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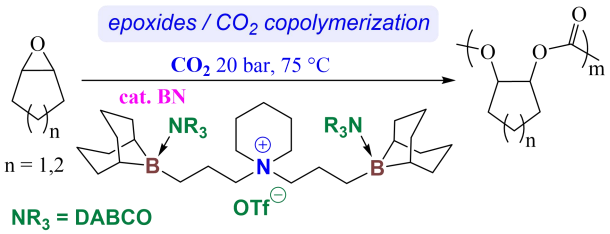
Carboxylation of epoxides using bifunctional ammonium-triorganoborane catalysts as borane-amine adducts

Nikolai Yu. Kuznetsov,*[a,b] Elena V. Chernikova[a,b] and Irina P. Beletskaya[a,b]

[a] *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: nkuznff@ips.ac.ru*
[b] *Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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Amine adducts of bifunctional ammonium-triorganoborane-catalysts of copolymerization of epoxides and CO_2 have higher stability than free ammonium-organoboranes, but at the same time, they are still active in copolymerization reactions.

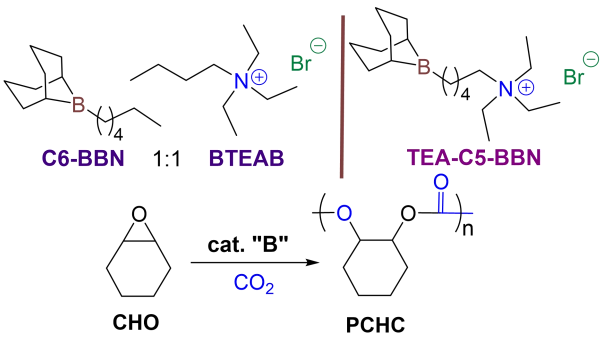


Keywords: CO_2, carbon dioxide, epoxides copolymerization, oganocatalysis, amine adducts of trialkylboranes, polycarbonates, cyclocarbonates.

Carboxylation of epoxides is an efficient way to convert CO_2, a major greenhouse gas, into such valuable chemical products as cyclic[1] and polymeric carbonates.[2] Cyclic carbonates (CC) have multiple areas of applications. They are not only chemical reagents and monomers,[3,4] but are also considered as truly "green," biodegradable polar aprotic solvents that can replace more toxic DMF, NMP, THF, or DMSO in a number of industrial processes.[5-7] CCs such as ethylene, propylene, fluoroethylene, and vinylene carbonate, which are components of electrolytes for lithium-ion batteries (LIB) are also of great importance.[8,9] At the same time, polycarbonates (PC), although they are biodegradable materials, are in a highly competitive environment with other polymers, which makes the question of their potential industrialization difficult leaving them at the beginning of their industrial application. Chernikova and Beletskaya[2] as well as Wu *et al.*[10] surveyed the data on the application, properties and prospects of PC obtained from CO_2. According to the analysis, applications of PC depend not only on their structure but also on their molecular weight. Hydroxyl-terminated oligomers and PCs are used to synthesize polyurethanes, while PC with a low glass transition temperature can form the basis of polymer carbonates for LIBs and find application as elastomers with high elongation. ZnO-filled polypropylene carbonate, with its good water and oxygen barrier properties and antibacterial properties, holds promise for packaging materials. The properties of block copolymers with polycarbonate units can be optimized across a wide range of applications, from durable plastics to adhesives. Good biocompatibility of PC is noted for their use in cellular medical technologies. Furthermore, this type of PC is effectively depolymerized to epoxides, which is important for the subsequent recycling of polymer waste.[11] Thus, polycarbonate materials will meet all requirements for reducing CO_2 emissions from the beginning of the product's "life cycle" to its end.[12]

Organocatalysts for the co-polymerization of epoxides and CO_2 derived from triorganoboranes are the most active and allow the preparation of pure polymers with easily removable traces of catalyst, unlike metal complexes.[10,13] Especially effective are catalysts having bifunctional structure combining Lewis acidic boron centers and onium salt fragments in co-polymerization of cyclohexene oxide (**CHO**)/CO_2 to poly(cyclohexene carbonate) (**PCHC**) (Scheme 1).[14-19]

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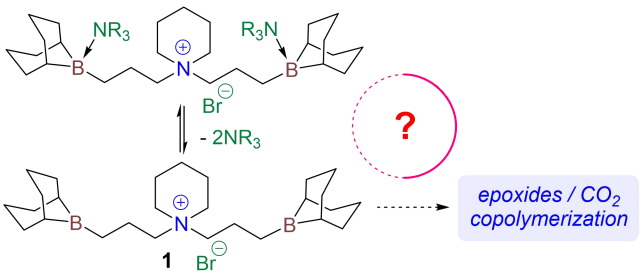
CHO / cat. "B"	C6-BBN & BTEAB (1:1)	TEA-C5-BBN
molar ratio	TOF, h^{-1}	TOF, h^{-1}
500	**11.7**	**710**
1000	**10.3**	**676**
3000	**6.2**	**601**

Scheme 1 Comparison mono- and bifunctional catalysts

However, one of the main obstacles for utilization of organoborane catalysts is their high sensitivity to atmospheric oxygen, which oxidizes C–B bonds thus deactivating catalyst.

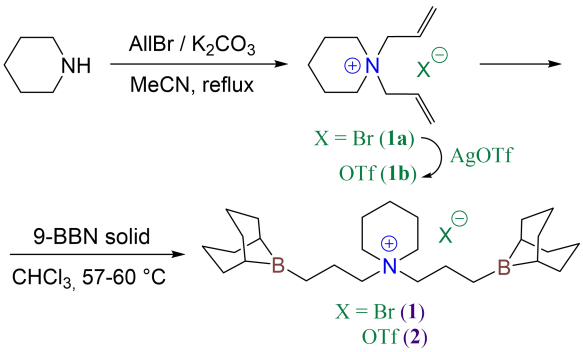
Previously, we developed efficient allylborating reagents based on amine adducts of allylic triorganoboranes which are survive under air atmosphere and totally retain intrinsic reactivity of organoborane due to dissociation onto components during reaction.[20-22] Based on these results, we proposed that converting bifunctional organoborane copolymerization catalysts into amine adducts could improve their stability and make them more convenient to use. However, the relationship between catalytic activity and the stability of the amine adducts required a separate study (Scheme 2), which is presented here.

This study was started using catalyst **1** developed by Wu *et al.*[13]



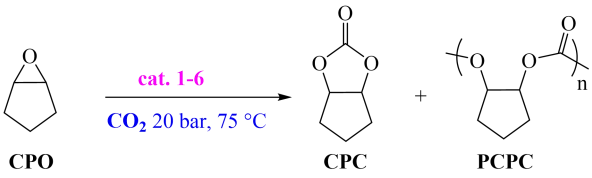
Scheme 2

Its quite straight and simple synthesis was carried out via sequential diallylation of piperidine followed by hydroboration with 9-BBN using modified Wu procedure (Scheme 3).[13]



Scheme 3

The progress of hydroboration was monitored by ^{1}H NMR on the disappearance of C=C bond signals. The resulting catalyst was washed with ether to remove excess 9-BBN, and its purity was confirmed by ^{11}B NMR, which shows a characteristic, strongly broadened boron peak at 88 ppm (see Online Supplementary Materials). All manipulations with the boron catalyst were performed under argon using the Schlenk technique. The cyclopentene oxide (**CPO**)/CO_2 copolymerization was carried out under CO_2 pressure (20 bar) at 75 °C with 0.5 mol.% **1** in a steel autoclave (Scheme 4). ^{1}H NMR spectra of the reaction mixture show a selective conversion of **CPO** to poly(cyclopentene carbonate) (**PCPC**) (70%), the molecular weight of which was 9.1 kDa after 4 h (Table 1, run 1). Since we performed the experiments not in a glovebox, but using conventional Schlenk vessel, we decided to examine whether increasing the **CPO** loading from 14 to 60 mmol with 0.4 mol% **1** will affect the reaction. This virtually has no effect on the polymer yield or its characteristics (Table 1, run 2), indicating a minor contribution of oxygen impurities to catalyst deactivation. At the same time, reducing the amount of **1** to 0.1 mol% leads to the formation of a mixture of cyclic carbonate **CPC** (26%) and polymer **PCPC** (11%) (Table 1, run 3).



Scheme 4

Table 1 **Catalyzed reaction of CPO and CO_2**

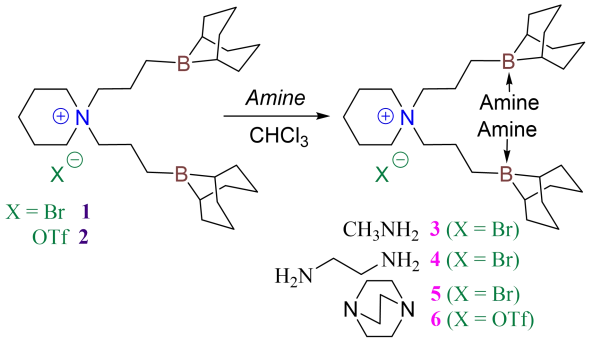
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run	*Cat., mol%*	*Time, h*	*Conv. **CPO**, %*	***CPC**, %*	***PCPC**, %*	*M_n, kDa; $Đ_M$*
1[a]	**1**, 0.5	4	70	---	70	9.1; 1.21
2[b]	**1**, 0.4	20	72	---	72	11.7; 1.44
3[a]	**1**, 0.1	20	37	26	11	---
4	**3**, 0.5	20	48	48	---	---
5	**4**, 0.5	20	55	55	---	---
6	**5**, 0.5	0.5	15	4	11	---
7[c]	**5**, 0.5	20	81	38	**43**	---
8[b,d]	**5**, 0.5	20	62	36	**26**	1.3; 1.3
9[a]	**5**, 1.0[e]	20	63	63	---	---
10[a]	**5**, 1.0[f]	20	74	74	---	---
11[a]	**5**, 1.0[g]	20	90	90	---	---
12[b]	**2**, 0.4	20	88	---	35(53[h])	3.1; 1.91
13[b]	**6**, 0.4	20	**84**	8	**76**	9.0; 1.51
14[b,d]	**6**, 0.4	20	**78**	6	**72**	---

[a] **CPO** (14 mmol) loading using Schlenk technique; [b] **CPO** (60 mmol) loading using Schlenk technique; [c] **CPO** (10 mmol) loading in glove box; [d] exposure of cat **5** or **6** on air for 5 min.; [e] additive (2-chloromethyl)allylchloride 2 mol%; [f] additive methallylchloride 2 mol%; [g] additive allylbromide 2 mol%; [h] yield of polyether from **CPO**.

This result is apparently due to catalyst oxidative degradation, which demonstrates the limits of **1** loading in our conditions. Indeed, catalyst **1** is extremely sensitive to oxygen. When exposed to air, it almost immediately heated up and melted, completely losing its polymerization activity. Therefore, the problem of stabilizing the catalyst with respect to air is indeed of great practical importance.

To study the effect of amines on the stability and catalytic activity of the bifunctional system **1**, mono- and diamines (methylamine, 1,2-ethylenediamine, and DABCO) were selected. The amine adducts were synthesized by adding the amine to a solution of **1** in degassed $CHCl_3$ (Scheme 5). Methylamine was used first, added as a methanol solution. Previous data showed,[20-22] that methylamine should produces the most stable adduct with the alkylborons (Scheme 2 and 5). After the removal all volatiles *in vacuo*, the residue was analyzed by ^{11}B NMR, confirming the formation of the methylamine adduct **3** by a chemical shift of the boron signals to the region of -5.5 ppm. Adducts **4** from ethylenediamine and **5** from DABCO were obtained similarly (Scheme 5). According to the NMR spectra, **4** lost the symmetry inherent in the structure of the original catalyst **1**, apparently due to intermolecular bonding of the two amino groups of the diamine with the boron centers.



Scheme 5

At the same time, the NMR spectrum on ^{11}B nuclei confirms an adduct formation (δ -5.5 ppm). The epoxide/CO_2 reactions catalyzed by adducts **3** and **4** have fundamental difference from the reaction with **1**. The sole product in these experiments was **CPC** (48% and 55%) without any traces of the polymer (Table 1, runs 4 and 5). Apparently, the strength of the resulting adducts (**3**, **4**) is not enough balanced to effectively catalyze epoxide ring-opening and copolymerization, since the ammonium salt moiety containing the bromide anion is effectively catalyze the cyclocarboxylation reaction.[23] As expected an adduct **5** with tertiary amine DABCO would be more easily dissociate to generate free borane and **PCPC** in the course of the reaction. However, in fact, with this catalyst, the amount of a polymer was not high and cyclocarboxylation was still a main process. Over a period of 0.5 h, the **CPO** conversion was 15%, with a product composition of **PCPC** (11%) and **CPC** (4%) (Table. 1, run 6). Conduction of the reaction under standard conditions with reagents loading in an argon box to exclude the ingress of oxygen led to 81% conversion of **CPO** for 20 h, which corresponds to the formation of polymer **PCPC** (43%) and **CPC** (38%) (Table 1, run 7). Thus, amine adducts can indeed serve as a source of *in situ*-generated boron catalyst. At the same time, the introduction of an amine component enhance the stability of the catalyst under air. When the manipulations on weighting and transferring of the catalyst were performed under air (only with final degassing), the polymerization took place producing a mixture **PCPC** (26%) and **CPC** (36%) (Table 1, run 8).

Attempts to activate catalyst *via in situ* removing of amine by action of allylating agents (allylbromide, methallylchloride and (2-chloromethyl)allylchloride) were unsuccessful, because the predominating process became cyclocarboxylation and **CPC** content was increased up to 90% (Table 1, runs 9-11). These experiments indicate importance of the anion, which directs the reaction along the cyclocarboxylation pathway, *i.e.*, the *in situ* formation of additional amounts of bromoammonium salts from allyl bromide catalytically accelerates the synthesis of **CPC**. An evident solution to this problem was replacing of the nucleophilic halide anion on a weakly nucleophilic triflate anion that was done *via* metathesis of bromide in the initial diallylpiperidinium salt **1a** to triflate **1b** by treatment with AgOTf that finally gave rise to catalyst **2** (Scheme 3). Test of catalyst **2** with **CPO**/CO_2 revealed an interesting feature of this system. Along with polymeric **PCPC** (35%), significant amounts of carboxylate-free polymer (53%) was obtained, with a total **CPO** conversion 88% (Table 1, run 12). Thus, this experiment showed that the role of the anion in the bifunctional catalyst is not only to participate in the opening of the epoxide, but also to neutralize the Lewis acidity of the boron catalytic center through coordination.

Further, an amine adduct **5** from **2** and DABCO was tested in copolymerization. Catalyst **5** demonstrated high activity: **CPO** conversion reached 84%, and **PCPC** and **CPC** contents were 76% and 8%, respectively (Table 1, run 13). Although the selectivity in this process is somewhat lower than with **1** (Table 1, run 1), in practice low molecular weight CCs are easily separated from the polymer. Testing the effect of air on **5** (passing dry air through a vessel containing the catalyst) also demonstrated its greater stability. After degassing, copolymerization with **6** yields primarily **PCPC** (72%) (Table 1, run 14), demonstrating the advantage of amine adducts under the air atmosphere.

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The kinetics of copolymerization of epoxides **CPO** and **CHO** with CO_2 in the presence of **6** was studied at epoxide/catalyst molar ratio of 250 (Fig. 1). Figure 1a shows the dependences of epoxides conversion on time during the copolymerization of **CPO** and **CHO** at CO_2 pressure of 2.0 MPa at 65 and 70 °C, respectively. As can be seen both kinetic curves are S-shaped. Moreover, the rate of copolymerization with CO_2 for **CPO** is ~5.8 times lower than for **CHO**. The kinetic curves reconstructed in the coordinates of the first-order reaction turn out to be non-linear (Fig. 1b), which may indicate a slow initiation of polymerization.

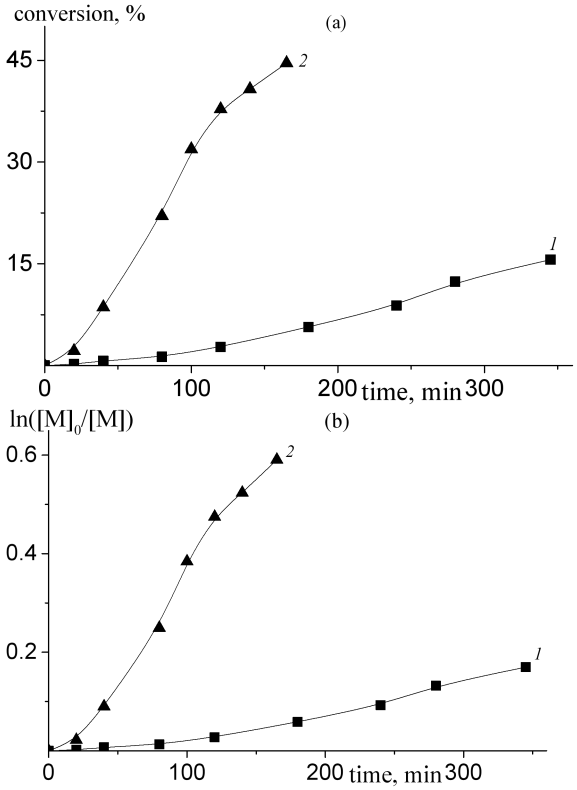
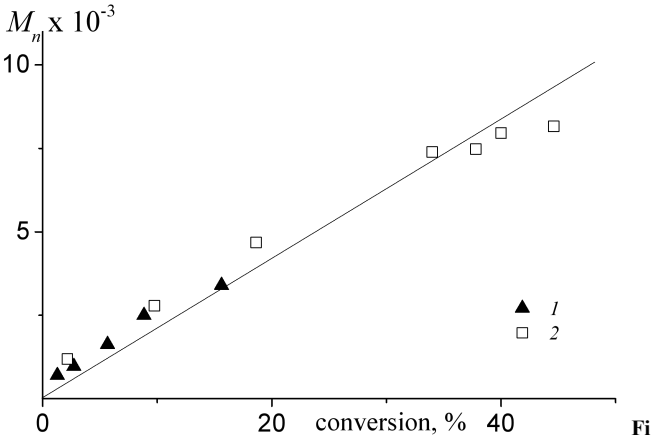


Figure 1. Dependences of epoxide conversion (a) and the logarithm of the ratio of the initial to current epoxide concentration ($\ln([M]_0/[M])$) (b) on time during the copolymerization of **CPO** (1) and **CHO** (2) in the presence of **6** catalyst under CO_2 pressure of 2.0 MPa, T = 65 (1) and 70 °C (2).

The molecular weight characteristics of the resulting polycarbonates were studied using gel permeation chromatography (GPC). Figure S4 shows the MWD curves of the polycarbonates. It is clear that with increasing epoxide conversion, the MWD curves shift toward higher molecular weights, indicating a "living" polymerization mechanism. The dependences of the number-average molecular weight M_n on conversion are also linear for both epoxides. Importantly that, at the same molar ratio [epoxide]/[catalyst], all experimental values of M_n are described by a single linear dependence, which also proves the “living” mechanism of the process (Fig. 2). The values of dispersion of polycarbonates $Đ_M$ are 1.2 – 1.4, which is typical for “living” processes with slow initiation.



gure 2. Conversion dependences of M_n of **PCPC** (1) and **PCHC** (2) formed during copolymerization with CO_2 in the presence of **6** catalyst under CO_2 pressure of 2.0 MPa. T = 65 (1) and 70 °C (2).

The overall mechanism of the process involves two independent catalytic cycles (Scheme S1). The cycle for the formation of the cyclic carbonate **CPC** is shown on the left, where the X anion opens the epoxide, and CO_2 adds to the intermediate alkoxide, forming a precursor for closure into the CC. The boron center in this case is completely blocked by the amine and does not contribute to polymerization. On the other hand, the catalytic polymerization cycle begins with the thermal dissociation of the boron-amine complex, forming amine and free alkylboron catalyst. The latter activates the opening of the epoxide with the participation of nucleophile X. However, along with X, the amine complexing agent can also participate in the epoxide opening process, and such a process will be predominant in the case of the weakly nucleophilic triflate anion. The exchange process between the boron center and the ammonium group regenerates the catalytic boron center and facilitates carboxylation. This is followed by a stage of polymer chain growth with similar sequential insertion of epoxide and CO_2. Chain termination occurs through protonation of the alkoxide anion or deactivation of the alkylborane. In the latter case, the catalytic cycle stops.

To conclude, amine adducts of bifunctional organoboron catalysts may be promising systems for the synthesis of polycarbonates, as they exhibit higher oxygen stability than free boranes. The latter oxidize almost instantly and can pose a serious hazard due to their pyrophoricity, whereas amine adducts are completely safe. Further study of the effect of the onium salt counterion is also of interest for controlling the catalytic activity of bifunctional epoxide carboxylation catalysts.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:

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