecular weights and a narrow Đ. No crotonate species were detected, and the polymers were entirely acetate-initiated. At elevated temperatures, pathways **II**, **VI**, and **VII** contributed to an increase in crotonate species, as evidenced by an *in situ* FTIR analysis. However, the *in situ* FTIR experiment revealed that the response of C═C in crotonate increased at the initial 1 h and remained constant at the late stage of polymerization (Figure 5B,C). At the initial 1 h stage, pathways **II** and **IV** likely contributed to the generation of crotonate species. However, the analysis of ^{1}H NMR spectra revealed the absence of *cis*- or *trans*-crotonic acid, suggesting that the predominant production of crotonate species occurred through pathway **II**. The activity of pathway **IV** was constrained by inadequate hydrogen bonding between the crotonate anion and the N−H moiety. The response of C═C in crotonate remained constant after 1 h, indicating limited proton abstraction (pathway **VI**) and cleavage of the polymer chain (pathway **VII**) at the late stage of polymerization. This phenomenon was attributed to the interaction between the N−H moiety and the active growing chain ends. However, hydrogen bonding at high temperature was weaker than that at low temperature. For comparison, stronger interactions, such as those observed with organoboron catalysts,[41] activated both monomer and carbonyl in the polymer main chain, resulting in high activity and molecular weight loss at the late stage of polymerization (pathway **VII**).

■ CONCLUSIONS

In conclusion, we present a series of aminocyclopropenium catalysts with adjustable hydrogen bond donors that were utilized in the ROP of BBL and BPL to generate PHAs with optimal activity and molecular weights (over 200 kg·mol^{-1} for P3HP). The capacity of catalysts to establish hydrogen bonds with monomers can be modulated by modifying the substituents at the N-position. In comparison with catalysts bearing electron-donating groups, catalysts with electron-withdrawing groups exhibited enhanced hydrogen bond donor properties and promoted ROP, resulting in augmented catalyst activity and elevated molecular weights of PHAs. It was observed that BBL exhibited a significantly slower rate of polymerization compared to its analogue BPL. This disparity can be attributed to the steric methyl group present in BBL, which significantly hinders the attack of the carboxylate anion at the β-C position. This hypothesis was validated through quenching experiments. The aminocyclopropenium cation with an N−H moiety was observed to form a hydrogen bond with monomers and active carboxylate chain ends, which was verified by ^{1}H NMR titration experiments. Hydrogen bonding promoted fast polymerization through activation of monomers. The stabilization of the active carboxylate end by hydrogen bonding prevented the activation of the monomer and polymer chain during polymerization, limiting the acidic abstraction of the α-H at β-lactones or the polymer chain at high temperatures to produce crotonate species and increasing the molecular weight. The hydrogen bonding-driven ROP of β-lactones has the potential to expand the application of organocatalysis in PHA preparation.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00165.

> Experimental details; characterization of aminocyclopropenium catalysts and PHAs; MALDI TOF spectra; DSC and TGA curves of P3HP; and solvent screening and regioselectivity of ROP (PDF)

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Notes

The authors declare no competing financial interest.

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