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A genuine H-bond donor and Lewis base amine cocatalyst in ring-opening polymerizations

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ABSTRACT

Hydrogen bond donor (HBD) and organic base binary cocatalyst established a gold standard in organocatalytic ring-opening polymerizations (ROPs). In depth probe of the mechanisms revealed that proton abstraction of the acidic H on the HBDs by the bases do occur frequently. A truly simple HBD and Lewis base (LB) cocatalysis, however, was elusive. We proposed genuine HBD/LB cocatalyst for ROPs by introducing 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) as a bidentate H-bond donor and triethylamine (TEA) as a mild Lewis base. ROPs of lactide (LA) and trimethylene carbonate (TMC) in solutions at room temperature were success. The mild ROPs produced polylactide (PLA) of predictable molecular weights (from 1.6 to 26.7 kg mol^{-1}) and extremely narrow dispersities (Đ 1.01 to 1.06). Furthermore, well-defined diblock copolymers PTMC-b-PLA were synthesized. NMR titration experiments verified exclusive H-bond donor activation of the monomer and TEA activation of the hydroxyl chain end without trace of proton abstraction.

1. Introduction

Hydrogen bond donor (HBD) and organic base binary cocatalyst [1–3] became accepted protocol in organocatalytic ring-opening polymerizations (ROPs) since Takemoto thiourea-amine catalyst [4–6] was firstly introduced in ROP of lactide (LA) by Waymouth and Hedrick [7–9]. The catalysis proceeds via bifunctional activation of the monomer by hydrogen bonding with Lewis acidic thiourea moiety, and of the initiator or propagating chain end by the Lewis basic amino group (Scheme 1a) [7,10,11]. The unimolecular bifunctional Takemoto catalyst was evolved into binary cocatalyst of thiourea and amine (Scheme 1b) [8] which exhibited combinatory diversity in general HBD/base binary cocatalyst design for ROPs [12–15]. Cooperative activation mechanisms of the HBD thiourea to carbonyl of the monomer, and the base to the hydroxyl of the propagating chain end were respectively confirmed by ^{1}H NMR titrations (Scheme 1c, mechanism 1) [7–11]. Enhancing the donating ability of HBD [15–19] and/or strengthening the receipting ability of base [9,12,20] were useful to increase cocatalytic efficiency. However, if base is more basic, the base would exhibit Brønsted basicity rather than Lewis basicity in H-bonds and abstract hydrogen of bidentate HBD. Similarly, more acidic H-bond donors have stronger proton donating ability. However, most of reported bases were strong enough to abstract the acidic proton of the HBD (i.e. proton of N–H on thiourea) and produce anions (i.e. thioureate anion), resulted in mixed ROP mechanisms of HBD/base catalysis and anionic catalysis. Kiesewetter et al. and Waymouth et al. proposed a rapid and complicated equilibrium between neutral H-bond mechanism and anion mechanism (Scheme 1c, mechanism 1 + 2) [13,14,21–23]. If the base is stronger, ROP even could be promoted by pure anionic catalysis (Scheme 1c, mechanism 2). Waymouth et al. treated (thio)ureas with alkoxides, forming urea anions to catalyze ROP via (thio)urea imidate activation mechanism [24,25]. The proton abstraction of the acidic H on the HBD by the base does occur frequently. Once deprotonation happened, it is hard to process an absolute hydrogen bonding mediated ROP mechanism. Does genuine cooperative H-bond activation ROP mechanism as originally designed really exist (Scheme 1d)?

The ROP catalyzed by HBD/base exists a conflict between the polymerization mechanism and H-bonds intensity. Stronger H-bond receptors exhibiting more Brønsted basicity and higher nucleophilicity to the hydrogens of HBDs result in mixed ROP mechanisms of HBD/base catalysis and anionic catalysis or pure anion mediated mechanism. By screening bases, we found that tertiary amines (TA) as weak bases were

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unable to abstract hydrogen of proton donators [26–29]. And the tertiary amino group of the Takemoto catalyst could activate the initiators or propagating chain ends [7]. Thereby, Lewis basic tertiary amine might be the possible pathway to control polymerization mechanism. However, compared with amine-tethered H-bond donor, corresponding HBD/TA could even retard ring-opening polymerization, for example thiourea/TA [8] and squaramide/TA [30,31] versus corresponding unimolecular bifunctional catalyst [7,30,31]. There were only a few metal-free and nonionic HBDs and TA could organic catalyze ROP of cyclic esters with long polymerization time (almost over one day) via proposed H-bonding activation mechanism [8,15,16,18,19,32]. Keeping catalytic activity of ROP is necessary when employing mild Lewis bases.

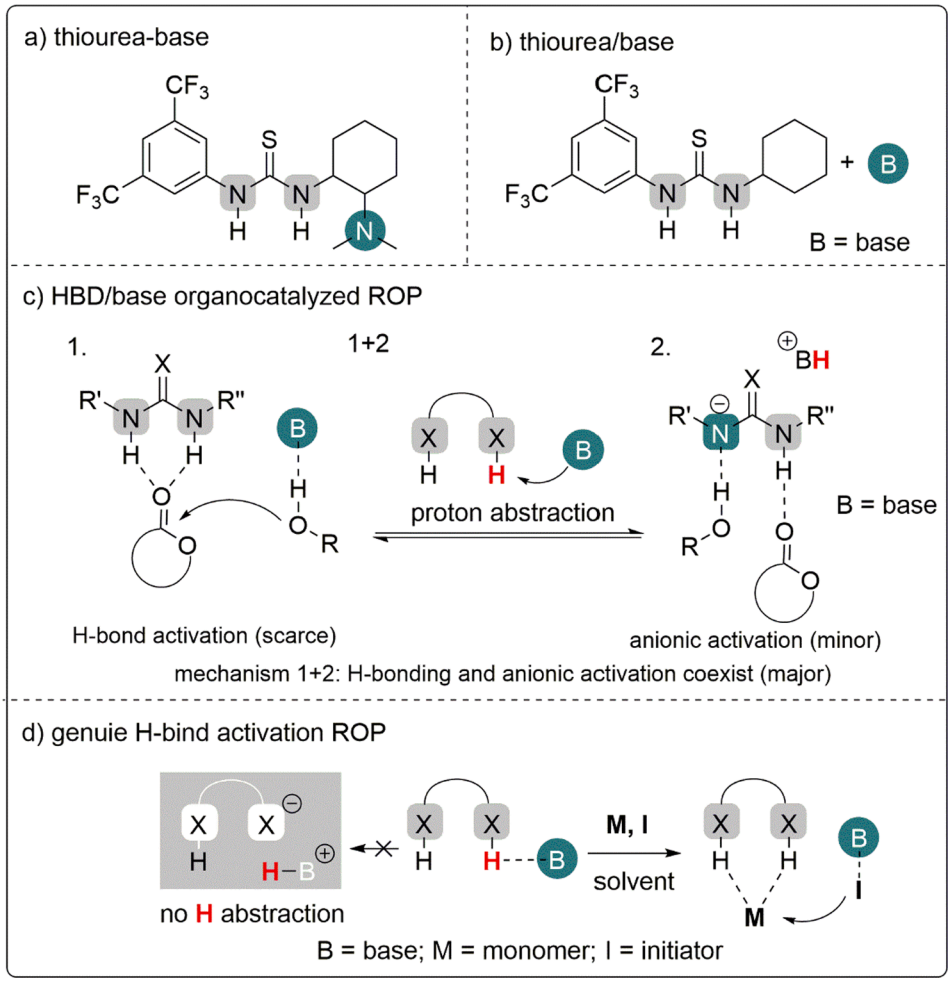
To improve catalytic activity of ring-opening polymerization, increasing the intensity of the hydrogen bond of HBD is useful. The HBD catalyst could be also considered as anion receptor which is famous in the anion recognition [33–35]. Thiourea with two appropriate distance of N-H protons has been recognized as one of the most successful and effective H-bond donating structures [36,37]. Among anions receptors, 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) [37–41], a thiourea isostere, was considered as a stronger anion receptor compared with thioureas. The stability constants of ABTD binding with anions, such as sulfate, benzoate and acetate, are well above the stability constants of thiourea (>4 vs 3) [37]. ABTD was also applied to highly enantioselective isomerization of alkynoates to allenoates [38]. In addition, our group used bidentate ABTD to promote benzoic acid activity in the ROP of δ-valerolactone (VL) through noncovalently activated [39]. Therefore, we considered that ABTD could act as a strong bidentate HBD and efficiently catalyze ROP with mild Lewis base through genuine H-bond donor/base activation without proton abstraction.

Despite advancements in ring-opening polymerization binary catalysts systems, the challenge of processing a genuine H-bond activation mechanism with high catalytic efficiency remains. Herein, we describe a catalytic combination of a genuine H-bond donor and Lewis base amine cocatalysts, bidentate ABTD and TA, promoting ring-opening polymerizations by strict H-bond activation mechanism without trace of proton abstraction (Scheme 2). To support the assumptions, ABTD/TEA cocatalyst was used to promote ring-opening polymerizations of cyclic esters, for example lactide, cyclic carbonate and lactone. The controlled and 'living' nature of the ROP was supported by ^{1}H NMR, ^{13}C NMR, and MALDI-ToF MS, kinetic studies and chain extension experiments. Furthermore, a strict H-bond donor and Lewis base cocatalysis mechanism as originally proposed was verified by NMR titration experiments.

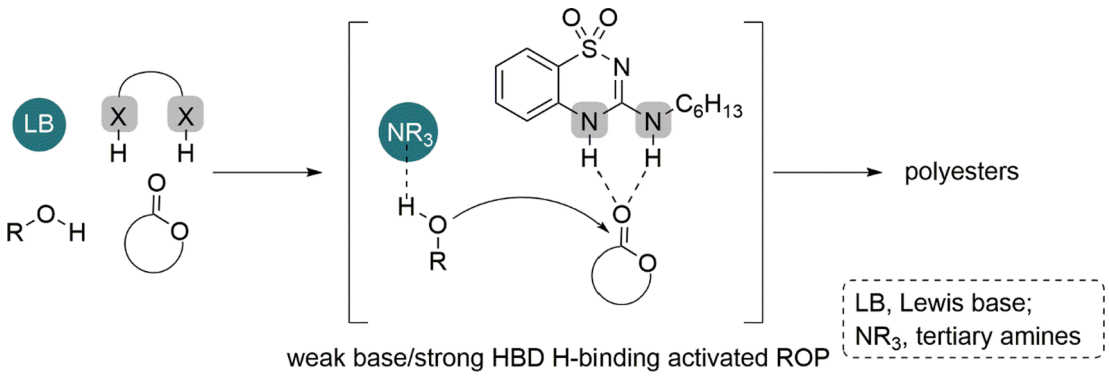
2. Results and discussion

2.1. Ring-opening polymerizations of lactide catalyzed by ABTD and triethylamine

To assess the effectiveness of 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) for the ring-opening polymerization, ABTD was firstly employed with the most used base (−)-sparteine and investigated the polymerization of lactide. The designed model ring-opening polymerization of lactide (LA) proceeded in dichloromethane (CH_2Cl_2) at room temperature using benzyl alcohol as initiator with the catalysis system of ABTD and base ($[LA]_0/[BnOH]_0/[ABTD]_0/[Base]_0$ = 30/1/1/1 and



Scheme 1. a. (Thio)urea-base (Takemoto thiourea) catalyzed ROP; b. (Thio)urea/base catalyzed ROP; c. The mixed ROP mechanisms of HBD/base catalysis and anionic catalysis (mechanism 1 + 2) is the commonest in the HBD and base cocatalyzed ring-opening polymerization. The ROPs only via anion activation (mechanism 2) were possible when using super-base. Genuine classic H-bond activation (mechanisms 1) was scarce; d. HBD/base catalyzed ROP via genuine H-bond activation mechanism with no proton abstraction.

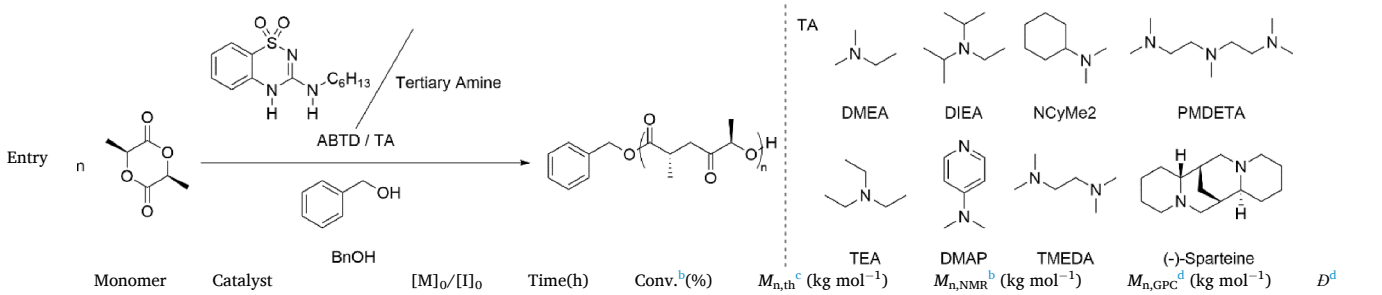


Scheme 2. ABTD organocatalyzed ROP with Lewis basic TA via genuine H-bond activation mechanism in this work.

monomer concentration of $[LA]_0 = 1$ mol L^{-1}). ABTD combined with the stronger base (−)-sparteine could effectively catalyze the ROP of lactide and resulted in polylactide (PLA) with accurate molecular weight and narrow molecular-weight distributions (MWD) (94.4% in 2 h, $Đ$ = 1.045, Table 1, entry 1). Seven various tertiary amines were picked and applied to catalyze the ROP of cyclic ester, given the economy and biosafety of catalyst. All resultant PLAs displayed expected molecular weight and remarkably narrow dispersity ($Đ$ between 1.003 and 1.030) which indicated transesterification scarcely occurred (Table 1, entries 2–8). Surprisingly, triethylamine (TEA), a cheap and available base, could efficiently catalyze the ROP of LA (Table 1, entries 4). Alone ABTD or TEA was basically inactive to the ROP of LA (Table 1, entries 9 and 10) confirmed that hydrogen bond donor ABTD and base are indispensable in the bicomponent catalyzed ROP of LA.

TEA plus ABTD catalyzed the ROP of LA with comparatively good catalytic efficiency (89.5% in 12 h, Table 1, entry 13) and higher turnover frequency (TOF) calculated as 1.43 h^{-1} (Table S1). More remarkable, the catalytic effect (TOF) of ABTD is better than the thiourea, squaramide and other HBDs [8,16,18,19,30,32] proposed before. And the PLAs produced by the combination of TEA and ABTD had precise molecular weight and narrow dispersity ($Đ$ was around 1.01, Table 1, entries 4 and 13). Besides, triethylamine has a huge advantage in price. ((−)-sparteine, Aladdin, 2519.1 ¥/500 mg; TEA, Aladdin, 32.76 ¥/500 mL). TEA is a cheap, available, and efficient basic cocatalyst to promote

Table 1
ROP of Lactide and trimethylene carbonate initiated from BnOH by ABTD and base.[a]



	Monomer	Catalyst	$[M]_0/[I]_0$	Time(h)	Conv.[b](%)	$M_{n,th}$[c] (kg mol^{-1})	$M_{n,NMR}$[b] (kg mol^{-1})	$M_{n,GPC}$[d] (kg mol^{-1})	$Đ$[d]
1	LA	ABTD/(−)-sparteine	30	2	94.4	4.2	4.2	3.3	1.045
2	LA	ABTD/DIEA	30	20	98.5	4.4	4.4	4.3	1.022
3	LA	ABTD/PMDETA	30	20	97.0	4.3	4.2	4.1	1.030
4	LA	ABTD/TEA	30	20	95.4	4.2	4.2	4.2	1.003
5	LA	ABTD/NCyMe2	30	20	93.1	4.1	4.0	3.7	1.022
6	LA	ABTD/DMEA	30	20	69.1	3.1	2.9	2.7	1.025
7	LA	ABTD/DMAP	30	20	66.5	3.0	2.8	2.0	1.013
8	LA	ABTD/TMEDA	30	20	32.9	1.4	–	–	–
9	LA	ABTD	30	24	–	–	–	–	–
10	LA	TEA	30	24	–	–	–	–	–
11	LA	ABTD/TEA	10	8	99.1	1.5	1.6	1.7	1.009
12	LA	ABTD/TEA	20	8	86.7	2.6	2.7	2.6	1.023
13	LA	ABTD/TEA	30	12	89.5	4.0	3.9	4.2	1.011
14	LA	ABTD/TEA	40	16	90.1	5.3	5.3	5.5	1.010
15	LA	ABTD/TEA	80	30	84.7	9.9	9.7	9.8	1.014
16	LA	ABTD/TEA	150	96	93.8	20.3	20.9	20.8	1.058
17	LA	ABTD/TEA	200	120	95.0	27.4	26.7	26.9	1.052
18	TMC	ABTD/TEA	30	96	83.7	2.7	2.7	2.9	1.026
19	VL[e]	ABTD/TEA	30	24	–	–	–	–	–
20	CL[e]	ABTD/TEA	30	24	–	–	–	–	–
21	LA[f]	ABTD/TEA	30	20	49.5	2.2	2.4	1.9	1.009

[a] Keeping $[ABTD]_0/[TEA]_0/[BnOH]_0 = 1$; $[M]_0 = 1$ mol L^{-1}; temperature, room temperature (rt.); solvent, CH_2Cl_2.
[b] Determined by ^1H NMR in $CDCl_3$.
[c] $M_{n,th}$ values were calculated from $([M]_0/[I]_0) \times$ conv. $\times$ (M_W of monomer) + (M_W of BnOH).
[d] Determined by GPC in THF using PSt Standards and correction factors.
[e] Keeping $[ABTD]_0/[TEA]_0/[BnOH]_0 = 1$; $[M]_0 = 3$ mol L^{-1}; temperature, rt.; solvent, CH_2Cl_2.
[f] Keeping $[ABTD]_0/[TEA]_0/[BnOH]_0 = 1$; $[M]_0 = 1$ mol L^{-1}; temperature, rt.; solvent, acetonitrile.

the ROP of LA with ABTD.

According to the cheapness, controllability, and activity of TEA, we hence explored the catalysis system ABTD/TEA for the ROP. Furthermore, ABTD and TEA were extended to catalytic ROPs of representative cyclic monomers of trimethylene carbonate (TMC), δ-valerolactone (VL) and ε-caprolactone (CL) (Table 1, entries 18–20). The ROP of TMC reached about 87% conversion after 96 h and synthesized PTMC with narrow dispersity ($M_{n,NMR}$ = 2.7 kg mol^{-1}, $Đ$ = 1.026) (Figs. S3 and S4); however, parallel ROPs of VL and CL did not yield any appreciable homopolymers. These observations suggested that ABTD combined with TEA was a mild and effective catalytic pathway in ROPs of lactides and cyclic carbonates and could synthesize well-defined PLA and PTMC with narrow dispersity and predicted molecular weights.

To garner insight into the catalytic performances of ABTD/TEA in the ROP of LLA, kinetic data were measured in the ROPs at 2, 4, 6, 8, 10, 12, and 24 h during the polymerizations (Fig. 1). In the kinetics plots (Fig. 1a), ln([LA]$_0$/[LA]) versus polymerization time exhibited as first order kinetics. Similarly, all PLAs sampled during polymerization still kept with predicted molecular weights and remarkably low dispersity values ($Đ$) (below 1.03) (Fig. 1b). The linear relationship between the molecular weight of the PLA and monomer conversion reveals that the ROP process was controlled and 'living'.

To further confirm the controlled nature of the polymerization, the chain structures of the obtained PLA samples were analyzed by using ^{1}H and ^{13}C NMR spectra (Fig. 2). Fig. 2a demonstrated that the peaks at around 1.57 ppm and 5.17 ppm were attributed to the repetitive structure of unit LA. The peaks of the aromatic terminal backbone were observed at about 7.34 ppm; the peaks of the methine proton closest to the hydroxyl chain end were considered at 4.35 ppm. In addition, the feed ratios close to the integration ratios of the repeating unit (peak C or D) to the chain-ending hydrogen (aromatic hydrogen and peak D') indicated PLA samples were initiated by exact BnOH. In addition, the methine carbon signal (69 ppm, peak D in Fig. 2b) and the methine hydrogen signal exhibited (5.17 and 4.35 ppm, peak D and D' in Fig. 2a) exhibited singlet and quartet peak, respectively. According to the NMR data, we could affirm that the ROP of LA without any racemization employing ABTD/TEA system [42].

Similarly, in the ^{1}H NMR spectrum of PTMC (Fig. S3), the appearances of the peaks at 2.01–2.07 ppm and 4.21–4.30 ppm were due to the main chains of the PTMC. The peaks at 3.74 ppm represented the methylene protons next to the chain end of the hydroxyl group; and the peaks at 5.15 and 7.31–7.39 ppm were contributed initiator BnOH. All these results indicated that the ROP of TMC was initiated by BnOH successfully. All NMR spectra proved the end-group fidelity of LA and TMC polymerization.

MALDI-ToF MS spectra (Fig. 3) provided further proof of the exact structures of the obtained PLA catalyzed by ABTD and TEA. Two main series of peaks were observed with molecular formulae of molar mass of M = 108.06 (M_w of BnOH) + n × 144.04 (M_w of LA) + 22.99 (Na$^+$) or M = 108.06 (M_w of BnOH) + n × 144.04 (M_w of LA) + 39.10 (K$^+$). For example, the experimental molecular weight of the 16-mer with K$^+$ 2451.80 and with Na + 2435.69 corresponded to theoretical values. And each neighboring peak showed a gap of 144 *m/z*, meeting with the molecular weight of the LA unit. Unfortunately, still minimum PLAs initiated by residual water were exhibited as the limit of experimental conditions. MALDI-ToF MS reaffirmed that the main PLA chains were initiated by BnOH.

Next, to further assess the 'living' nature, varying in monomer-to-initiator ratio ([LA]$_0$/[I]$_0$) from 10 to 200 and keeping the concentration of BnOH, we obtained controllable high molecular weight polylactides successfully (Table 1, entry 11–17). Even with lower catalyst loading ([I]$_0$/[ABTD]$_0$/[TEA]$_0$ = 1/1/1), the polymerization employing ABTD/TEA still exhibited higher or similar polymerization rate compared with the published work about TU/TEA ([I]$_0$/[ABTD]$_0$/[TEA]$_0$ = 1/10/10) [8]. The PLA samples were subjected to size-exclusion chromatography (SEC) analyses. With the increase of the ratios of [LA]$_0$/[BnOH]$_0$ from 10 to 200, the elution time of obtained PLA gradually decreased (Figs. 4 and S6). In other words, the molecular weights of obtained PLA linearly increased in direct proportion to the ratios. In addition, SEC traces of all PLAs revealed narrow and symmetrical monomodal peaks (the $Đ$ values ranging from 1.009 to 1.023). Besides, the $M_{n,GPC}$ values of the obtained PLAs fairly agreed with the $M_{n,th}$ values calculated by the monomer conversions reaching 27,000 kg mol^{-1}. These data confirmed that the ROP of LA employing ABTD/TEA system was very controlled and efficient in a range of degree of polymerization (DP) from 10 to 200.

Then the chain extension experiments were carried out to confirm the controllability and livingness of the ROP of LA. After the first ROP reached nearly complete conversion ($M_{n,\ NMR}$ 4.4 kg mol^{-1}, $Đ$ 1.003), another 30 equiv. of LA monomer were added in the polymerization solution at room temperature, keeping [LA]/[BnOH]/[ABTD]/[TEA] = 30/1/1/1. And then the polymerization restarted and proceed to full conversion ($M_{n,\ NMR}$ 8.3 kg mol^{-1}, $Đ$ 1.010). As shown in Fig. 5, the SEC trace peak of the second polymerization shifted significantly to the lower elution time compared with the first polymerization. The SEC graph proved that the chain end group of polymer and catalysis system truly kept active in the whole polymerization. In other words, the ROP of LA by ABTD/TEA was an ideal controlled and living polymerization.

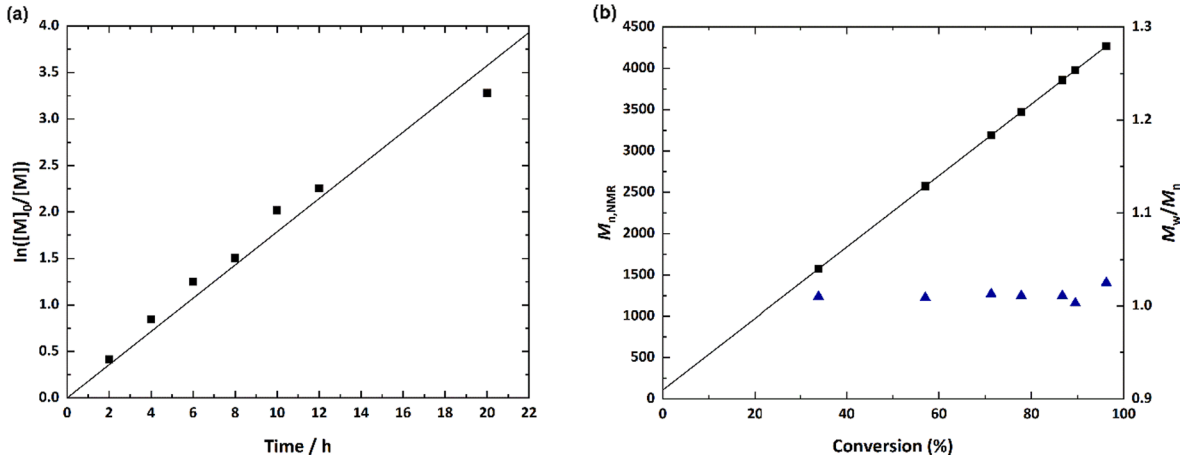


Fig. 1. (a) The semi-logarithmic kinetics plot for polylactide (PLA)([LA]$_0$/[BnOH]$_0$/[TEA]$_0$[ABTD]$_0$ = 30/1/1/1, CH_2Cl_2, rt.). (b) Dependence of molecular weight ($M_{n,NMR}$) and dispersities ($Đ$) versus the monomer conversion (conv.). The solid line shows the $M_{n,th}$ values equated ([LA]$_0$/[BnOH]$_0$) × conv. × (M_W of LA) + (M_W of BnOH).

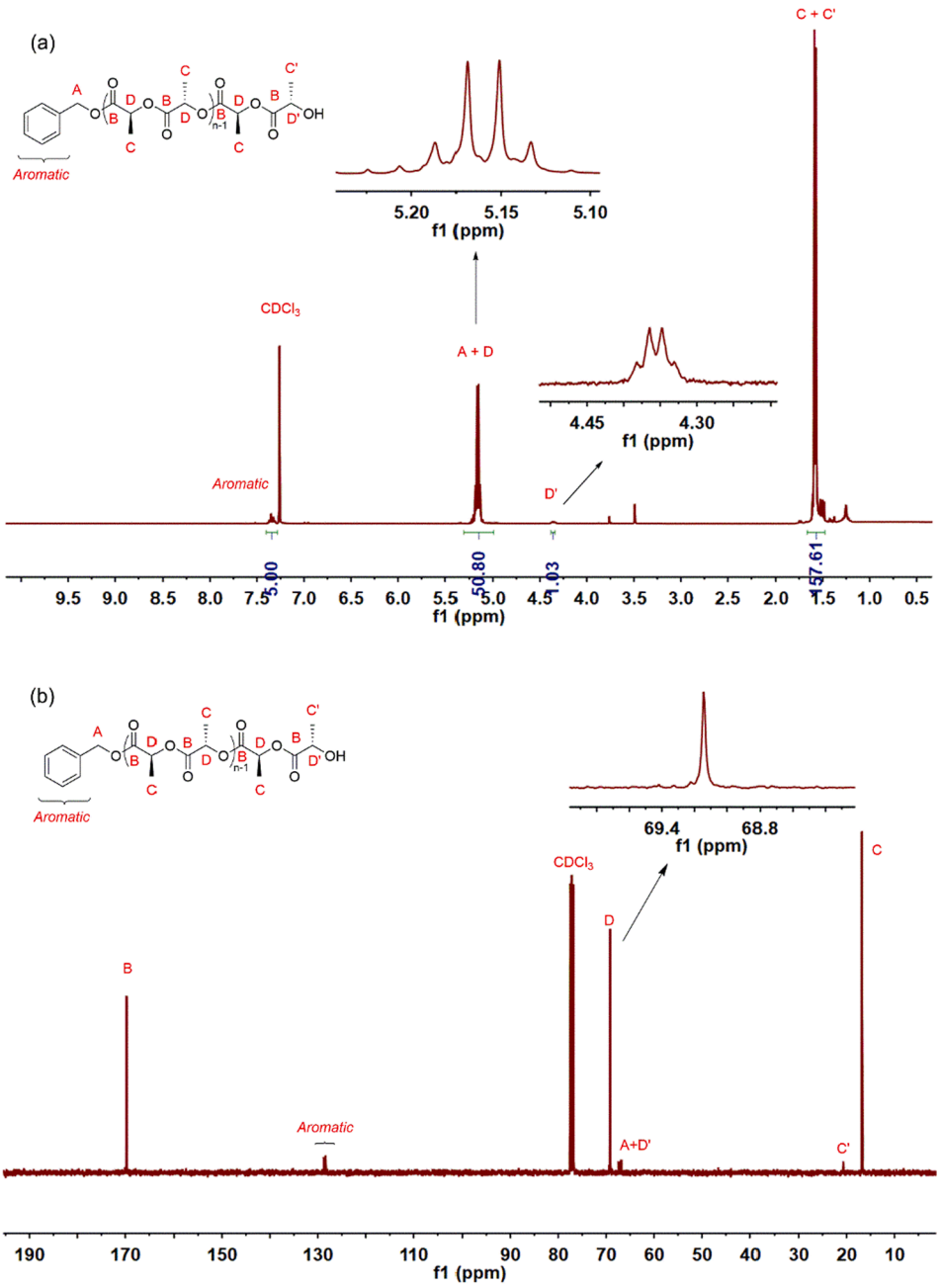
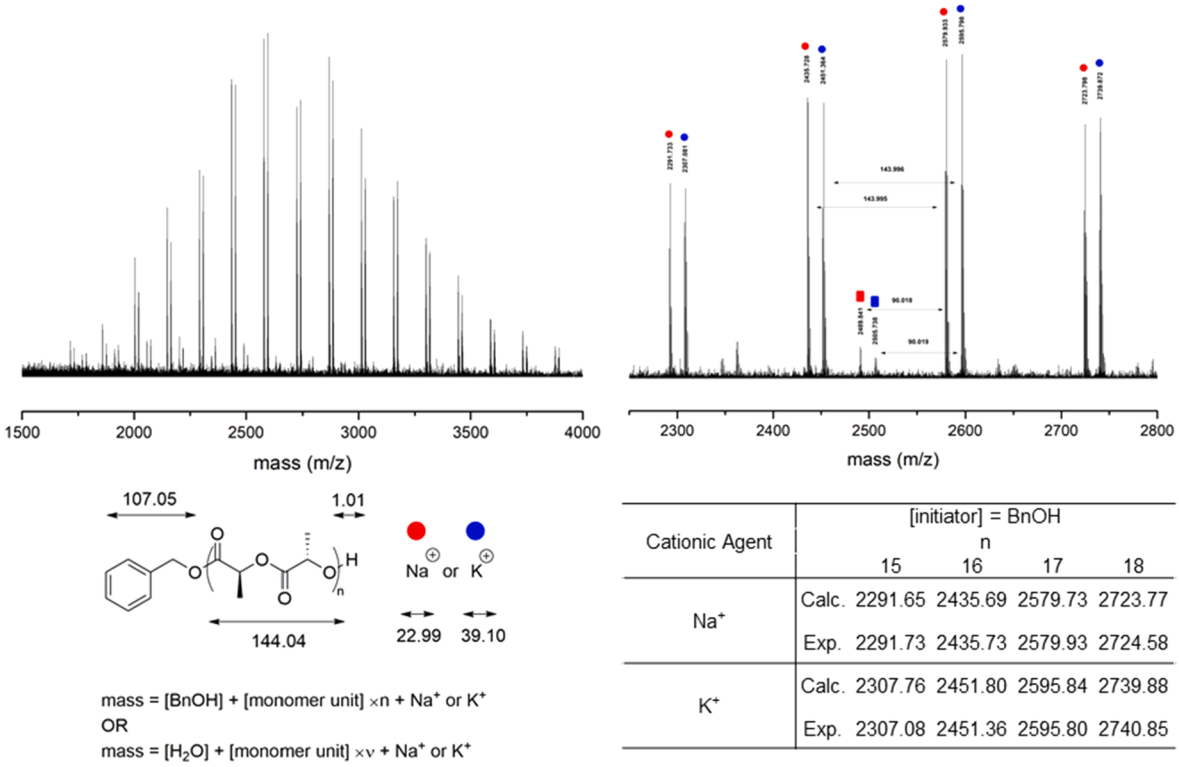


Fig. 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectrum of BnOH initiated PLA (Table 1, entry 13).

2.2. Proposed mechanisms for ROP initiated with BnOH catalyzed by ABTD and triethylamine

To explore the interactions between initiator BnOH, triethylamine, ABTD and monomer LA and certify exact polymerization mechanism, NMR titration experiments were carried out. Firstly, as the molar ratio of [TEA]/[BnOH] gradually increasing from 1/0 to 1/3, the chemical shifts of the adjacent methylene hydrogen of benzyl alcohol fielded from 4.576 to 4.562 ppm (Fig. 6). And the peaks of the methylene protons exhibited instant coalescing of the doublet into sharp singlet. At the same time, we observed that the chemical shift and peak shape of the hydrogen on the alcohol had undergone tremendous changes (from 1.678 to 4.238 ppm). TEA can activate the alcohol of initiator. Then the activation between ABTD and monomer was verified. Titrating the monomer LA with ABTD, we observed the chemical shifts of the carbonyl carbon of LA was shifted from 167.465 ppm to 167.484, 167.496, 167.500 and 167.515 ppm in the ^{13}C NMR spectra by increasing the molar ratio of [ABTD]/[BnOH] from 0 to 2 (Fig. 7). The changes of chemical shifts in Figs. 6 and 7 were attributed to the activation of hydroxyl by base and carbonyl carbon by ABTD through H-bonds interaction.

In addition, NMR titration experiments also certified that TEA is hard to deprotonate ABTD (Fig. 8). Once proton abstraction happened, the peaks of active hydrogens on the HBD would disappear or have merger into a single proton in NMR data [22,24]. At the same time, the chemical shift of adjacent aromatic hydrogens would change obviously. In contrast, in the ABTD/TEA cocatalysis system, the active hydrogens both existed; aromatic hydrogens did not have any noticeably shift. Titrating ABTD by gradient addition of TEA from 0 to 1 equivalent, two active hydrogens on the ABTD only exhibited slight upfield shifts. And the peak area was still about '1' ($[ABTD]_0/[TEA]_0 = 1/1$), although the peak pattern of the left active hydrogen significantly changed. This



Cationic Agent	[initiator] = BnOH, n			
	15	16	17	18
Na^+ Calc.	2291.65	2435.69	2579.73	2723.77
Na^+ Exp.	2291.73	2435.73	2579.93	2724.58
K^+ Calc.	2307.76	2451.80	2595.84	2739.88
K^+ Exp.	2307.08	2451.36	2595.80	2740.85

Fig. 3. MALDI-ToF MS spectrum of the PLA ([LA]/[ABTD]/[TEA]/[BnOH] = 20/1/1/1, 25 °C, conversion = 80%, $M_{n,\ NMR}$ = 2.7 kg mol^{-1}, $Đ$ = 1.012; PLAs initiated by BnOH or water were respectively marked with solid circle and rectangle).

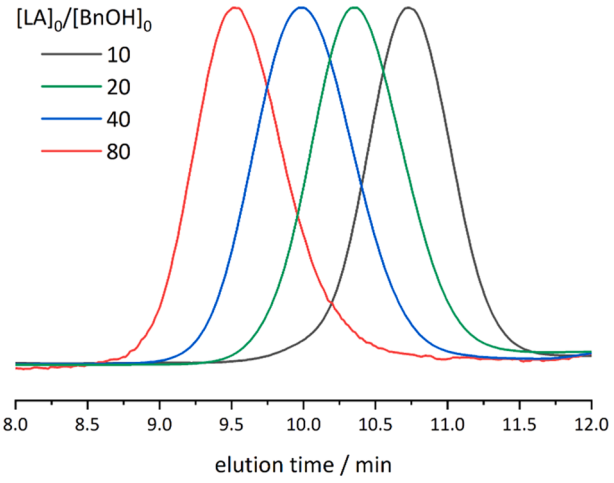


Fig. 4. SEC traces of the obtained PLA samples with various ratios of $[LA]_0/[BnOH]_0$ = 10; 20; 40 and 80 (entry 11, 12, 14, 15; eluent, THF; flow rate, 0.7 mL min^{-1}).

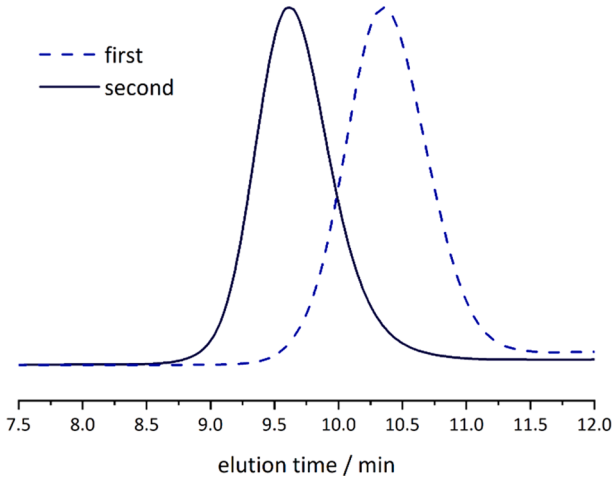


Fig. 5. SEC traces of first polylactide and post-polymerization (dashed and solid line respectively) (eluent, THF; flow rate, 0.7 mL min^{-1}).

result implied no proton abstraction and weak interaction after treating ABTD with weak base TEA. Moreover, the polymerization solvent also has a great influence on the tendency of mechanism. Polar solvents favored forming (thio)urea anions while nonpolar reaction solvents favored the classic H-bond mediation [22]. When acetonitrile was used, a significant decrease of the polymerization rate indirectly supported that the ROP was carried out through the H-Bonds activation mechanism (Table 1, entry 21). Proton abstraction did not exist during ABTD/TEA catalyzed ROP.

According to the results of NMR titration spectra, we considered that the possible mechanism of ring-opening polymerization of lactides and cyclic carbonates using ABTD/TEA were through a neutral H-bonding mechanism rather than anion mechanism (Scheme 4). Triethylamine could not interact with ABTD but activate the hydrogen of the initiating or propagating alcohol becoming more nucleophilic. At the same time, sulfonyl guanidine as a strong H-bonding donor activates the carbonyl group of the monomer becoming more electrophilic. Then nucleophilic hydroxyl group attacking the electrophilic carbonyl and opening the ring of monomer accomplished the propagating step. Finally, the polymerization catalytic cycle was terminated by the complete consumption of monomers.

2.3. Copolymerization of lactides and cyclic carbonates

The generation of well-defined block copolymer is significant in the

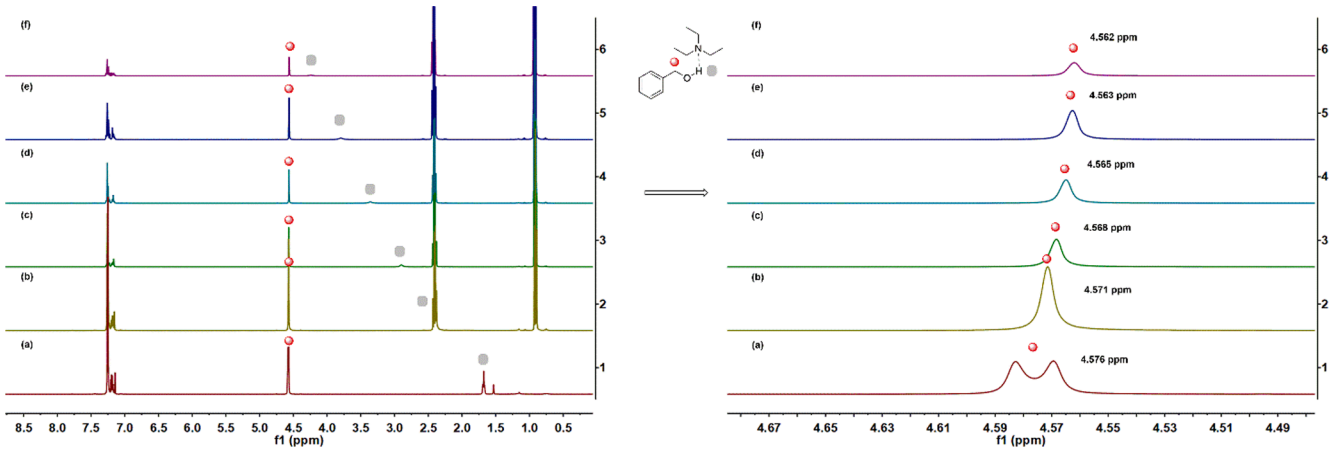


Fig. 6. The chemical shifts of the alcoholic protons in the presence of varied amounts of triethylamine were observed in the ^{1}H NMR spectra ($CDCl_3$): (a) BnOH; (b) triethylamine/BnOH = 0.5/1; (c) triethylamine/BnOH = 1/1; (d) triethylamine/BnOH = 1.5/1; (e) triethylamine/BnOH = 2/1; (f) triethylamine/BnOH = 3/1.

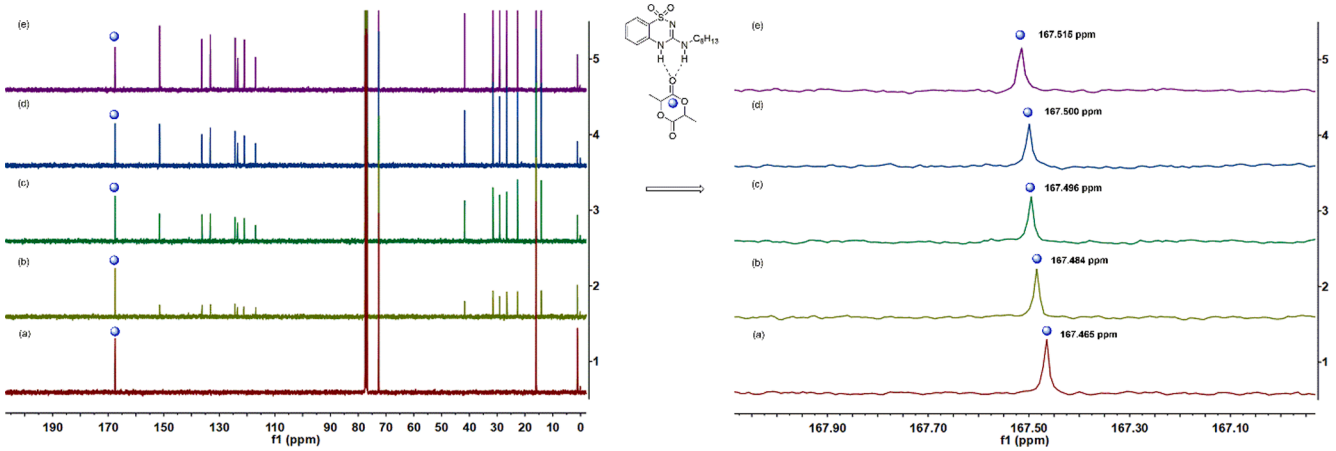


Fig. 7. The chemical shifts of the carbonyl-carbon of LA in the ^{13}C NMR spectra ($CDCl_3$) were observed. (a) LA; (b) ABTD/LA = 0.5/1; (c) ABTD/LA = 1/1; (d) ABTD/LA = 1.5/1; (e) ABTD/LA = 2/1.

field of nanoparticles and functional bioactive polymers [43–45]. Block copolymerization has a huge advantage in terms of the number of different possible products, compared to the polymerization of a single monomer [46]. However, different carbonyl-containing cyclic monomers of ROP, such as lactides, lactones and cyclic carbonates, are scarcely co-polymerizable under identical catalytic system [45,47,48]. An ideal pattern to prepare multiblock copolymers was ring-opening copolymerization (ROCOP) in one pot with one catalyst by sequential multi-feeding of various monomers. We focused on the diblock ROCOP of TMC and LA catalyzed by ABTD and triethylamine (Scheme 5). In this case, primary hydroxyls contained better controllability and higher polymerization rate compared to the secondary hydroxyls at the end of chain. Therefore, monomer LA was added into the prepared PTMC precursor solutions, then the second polymerizatio converted PTMC into PTMC-*b*-PLA (Table 2, entry 1 and 2). The molecular weights of PTMC-*b*-PLAs detected by NMR and GPC were close to the theoretical molecular weight. ^{1}H NMR and SEC results (Figs. 9 and 10) indicated that well-defined diblock polyester PTMC-*b*-PLA was synthesized successfully. ABTD plus TEA binary cocatalyst is an excellent pathway to control the copolymerization of LA and TMC with extremely narrow MWD ($Đ$ = 1.055).

3. Conclusions

Binary H-bond catalytic ring-opening polymerization were validated existing the mixed mechanism of HBD/base catalysis and anionic catalysis. Simple genuine HBD/base catalysis does rarely occur. In this work, Lewis basic triethylamine and bidentate 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) efficiently mediated the ROP of lactide and cyclic carbonate at room temperature and controlled polymerization by HBD/base mechanism without proton abstraction. ABTD/triethyl amine promoted ROPs to produce polyesters with predictable molecular weights (from 1.6 to 26.7 kg mol^{-1}) and extremely narrow dispersities ($Đ$ 1.003 to 1.058). Considering the weak basicity of triethylamine and the results of NMR titration experiments, we discovered that the ABTD/TEA cocatalysis was through the genuine hydrogen bonds activation mechanism without proton abstraction. Produced copolymers, PTMC-*b*-PLA, were still possessed with predictable molecular weight and extremely narrow dispersity. ABTD/TEA binary catalytic system has paved a mild, cheap, and effective avenue to ring-opening polymerization through genuine HBD/base catalysis as original designed. More generally, the adjustment of the intensity of cocatalysts and HBD is a general and useful pathway to balance the ring opening polymerization mechanism and catalytic activity.

4. Experimental section

4.1. Materials

Lactide (LA; 99.5%, Jinan Daigang Biomaterial Co.) was

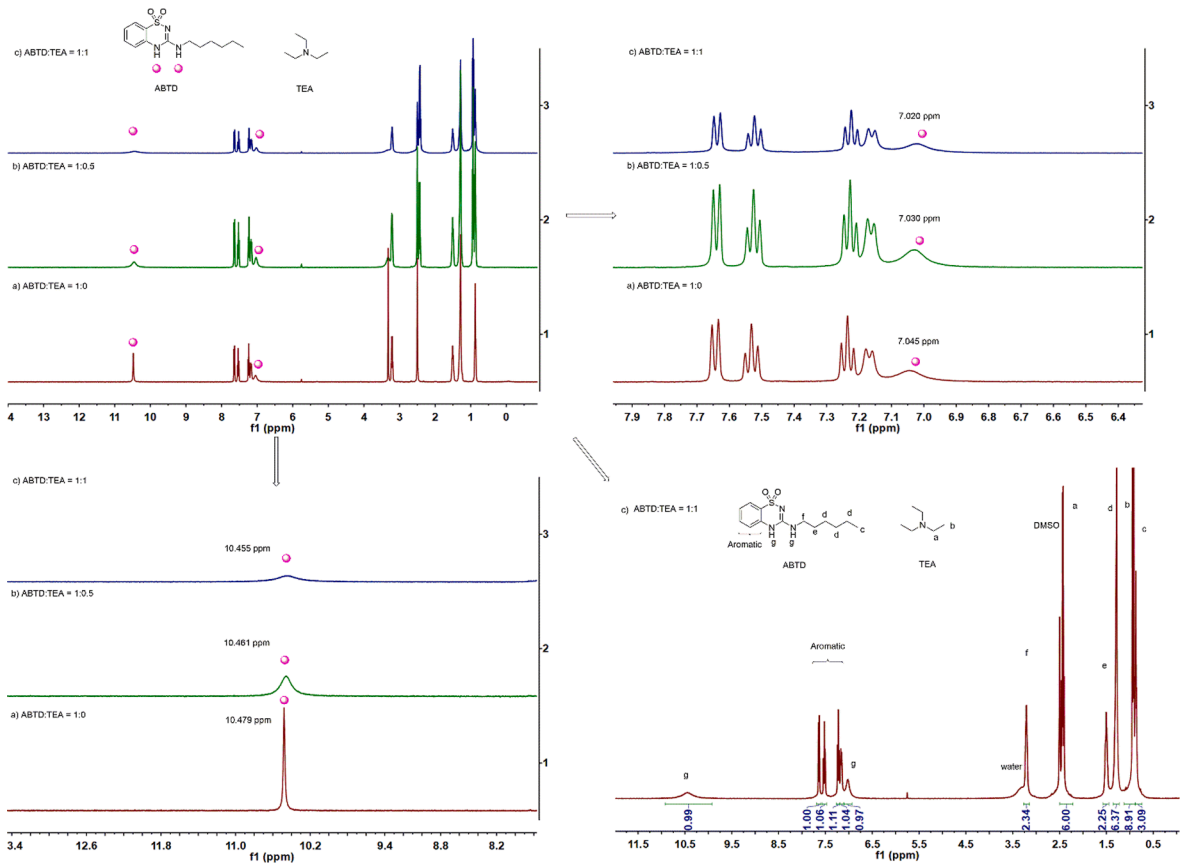
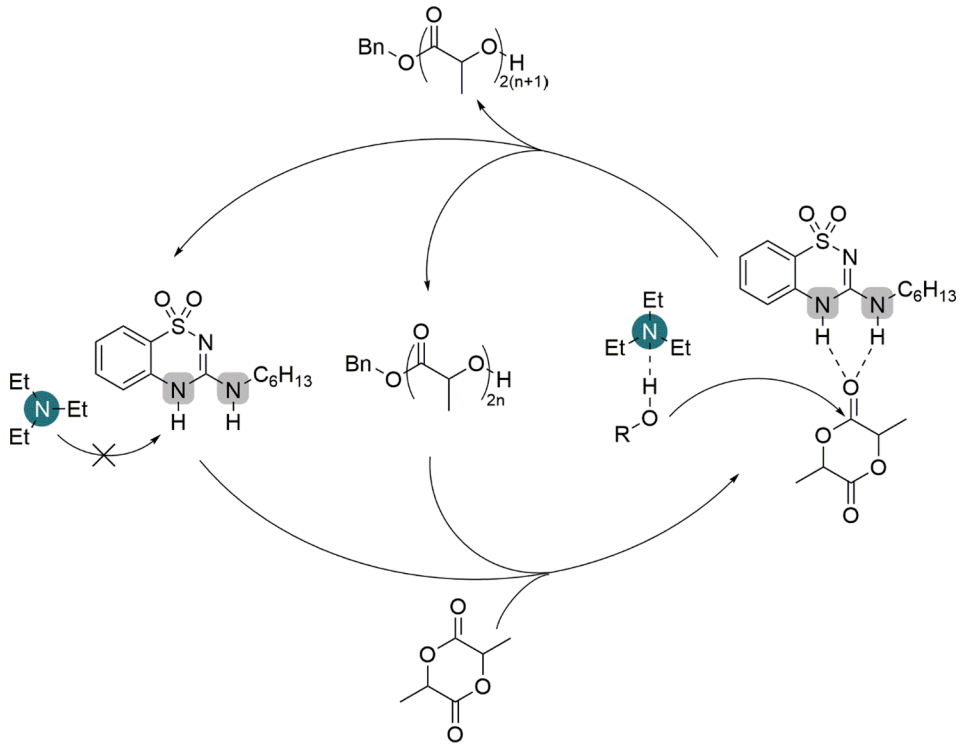
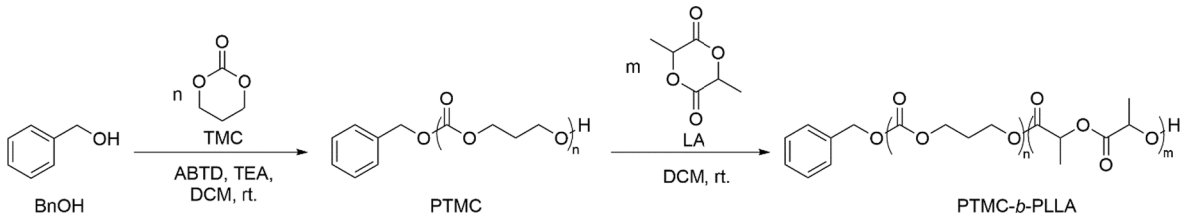


Fig. 8. The chemical shifts of active hydrogens of ABTD in the ^{1}H NMR spectra (DMSO) were observed. (a) ABTD; (b) ABTD/TEA = 1/0.5; (c) ABTD/TEA = 1/1.



Scheme 4. Plausible H-bonding activation mechanisms for the ROP of LA catalyzed by ABTD/TEA.



Scheme 5. One-pot synthesis of diblock copolymers by ROP of TMC and LA using ABTD and triethylamine as cocatalyst.

Table 2
ROP conditions and characterization of Homopolymers and Copolymers.[a]

Entry	M_1	M_2	Catalysts	$[M_1]_0/[M_2]_0/[I]_0$	Time (h)		Conv.[b] (%)		$M_{n,th}$[c] (kg mol^{-1})	$M_{n,NMR}$[b] (kg mol^{-1})	$M_{n,GPC}$[d] (kg mol^{-1})	$Đ$[d]
					ROP_1	ROP_2	ROP_1	ROP_2				
1	TMC		TEA	20/0/1	72	–	92	–	2.0	2.0	1.9	1.032
2	TMC	LA	TEA	20/20/1	72	10	92	85	4.4	4.3	4.1	1.055

[a] Keeping $[ABTD]_0/[TEA]_0/[BnOH]_0 = 1$; $[M]_0 = 1$ mol L^{-1} as a constant in CH_2Cl_2, polymerization at room temperature (rt.).
[b] Determined by ^{1}H NMR in $CDCl_3$.
[c] Calculated from $([M]_0/[I]_0) \times$ conv. $\times$ (M_W of monomer) + (M_W of BnOH).
[d] Determined by GPC in THF using PSt Standards and correction factors.

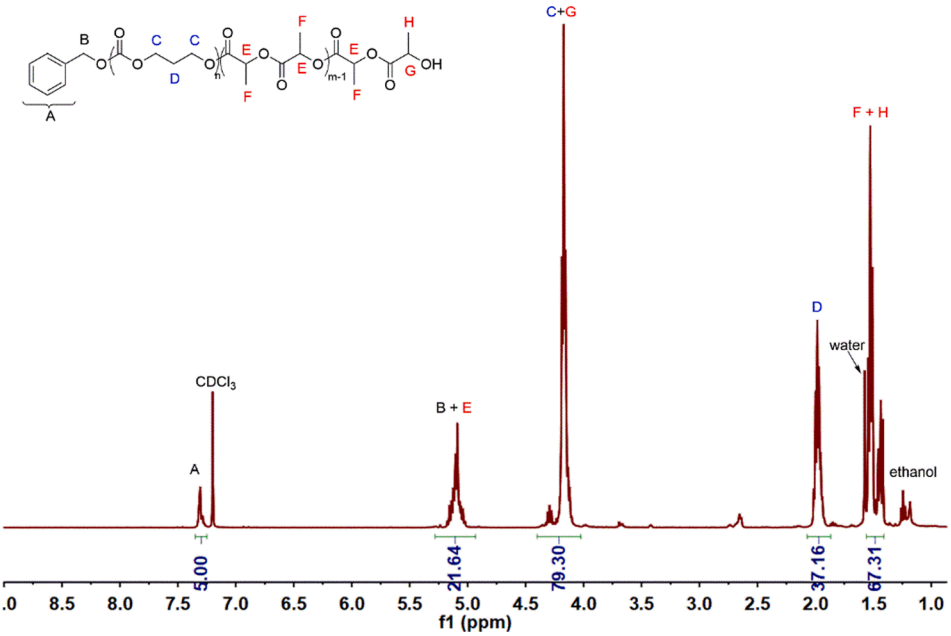


Fig. 9. ^{1}H NMR spectrum ($CDCl_3$) of PTMC-*b*-PLA initiated from BnOH using ABTD/TEA.

recrystallized using dry toluene for three times to obtain white crystals, the LA samples were dried under high vacuum for 72 h. Trimethylene carbonate (TMC; 99%, Sinopharm Chemical Reagent Co.) was purified three times by benzene–n–hexane to afford white crystals and dried under vacuum for 24 h. Benzyl alcohol (BnOH; 99%, Acros) was refluxed over CaH_2 for 48 h before distillation. Dichloromethane (CH_2Cl_2; >99.5%, Sinopharm Chemical Reagent Co.) was distilled over CaH_2 under argon atmosphere. Triethylamine (TEA; 99%, J&K), (−)-sparteine (98%, TCI), *N,N*-Dimethylcyclohexylamine ($NCyMe_2$; 98%, TCI), *N,N*-Diisopropylethylamine (DIEA; 99%, Aladdin), 4-Dimethylaminopyridine (DMAP; 99%, TCI), *N,N*-dimethylethylamine (DMEA; 98%, TCI), *N,N,N',N'*-Tetramethylethylenediamine (TMEDA; 99%, sigma), and Pentamethyldiethylenetriamine (PMDETA; 98%, TCI) were directly used as received.

3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) was prepared by a literature method [37–39,41]. In brief, 2-amino-benzenesulfonamide was converted into the sulfonylthiourea after reaction with hexyl isothiocyanate; and then ABTD was produced by ring closure reaction. The product was purified by column chromatography and recrystallization (Figs. S1 and S2). All the other reagents were purchased from Aldrich and used without further purification.

4.2. Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy was carried out on a Bruker Ascend TM-400 (400 MHz) spectrometer for ^{1}H, ^{13}C, NMR titration experiments and the calculation of the number-average molecular weights ($M_{n,\ NMR}$) and monomer conversions using $CDCl_3$ or DMSO as the solvent at 20 °C.

Gel Permeation Chromatography (GPC) was measured on the Wyatt Astra GPC system equipped with a SSI 1500 pump and the flow rate of 0.7 mL min^{-1}, the machine was equipped with a Waters Styragel HR 2.5 μm, 300 mm × 7.8 mm column, a Waters Styragel HR 4 μm, 300 mm × 7.8 mm column and a Wyatt Optilab rEX differential refractive index

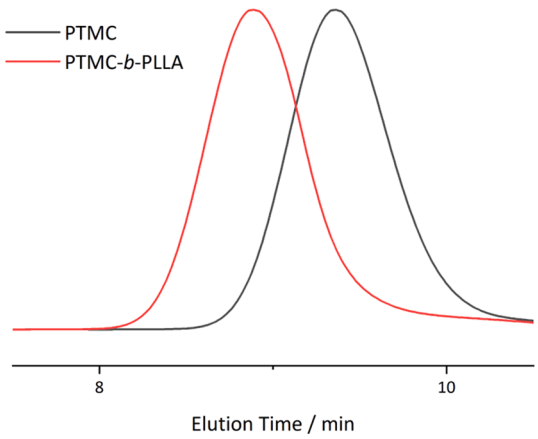


Fig. 10. SEC traces of the first sequence of PTMC (black line) with $M_{n,\ NMR}$ = 2.0 kg mol^{-1} and $Đ$ = 1.032 and the PTMC-*b*-PLA (red line) with $M_{n,\ NMR}$ = 4.3 kg mol^{-1} and $Đ$ = 1.055 (eluent, THF; flow rate, 0.7 mL min^{-1}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(DRI) detector with a 658 nm light source. HPLC-grade tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.7 mL/min at 35 °C. The number-average molecular weights ($M_{n,\ GPC}$), weight-average molecular weights (M_w) and dispersities ($Đ$) were calculated by standard polystyrene samples (M_n = 0.5000–20.00 kg mol^{-1}, Polymer Laboratories, Inc.) calibration.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) of the obtained polymers was performed using a mass spectrometer (ultraflextreme; Bruker) equipped with a Smartbeam/Smartbeam II modified Nd:YAG laser. Mass spectra of five hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflector mode. The polymer sample was dissolved in $CHCl_3$ at a concentration of 5 mg mL^{-1}, and the matrix 2,5-DHB (2,5-dihydroxybenzoic acid) was dissolved in the solution of water and acetonitrile (volume ratio = 70/30) with trifluoroacetic acid (1%, 10 μL). Then the matrix and polymer were mixed with ratio of 1:1 as samples for MALDI-ToF MS.

4.3. General procedure for ring-opening polymerization of lactide or trimethylene carbonate (TMC)

4.3.1. Ring-opening polymerization of lactide as model reaction

In glove box under nitrogen atmosphere, lactide (0.432 g, 3.0 mmol, 30 equiv.) was weighed and dissolved in CH_2Cl_2 (3.0 mL, $[LA]_0$ = 1.0 mol L^{-1}) in a dry Schlenk tube. Benzyl alcohol (10.4 μL, 0.1 mmol) as an initiator was dropped in using a micro syringe. 3-amino-1,2,4-benzothiadiazine-1,1-dioxide (ABTD) (0.028 g, 0.1 mmol) and triethylamine (13.9 μL, 0.1 mmol) as catalysts were added and injected. The mixture was stirred at room temperature and sampled after start of the reaction at designated time intervals. The conversions of the monomer were monitored by ^{1}H NMR. The crude polymer was separated by precipitation in cold methanol, and then was filtered and dried under vacuum. $M_{n,\ NMR}$, 3.9 kg mol^{-1}; $Đ$, 1.011, $M_{n,SEC}$, 4.2 kg mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm), 1.55–1.60 (m, 3H × n, (–C*H*$_3$)$_n$), 4.35 (q, 1H, –C*H*(CH$_3$)OH), 5.11–5.23 (q, 1H × (n-1), –C*H*(CH$_3$)O–; 2H, ArC*H*$_2$O–), 7.30–7.39 (m, 5H, aromatic).

4.4. Diblock copolymerization of TMC and lactide

In glove box under nitrogen atmosphere, TMC (0.312 g, 3.0 mmol, 30 equiv.) was weighed and dissolved in CH_2Cl_2 (3.0 mL, $[TMC]_0$ = 1.0 mol L^{-1}) in a dry Schlenk tube. Benzyl alcohol (10.4 μL, 0.1 mmol) as an initiator was dropped in using a micro syringe. ABTD (0.028 g, 0.1 mmol) and triethylamine (13.9 μL, 0.1 mmol) as catalysts were added and injected. The mixture was stirred at room temperature for predesigned time. Then lactide (0.432 g, 3.0 mmol, 30 equiv.) was fed to the polymerization mixture ($[LA]_0$ = 1.0 mol L^{-1}) under nitrogen atmosphere. The mixture reacted at room temperature for a predetermined time. The copolymer was separated by precipitation in cold methanol, and then was filtered and dried under vacuum. $M_{n,\ NMR}$, 4.3 kg mol^{-1}; $Đ$, 1.055, $M_{n,SEC}$, 4.1 kg mol^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm), 1.48–1.60 (m, 3H × n, (–C*H*$_3$)$_n$), 2.00–2.07 (m, 2H × n, –COCH$_2$C*H*$_3$CH$_2$O–), 4.16–4.38 (t, 4H × n, –COC*H*$_2$CH$_3$C*H*$_2$O–; m, 1H, –C*H*(CH$_3$)OH), 5.08–5.23 (m, 1H × (m-1), –C*H*(CH$_3$)O–; 2H, ArC*H*$_2$O–), 7.33–7.41 (m, 5H, aromatic).

Data availability

All data included in this study are available upon request by contact with the corresponding author.

CRediT authorship contribution statement

Yuejia Zhu: Methodology, Data curation, Investigation, Writing - original draft, Formal analysis. **Yongzhu Hu:** Investigation. **Zhenjiang Li:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - review & editing. **Bo Liu:** Writing - review & editing. **Yuanyuan Qu:** Data curation. **Zhihao Zhang:** Data curation. **Tianfo Guo:** Data curation. **Yongqiang Li:** Data curation. **Luoyu Gao:** Data curation. **Kai Guo:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2020.110184.

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