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ARTICLE

Ionic Hydrogen Bond Donor Organocatalyst for Fast Living Ring-Opening Polymerization†

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H-bonding organocatalysis using (thio)urea and amine received massive success. Ionic H-bonding catalysis, especially in polymerizations, was scarcely explored. Here we disclosed guanidinium **h**exahydro-2*H*-**p**yrimido[1,2-*a*] **p**yrimidin-1-ium [$(HppH_2)^+$] as representative ionic H-bond donor (IHBD), combined with tertiary amines as H-bond acceptor (HBA), promoted fast ring-opening polymerization (ROP) of L-lactide (LLA). The positively charged IHBD guanidinium exhibited exceptional activating ability towards monomer LLA. Its partnership with (−)-sparteine demonstrated excellent IHBD–HBA binary catalysts in the ROP of LLA, which featured with 97% up conversions, predicted molecular weights (from 2,550 to 17,900 g mol^{-1}), narrow dispersities ($Đ \leqslant 1.12$), and short reaction time of 30 to 180 minutes. A bifunctional synergistic activation mechanism by $(HppH_2)^+$ and (−)-sparteine was proposed, and was supported by NMR measurements. The controlled/living nature of the ROP was confirmed by kinetics and chain extension experiments. ^{1}H NMR, SEC, and MALDI-ToF MS analyses strongly indicated that the obtained poly(L-lactide)s were exactly the designated ones. The successful synthesis of well-defined poly(trimethylene carbonate)-*block*-poly(L-lactide) verified again that the catalytic ROPs were in controlled/living manner, and suggested that the IHBD–HBA binary catalysis system were a generally applicable method.

Introduction

Hydrogen bonding is the most important one of the noncovalent interactions[1], which is operative in determining molecular conformations, influencing supramolecular aggregations, functioning of biological systems, and promoting noncovalent catalysis.[2, 3] In terms of organocatalysis, H-bond is understood exerting crucial role in control of chemical reactions by attractive interactions,[4-6] in particular of its primacy in activating carbonyl in stereoselective transformations.[7-10] Meanwhile, hydrogen bond donor (HBD) has turned up a widely applicable class of catalyst in ring-opening polymerization (ROP).[11-21]

Over the last few years, hydrogen-bonding organocatalysis has received tremendous attentions in the field of ROPs.[12-19, 22, 23] Since the first report on thiourea/amine catalysis in the controlled/living ROP of lactide by Hedrick and Waymouth in 2005[12], an HBD in cooperation with a hydrogen bond acceptor (HBA) has been developed into a general consensus HBD–HBA bifunctional catalysis protocol.[22, 24-26] Furthermore, in partnership with appropriate tertiary amines as the HBA,[27] a wide range of classical neutral HBDs (Scheme 1, A) could synergistically catalyze the ROPs through bifunctional activation mechanisms.[21, 28-31] These ROPs proceeded cooperatively through activation of the carbonyl of the monomers by the neutral HBD, and the activation of the hydroxyl of the initiator or the propagating chain end by HBA. As shown in Scheme 1 (A), these neutral HBDs are finely tailored by bearing suitable electron-withdrawing group (EWG) to modulate their catalysis performance.[32-37] Furthermore, EWGs such as trifluoromethyl and sulfonyl groups in conjugation with typical HBDs increased the acidity of the hydrogen donor moiety, and enhanced its ability to electrophilically activate the carbonyl-containing monomers.[14, 25] In parallel with the privileged role of trifluoromethyl and sulfonyl as EWGs in enhancing neutral HBD,[38, 39] its counterpart charged HBD (the ionic hydrogen bond donor, IHBD), which is widely presented in recognition with anions and neutral HBAs in artificial sensors, crystals, and living systems,[40] remained largely unaware in H-bonding catalysis.[41, 42]

Recently, a series of metal-templated “organocatalysts" are developed into a new family of HBDs that catalyzed the condensation reactions as well as the polymerization of DL-lactide.[19, 43, 44] The guanidino-containing moiety of the ligands of the organometallic complex was exploited as new type of HBD (Scheme 1, B), the “inert central-metal” worked as positively charged EWG to tune the HBD mediated transformations.[45] Gladysz reported that cobalt chelate complexes of 2-guanidinobenzimidazole (GBI) combined with a tertiary amine are effective in ROP of DL-lactide,[19] while removing off the metal left GBI incompetent in the same reactions. Clearly, the electron-withdrawing effect of the metal is essential to promote the ROPs.

Inspired by the two successful strategies in HBD catalysis modulated by EWG and metal-template, and motivated by a

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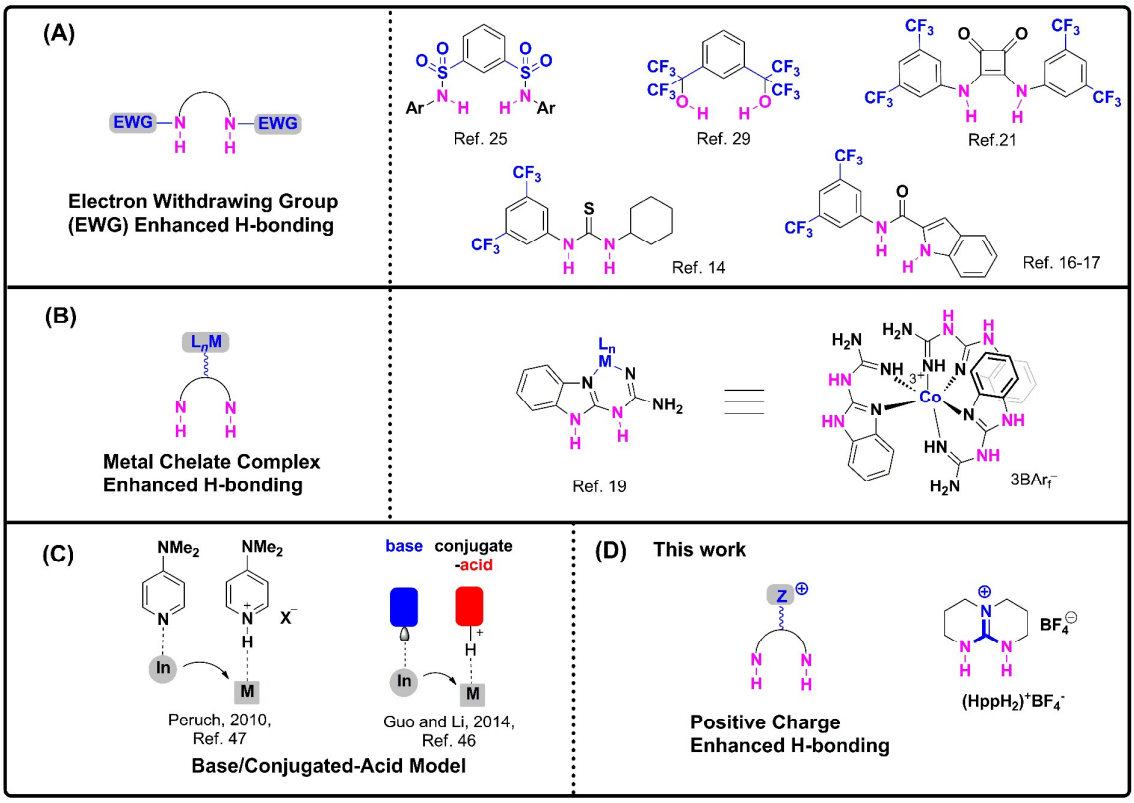


Scheme 1 Representative structures of hydrogen-bonding donor catalysts

base–conjugated-acid model we; guanidinium in its inium form as a catalyst in the field of polymerizations was unreported (or unknown) have clarified lately (Scheme 1, C)[46], we suggested positive charge enhanced H-bonding being a potential HBD in ROPs (Scheme 1, D).

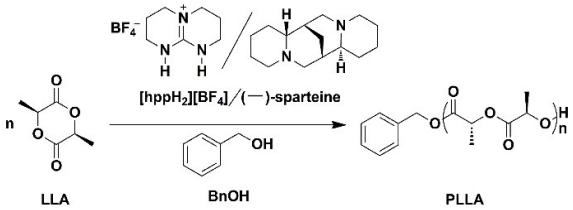
In previous work, we summarized the acidic and basic cocatalysis proposed by Peruch[47] and developed by others[48] into a base–conjugated-acid mechanism. As we re-scrutinizing the nature of the base–conjugated-acid model, we reasoned the conjugated-acid is essentially an ionic H-bond donor. As such, we anticipated that IHBD compounds are untapped new category of tunable IHBD catalyst in ROPs. By introducing positive charge(s) onto the HBD moiety, the binding ability of the IHBD is enhanced, and the catalytic performances of this new IHBD–HBA bifunctional catalysis system are hopefully of broad-spectrum and high efficiency.

In order to corroborate our assumptions, we focused on a representative guanidinium salt, $(HppH_2)^+BF_4^-$ (3,4,6,7,8,9-**h**exahydro-2*H*-**p**yrimido[1,2-*a*] **p**yrimidin-1-ium tetrafluoroborate), as the model IHBD featured with dual sites of H-bonding and unit positive charge (Scheme 1, D). Traditionally, guanidinium on residue of arginine in peptides or on synthetic non-peptide vectors has been most widely presented in biological transporting processes.[49, 50] Many artificial anion receptors of guanidinium type were well documented.[51] Recently, Tan[18a] employed chiral bicyclic guanidine in a Diels-Alder reactions in which guanidimium was attributed to induce enantioselectivity. The explicit guanidinium HBD catalysis was firstly disclosed by Jacobsen[52, 53b] in an elegantly designed Claisen rearrangement by HBD coordinating with oxygen of the vinyl ether. However, guanidinium in its inium form as a catalyst in the field of polymerizations was unaware.

Based on our interest in organocatalytic polymerizations, we begin to appreciate the tremendous potential offered by guanidinium as the IHBD in ROPs. With tertiary amines as HBA, and guanidinium as IHBD, this IHBD–HBA pair could work synergistically to catalyse the ROPs through bifunctional activations. Here, inium moiety $R_2N^+=C$ as an EWG could confer the double N–H hydrogen bond with increased binding ability, realize high efficiency in activation of the monomers.

In this article, we reported that $(HppH_2)^+BF_4^-$ and (−)-sparteine was optimal binary catalyst system for controlled/living ROPs of LLA to obtain well-defined poly(L-lactide) (PLLA) (Scheme 2).

We described (1) a conceptually new family of positive charge enhanced hydrogen bond donor exhibiting high



Scheme 2 ROP of LLA using $(HppH_2)^+BF_4^-$ and (−)-sparteine

performance in monomer activation of LLA; (2) guanidinium $(HppH_2)^+$ as ionic H-bond donor (IHBD) working cooperatively with tertiary amines to promote the ROP of LLA in solution at room temperature; (3) polymerizations of LLA by high conversions (>97%), narrow dispersities (1.12–1.17), and predicted molecular weights (up to 17,900 g mol^{-1}) within short time (30–180 min) were realized; (4) chain extension and kinetics experiments supported the controlled/living nature; (5) diblock copolymerization of poly(TMC-*b*-LLA) *via* one-pot sequential feed of TMC and LLA reconfirmed the living character, and showed the IHBD–HBA catalyzed ROPs generally workable.

Experimental section

Materials

L-Lactide (99.5%, LLA) was obtained from Jinan Daigang Biomaterial Co. and recrystallized three times from dry toluene. Dichloromethane (99.5%, DCM) was distilled over CaH_2 under an argon atmosphere. Benzyl alcohol (99.0%, BnOH) was dried over 4 Å molecular sieves and distilled under reduced pressure. (−)-Sparteine was dried over CaH_2, distilled, degassed, and stored under a nitrogen atmosphere. These reagents are provided by Sinopharm Chemical Reagent Co., Ltd. TMC was prepared by the literature method and recrystallized from benzene/*n*-hexane three times to obtain white crystals.[54] $(HppH_2)^+BF_4^-$ was prepared by literature procedures.[55] All the other reagents were purchased from Aldrich and used without further purification.

Instruments

^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Ascend TM-400 spectrometer operating at 400 MHz at room temperature. The size exclusion chromatography (SEC) was performed at 30 °C in THF at the flow rate of 0.7 mL min^{-1} using a Wyatt Astra V 6.1.1 software, the machine was equipped with a SSI 1500 pump equipped with Waters Styragel® HR 2 THF column (300 × 7.8 mm^2, 5 μm), Wyatt Optilab rEX differential refractive index (DRI) detector with a 658 nm light source. The experimental number-average molecular weights ($M_{n,SEC}$) and the molecular weight distribution (M_w/M_n) of the polymers were calculated by SEC from analysis with a calibration curve on the basis of a polystyrene calibration. These SEC values were corrected using the correction coefficients *X* determined by Guillaume[56, 57]:

- X = 0.57 for M_n (SEC raw data) < 5000 g mol^{-1}
- X = 0.88 for M_n (SEC raw data) > 10,000 g mol^{-1}
- X = 0.73 for 5000 g mol^{-1} < M_n (SEC raw data) <10,000 g mol^{-1}

  an average value between these two data was applied.

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 Smartbeam/Smartbeam II modified Nd:YAG laser. Mass spectra of five hundred shots were accumulated for the spectra at a 25 kV acceleration voltage. The polymer sample was dissolved in $CHCl_3$ at a concentration of 5 mg mL^{-1}. The matrix 2,5-DHB (2,5-dihydroxybenzoic acid) was dissolved in solution of trifluoroacetic acid and acetonitrile (volume ratio = 70/30) in water (1%, 10 μL). Samples for the MALDI-ToF MS were prepared by mixing the matrix and polymer.

General procedure for polymerization of L-lactide in solution

Under nitrogen, in a dry Schlenk tube, L-lactide (0.435 g, 3 mmol, 30 equiv.) was dissolved in dichloromethane (3 mL, $[L\text{-lactide}]_0$ = 1.0 mol L^{-1}). Benzyl alcohol (10.3 μL, 0.1 mmol, 1 equiv.) as an initiator was added by micro syringe. $(HppH_2)^+BF_4^-$ (0.0345 g, 0.15 mmol, 1.5 equiv.) and (−)-sparteine (34.5 μL, 0.15 mmol, 1.5 equiv.) as the binary catalyst system were then successively added. The reaction mixture was stirred for 30 min at room temperature. An excess of benzoic acid was added to neutralize the catalyst, and the mixture was concentrated under reduced pressure. Before the concentrated product was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol, a small portion of the concentrated product was sampled to determine the monomer conversion *via* the ^1H NMR measurement. The precipitate was filtered and dried under vacuum. Yield, 62.8%; $M_{n,NMR}$, 4400 g mol^{-1}; $M_{n,SEC}$, 5100 g mol^{-1}; M_w/M_n, 1.12. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm), 1.57 (m, 3H × n, $(-CH_3)_n$), 4.34 (m, $-CH(CH_3)OH$), 5.13–5.21 (q, 1H × n-1, *J*=7.0, $-CH(CH_3)O-$; 2H, $ArCH_2O-$), 7.33–7.34 (m, 5H, aromatic).

Diblock copolymerization of L-lactide (LLA) and trimethylene carbonate (TMC)

Under nitrogen, in a dry Schlenk tube, TMC (0.306 g, 3 mmol, 30 equiv.) was dissolved in dichloromethane (3 mL, $[TMC]_0$ = 1.0 mol L^{-1}). Benzyl alcohol (10.3 μL, 0.1 mmol, 1 equiv.) was added to the solution to trigger the polymerization. $(HppH_2)^+BF_4^-$ (0.0345 g, 0.15 mmol, 1.5 equiv.) and (−)-sparteine (34.5 μL, 0.15 mmol, 1.5 equiv.) as the binary catalyst system was then successively added. After the first reaction was stirred for 60 h at room temperature, 30 equiv. of L-lactide (0.435 g, 3 mmol) was added to start the block polymerization. Then the polymerization was quenched by an excess of benzoic acid and the mixture was concentrated under reduced pressure, to a small portion of the concentration production as sample determined the monomer conversion *via* the ^1H NMR measurement. The concentrated crude polymer was dissolved in a minimum of dichloromethane and reprecipitated in cold methanol. After filtered and dried under vacuum, we can obtain the poly(trimethylene carbonate)-*block*-poly(L-lactide) (PTMC-*b*-PLLA). Yield, 70.2%; $M_{n,NMR}$, 7200 g mol^{-1}; $M_{n,SEC}$, 8300 g mol^{-1}; M_w/M_n, 1.05. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm), 1.57 (q, *J* = 7.3 Hz, 3H × m, $(-CH_3)_m$), 2.03–2.07 (m, 2H × n, $(-OCH_2CH_2-)_n$), 4.24 (t, 4H × n, $(-OCH_2CH_2-)_n$), 4.35 (m, $-CH(CH_3)OH$), 5.11–5.23 (q, 1H × m-1, *J* = 7.2 Hz, $(-CH(CH_3)O-)_{m-1}$, s, 2H, $ArCH_2O$), 7.25–7.37 (m, 5H, aromatic).

Results and Discussion

Ring-Opening Polymerization of L-Lactide Catalyzed by 3,4,6,7,8,9-hexahydro-2*H*-pyrimido[1,2-*a*] pyrimidin-1-ium tetrafluoroborate [$(HppH_2)^+BF_4^-$] and (−)-Sparteine

To the best of our knowledge, guanidinium has been exploited for anion recognition as well as co-catalysis in aldol reactions.[55, 58-61] In our catalyst system, guanidinium was anticipated to form double H-bonding with the monomers. In order to clarify the catalytic performances of $(HppH_2)^+BF_4^-$ as IHBD, and (−)-sparteine as HBA, ring-opening polymerizations of L-lactide were investigated in dichloromethane at room temperature using benzyl alcohol as the initiator. Under these conditions,

Table 1 ROP of L-lactide (LLA) initiated by BnOH and catalyzed by the combination of $(HppH_2)^+BF_4^-$/(−)-sparteine[a]

Entry	$[LLA]_0/[BnOH]_0$	Time /min	Conv.[b]/%	$M_{n,theo}$[c]/g mol^{-1}	$M_{n,NMR}$[b]/g mol^{-1}	$M_{n,SEC}$[d]	M_w/M_n[d]
1	20	10	91.2	2700	2600	3800	1.12
2	30	30	97.7	4300	4400	5100	1.12
3	50	40	97.6	7100	7500	8200	1.17
4	80	120	97.4	11300	11300	11900	1.14
5	100	150	97.3	14100	14600	15100	1.25
6	120	180	97.9	17000	17900	18600	1.29
7[e]	30	23(h)	0	–	–	–	–
8[f]	30	72(h)	6.0	–	–	–	–

[a] Temperature, room temperature; solvent, CH_2Cl_2; $[LLA]_0$ = 1 mol L^{-1}; 5 mol % $(HppH_2)^+BF_4^-$; 5 mol % (−)-sparteine. [b] Determined by ^{1}H NMR in $CDCl_3$. [c] Calculated from $([LLA]_0/[BnOH]_0)$ × conv. × (MW of LLA) + (M_W of BnOH). [d] Determined by SEC in THF using PSt Standards and correction factors. [e] $[LLA]_0/[BnOH]_0/[(HppH_2)^+BF_4^-]_0/[(-)\text{-sparteine}]_0$ = 30/1/1.5/0. [f] $[LLA]_0/[BnOH]_0/[(HppH_2)^+BF_4^-]_0/[(-)\text{-sparteine}]_0$ = 30/1/0/1.5.

$(HppH_2)^+BF_4^-$ alone was unable to catalyse the ROP of LLA, ^{1}H NMR spectra showed no monomer conversion after 23 h (Table 1, entry 7). By alternative, (−)-sparteine alone was not efficient since the conversion of monomer LLA just reached 6% after 72 h (Table 1, entry 8). It may be concluded that either of the IHBD–HBA catalysts was not effective in the ROP of LLA.

Combination of $(HppH_2)^+BF_4^-$ with (−)-sparteine showed highly efficient catalysis for the controlled ROP of LLA. As listed in Table 1, to evaluate the performance of the binary catalysts system in the ROP of LLA, we firstly carried out the polymerizations at ratios of $[LLA]_0/[BnOH]_0/[(HppH_2)^+BF_4^-]_0/[(-)\text{-sparteine}]_0$ at 30/1/1.5/1.5 (Table 1, entry 2). Within 30 min, LLA was quantitatively converted into polymers. The observed number average molecular weight ($M_{n,NMR}$) of the obtained polymer of 4400 g mol^{-1} and the number average molecular weight determined by SEC of 5100 g mol^{-1} agreed well with the theoretical value ($M_{n,theo}$) of 4300 g mol^{-1}. The polydispersity (M_w/M_n) of 1.12 estimated by SEC measurement was relatively low. Interestingly, as we prolonged the reaction time for several days without quenching by benzoic acid, the polydispersity only increased slightly from 1.12 to 1.22. It indicated that the binary catalysts system was mild and the transesterifications were kept at a minimal level. Importantly, all previous HBD/amine catalysts in ROPs of LLA under comparable conditions (5% catalyst loading, LLA 1 mol L^{-1}, DCM solution, r.t., target degree of polymerization of 50) required 24 to 72 hours to receive 95% conversion (cf. entry 2, Table 1).[5, 9] Our $(HppH_2)^+$ and (−)-sparteine binary system finished by 40 min.

The chemical structures of the obtained PLLA were determined clearly by ^{1}H NMR spectrum (Fig. 1, corresponding to entry 2, Table 1). The distinct peaks of the initiator residue (BnOH) were observed at 7.33–7.34 ppms due to the phenyl protons adjacent to the ester linkage, and the peak to the terminal methine protons adjacent to the ω-chain end of the hydroxyl group was clearly observed at 4.34 ppm. Additionally, the polymer main chain attributed to the remaining peaks at 1.57 ppm and 5.13–5.21 ppms. These results demonstrated that the polymer chains had been initiated by the BnOH, and therefore, they are all capped with the corresponding ester moiety.

Furthermore, MALDI-ToF MS spectra (Fig. 2) of PLLA were used to provide direct evidence that the ROP of LLA was initiated by BnOH. As shown in Fig. 2, one series of main peaks ionized by potassium appeared at regular intervals of 144 m/z, which perfectly agreed with the molecular weight of the LLA. The other series of main peaks with the same 144 periodicity just switched the cationized molecular ion to sodium. Importantly, the values of peaks were correspond to the theoretical molecular weight of the polymer from LLA possessing the BnOH residue and the hydroxyl chain-end; for example, for the 20-mer, the measured value with Na^+ 3016.40 and with K^+ 3032.39 corresponded with the calculated value with Na^+ 3011.86 and with K^+ 3027.86. In view of the calibration issue of the spectrometer, the small systematic difference values can be observed. Meanwhile, a very small amount of PLLA initiated by residual H_2O was identified due to the limitations of the operation conditions.

Notably, only even numbers of lactate units (*viz.* 2 × 72 m/z = 144 m/z) demonstrated that no transesterification reactions occurred under these conditions. Indeed, the side reactions such as intermolecular redistributions and intramolecular backbitings could lead to odd numbers of lactate units (72 m/z). Besides, ^{13}C NMR spectroscopy of a PLLA in $CDCl_3$ (Fig. S2) exhibiting the singlet of 69 ppm corresponding to the methine group which indicated that the poly(L-lactide) exhibit a fully isotactic structure. Therefore, these data strongly suggested the absence of side transesterification reactions, which would lead to racemization. It demonstrated $(HppH_2)^+$ possessed strong preference to activate the LLA rather than the polymer chain.

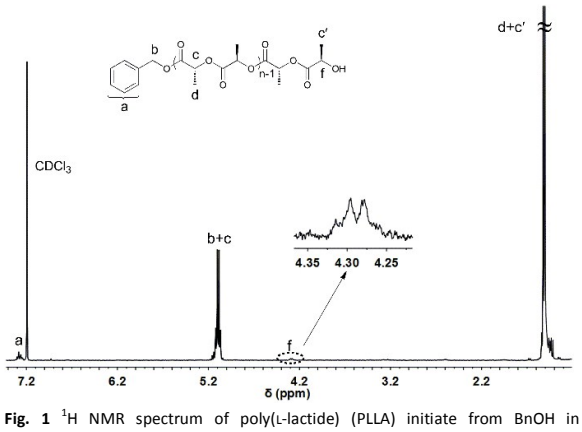
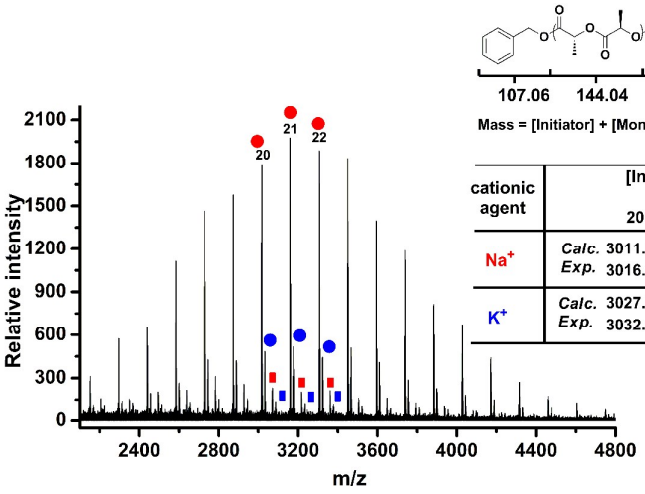


Fig. 1 ^{1}H NMR spectrum of poly(L-lactide) (PLLA) initiate from BnOH in $CDCl_3$ (corresponding to entry 2, Table 1).

To further investigate the controlled/living feature of the polymerization system, the ROP of LLA with varied $[LLA]_0/[BnOH]_0$ ratios from 20 to 120 were carried out (Table 1, entries 1–6). The molecular weights $M_{n,NMR}$ (measured by ^1H NMR) of the obtained PLLAs increased linearly with increasing initial ratios of $[LLA]_0/[BnOH]_0$, and the $M_{n,NMR}$ values were consistent with the $M_{n,theo}$ ones calculated by the $[LLA]_0/[BnOH]_0$ values and the monomer conversions. The corresponding SEC traces (Fig. 3) of these obtained polymers showed monomodal peaks with narrow distributions, and the molecular weight distributions (M_w/M_n) were as low as 1.12–1.29. The molecular weights $M_{n,NMR}$ (measured by ^1H NMR) of the obtained PLLAs increased linearly with increasing initial ratios of $[LLA]_0/[BnOH]_0$, and the $M_{n,NMR}$ values were consistent with the $M_{n,theo}$ ones calculated. All of the above data prove that the ROP of LLA catalyzed by $(HppH_2)^+BF_4^-$/(−)-sparteine possesses a controlled/living nature.

Variation of Tertiary Amine as the Hydrogen Bond Donor Cocatalyst

In order to obtain deeper insight into the tertiary amine cocatalyst efficiency in this IHBD–HBA binary catalysts system, a series of commercially available amines were tested, with results givenin Table 2. $NCyMe_2$ is more basic than PMDETA (basicities in acetonitrile: $NCyMe_2$-H^+ = 10.72; PMDETA-H^+ = 9.10), however, under the same reaction conditions the catalytic activity of PMDETA was better than that of $NCyMe_2$. Obviously, the catalytic activity was not simply determined by the basicity of the tertiary amines. All the other tertiary amines induced slower polymerization rates, and (−)-sparteine is the optimal base to combine with $(HppH_2)^+BF_4^-$. This is contrast with the situation where DMAP showed the optimal cocatalyst



cationic agent		[Initiator] = BnOH n 20	21	22	[Initiator] = H_2O n 20	21	22
Na^+	*Calc.*	3011.86	3155.90	3299.94	2921.80	3065.84	3209.88
	Exp.	3016.40	3160.62	3304.85	2926.24	3070.47	3214.69
K^+	*Calc.*	3027.86	3171.90	3315.94	2937.80	3081.84	3225.88
	Exp.	3032.39	3176.61	3320.83	2842.20	3086.45	3230.57

Fig. 2 MALDI-ToF MS spectrum of the PLLA (Table 1, entry 2).

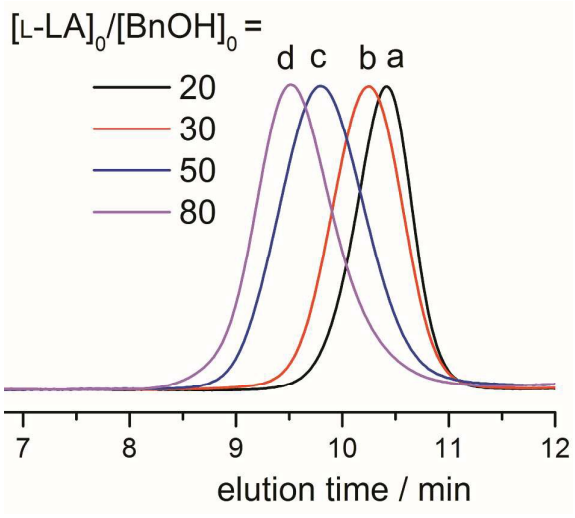


Fig. 3 SEC traces of the obtained poly(L-lactide)s (PLLA) with the molar ratio of L-lactide (LLA) and BnOH ($[LLA]_0/[BnOH]_0$) of (a) 20, (b) 30, (c) 50,(d) 80 (eluent, THF; flow rate, 0.7 ml min^{-1})

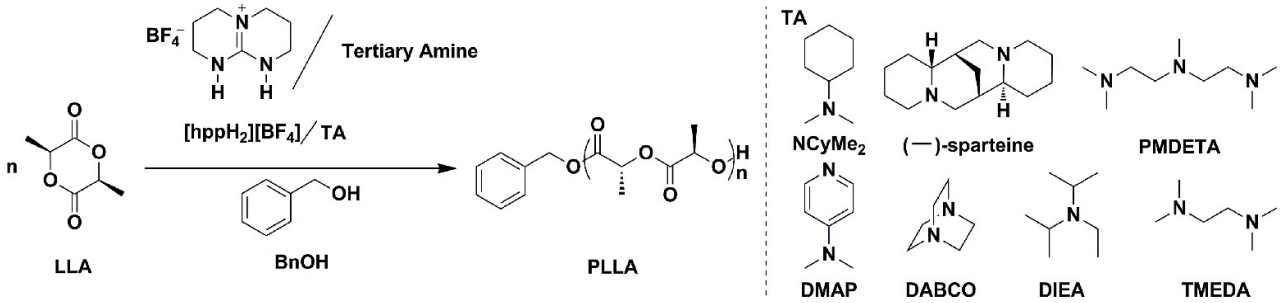
with the situation where DMAP showed the optimal cocatalyst in DPP/DMAP system reported by Kakuchi et al.[48] Together with previous studies, the activity of bifunctional binary catalysts system can be affected by three factors: (1) basicity;[62-64] (2) conformation;[27, 65] (3) cocatalyst binding constant.[22] In our system, appropriate binding between $(HppH_2)^+$ and (−)-sparteine was proposed, in which Kiesewetter's model[22] applied.

Living/Controlled Property of $(HppH_2)^+BF_4^-$ and (−)-Sparteine for Ring-Opening Polymerization of L-Lactide

Chain extension and kinetics experiments were carried out to check the living character of the polymerizations. Figure 4 showed the SEC traces for the chain extension experiments. The polymerization proceeded with ratio of $[LLA]_0/[BnOH]_0/[(HppH_2)^+BF_4^-]_0/[(-)\text{-sparteine}]_0$ = 40/1/2/2 in dichloromethane at room temperature to afford PLLA with $M_{n,NMR}$ = 5700, M_w/M_n = 1.10, at monomer conversion of 97.3%. Additional 40 equiv. of LLA was subsequently added to obtain PLLA with $M_{n,NMR}$ =11200, M_w/M_n=1.15, indicating that the chain end group of PLLA clearly sustained a living nature.

To further demonstrate the controlled/living feature, we carried out kinetics experiments. A plot of $M_{n,NMR}$ *versus* monomer conversion (measured by ^1H NMR) for the ROP of

Table 2 ROP of L-lactide (LLA) initiated by BnOH and catalyzed by the combination of $(HppH_2)^+BF_4^-$ and different tertiary amines[a]



Entry	$[LLA]_0/[BnOH]_0$	amine	Time /min	Conv.[b] /%	$M_{n,NMR}$[b]	$M_{n,SEC}$[c]	M_w/M_n[c]
1	30	(−)-Sparteine	40	97	4300	5200	1.13
2	30	$NCyMe_2$	40	15	–		–
3	30	DMAP	40	10	–		–
4	30	PMDETA	40	67	3200	3800	1.15
5	30	TMEDA	40	4	–		–
6	30	DABCO	40	7	–		–
7	30	DIEA	40	29	1500	2200	1.21

[a] Temperature, room temperature; solvent, CH_2Cl_2; $[LLA]_0$ = 1 mol L^{-1}; 5 mol % $(HppH_2)^+BF_4^-$; 5 mol % amines. [b] Determined by ^1H NMR in $CDCl_3$. [c] Determined by SEC in THF using PSt Standards and correction factors.

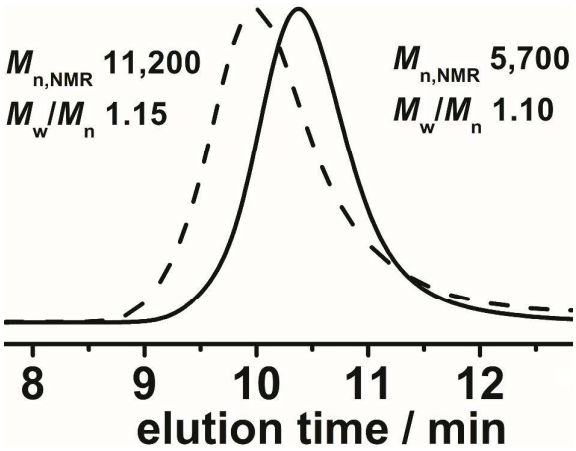


Fig. 4 SEC traces of first poly(L-lactide) (solid line) and postpolymerization (dashed line) (eluent, THF; flow rate, 0.7 ml min^{-1}).

LLA showed a linear correlation with narrow polydispersities (measured by SEC, Fig. 5 A). This result implied that there was little chain transfer occurred during the living polymerization. In addition, the kinetics plots were shown in Fig. 5 B. A distinct first-order relationship between $ln([LLA]_0/[LLA])$ versus the reaction time was observed, showed that the monomer consumption rate was constant during the polymerization. These experimental results provided favorable evidence that the ROP of LLA using $(HppH_2)^+BF_4^-$ and (−)-sparteine as the binary system possessed definitely controlled/living properties.

Proposed Mechanism for the Ring-Opening Polymerization of L-lactide

For the ROP of LLA leading to well-defined poly(L-lactide) using $(HppH_2)^+BF4^-$ and (−)-sparteine as the binary catalysts system, a plausible H-bonding bifunctional synergistic activation mechanism was proposed (Scheme 3). In the binary catalysts system, the guanidinium core of $(HppH_2)^+BF4^-$ as HBD could form double H-bonded motifs with the carbonyl, thus enhancing the electrophilicity of the monomers. (−)-Sparteine as HBA could form multiple H-bonds with the hydroxyl group of the initiator or the polymer chain end, the oxygen of the hydroxyl at the terminal of the propagating chain was activated.

In order to provide a fundamental insight into the mechanism, NMR spectroscopy has been used to investigate the strength of the hydrogen-bonding interactions. As shown in Fig. 6, in the ^{13}C NMR spectrum, the chemical shift of carbonyl carbon of the original LLA at room temperature was 166.49 ppm in $CDCl_3$. Titration experiments on $(HppH_2)^+BF_4^-$ and LLA were conducted with various molar ratios of $(HppH_2)^+BF_4^-$ and LLA ($[(HppH_2)^+BF_4^-]_0/[LLA]_0$, from 0/1 to 2/1). With increasing molar ratios of $(HppH_2)^+BF_4^-$ to LLA, the chemical shifts for the carbonyl carbon of LLA were more affected and downfield from 167.14 to 168.39 ppms, as indicated by the large change in chemical shift of the carbonyl carbon resonance. This shift manifested that a strong doubly hydrogen bonding interaction happened between L-lactide and the HBD, and attributed to the proximity of the carbonyl carbon and the double N–H. Additionally, we could make prediction that the counterpart BF_4^- of $(HppH_2)^+BF_4^-$ as a bulky anion has little influence on the double N–H.

In respect to the nucleophilic partner in the ROP, ^1H NMR spectrum was measured to confirm the interaction between (−)-sparteine and BnOH (Fig. 7). With titration of (−)-sparteine, we can observe that α-methylene protons of benzyl alcohol has shifted from 4.597 to 4.613 ppms, indicated that a deshielding effect of the proton resonance appeared. Because

(−)-sparteine has optimal spacing of intramolecular nitrogens and corresponding fixed lone pair orientations, this allowed (−)-sparteine provided sufficient nucleophilic activation to the hydroxyl of BnOH to form hydrogen-bonded complex. Therefore all of the results discussed above are in agreement with the bifunctional mechanism in which $(HppH_2)^+BF_4^-$ activated the monomer and (−)-sparteine activated the alcohol.

Diblock Copolymerization of L-Lactide and Trimethylene Carbonate

We made extension of the $(HppH_2)^+BF_4^-$ and (−)-sparteine system in sequential copolymerization of LLA and TMC[66] (Scheme 4). First step was the ROP of TMC using BnOH to initiate the reaction without quenching. Subsequently, LLA was added to polymerize as the second monomer.[67-69] By ^{1}H NMR measurements, the structure of PTMC-*b*-PLLA can be observed (Fig. 8). The characteristic signals of PTMC and residual BnOH were observed at 2.03–2.07, 4.24, and 7.25–7.37 ppms. Meanwhile, the appearance of peaks of second segment of PLLA were observed at 1.57 and 5.11–5.23 ppms. The chemical structure of the PTMC-*b*-PLLA also confirmed by ^{13}C NMR spectrum.[70, 71] In Fig. S3, the PTMC-*b*-PLLA junction units were clearly observed, which precisely corresponded to hydrogen signals of F, H, G, J and I. Furthermore, these junction units demonstrated the tacticity of the obtained PTMC-*b*-PLLA. In the process of the polymerization, sample of PTMC was withdrawn at the end of the first polymerization, and its SEC trace showed monomodal at 3100 g mol^{-1} (Fig. 9); after second feed of LLA until its full conversion, sample of the diblock copolymer showed a monomodal in SEC trace, and the $M_{n,NMR}$ value increased from 3100 to 7300 g mol^{-1} (Fig. 9). These results validated that $(HppH_2)^+BF_4^-$ and (−)-sparteine were an efficient binary catalysts for diblock copolymerization of TMC and LLA. In the process of sequential copolymerization of TMC and LLA, we found that the rates of polymerizations of LLA was faster than that of TMC by using $(HppH_2)^+(BF_4)^-$/(−)-sparteine binary system. This is similar with thiourea/amine as typically hydrogen-bonding organocatalyst during the polymerization of LLA.[72, 73]

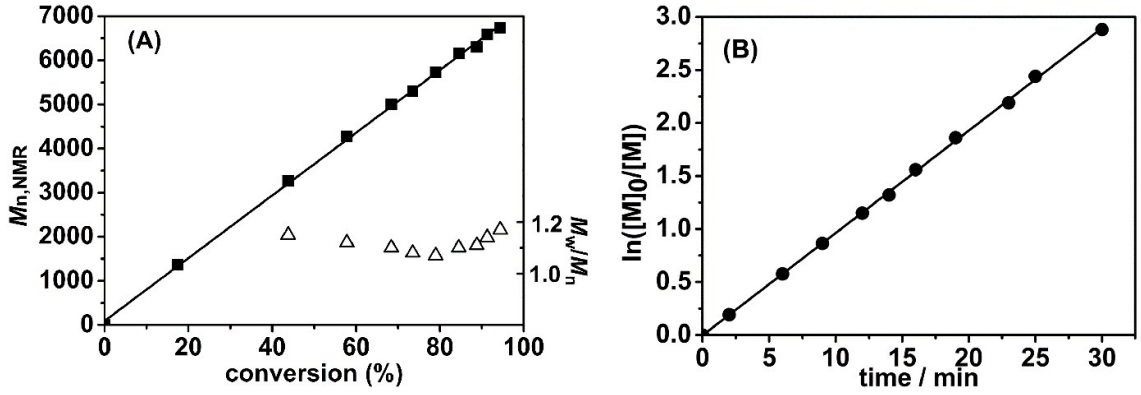
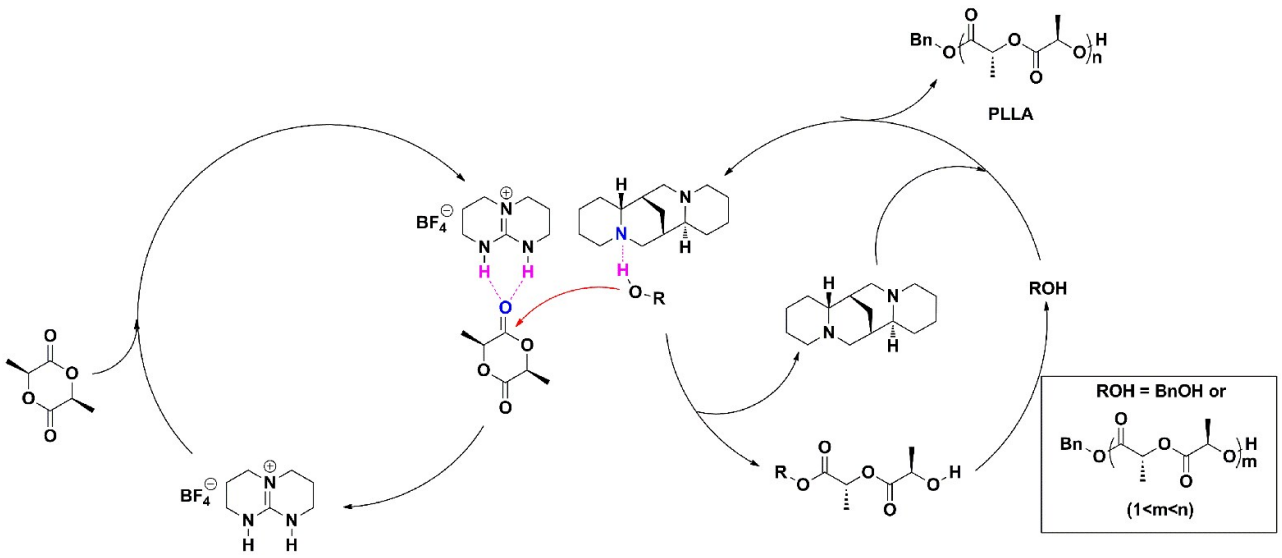


Fig. 5 (A) Dependence of molecular weight ($M_{n,NMR}$) and polydispersity (M_w/M_n) *versus* the monomer conversion (conv). Solid line shows the $M_{n,theo}$ values calculated from the equation ([LLA]$_0$/[BnOH]$_0$) × conv × (MW of LLA) + (MW of BnOH) (B) the semi-logarithmic kinetic plot for poly(L-lactide) (PLLA) ([LLA]$_0$/[BnOH]$_0$/[$(HppH_2)^+BF_4^-$]$_0$/[(−)-sparteine]$_0$ = 30/1/1.5/1.5, CH_2Cl_2, room temperature).



Scheme 3 A bifunctional activation mechanism for the ROP of L-lactide using $(HppH_2)^+BF_4^-$ and (−)-sparteine

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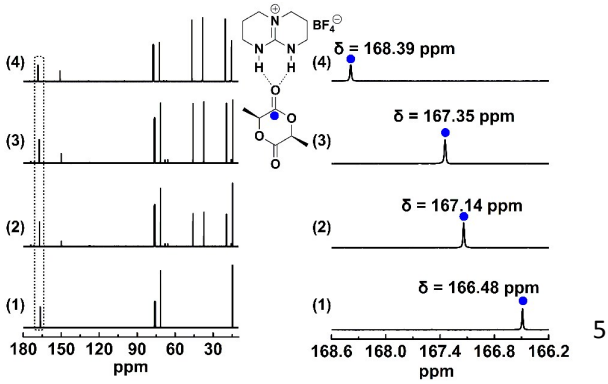


Fig. 6 ^{13}C NMR spectra of the carbonyl carbon signals in $CDCl_3$ for (1) free LLA, (2) $(HppH_2)^+BF_4^-$/LLA = 0.5/1, (3) $(HppH_2)^+BF_4^-$/LLA = 1/1, (4) $(HppH_2)^+BF_4^-$/LLA = 2/1.

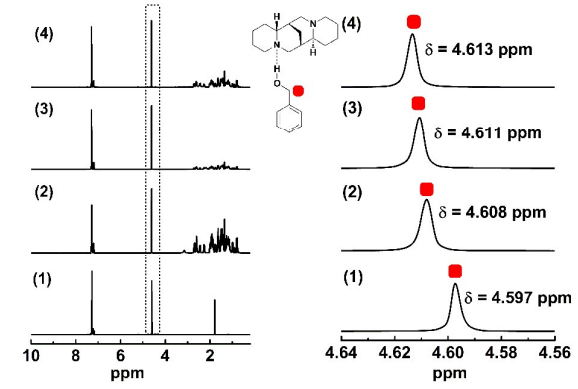
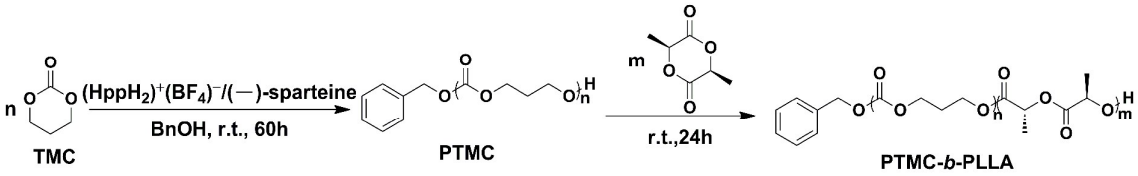


Fig. 7 ^1H NMR spectra of the alcoholic methylene protons signals for (1) BnOH, (2) (−)-sparteine/BnOH =0.5/1, (3) (−)-sparteine/BnOH =1/1, (4) (−)-sparteine/BnOH =2/1.



Scheme 4 One-pot Synthesis of diblock copolymers by ROP of TMC with LLA using $(HppH_2)^+BF_4^-$ and (−)-sparteine.

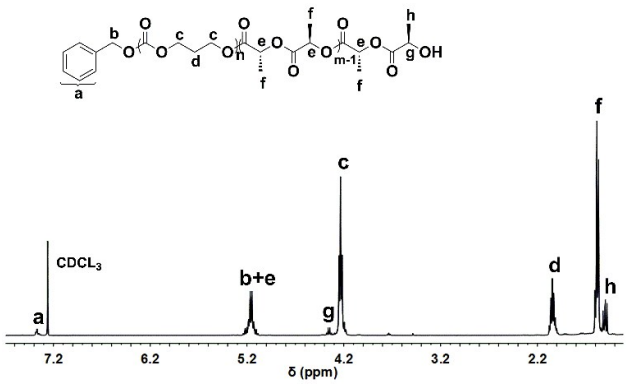


Fig. 8 ^1H NMR spectrum of PTMC−*b*−PLLA initiate from BnOH in $CDCl_3$.

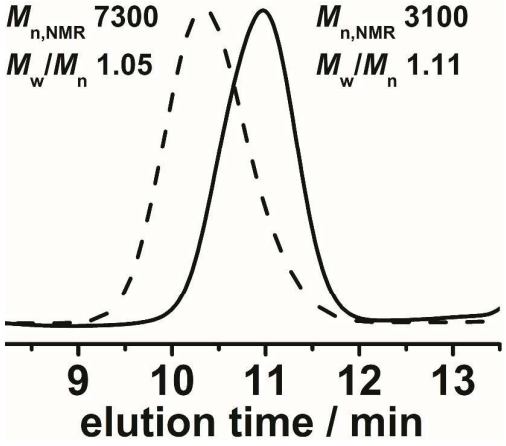


Fig. 9 SEC traces of first sequence of poly(trimethylene carbonate) (PTMC; solid line) and poly(trimethylene carbonate)-*block*-poly(L-lactide) (PTMC-*b*-PLLA; dashed line) (eluent, THF; flow rate, 0.7 ml min^{-1}

Conclusions

$(HppH_2)^+BF_4^-$ and (−)-sparteine as a binary catalysts system exhibited strict selectivity and high activity in the ROP of L-lactide under mild conditions. This guanidinium and amine

system exemplified a fastest ROPs of LLA by general HBD–HBA organocatalysis mechanism. The assumption that ionic hydrogen bond donor was efficient H-bond organocatalyst in ROP was validated. $(HppH_2)^+BF_4^-$ and (−)-sparteine was the optimal catalysts combination, and a variety of amines worked compatible with the hydrogen bond donor to catalyse the controlled/living ROP of L-lactide to generate well-defined homopolymers. Mechanistic studies showed that $(HppH_2)^+$ and (−)-sparteine cooperatively activated both the monomer and the chain end to increase the reactivity. In addition, the binary catalysts performed as versatile organocatalyst for ROPs of L-lactide as well as TMC to obtain diblock polymer PTMC-*b*-PLLA. An extension of IHBD in catalysis of ROPs of diversity of monomers may result in rewarding area of widely compatible and fast polymer preparations. An in-depth probe into the interactions amongst the IHBD, HBA, monomer, and the propagating chain is one of our future works. Furthermore, chiral elements deserved to be incorporated at the vicinity to the IHBD center(s) to evaluate stereochemistry in ring-opening polymerizations.

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Graphical and Textual Abstract

Positive charge enhanced H bond donor combined with H bond acceptor as bifunctional organocatalyst enabled fast living ring-opening polymerization of lactide.