

Borinane Boosted Bifunctional Organocatalysts for Ultrafast Ring-Opening Polymerization of Cyclic Ethers

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Abstract

The design of reactive species that can either serve to initiate the ring-opening polymerization (ROP) of epoxides for the synthesis of high molar mass polyethers or be alternatively used to catalyze the synthesis of polyether telechelics in the presence of chain transfer agents (CTAs) has long been an elusive goal. Here we report the synthesis of a series of bifunctional borinane-based catalysts that enable the living ROP of epoxides with unprecedented activity ($\text{TOF} \geq 1.8 \times 10^5 \text{ h}^{-1}$) and molar mass up to 10^6 g/mol under mild conditions. When used along with CTAs to generate low M_n telechelics, the same borinane-based catalysts exhibit ultrahigh productivity even for loading amounts as low as 50 ppb for ethylene oxide polymerization. These newly designed catalysts also afford the polymerization of oxetane with record TOF values and molar masses. DFT computation provides a full understanding of how these bifunctional catalysts operate when used in the ROP of epoxides.

Introduction

Aliphatic polyethers, namely poly(propylene oxide) (PPO), poly(ethylene oxide) (PEO) and their copolymers are industrially produced in megaton scale with molar masses ranging from a few hundreds g/mol to ultrahigh millions g/mol. These polyethers have found applications in a variety of situations such as nonionic surfactants, biomedical materials, polyelectrolytes, elastomers^{1, 2, 3, 4, 5, 6, 7} or as precursors for polyurethane.^{8, 9} The synthesis of high molar mass PPO is a challenge because of the occurrence of transfer reactions which prevent the formation of well-defined PPO beyond 10 kg/mol. Aluminum-based Vandenberg's catalyst¹⁰ which implies monomer coordination before insertion affords high molar mass PPO but the polymerization is not well controlled. Even zinc/cobalt double metal cyanide (DMC)^{11, 12, 13, 14, 15} catalyst which is employed for PPO production in industry is not without drawbacks such as long induction time, specific equipment to meet harsh polymerization conditions (high temperature and pressure build-up during polymerization), high molar mass impurities (100–400 kg/mol), necessity of specific chain transfer agents (CTAs), and unsuitability for ROP of EO. Other outstanding metallic catalysts have been specially designed for the synthesis of PPO by Coates^{16, 17, 18, 19} and Deffieux,^{20, 21, 22, 23} respectively. The Coates group synthesized perfectly isotactic PPO with molar masses up to 290 kg/mol using monometallic Co(III) complex fitted with a salicylidine ligand.^{16, 17} Deffieux and Carlotti et al. on the other hand resorted to the formation of an "ate complex" between trialkylaluminum and the growing oxyanion to obtain high molar mass PPO free of chain transfer reactions.

In order to broaden the applications of polyethers and avoid the presence of metal residues resulting from the use of metal complexes, several efforts have been made to prepare polyethers under metal-free conditions. Organocatalysts such as phosphazene base,²⁴ N-heterocyclic carbenes (NHC),^{25, 26, 27} N-heterocyclic olefins (NHO)^{7, 28, 29}, triethylborane (TEB)^{30, 31, 32}, and 9-borabicyclo[3.3.1]nonane (9-BBN) based catalysts³³ have been utilized for ROP of epoxides. The TEB system enables the synthesis of well-defined polyethers, but is not suitable for the preparation of low molar mass polyols. In contrast, NHO does provide an efficient route to ultrahigh molar mass polyethers but it lacks control as the molar masses eventually obtained generally deviate from the expected values. Overall, rare are organocatalysts that are capable to produce ultrahigh molar mass polyethers without entailing long reaction time, harsh conditions, and low turnover numbers (TON). As a consequence, there is a dearth of articles reporting the organocatalyzed synthesis of telechelic polyether diols carried out in the presence of transfer agents yet the use of CTA is beneficial as it allows the generation of numerous chains from a very limited number of catalyst centers; it also allows the control of polymer molar mass and of its architecture. The development of very reactive organocatalysts that enable the synthesis of polyethers with a high reactivity, productivity, ultrahigh molar mass, broad monomer scope, and that can be simultaneously compatible with CTAs for the synthesis of telechelic polyether diols is a long-standing goal that this work aims to address.

From the examples of highly active metallic catalysts that have been utilized along with transfer agents,^{34, 35, 36} we reasoned that organoboron catalysts can serve the same purpose provided their activity is dramatically boosted. On the other hand, our experience in alkylborane mediated polymerization showed us that the steric hindrance around boron centers is an important factor affecting the polymerization of epoxides. By covalently attaching 2, 3 and 4 borinane moieties to ammonium salts (Scheme 1), we wanted to ease steric hindrance around the boron centers of these catalysts. As a result, this novel generation of borinane-based catalysts exhibited outstanding performance when directly used in the ROP of epoxides and oxetane; in the presence of CTAs they could catalyze in minute amounts the synthesis of low molar mass telechelic polyether diols.

Results And Discussion

Synthesis of borinane based bifunctional catalysts

The six-membered cyclic borinane (shown in **Scheme S1**) was synthesized by cyclization of 1,4-pentadiene with borane.³⁷ Pure borinane was finally obtained with a total yield of 95% as a white solid. Once enough borinane was isolated it was used as seeds: as shown in **Scheme S1**, 2 moles of borinane could indeed afford up to 3 moles of borinane through direct hydroboration of 1,4-pentadiene using borinane followed by treatment with borane. The obtained borinane was fully characterized by ¹H, ¹³C and ¹¹B NMR spectroscopy (**Figure S1-S3**), confirming its high purity without contamination of 9-BBN and other boranes.

The subsequent hydroboration of allyl-containing ammonium salts carrying different numbers of terminal double bonds was carried out after quaternization of the initial tertiary amine using a stoichiometric amount of 5-bromo-1-pentene (SI Experimental, **Scheme S2, S3** and **Figure S4-S9**). Upon hydroboration of terminal double bonds carried by the above obtained ammonium chloride, bifunctional catalysts possessing one ammonium cation and 2, 3, 4 borinane moieties named **B2, B3**, and **B4** could be easily prepared in quantitative yield, the structure of obtained catalysts were determined by ¹H NMR, ¹³C NMR and ¹¹B NMR spectroscopy (**Scheme 1, Figure S10-S18**). In all cases, the signals in ¹H or ¹³C NMR spectra corresponding to double bonds completely vanished after hydroboration; instead, a broad peak at 85.5 ppm in ¹¹B NMR spectra was clearly detected, indicating the successful synthesis of bifunctional catalysts **B2, B3**, and **B4**.

Table 1. Comparison of catalysts **B2, B3**, and **B4** with other catalyst system for the ROP of PO.^a

Entry	Catalysts	Monomer	M:Cat	T (°C)	Time (h)	Conv. (%) ^b	TOF (h ⁻¹) ^c	$M_{n,GPC}^d$ (kg/mol)	\mathcal{D}^e
1	B2	PO	10000:1	25	10 min	100	60000	465	1.12
2	B4	PO	30000:1	0	10 min	100	180000	1539	1.18
3	B3	PO	30000:1	0	10 min	68	122400	957	1.23
4	B2	PO	30000:1	0	10 min	21	37800	278	1.25
5	B4	BO	30000:1	0	1	100	30000	1441	1.23
6	B4	AGE	30000:1	25	1	100	30000	1174	1.26
7	B4	EO	30000:1	25	1 min	97	1.7×10 ⁶	538	1.28
8 ^f	B4	EO	30000:1	25	1	100	30000	811	1.12
9 ^{g,27}	ⁱ Pr /TiBAI	PO	1500:1	25	0.7	84	1800	62.1	1.56
10 ^{h,22}	P4/TiBAI	PO	2586:1	20	3	100	862	12.4	1.15
11 ^{i,23}	TBACl/TiBAI	PO	350:1	0	0.5	100	700	13.8	1.77
12 ^{j,19}	(salen)Co	PO	2000:1	0	0.25	34	2720	26.4	1.8
13 ^{k,18}	(salen)Cr	PO	32000:1	23	24	61.5	1333	104	2.68
14 ^{l,29}	NHO	PO	1000:1	r.t.	5 min	100	12000	61	1.47
15 ^{m,38}	Co-Ni-DMC	PO	2530:1	70	1	78	1990	188	2.3
16 ^{n,26}	ⁱ Pr /TEB	PO	1000:1	25	4	89	223	49.9	1.13
17 ^{o,30}	P2/TEB	PO	250:1	0	2 min	100	7500	18.9	1.06
18 ^{p,33}	N ⁺ [(9-BBN) ₂]	PO	10000:1	25	1	23.7	2370	80.7	1.33

^a Polymerizations were performed in neat condition unless otherwise mentioned. ^b Conversion was determined by ¹H NMR. ^c Turnover frequency (TOF) = TON/ time (h). ^{d,e} Determined by GPC in THF using multidetectors corrected by the dn/dc values of PPO, PBO and PAGE. ^f EO was polymerized in THF with [EO]= 10 M, the molar mass was determined by GPC calibrated by PEO linear standards. ^g 1,3-bis(isopropyl)-4,5(dimethyl)imidazol-2-ylidene (ⁱPr): triisobutylaluminum (TiBAI) = 1: 3, in 2-Methyltetrahydrofuran with [PO]= 10 M. ^h Phosphazene base (P4): TiBAI= 1:3 in toluene with [PO]= 2 M. ⁱ Tetrabutylammonium chloride (TBACl): TiBAI= 1:3 in toluene with [PO]= 4 M. ^j Catalyst (salen)Co: bis(triphenylphosphine)iminium acetate (PPNOAc)= 1:2 in toluene with [PO]= 2 M, produced highly isotactic PPO. ^k (salen)Cr: bis(triphenylphosphine)iminium chloride (PPNCl): 1,6-hexanediol = 1:2:15 in dimethoxyethane with [PO]= 27.6 M, produced highly isotactic PPO. ^l NHO: magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂)= 1:5 with [PO]= 5 M in pentane. ^m Double metal cyanide catalyst (Co-Ni-DMC) with [PO]= 7.1 M in toluene. ⁿ ⁱPr: TEB: benzyl alcohol= 1:3:1.5 in neat PO. ^o

Phosphazene base (P2):TEB=1:3 in neat PO. ^p Ammonium bromide carrying two 9-borabicyclo (3.3.1) nonane (9-BBN) moieties, polymerization was run in neat PO.

ROP of epoxides for ultrahigh molar mass polyethers and the comparison of catalytic performance of bifunctional catalysts with reported ones

As mentioned in the introduction, the access to high molar mass polyethers is challenging especially for substituted epoxides due to potential transfer reactions. The efficiencies of bifunctional borinane-bearing ammonium salts **B2**, **B3** and **B4** carrying 2, 3 and 4 borinane moieties were respectively evaluated through the ROP of PO carried out in bulk under a feeding molar ratio of [PO]/[**B2**] or [PO]/[**B3**] or [PO]/[**B4**] of 30,000. After 10 mins of reaction aliquots were sampled out: with **B4** 100% conversion of PO was reached, whereas with **B3** and **B2** conversion reached 68% and 21%, respectively. Higher the number of borinane moieties carried by these three ammonium salts, higher the corresponding rate of polymerization of PO. In fact, the TOF value measured in the case of entry 2 was $1.8 \times 10^5 \text{ h}^{-1}$ with **B4**, which is 5 times higher than that measured in the case of entry 4 with **B2** as catalyst (37800 h^{-1}), and also significantly higher than for entry 3 involving **B3** as catalyst (122400 h^{-1}). Remarkable synergistic effects were thus observed when borinane moieties carried by this family of ammonium salts were increased from 2 to 3 and then from 3 to 4. As summarized in **Table 1**, all these catalysts showed unprecedented activity in comparison to any other reported catalysts. Importantly, comparison with recently described bifunctional catalysts carrying two 9-BBN moieties ($\text{TOF } 2370 \text{ h}^{-1}$, entry 18, **Table 1**) shows that **B2** exhibits an activity that is at least one order of magnitude higher ($60,000 \text{ h}^{-1}$, entry 1, **Table 1**) under the same polymerization conditions. Actually, both types of bifunctional catalysts benefit from the reduced entropy due to the proximity of the anionic growing centers with the boron-based monomer activating centers. Because boron centers carried by 9-BBN are more hindered than those carried by borinane, monomer activation is more efficient in the latter case resulting in turn in a significant enhancement of the catalyst activity. With the borinane family of bifunctional ammonium salts the molar masses of obtained PPO samples reach up to $1.5 \times 10^6 \text{ g/mol}$ with monomodal and narrow molar mass distributions (< 1.2). To the best of our knowledge, only two examples of PPO were reported with $M_n > 10^6 \text{ g/mol}$ ($\mathcal{D} > 1.2$),^{29,33} but with **B4** as catalyst the synthesis of a sample of $1.5 \times 10^6 \text{ g/mol}$ could be obtained in milder conditions. As seen from the ¹H NMR spectrum, no vinyl group could be detected (**Figure S19**), confirming the living character of the polymerization carried out in the presence of borinane-based bifunctional catalysts. Indeed, the molar masses drawn from by MALLS are close to their theoretical values calculated based on monomer conversion. Overall, **B4** represents the first example of catalyst that allowed the synthesis of ultrahigh molar mass polyether with a very high rate of polymerization. Notably, the difference is striking between the PPO sample of $0.46 \times 10^6 \text{ g/mol}$ which is a viscous liquid (**Figure 1A**, entry 1, **Table 1**) and the PPO sample of $1.5 \times 10^6 \text{ g/mol}$ molar mass which is a soft solid (**Figure 1B**, entry 2, **Table 1**).

The efficiency of borinane-based bifunctional catalysts at bringing about the ROP of other epoxides was tested with EO, BO and AGE. Being the most active catalyst for PO **B4** was chosen for this screening. As seen in **Table 1**, EO, BO and a functional epoxide such as AGE could be efficiently initiated by **B4** and polymerized with TOF values up to $30,000 \text{ h}^{-1}$; in all these cases, the obtained polyethers exhibited monomodal and narrow distribution of molar masses (~ 1.20 , **Figure 1C**), whose values could easily reach around 10^6 g/mol level. In the case of EO, supposedly the most reactive monomer among epoxides, its polymerization had to be carried out in the presence of a solvent rather than in bulk due to its tendency to crystallize in order to obtain PEO samples with a narrow distribution of molar masses. As anticipated, the presence of **B4** enabled the ROP of EO with a record TOF value up to $1.7 \times 10^6 \text{ h}^{-1}$, in other words one gram of **B4** could produce 117.5 kg PEO per hour.

The scope of CTAs and their effect on polymerization

One of the very important applications of polyethers is their use as precursors for the synthesis of polyurethanes that require telechelic samples with very well defined terminal functionality, generally hydroxyl functions, and molar masses below 10,000 g/mol. Unlike the preparation of polymers of large molar mass, the synthesis of low molar mass telechelics would require large amounts of borinane-based catalysts. One way to reduce the amount of borinane-based catalyst load is to use them in catalytic quantity and to resort to CTAs to precisely control the molar mass of the telechelics formed. In other words, after demonstrating that borinane-based ammonium salts are remarkable catalysts for ROP of epoxides we wanted next to investigate their potential in the presence of protic transfer agents when the ROP of cyclic ethers involve exchange reactions between minute concentration of active oxyanions and a large amount of dormant hydroxyls. First, various CTAs with different structures and functionalities, including water, monofunctional species and tetrafunctional star-shaped PEOs were screened for ROP of PO (**B4**: CTA: PO=1:1000:20000) at room temperature using **B4** as catalyst (**Table S1**, **Figure S20-29**). We were delighted to see that the borinane-based bifunctional catalysts were tolerant of the various protic functional groups carried by CTAs, including water. Among all the protic CTAs tested, the highest activity was observed for benzyl alcohols (BnOH and DBnOH) and propargyl alcohol (PA) with super-conjugated structure, with around 90% of PO conversion within 10 minutes, which is almost 10 times faster than the activity measured for other aliphatic alcohols, thiol and water. In comparison, the ROP of PO carried out in the presence of the binary system composed of TEB and tetrabutylammonium chloride (TBACl) (4:1) that we reported previously afforded only 5% of conversion in (**Table S1**, entry 1) which is 18 times lower than that catalyzed by **B4** (**Table S1**, entry 4), confirming the synergistic effect of bifunctional catalysts where ammonium cation and chloride anion stand in a close proximity with monomer-activating boron centers. Similar catalytic activities to that measured for **B4** (**Table S1**, entry 2-4,) were also observed in the cases of **B2** and **B3** (**Table S1**, entry 2 and 3) when used to prepare PPO telechelics. Logically **B4** with its 4 boron centers and **B3** with 3 boron centers exhibited higher activities than **B2**. In summary, borinane-based bifunctional ammonium salts present broad tolerance to various protic functional transfer agents including water, vinyl, alkynyl, fluorine moieties allowing the synthesis of α -vinyl, ω -OH PPO macromonomers, α -, ω - diOH PPO telechelics and even hydroxyl-ended 4-arm PPO stars.

Molar mass control by CTA

The four boron centers carried by the ammonium salt (**B4**) induce such a synergistic effect that its catalytic performance is unrivalled compared to any other catalysts used for the ROP of epoxides. To demonstrate the unmatched advantages of **B4**, we further investigated its catalytic performance and efficiency for the ROP of PO carried out in the presence of a CTA: various [PO] to [CTA] (BnOH) ratios for a same [PO] to [**B4**] ratio (detailed data was shown in **Table S2**) and various [CTA] to [**B4**] ratios for a same [PO] to [CTA] ratio were applied. As shown in **Figure 2A**, the molar mass of resulting PPO samples could be controlled independently of the [PO] ratio to [**B4**] ratio. As expected, increasing the amount of CTA resulted in a decreased molar mass. On the other hand, an excellent control of molar mass could also be achieved for all samples prepared with a same [PO] to [CTA] ratio but varying loading of **B4** (**Figure 2B**). Notably, decreasing the **B4** loading had no obvious effect on the resulting molar mass of the samples obtained. Moreover, the GPC traces for all PPO samples exhibited symmetrical and narrow molar mass distributions ($\mathcal{D} < 1.10$, **Figure S30**); the characterized molar masses were found very close to the expected values which were calculated upon taking into account the monomer conversion and the ratio of PO to the amount of BnOH and **B4** used. The above results revealed the remarkable advantages provided by the bifunctional ammonium salt **B4** for the preparation of polyols, allowing one to perfectly control the molar mass of the polyether samples synthesized using **B4** as a catalyst at ultralow loading. Compared to the industrial scale production of PPO diols relying on the use of DMC as catalyst, and necessitating oligomers or noncomplexing alcohols³⁹ as CTAs which tend to generate higher molar mass chains,^{40, 41} the process catalyzed by **B4** not only affords sample free of any high molar mass contaminant, but it can also be carried out under much milder conditions, using standard protic CTAs to generate well-defined PPO diols.

Ultra low catalysts loading for polyols preparation with broad monomer scope

After demonstrating that borinane-based ammonium salts are excellent catalysts for the ROP of various epoxides carried out in the presence of CTAs and for the preparation of ω -functional low molar mass samples, we wanted to explore the catalytic limit of **B4**. Hence, the catalyst loading was thus decreased to 2 ppm to polymerize PO (**Table 2**, entry 3): yet a high reactivity characterized by a TOF value of 18,125 was observed with DBnOH as CTA. More interestingly, **B4** still showed a remarkable activity with a catalyst loading as low as 2 ppm (**Table 2**, entry 4) in the case of water as CTA and PO as monomer. In the latter case, the rate of polymerization was found to be slower in comparison with that measured using DBnOH as CTA but the TOF value was only divided by a factor of 2. With a view of exploring the catalytic limits of **B4** for the ROP of EO, the catalyst loading was further decreased to ppb level (**Table 2**, entry 6): in EO case TON and TOF values of 9×10^6 and $1.9 \times 10^5 \text{ h}^{-1}$ were respectively measured, positioning **B4** as the most efficient catalyst ever synthesized for the synthesis of PEO telechelics. In other words, one gram of **B4** can produce no less than 606 kg PEO in 48h in the presence of CTA, which is an unrivalled value reached by any other catalyst. NMR spectra confirm the successful incorporation of CTA motifs into PEO diols (**Figure S31-S33**). Next, we evaluated the catalytic performance of **B4** with a broad range of epoxide monomers in the presence of water as CTA. In the case of epoxides substituted by long chains, namely butylene oxide (BO, **Figure S34**) and octene oxide (OO, **Figure S35**), negligible differences were observed between their rates of polymerization and that of PO. In contrast, the polymerization rate of allyl glycidyl ether (AGE, **Figure S36**) and phenyl glycidyl ether (PGE, **Figure S37**) were slower compared to that of PO likely because of the interaction of the extra oxygen atom carried by PGE and the double bond carried by AGE with the boron centers of **B4**. Nevertheless, the molar mass of all the diols obtained showed excellent agreement with the expected values; a narrow distribution of molar mass and no high molar mass impurities were observed (**Figure S3A**).

Table 2. **B4** catalyzed ROP of epoxides for polyols in the presence of CTA.^a

Entry	monomer	CTA	M:Cat:CTA	T (°C)	Time (h)	Conv. (%) ^b	TON ^c	TOF (h ⁻¹) ^d	$M_{n,thero.}^e$ (kg/mol)	$M_{n,GPC}^f$ (kg/mol)	\mathcal{D}^f
1	PO	H ₂ O	20000:1:250	25	4	95	19000	4750	4.4	4.8	1.03
2	PO	PEG4OH	20000:1:250	25	3	89	17800	5933	4.9	5.7	1.05
3	PO	DBnOH	5×10^5 :1:25000	60	24	87	435000	18125	1.1	1.1	1.04
4	PO	H ₂ O	5×10^5 :1:25000	60	48	81	405000	8438	0.9	1.3	1.04
5	PO	PEG4OH	5×10^5 :1:25000	60	48	96	480000	10000	1.9	2.3	1.03
6	EO	DBnOH	1×10^7 :1:25000	40	48	90	9×10^6	187500	1.7	1.8	1.03
7	EO	DBnOH	2×10^7 :1:250000	40	48	9	1.8×10^6	37500	0.3	0.5	1.08
8	EO	H ₂ O	1×10^7 :1:250000	40	48	47	4.7×10^6	97917	0.8	0.8	1.06
9	EO	PEG4OH	1×10^7 :1:250000	40	48	77	7.7×10^6	160417	2.2	2.4	1.05
10	BO	H ₂ O	5×10^5 :1:25000	60	48	65	325000	6771	0.9	1.2	1.05
11	PGE	H ₂ O	5×10^5 :1:25000	60	48	31	155000	3229	0.9	1.4	1.04
12	AGE	H ₂ O	5×10^5 :1:25000	60	48	26	130000	2708	0.6	0.7	1.06
13	OO	H ₂ O	5×10^5 :1:25000	60	48	52	260000	5417	1.3	1.5	1.05

^a Polymerizations were run in neat condition. ^b Conversion was determined by ¹H NMR. ^c Turnover number (TON) = moles of PO consumed/ moles of catalysts. ^d Turnover frequency (TOF) = TON/ time (h). ^e Determined by ¹H NMR. ^f Determined by GPC in THF using standard PEO as calibration.

Effective ROP of oxetane

The anionic ROP of oxetane has seldom been reported and the highest molar mass of polyoxetane ever obtained was limited to 19 kg/mol.^{42,43} On the other hand, Amass and coworkers⁴⁴ reported a controlled/"living" cationic ROP of oxetane carried out in 1,4-dioxane using a specially synthesized initiator 3-phenoxypropyl1-oxonia-4-oxacyclohexane hexafluoroantimonate (3-PPOA): polyoxetane with molar mass up to 160 kg/mol, containing 10 % of cyclic oligomers and incorporating dioxane units were obtained. Due to its high basicity and low ring strain, the ROP of oxetane through either cationic or anionic mechanism and thus the synthesis of high molar mass polyoxetane are still a challenge. As shown in **Table S3** entry 3, **B4** catalyzed polymerization of oxetane (TMO) shows a TOF value 1000 times higher than that of last reported value obtained by anionic means⁴⁵ in 2018 (entry 5). Moreover, the polyoxetane sample obtained by the use of **B4** exhibited an unprecedented molar mass value of 600 kg/mol (**Figure 3B**). The experimental molar mass showed an excellent agreement with the expected value, indicating that the polymerization of oxetane is living when initiated by **B4**.

Chain end group fidelity

Chain end group fidelity was confirmed by matrix-assisted laser desorption/ ionization time-of-flight (MALDI-TOF) mass spectrometry. The mass spectra of PPO (**Figure S38**) and PTMO (**Figure S39**) showed a single population indicating that chloride solely initiated polymerization in absence of CTA. Furthermore, in the presence of water as CTA only one single population (**Figure 3C**) is observed that appears to be in excellent agreement with the experimental mass obtained by GPC. The repeating intervals of 58 is in agreement with the molar mass of PO. Owing to the high ratio of CTA (water) to **B4**, the chloride initiated population was undetectable in spite of the single initiation nature by **B4**. Importantly, α -allyloxy, ω -OH PPO was not observed in MALDI-TOF, indicating the absence of any chain transfer reaction to monomer in **B4**-catalyzed polymerization. Additionally, the absence of any hydrogen abstraction side reaction was also supported by ¹H NMR since no allyl group was observed (**Figure S19**). Finally, **B4** effectively produced α,ω -diOH PPO and its molar mass was precisely controlled by the ratio of CTA: **B4**. The high fidelity of two primary hydroxyl ended PPO make this kind of diol precursors particularly valuable for high quality polyurethane preparation.

Mechanism investigation

Boron centers in organoboron catalysts play a double role when used in the ROP of epoxides: 1) activate the latter monomers; 2) form growing "ate complexes" through their interaction with oxyanions. In such "ate complexes" the nucleophilicity of oxyanions is decreased which helps to prevent side reactions. Because boron centers in borinane are more accessible to monomers than with any other bulky boron, the overall activity of such catalysts is enhanced by at least one order of magnitude compared to the best-known catalysts. In addition, the ring opening of PO in the presence of these borinane-based bifunctional ammonium salts strictly happened at the methylene C–O bond to produces regio-regular PPO as confirmed by the regioselective polymerization of chiral SPO (**Figure S40**). In the presence of CTA, no inhibition period is observed in the ROP of epoxides in the presence of borinane-based catalysts unlike other systems. In contrast, the binary system (TBACl/TEB) is inoperative when used for the ROP of epoxides in the presence of CTAs because of a low rate constant of initiation (k_1)/propagation (k_3) compared to the rate of exchange (k_2). On the other hand, the synergistic effect in borinane-based bifunctional catalysts likely results in a slightly higher value of k_1

compared to k_2 (**Figure 4**) which enabled initiation. In addition, the k_3 certainly lower than k_2 which allows a precise control of molar masses through fast exchange between dormant and active species (boron-based ate complex, **Figure S41**), thus affording polyols with a narrow dispersity. The above features indicate that borinane-based ammonium salts behave as excellent catalysts for the ROP of epoxides carried out in the presence of CTAs. To gain a deeper insight into the mechanism of bifunctional catalysts mediated ROP, DFT computation was performed (**Figure 5, Figure S42**). The energy barrier of the initiation step (25.11 kcal/mol), INT1-TS1, is lower than that of exchange (28.15 kcal/mol, INT2-TS2) which indicates a slightly higher value of k_1 compared to that of k_2 , confirming the above proposed mechanism. Furthermore, the increased energy barrier observed between INT3 and TS3 (35.43 kcal/mol) provides sufficient room for exchange between active chains and dormant chains which resulted in well-defined polyols. This DFT study thus provides perfect understanding of the mechanism in borinane-based bifunctional catalysts mediated ROP.

Conclusion

In this contribution, we described the rational design of a series of borinane-based bifunctional ammonium salts that proved to be excellent catalysts for the ROP of epoxides under mild conditions. Such bifunctional catalysts were synthesized by simple hydroboration of alkene ammonium salts using borinane in quantitative yield. In the presence of these bifunctional catalysts the ROP of epoxides is living, no side reaction and in particular no transfer to monomer could be detected; these catalysts afford a highly regioselective ring-opening of epoxides producing stereoregular polyethers. Ultrahigh molar mass polyether of $> 10^6$ g/mol could be obtained with narrow distribution upon using these bifunctional catalysts. Record TOF values were reached for PO ($1.8 \times 10^5 \text{ h}^{-1}$) and EO ($1.7 \times 10^6 \text{ h}^{-1}$), respectively. Significantly, the borinane-based bifunctional catalysts exhibit remarkable tolerance against various CTAs thus enabling the synthesis of polyols with precisely controlled molar mass and high end group fidelity using ppm level catalyst loading for PO and ppb level loading for EO. Moreover, an unprecedented productivity of 606 kg PEO/g **B4** catalyst in 48 h in the presence of CTA was achieved with polymers of well-defined structure. In the presence of **B4**, record values of TOF and of molar mass were reached for the ROP of oxetane. Finally, DFT computation gives a deep insight into the ROP of epoxides in the presence of these bifunctional catalysts and CTAs. Overall, such outstanding performance of these borinane-based bifunctional catalysts exhibit a great potential for an industrial preparation of polyols and can inspire the design of new generation of catalysts for effective ROP.

Methods

Materials

All the reagents were purchased from Sigma-Aldrich and used as received unless otherwise stated. Triethylborane (TEB, 1 M in THF), 9-Borabicyclo[3.3.1]nonane (9-BBN, 0.4 M in Hexane), borane dimethyl sulfide complex (BMS), boron trifluoride diethyl etherate and 1,4-Pentadiene was used as received. Tetrabutylammonium chloride (TBAC) were purified by recrystallization from cold n-hexane three times and followed by drying under vacuum to remove the solvents. The traces of water in the above ammonium salt were removed by drying under vacuum in the presence of P_2O_5 for 2 days. Tributyl amine and 5-bromo-1-pentene were purified by distillation. Propylene oxide (PO), oxetane, 1-butylene oxide (BO), 1-ocene oxide (OO), allyl glycidyl ether (AGE) and phenyl glycidyl ether (PGE) were purified by distilling firstly over CaH_2 and then over n-butyl lithium for two times using standard Schlenk technique. Ethylene oxide (EO) were purified by distilling over sodium. The purified monomers were stored in Schlenk flasks and kept in glovebox. Benzyl alcohol (BzOH), trifluoroethanol (TFE), propargyl alcohol (PA), 2-Hydroxyethyl acrylate (HEA), propylene glycol (PG), deionized water (H_2O) and pentaerythritol ethoxylate (PEG4OH, average $M_n \sim 797$) were degassed via three times of freeze-pump-thaw procedure. 1,4-Benzenedimethanol (DBnOH) and 1,4-Benzenedimethanethiol (DBnSH) were used as received. 1,4-diazabicyclo[2.2.2]octane (DABCO) was purified by two times of sublimation and stored in glove box.

Characterization

Nuclear magnetic resonance (NMR): ^1H , ^{11}B , ^{19}F and ^{13}C NMR spectra were recorded on a Bruker AVANCE III-400 Hz instrument in CDCl_3 .

Gel permeation chromatography (GPC): GPC traces were acquired on a VISCOTEK VE2001 system equipped with the Styragel HR2 THF and Styragel HR4 THF using THF (1 mL/min) as the eluent. The relative molar masses and distributions were obtained at 35 °C using a RID detector and against linear polystyrene standards.

The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on an Autoflex (Bruker) mass spectrometer. The trans-2-[3-(4-*t*-butyl-phenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as the matrix with a loading of 2:1 to sodium acetate which used as the ionizing agent.

Synthesis of borinane.

The six-membered cyclic borinane was synthesized as reported method.⁴⁶ A flame dried round bottom flask equipped with magnetic stir bar was cooled under vacuum and transferred to glove box. The flask was charged with 48.5 mL 9-BBN and 1 mL 1,4 pentadiene (9.7 mmol). The flask was stirred at room temperature in glove box overnight before adding 0.92 mL BMS. The reaction continued at room temperature for 24 h before anhydrous DABCO (0.54 g) THF solution was added to the above borane mixture solution. Borinane was immediately form complex with DABCO and precipitated. However, 9-BBN has no complexation with DABCO. In this case, pure borinane was separated with 9-BBN by filtration. And 9-BBN could be recycled for further reaction. The free borinane could be generated from the DABCO complex by reacting with boron trifluoride. The above solution was concentrated by distillation to yield pure borinane as white solid (0.76 g, 95% yield). Once the pure borinane was obtained, three moles of borinane could be easily generated from two moles of borinane (**Scheme S1**) without further separation or purification procedure.

Synthesis of catalysts

As shown in **Scheme 1**, all the bifunctional catalysts were synthesized via the direct hydroboration of borinane with vinyl groups. All the solvents utilized in this reaction were carefully dried to afford high yield and eliminate side reaction.

B4 mediated RD-ROP of PO

The obtained bifunctional borinane catalyst (**B4**) was dissolved in THF to obtain a 1 M solution. And the solution was further diluted 100 times to afford a 0.01 M THF solution. A typical polymerization procedure which corresponding to **Table 2**, entry 3 was described as follows: A flame dried Schlenk tube was transferred to glovebox. Then the tube was charged with 1 eq. **B4** (50 μL , 0.5 μmmol), 100 eq DBnOH (6.9 mg, 0.05 mmol) and 20000 eq. PO (0.7 mL, 10 mmol). The tube was stirred at room temperature for 30 min. The crude polymer was dried in vacuo at 50 °C to yield a viscous oil (0.58 g, 100% yield).

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Declarations

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Author contributions

Y.G. and X.F. directed the investigations, and revised the manuscript. C.C. carried out all experiments and analyses, and wrote the draft. All the authors participated in the discussions and revised the manuscript.

Additional information

Supporting Information. Details for synthesis of catalysts, and DFT computation. ^1H , ^{13}C , ^{19}F and ^{11}B NMR spectra and GPC Characterization data shown in **Scheme S1-S3**, **Table S1-S2**, **Figure S1-S43**.

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Competing interests

The authors declare no competing financial interests.

Schemes

Scheme 1 is available in the supplementary files section.

Figures

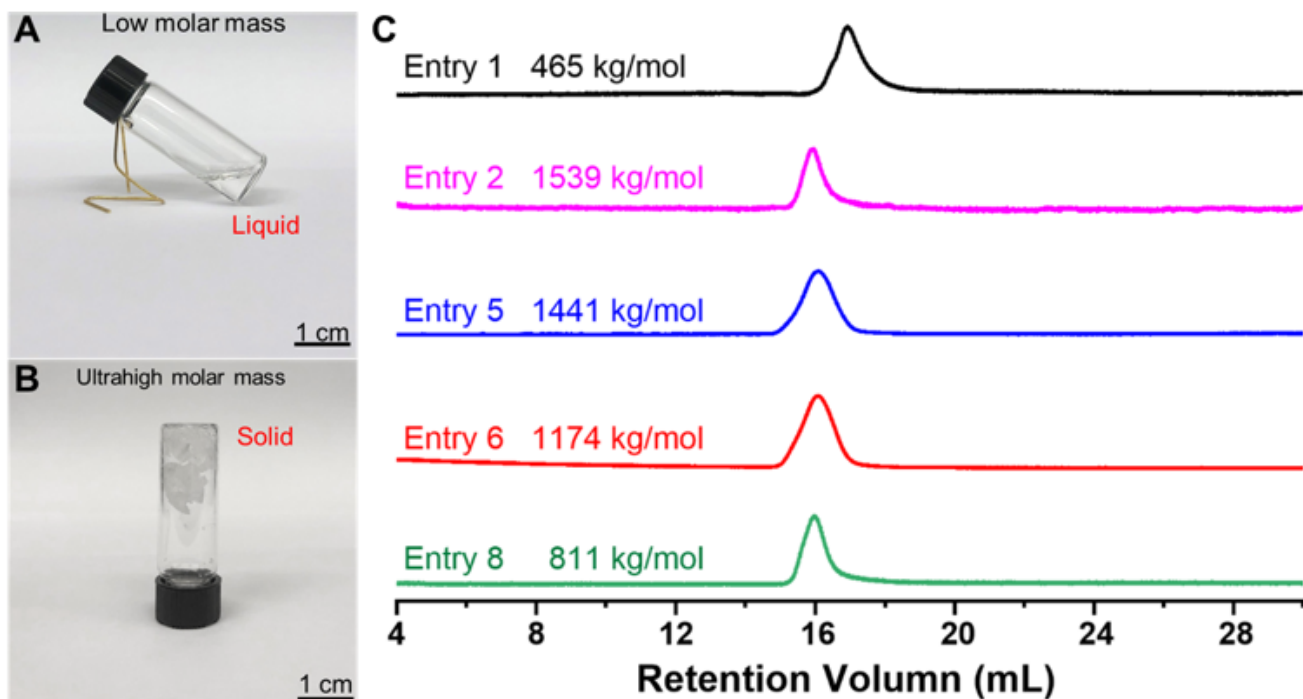


Figure 1

Digital photographs of (A) low (**Table 1**, entry 1) and (B) ultrahigh (**Table 1**, entry 2) M_n PPO, (C) SEC traces of ultrahigh M_n polyethers.

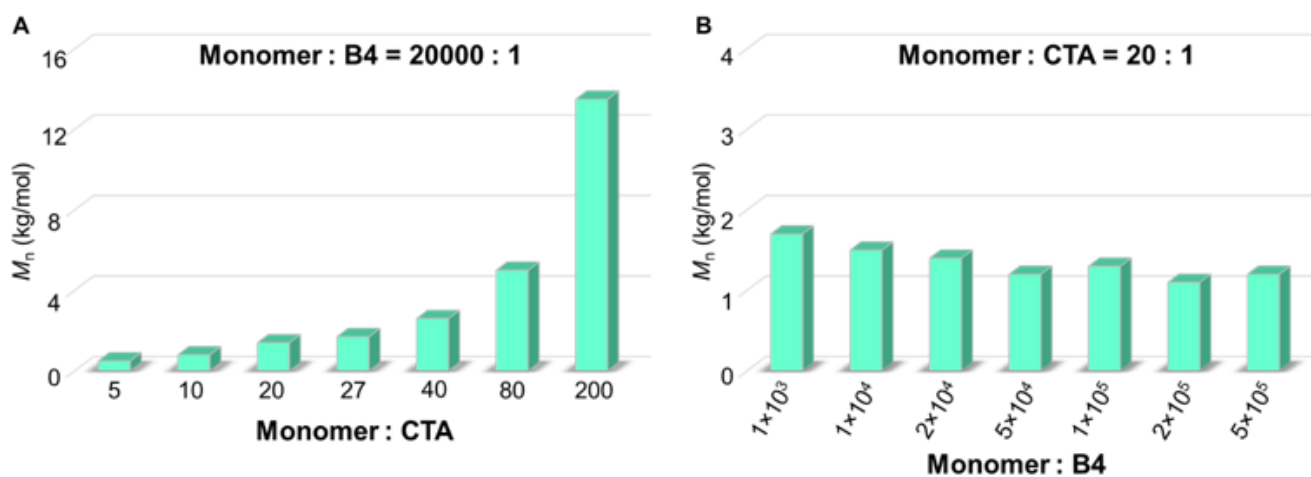


Figure 2

The effect of CTA (BnOH) on the polymerization of PO using bifunctional borinane-bearing ammonium salt **B4**. (A) Keeping the ratio of PO to **B4** constant and increasing the ratio of BnOH to **B4**. (B) Keeping the initiating species constant, varying the ratio of BnOH to **B4**. Detailed data are shown in **Table S2**.

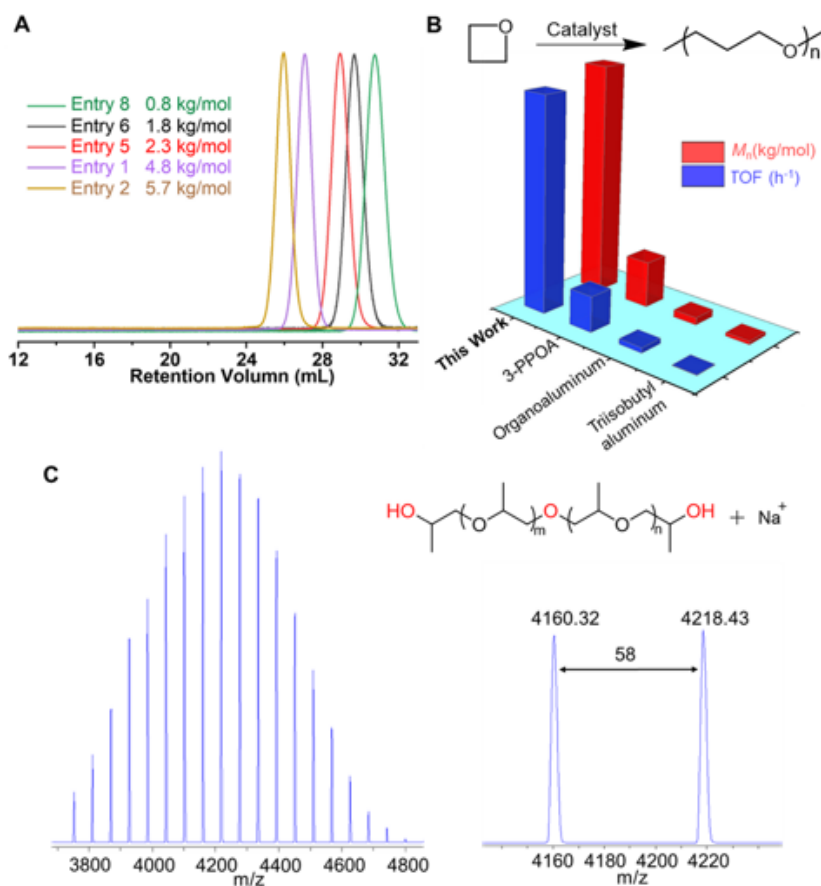


Figure 3

(A) SEC traces of polyethers with low M_n (Table 2). (B) Comparison of catalysts **B4** with other catalyst system for the ROP of oxetane and (C) MALDI-TOF spectra of PPO obtained using H_2O as CTA refer to Table 2, entry 1.

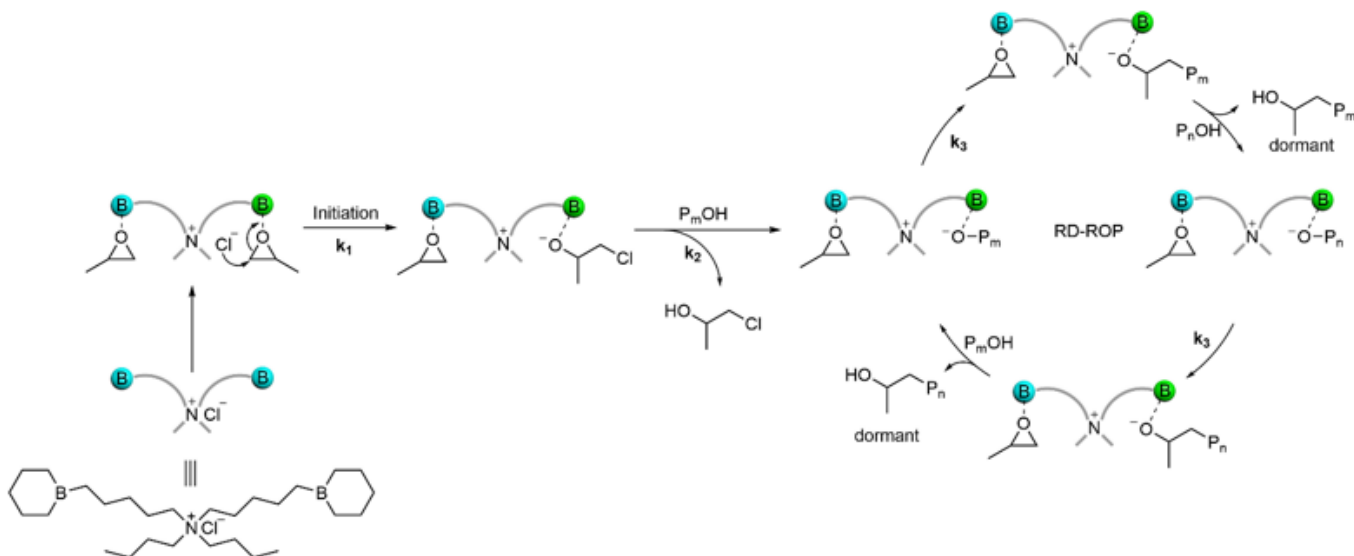


Figure 4

Proposed mechanism of **B2** mediated ROP of PO in the presence of CTA.

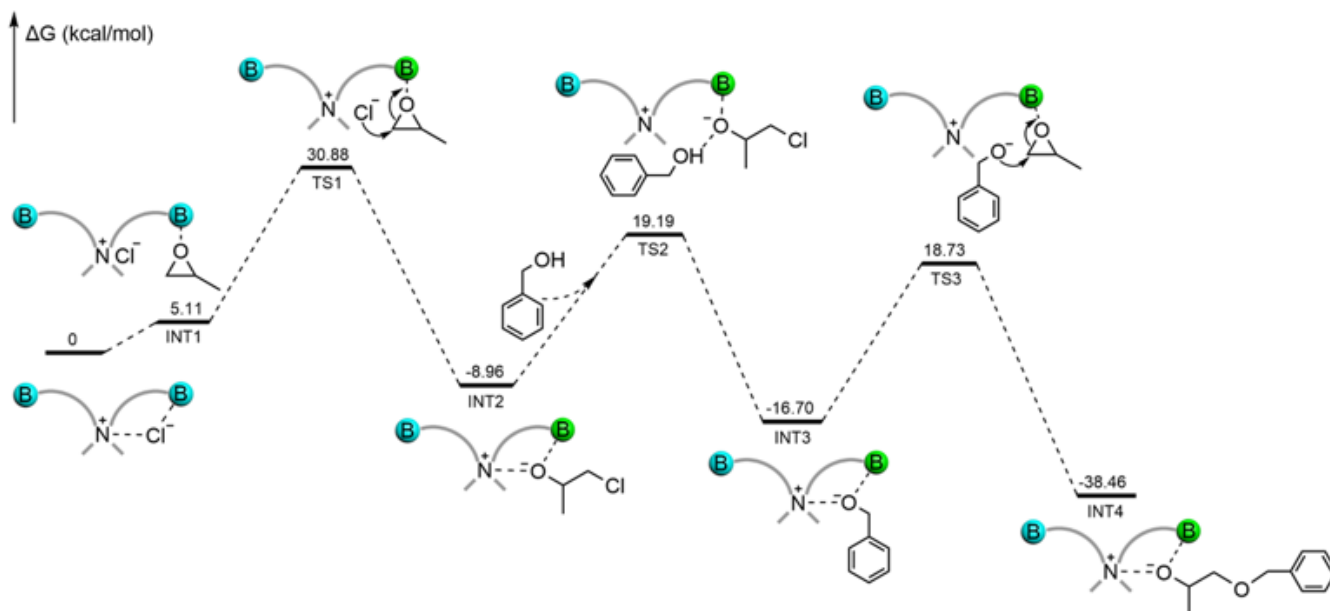


Figure 5

Gibbs free energy profile comprise intermediates (INT1-INT4) and transition states (TS1-TS3) for ROP of PO in the presence of BnOH as CTA.

Supplementary Files

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