1 Carboxylate Salts as Ideal Initiators for the Metal-Free 2 Copolymerization of CO₂ with Epoxides. Synthesis of Well-Defined 3 Polycarbonates Diols and Polyols

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8 **S** Supporting Information

9 **ABSTRACT:** Tetrabutylammonium carbonate (TBAC)
10 which is obtained by treating CO₂ with tetrabutylammonium
11 hydroxide is shown to perform as an ideal difunctional
12 initiator for the copolymerization of carbon dioxide (CO₂)
13 and propylene oxide (PO) in the presence of triethylborane
14 (TEB). In this system, CO₂ thus serves as the initiating
15 moiety of its own copolymerization with epoxides when used
16 in the form of a carbonate salt. Based on this remarkable
17 result, mono-, tri-, and tetrafunctional ammonium carboxylate
18 initiators and also other difunctional carboxylate initiators
19 were synthesized and used for the synthesis of well-defined ω -
20 hydroxyl-polycarbonates with linear and star structures. Well-defined telechelics, three- and four-armed star samples of molar
21 mass varying from 1 kg/mol to 10 kg/mol, with around 95% carbonate content, were successfully synthesized. The structure of
22 the obtained polycarbonate ω -polyols were characterized by ¹H NMR, MALDI-TOF, and GPC. The terminal hydroxyl
23 functionality of polycarbonate diol was further used for polycondensation with diisocyanates to afford polyurethanes. Finally,
24 taking TBAC as an example, the recyclability of this ammonium-based initiator is demonstrated for the preparation of
25 polycarbonate diols.

26 ■ INTRODUCTION

27 Because the rising concentration of CO₂ in the atmosphere is
28 currently a serious environmental concern due to the
29 greenhouse effect, a considerable amount of research effort
30 has thus been made to explore solutions aiming at reducing the
31 emission of CO₂ and utilizing it as a C1 resource.^{1–3} Pioneered
32 by Inoue et al.,⁴ research on the copolymerization of CO₂ with
33 epoxides resulted in the development of many catalysts,
34 including heterogeneous and homogeneous ones; CO₂-based
35 copolymers exhibiting different structures have found
36 applications as sacrificial binders, packaging and films, coatings,
37 adhesives, etc.^{5–7} Especially, polycarbonate diols and also
38 polyols of low molar mass are increasingly preferred to
39 conventional polyether polyols in applications such as
40 polyurethanes, as the latter exhibit better performance when
41 generated from polycarbonate polyols.^{8–12} For such applica-
42 tions, polycarbonate polyols are required to exhibit well-
43 defined terminal hydroxyl functionality, low polydispersity, and
44 tunable carbonate contents.

45 Although much progress has been made during the past two
46 decades in the preparation of polycarbonate of high molar
47 mass and high carbonate content,^{13–17} the preparation of low
48 molar mass polycarbonate diols and polyols with well-defined
49 structure is still challenging. When heterogeneous catalysts,

such as double metal cyanide (DMC), are used to prepare
polycarbonate diols, protic transfer agents such as alcohols and
acids are required;^{18–25} similarly for the synthesis of
polycarbonate triol and tetraols, multifunctional tri- or
tetraacid transfer agents are necessary.^{26,27} Although the
chain ends of such polycarbonate samples possess the expected
hydroxyl functionality, they generally suffer from a low
carbonate content, a lack of linear versus cyclic selectivity,
and a broad polydispersity.

Polycarbonate polyols have also been prepared using
homogeneous catalysts based on cobalt, zinc, or magne-
sium.^{28–35} In these cases, the polycarbonate polyols possess high
carbonate content and narrow polydispersity; however, the
anion which is carried by the metal center, and which triggers
polymerization, generates ω -monohydroxyl chains and thus the
polycarbonate diols and polyols eventually obtained under
these conditions are contaminated with monofunctional
chains, which is detrimental to the subsequent polycondensa-
tion applications. As clearly demonstrated by Sugimoto et al.,
polycarbonate tetrol and hexeol samples using 69

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70 tetraphenylporphyrinatocobalt(III) chloride as catalyst and
71 prepared in the presence of tetra- and hexafunctional
72 carboxylic acids are contaminated with linear polycarbonate
73 chains that have to be removed by fractionation.³⁶ In the case
74 of the synthesis of polycarbonate diols, such monohydroxyl
75 linear polycarbonate impurities are difficult to eliminate by
76 fractionation.

77 Polycarbonate diols can also be obtained by another
78 strategy, consisting of the preparation of a polycarbonate of
79 rather a high molar mass (80 to 100 kg/mol), followed by
80 alcoholysis in the presence of "molecular" diols and an
81 inorganic catalyst. Both the teams of Lee and Meng followed
82 this general strategy, although Lee started from a high molar
83 mass poly(butylene carbonate) prepared by polycondensa-
84 tion³⁷ while Meng used a polycarbonate obtained by
85 copolymerization of PO with CO₂.³⁸ In both cases rather
86 harsh conditions were used, which eventually afforded
87 polycarbonate diol samples of broad molar mass distribution
88 contaminated with cyclic byproducts.

89 In contrast to all catalytic systems investigated and
90 developed so far, our group recently proposed a new metal-
91 free approach allowing the successful copolymerization of CO₂
92 and epoxides by boron-based ate complexes.^{13,39} In the
93 presence of these ate complexes and an excess of trialkyl
94 borane, well-defined alternating copolymers of CO₂ and
95 epoxides could be obtained with high selectivity and an
96 activity comparable to some organometallic systems. Due to
97 the "livingness" of such copolymerizations, the molar mass is
98 controlled by the monomer conversion and the ratio of
99 monomer to the initiator, the structure and terminal
100 functionality of polycarbonates being strictly determined by
101 the initiators used. In our initial work, we found that
102 quaternary onium chloride salt initiators worked best for the
103 copolymerization of CO₂ with epoxides to afford α -chloro, ω -
104 hydroxyl polycarbonates. We serendipitously discovered that
105 tetrabutylammonium carbonate behaves as an ideal initiator for
106 the copolymerization of CO₂ with epoxides in the presence of
107 triethylborane (TEB), affording well-defined α,ω -hydroxyl
108 polycarbonate telechelics. This result prompted us to consider
109 ammonium salts of carboxylates as initiators for the
110 copolymerization of CO₂ with epoxides. Unlike onium
111 chloride salts, carboxylic acids are very common compounds
112 either as natural or synthetic products. In polymer chemistry
113 compounds fitted with carboxylic acids have been mainly used
114 as monomer in polycondensation reactions and seldom as an
115 initiator to ring-open the polymerization of cyclic monomers,⁴⁰
116 unlike hydroxyl-carrying compounds. In the present work we
117 show that carboxylate salts of tetrabutylammonium of various
118 functionality ranging from 1 to 4 can successfully be used to
119 initiate the copolymerization of CO₂ with propylene oxide
120 (PO) and generate poly(propylene carbonate) (PPC) samples
121 carrying one, two, three, and four terminal hydroxyl groups,
122 respectively, in the presence of TEB. Remarkably, tetrabutyl-
123 ammonium carbonate which is an ideal difunctional initiator
124 could be obtained upon treating tetrabutylammonium
125 hydroxide with CO₂. In addition, this tetrabutylammonium
126 carbonate initiator could be quantitatively recycled. Upon
127 changing slightly the polymerization conditions, the molar
128 mass (1000 to 10 000 g/mol) and carbonate content (50–
129 96%) could be easily tuned. All samples featured narrow PDIs
130 (GPC), and their carbonate content and terminal functionality
131 were confirmed by NMR and MALDI-TOF characterization.
132 The end group functionality of the obtained polycarbonate

diols and polyols was further demonstrated by carrying out
polycondensation reactions with hexamethylene diisocyanate
and phenyl isocyanate. The telechelic diols and the polyols
synthesized through this anionic approach thus satisfied all the
requirements as precursors for polyurethane production.

EXPERIMENTAL SECTION

Materials and Characterization. All chemicals were purchased
from Aldrich chemicals and used as received unless otherwise stated.
Propylene oxide was stirred over CaH₂ and distilled under reduced
pressure. Tetrahydrofuran (THF) and hexane were dried over sodium
metal and distilled under reduced pressure. The CO₂ (99.995%),
purchased from Abdullah Hashim Industrial & Gas Co., was further
purified by passing through a CO₂ purifier (VICI Co., US). All ¹H and
¹³C NMR spectra were recorded on a Bruker AVANCE III-400 and
500 MHz instrument. GPC traces were recorded by VISCOTEK
VE2001 equipped with Styragel HR2 THF and Styragel HR4 THF
using THF (1 mL/min) as eluent. Narrow Mw polystyrene standards
were used to calibrate the instrument. MALDI-TOF MS experiments
were carried out by using trans-2-[3-(4-*t*-butyl-phenyl)-2-methyl-2-
propenylidene] malononitrile (DCTB) as the matrix in THF at a
loading of 1:5 with sodium trifluoroacetate as an ionizing agent.

Synthesis of Initiators. *Synthesis of Tetrabutyl Ammonium Carbonate (TBAC).* The TBAC was prepared by modification of the
reported procedure.⁴¹ In a Schlenk flask, an aqueous solution of
tetrabutylammonium hydroxide (20 mL) was stirred under a positive
pressure of CO₂ and the reaction was followed by phenolphthalein
indicator until the disappearance of the pink color. The water was
removed by lyophilization. Further traces of water was removed by
lyophilization with anhydrous 1,4 dioxane to get TBAC as a white
powder.

¹H NMR (400 MHz, DMSO-*d*₆), δ 2.79 (t, 8H), 1.17 (m, 8H),
0.94 (m, 8H), 0.52 (m, 12H). ¹³C NMR (100 MHz, CDCl₃), δ
158.12, 57.48, 23.05, 19.17, 13.45.

General Procedure for Synthesis of Tetrabutyl Ammonium Salt of Carboxylic Acid. In a Schlenk tube an aqueous solution of
tetrabutylammonium hydroxide was charged under argon. An
equivalent quantity of carboxylic acid was added and stirred at 25
°C for 1 h. The completion of neutralization reaction was monitored
by phenolphthalein indicator. The water was removed by lyophiliza-
tion. Further traces of water was removed by lyophilization with
anhydrous 1,4 dioxane to get the corresponding ammonium
carboxylate salt as a white powder.

Tetrabutyl Ammonium Salt of Benzoic Acid (ABA). ¹H NMR
(500 MHz, DMSO-*d*₆), δ 7.81 (m, 2H), 7.21 (t, 3H), 3.18 (t, 8H),
1.57 (m, 8H), 1.32 (m, 8H), 0.92 (m, 12H). ¹³C NMR (125 MHz,
DMSO-*d*₆), δ 168.0, 142.2, 128.8, 127.6, 126.7, 57.5, 23.1, 19.2, 13.5.

Tetrabutyl Ammonium Salt of Succinic Acid (ASA). ¹H NMR
(400 MHz, DMSO-*d*₆), δ 3.18 (t, 16H), 1.81 (s, 4H), 1.57 (m, 16H),
1.32 (m, 16H), 0.92 (m, 24H). ¹³C NMR (100 MHz, DMSO-*d*₆), δ
176.2, 57.5, 37.9, 23.1, 19.2, 13.5.

*Tetrabutyl Ammonium Salt of *m*-Phthalic Acid (A-*m*PhA).* ¹H
NMR (500 MHz, DMSO-*d*₆), δ 8.25 (s, 1H), 7.64 (d, 2H), 6.99 (t, 1H),
3.17 (t, 16H), 1.56 (m, 16H), 1.31 (m, 16H), 0.92 (m, 24H).
¹³C NMR (125 MHz, DMSO-*d*₆), δ 168.8, 141.1, 129.9, 128.4, 124.7,
57.5, 23.1, 19.2, 13.5.

Tetrabutyl Ammonium Salt of Trimesic Acid (ATMA). ¹H NMR
(500 MHz, DMSO-*d*₆), δ 8.11 (s, 3H), 3.18 (t, 24H), 1.57 (m, 24H),
1.31 (m, 24H), 0.92 (m, 36H). ¹³C NMR (100 MHz, DMSO-*d*₆), δ
169.9, 139.5, 129.8, 57.5, 23.1, 19.2, 13.5.

1,2,4,5-Benzenetetracarboxylic Acid (APMA). ¹H NMR (500
MHz, DMSO-*d*₆), δ 6.90 (s, 2H), 3.18 (t, 32H), 1.56 (m, 32H),
1.31 (m, 32H), 0.93 (m, 48H). ¹³C NMR (100 MHz, DMSO-*d*₆), δ
173.56, 139.49, 126.02, 57.44, 23.06, 19.18, 13.49.

Polymerization. A typical experimental procedure, corresponding
to entry 4, is described below. A 50 mL Parr reactor with a magnetic
stir bar and a small glass vial inside was first dried in an oven at 120
°C overnight and then immediately placed into a glovebox chamber.
After keeping under vacuum for 2 h, the reaction vessel was moved 200

into the glovebox under argon atmosphere. The reactor was charged with difunctional initiator (0.2 g 0.367 mmol), triethyl borane (1.03 mL, 1 molar solution in THF, 1.03 mmol), and THF (1.0 mL). The propylene oxide (2.05 mL, 29.3 mmol) was then added in the glass vial inside the reactor, the reactor was quickly sealed, taken out from the glovebox and charged with CO₂ to a pressure of 10 bar, and reaction was carried out at 40 °C for 14 h with stirring. The reactor was cooled, the unreacted CO₂ was slowly released, and the polymer solution was quenched with 1 M HCl solution in methanol. The crude product was diluted with tetrahydrofuran and purified by precipitation in methanol. The product was collected and dried in vacuum at 40 °C.

Procedure for the Recycling of Ammonium Carbonate Initiator. After polymerization, the polymer solution was directly precipitated from the autoclave in deionized water. Poly(propylene carbonate) (PPC) carrying Bu₄N⁺ cation at the chain ends undergoes hydrolysis to form Bu₄NOH which dissolves in the aqueous layer leaving behind PPC as precipitate. The aqueous solution obtained after precipitation of PPC diol was neutralized through bubbling CO₂ to transform from ammonium hydroxide into ammonium carbonate salts (TBAC). After the volatiles were removed by rotovap, the obtained aqueous solution were further dried by lyophilization. The obtained TBAC was washed with dry toluene in order to remove any residual propylene carbonate. In all the cases studied such recovered TBAC was reused for the next cycle.

Representative Procedure for the Reaction of PPC with Phenyl Isocyanate. In a typical procedure, PPC-diol (0.2 g, 0.100 mmol) and phenyl isocyanate (0.2 g, 170 mmol) were dissolved in 2.0 mL anhydrous DMF, followed by the addition of 0.1 wt % dibutyltin dilaurate (DBTDL) as a catalyst. The reaction was carried out at 70 °C for 10 h with vigorous stirring and then quenched by precipitation in methanol. The obtained polymer was dried under vacuum at 40 °C for 24 h.

RESULTS AND DISCUSSION

Synthesis of Initiators for Linear and Star PPCs. In our initial work we reported that the onium chloride salts act as excellent initiators for PPC synthesis in the presence of TEB as activator.^{13,42} α,ω -Heterobifunctional PPCs were obtained, with one end of PPC chains being capped by chloride and the other by hydroxyl group, which made them unsuitable for an application such as precursors of polyurethanes. After discovering that TBAC affords PPC telechelic samples terminated at both ends with hydroxyl groups, we designed and prepared a group of initiators all based on tetrabutylammonium carboxylate salts to produce linear and star PPCs. As shown in Figure 1, the functionality of these initiators range from 1 to 4. These carboxylate salts were prepared by neutralization of the corresponding acids using tetrabutylammonium hydroxide. As for TBAC, the difunctional initiator, it is easily isolated upon bubbling CO₂ in a solution of

tetrabutylammonium hydroxide. The choice of tetrabutylammonium carboxylate salts as initiators was actually dictated by two criteria: first onium cations and, namely, tetrabutylammoniums afford high linear versus cyclic selectivity and, at the same time, rather high activity, and second, carboxylic acids are available in various functionality (1, 2, 3, and more) and they can be easily transformed into the corresponding ammonium carboxylate salts upon reaction with tetrabutylammonium hydroxide (see Figures S1 and S2 for ¹H and ¹³C NMR characterization). As our chemistry requires an excess of TEB to activate the epoxide monomer, even a weak nucleophile—actually an ate complex—formed by the addition of such tetrabutylammonium carboxylate salts to 1 equiv of TEB is expected to initiate the copolymerization of CO₂ with PO (Scheme 1).

ω -Hydroxyl Polycarbonate. Although less nucleophilic than its alkoxide counterpart, the boron ate complex resulting from the reaction of TEB with tetrabutylammonium benzoate (ABA) salt efficiently initiates the copolymerization of CO₂ with PO, in the presence of a slight excess of TEB (entry 1, Table 1). ABA afforded a PPC sample of high carbonate content and good selectivity (Figures S3, S4), exhibiting a similar activity to that chloride and alkoxide onium salts.¹² After this successful attempt at preparing ω -hydroxyl polycarbonate, we then tried to prepare low molar mass PPC diols and polyols using di- and multifunctional initiators.

α,ω -Dihydroxyl End-Capped Polycarbonates. As mentioned above, the use of TBAC as cheap and easy to obtain difunctional initiator triggers this investigation on the relevance of ammonium carboxylate salts as initiators for the copolymerization of CO₂ with epoxides. TBAC is merely obtained by reaction of tetrabutylammonium hydroxide with CO₂. Upon adding 1.4 equiv of borane to TBAC, a polycarbonate sample with high carbonate content and high linear/cyclic selectivity could be obtained (entry 2, Table 1, Figure S5). In all other attempts at copolymerizing CO₂ and PO using TBAC as difunctional initiator, the conditions were the same as those of entry 2 in Table 1, implying an excess TEB of 2.8 mol with respect to TBAC. These experiments yielded polycarbonate diol samples of molar masses ranging from 1000 to 10 000 g/mol. As listed in entries 2 to 6 in Table 1, in all cases, the carbonate contents were above 90% as characterized by NMR spectroscopy. GPC traces of all the polycarbonate diol samples exhibit a narrow and monomodal distribution of molar masses as shown in Figure 2A.

Subsequent efforts were devoted to characterize the terminal functionality of these telechelic samples, which is a very important factor to verify before considering such putative telechelics for applications such as precursors of polyurethanes. These diol samples were thus first submitted to MALDI-TOF analysis. With tetrabutylammonium carbonate used as initiator, two main populations and a small third population matching exactly the expected structure can be seen: all these populations of PPC chains correspond to two hydroxyl-ended PPC diol chains (Figure 3A), all initiated by the ammonium salt of carbonic acid. Indeed, the molar mass values of the main population satisfy the following formula: $m/z = 102.09n + 62 + 3 \times 58.1 + 23$, $102.09n + 62 + 2 \times 58.1 + 23$, and $102.09n + 62 + 4 \times 58.1 + 23$, where 102.09, 62, 58.1, and 23 are, respectively, the molar masses of propylene carbonate unit, of carbonic acid, of PO and of sodium. In comparison to the main population of chains corresponding to perfectly alternating structure, the two other populations of chains 313

Figure 1. Structural representation of functional initiators ABA (mono), TBAC (di), ASA (di), A-*m*PhA (di), ATMA (tri), and APMA (tetra) for copolymerization of CO₂/epoxide used in this work.

Scheme 1. Schematic Representation with Proposed Mechanism for Ammonium Carboxylate Initiated Copolymerization of Epoxide and CO₂

Table 1. Triethyl Borane Assisted Copolymerization of Propylene Oxide and Carbon Dioxide

Entry	Initiator	[M]:[I]:[A]	Selectivity ^b (%)	PC ^c (%)	Yield ^d (%)	$M_{n(\text{NMR})}$ ^e (kg/mol)	$M_{n(\text{GPC})}$ ^f (kg/mol)/Đ
1	ABA	500:1:2	>99	95	43	19.0	16.8/1.1
2	TBAC	40:1:2.8	95	91	93	-	4.1/1.1
3	TBAC	10:1:2.8	>99	90	95	-	1.1/1.4
4	TBAC	20:1:2.8	>99	93	96	-	2.1/1.2
5	TBAC	80:1:2.8	93	96	95	-	7.3/1.1
6	TBAC	100:1:2.8	95	99	90	-	9.2/1.1
7 ^g	TBAC	40:1:2.8	95	86	92	-	3.6/1.1
8 ^h	TBAC	40:1:2.8	95	53	90	-	3.4/1.1
9	ASA	40:1:4.0	95	63	92	3.6	3.5/1.2
10	ASA	40:1:3.0	92	80	90	3.7	3.9/1.1
11	ASA	40:1:2.0	92	98	95	3.9	4.3/1.1
12	A- <i>m</i> PhA	40:1:2.0	98	98	96	4.2	5.0/1.1
13	ATMA	40:1:3.0	>99	99	96	4.3	4.6/1.1
14	ATMA	60:1:3.0	95	99	95	5.5	6.6/1.1
15	ATMA	100:1:3.0	96	99	94	9.3	9.3/1.0
16	APMA	40:1:3.6	98	97	95	4.8	4.2/1.1
17	APMA	60:1:3.6	94	98	94	6.2	5.6/1.1

^aPolymerizations were carried out in 50 mL Parr reactor under 10 bar CO₂ with stirring at 40 °C. ^bThe ratio of linear to cyclic carbonate was determined by ¹H NMR of crude product. ^cDetermined from ¹H NMR. ^dCalculated by gravimetry. ^e $M_{n(\text{NMR})}$ was calculated based NMR data (due to lack of initiating protons of initiator TBAC, no values were provided for entries 2–8). ^fDetermined by GPC with THF as eluent and calibrated by polystyrene standard. ^gUnder 2 bar of CO₂. ^hunder 1 bar of CO₂ in glass reactor.

contain one and two additional PO units, respectively. To further confirm the terminal functionality of the polycarbonate sample prepared, one of the samples was stoichiometrically reacted with hexamethylene diisocyanate (HMDI) using Sn catalyst.⁸ The resulting reaction mixture was precipitated using water to achieve full recovery of all the polycondensates produced and even the nonreacted precursor as well. The obtained polycondensates were characterized by GPC and ¹H NMR (Figures 2B, S6). As can be seen, in comparison to its precursor, the GPC trace was symmetrical and completely shifted to high molar mass from 2.1 kg/mol to 20.7 kg/mol. No trace of the precursor was detected, indicating the absence of any monohydroxyl terminated PPC contained in the initial macrodiol prepared.

Besides TBAC tetrabutylammonium salts of succinic acid (ASA) and *m*-phthalic acid (A-*m*PhA) were also tried as difunctional initiators of the copolymerization of CO₂ with epoxides. In our first attempt to use ASA we targeted a DP of 40 for the copolymerization of CO₂ and PO and employed the same conditions as the one of entry 1 in Table 1, which aimed a DP of 500. To our surprise, although a high selectivity was eventually obtained, the carbonate content of resulting

polycarbonate diol decreased to 63% (entry 9). As discussed in detail in our previous work, besides the two copolymerization reactions between CO₂ and epoxides that afford the expected polycarbonate, other reactions can also occur such as the homopolymerization of cyclic ether which give polyether linkages and also backbiting reactions.^{13,39,42} If the amount of Lewis acid TEB added in excess is too large, the epoxide monomer can be too activated, and thus the formation of polyether can be favored. When synthesizing a polycarbonate diol sample of low DP maintaining a ratio of TEB to the initiating species equal to 2 as in the case of DP of 500 dramatically modified the ratio of [PO] to [TEB], and thus favored the activation of the epoxide and its homopolymerization. Upon decreasing the ratio of TEB to initiating species to 1.5 (entry 10, Table 1), the carbonate content in the corresponding sample increased from 63% to 80% with a 92% linear versus cyclic selectivity. Upon further decreasing the amount of TEB to initiator to 1.0 equiv, the carbonate content could be further increased to 98% and the selectivity kept unchanged (entry 11, Table 1, Figure S4, S7). The α,ω -dihydroxyl end-capped structure could be confirmed by MALDI-TOF analysis (Figure 3B). Using aromatic ammonium

Figure 2. Representative GPC traces of polycarbonate polyol samples from Table 1. (A) PPC-diol-1 (entry 3), PPC-diol-2 (entry 2), PPC-diol-3 (entry 5); (B) GPC overlay of PPC-diol-4 (entry 4) and polyurethane after its polycondensation with HMDI; (C) PPC-triol-1 (entry 13), PPC-triol-2 (entry 14), PPC-triol-3 (entry 15); and (D) PPC-tetraol-1 (entry 16), PPC-tetraol-2 (entry 17).

Figure 3. Representative MALDI-TOF characterization results of polycarbonate samples of diol and polyol. (A) PPC diol (entry 4, Table 1), (B) PPC diol (entry 11, Table 1), (C) PPC-triol (entry 13, Table 1), and (D) PPC tetraol (entry 16, Table 1).

(a) to (e) and (d) are found close to 1:1:5 and 1:2:10 (Figure 3A,D), confirming their triol and tetraol structure. Further, PPC triol and tetraol stars were characterized by MALDI-TOF mass spectrometry. As shown in Figure 3C and D, the main populations correspond perfectly to the alternating structure, and only one small population due to one more PO units incorporated into the backbone of the alternating carbonate is seen. In any case, both populations carry the same terminal hydroxyl groups as interpreted in Figure 3C and D, corroborating their triol and tetraol structure.

To demonstrate the versatility of our method of synthesis of polycarbonate polyols we carried out experiments aiming at fine-tuning the carbonate content of our samples, with in mind a variety of other applications than those mentioned above. For instance, more TEB was added to increase the incorporation of ether linkages in the copolymer (entry 9 and 10, Table 1). In another experiment, the pressure of CO₂ was decreased to lower the carbonate content in the polyol formed which is undoubtedly more economic than adding more TEB. With a

carboxylate salts obtained from *m*-phthalic acid similar polymerization results to that of ASA were obtained with A-mPhA as difunctional initiator (entry 12, Table 1, Figure S4).

Tri- and Tetrafunctional Polycarbonates. Besides linear polyurethanes that can be obtained by reacting PPC macrodiol with diisocyanate, cross-linked polyurethanes are also desired especially for applications requiring polyols as precursors. After the successful synthesis of PPC diols using the above-described difunctional ammonium salt initiator, we attempted the synthesis of PPC polyol stars.

The polymerization was carried out under similar conditions to the ones applied for the PPC diols, except that tri-(ATMA) and tetrafunctional (APMA) carboxylate ammonium salts were used as initiators. In these cases, 1.0 equiv of TEB to ATMA and 0.9 equiv to APMA were respectively charged to achieve alternating polycarbonate triols and tetraols, the molar masses of the various polyols could be varied by changing the ratio of PO to ATMA or APMA used as initiators. The results are listed in entries 13 to 17 in Table 1. ¹H NMR characterization gave access not only to the carbonate content but also to the molar mass of the sample thanks to the presence of the initiator aromatic moieties as shown in Figure 4A,C. Upon using the peak of the initiator aromatic proton as a reference, the molar masses of the obtained PPC stars could be calculated. The GPC analysis showed also unimodal and narrow distribution of molar masses (Figure 2C and D). The terminal functionality of hydroxyl groups was first characterized by ¹H NMR through derivatization of all the hydroxyls into urethane linkages, which is a technique widely applied for the hydroxyl quantification of hydroxyl functions in polymers.⁴³ After formation of urethane linkages upon reaction with phenyl isocyanate, a new group of peaks (d) unambiguously appeared at δ 6.9–7.5 ppm corresponding to phenyl group and (e) at δ 9.6–9.8 ppm from –NH protons of the urethane linkages (Figure 4B,D). Using the peak a from the initiator core moiety as reference, the intensity ratios of peak

Figure 4. ^1H NMR characterization results of polycarbonate polyols and their derivatized polymer with isocyanate. (A) PPC-triol (entry 13, Table 1, in CDCl_3) and (B) its derivative with phenyl isocyanate in $\text{DMSO}-d_6$; (C) PPC-tetraol (entry 16, Table 1, in CDCl_3) and (D) its derivative with phenyl isocyanate in $\text{DMSO}-d_6$.

undoubtedly an economic advantage. TBAC serves as an example for our recyclability study. After polymerization, the poly(propylene carbonate) chains that are formed and carry Bu_4N^+ cation at their ends are treated with water, leading to the formation of Bu_4NOH which readily migrate to the aqueous phase. Upon neutralization the latter phase with CO_2 TBAC is generated. Upon drying TBAC, it can be reused in the next cycle of polymerization under the same conditions as in the previous case: the polymerization results are listed in Table 2. As can be seen, very similar results were obtained, indeed, the molar masses of the PPC diols match well with the expected values, indicating the quantitative recovery of TBAC.

CONCLUSION

After serendipitously discovering that TBAC functions as an ideal initiator for the copolymerization of CO_2 with PO, mono, other di-, tri-, and tetrafunctional ammonium carboxylate initiators were synthesized and used, in the presence of TEB, to prepare ω -hydroxyl-polycarbonates with perfectly defined linear and star structures. Trialkyl boron ate complexes, formed between the latter Lewis acid and tetrabutylammonium carboxylates, turn to be efficient initiators for the synthesis of these mono-, di, tri, and tetrafunctional polycarbonate samples. Indeed, well-defined ω -hydroxyl-polycarbonates with linear and star structures and tunable carbonate content (50–96%), exhibiting molar mass from 1.0 to 10.0 kg/mol, were synthesized. These ω -hydroxyl low molar mass polycarbonates are perfectly suited to serve as precursors for polyurethane synthesis in a variety of applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00122.

Characterization data of initiators and polycarbonate samples: NMR, GPC (PDF)

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pressure of CO_2 of 2 bar, the carbonate content in the polycarbonate produced decreased to 86% (entry 7, Table 1) and when the polymerization was carried out in a glass reactor under 1 bar, the carbonate content of the produced macrodiol further dropped to 53% (entry 8, Table 1).

Recyclability of Ammonium-Based Initiators. As our strategy of PPC synthesis resorts to the use of initiators it necessarily requires a large amount of initiators when telechelics of low molar mass are targeted. We thus developed a method to recycle these ammonium-based initiators and showed that they can be reused several times, which is

Table 2. Recyclability of TBAC for the preparation PPC-diol^a

Entry	Initiator TBAC	[M]:[I]:[A]	Selectivity ^b (%)	PC ^c (%)	Yield ^d (%)	$M_{n(\text{theo})}$ ^e (kg/mol)	$M_{n(\text{GPC})}$ ^f (kg/mol)/Đ
1	Fresh	50:1:2.8	93	95	66	3.3	3.0/1.1
2	cycle- I	50:1:2.8	94	91	59	2.9	2.8/1.3
3	cycle- II	50:1:2.8	98	90	52	2.6	2.7/1.2
4	Fresh	20:1:2.8	95	93	69	1.4	1.6/1.5
5	cycle- I	20:1:2.8	98	96	71	1.4	1.6/1.3
6	cycle- II	20:1:2.8	91	99	73	1.5	1.4/1.4
7	cycle- III	20:1:2.8	95	86	74	1.5	1.6/1.3

^aPolymerizations were carried out in 50 mL Parr reactor under 10 bar CO_2 with stirring at 40 °C. ^bRatio of linear to cyclic carbonate was determined by ^1H NMR of crude product. ^cDetermined from ^1H NMR. ^dCalculated by gravimetry. ^eCalculated based on the formula: $M_{n(\text{theo})} = 102 \times \text{DP}_{\text{target}} \times \text{yield}\%$. ^fDetermined by GPC with THF as eluent and calibrated by polystyrene standard.

467 **Notes**

468 The authors declare no competing financial interest.

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