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

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ABSTRACT: Tetrabutylammonium carbonate (TBAC) which is obtained by treating CO₂ with tetrabutylammonium hydroxide is shown to perform as an ideal difunctional initiator for the copolymerization of carbon dioxide (CO₂) and propylene oxide (PO) in the presence of triethylborane (TEB). In this system, CO₂ thus serves as the initiating moiety of its own copolymerization with epoxides when used in the form of a carbonate salt. Based on this remarkable result, mono-, tri-, and tetrafuctional ammonium carboxylate initiators and also other difunctional carboxylate initiators were synthesized and used for the synthesis of well-defined ω-hydroxy-polycarbonates with linear and star structures. Well-defined telechelics, three- and four-armed star samples of molar mass varying from 1 kg/mol to 10 kg/mol, with around 95% carbonate content, were successfully synthesized. The structure of the obtained polycarbonate ω-polyols were characterized by 1H NMR, MALDI-TOF, and GPC. The terminal hydroxyl functionality of polycarbonate diol was further used for polycondensation with diisocyanates to a functionality of polycarbonate diol was further used for polycondensation with diisocyanates to a

INTRODUCTION

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

Although much progress has been made during the past two decades in the preparation of polycarbonate of high molar mass and high carbonate content,¹³–¹⁷ the preparation of low molar mass polycarbonate diols and polyols with well-defined 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 magnesium.²⁸–³² 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 polycondensation applications. As clearly demonstrated by Sugimoto et al.,³³ polycarbonate tetrol and hexeol samples using...
tetraphenylporphyrinatocobalt(III) chloride as catalyst and prepared in the presence of tetra- and hexafunctional carboxylic acids are contaminated with linear polycarbonate chains that have to be removed by fractionation. In the case of the synthesis of polycarbonate diols, such monohydroxyl linear polycarbonate impurities are difficult to eliminate by fractionation.

Polycarbonate diols can also be obtained by another strategy, consisting of the preparation of a polycarbonate of rather a high molar mass (80 to 100 kg/mol), followed by alcoholysis in the presence of “molecular” diols and an inorganic catalyst. Both the teams of Lee and Meng followed this general strategy, although Lee started from a high molar mass poly(ethylene carbonate) prepared by polycondensation while Meng used a polycarbonate obtained by copolymerization of PO with CO2. In both cases rather harsh conditions were used, which eventually afforded polycarbonate diol samples of broad molar mass distribution contaminated with cyclic byproducts.

In contrast to all catalytic systems investigated and developed so far, our group recently proposed a new metal-free approach allowing the successful copolymerization of CO2 and epoxides by boron-based ate complexes. In the presence of these ate complexes and an excess of trialkyl borane, a quaternary onium salt so far used as initiator for the copolymerization of CO2 with epoxides to afford α-chloro, α-ω-hydroxyl polycarbonates. We serendipitously discovered that tetrabutylammonium carbonate behaves as an ideal initiator for the copolymerization of CO2 with epoxides in the presence of triethylborane (TEB), allowing well-defined α,ω-hydroxyl polycarbonate telechelics. This result prompted us to consider polycarbonate initiators worked best for the copolymerization of CO2 with epoxides. Unlike onium chloride salts, carboxylic acids are very common compounds either as natural or synthetic products. In polymer chemistry compounds fitted with carboxylic acids have been mainly used as monomer in polycondensation reactions and seldom as an initiator to ring-open the polymerization of cyclic monomers. Unlike hydroxyl-carrying compounds. In the present work we show that carboxylate salts of tetrabutylammonium of various functionality ranging from 1 to 4 can successfully be used to initiate the copolymerization of CO2 with propylene oxide (PO) and generate poly(propylene carbonate) (PPC) samples carrying one, two, three, and four terminal hydroxyl groups, respectively, in the presence of TEB. Remarkably, tetrabutylammonium carbonate which is an ideal difunctional initiator could be obtained upon treating tetrabutylammonium hydroxide with CO2. In addition, this tetrabutylammonium carbonate initiator could be quantitatively recycled. Upon changing slightly the polymerization conditions, the molar mass (1000 to 10 000 g/mol) and carbonate content (50–96%) could be easily tuned. All samples featured narrow PDI s (GPC), and their carbonate content and terminal functionality were confirmed by NMR and MALDI-TOF characterization. The end group functionality of the obtained polycarbonate diols and polyls was further demonstrated by carrying out polycondensation reactions with hexamethylene diisocyanate and phenyl isocyanate. The telechelic diols and the polyls 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-butyl-phenyl)-2-methyl-1-propanylidene] mononitrile (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. 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.

Tetrabutyl Ammonium Salt of Benzoic Acid (ABA). 1H NMR (400 MHz, DMSO-d6), δ 7.79 (t, 8H), 1.22 (m, 12H), 0.86 (m, 18H). 13C NMR (100 MHz, CDCl3), δ 150.7, 57.4, 23.1, 19.2, 13.5. General Procedure for Synthesis of Tetrabutyl Ammonium Salt of Carboxylic Acid. In a Schlenk tube 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 the corresponding tetrabutylammonium carboxylate salt as a white powder.

Tetrabutyl Ammonium Salt of P-Methacrylic Acid (A-MpA). 1H NMR (500 MHz, DMSO-d6), δ 8.52 (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 (100 MHz, DMSO-d6), δ 176.2, 57.3, 37.9, 23.1, 19.2, 13.5. Tetrabutyl Ammonium Salt of M-Phthalic Acid (A-MpA). 1H NMR (500 MHz, DMSO-d6), 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-d6), δ 168.8, 141.1, 129.9, 128.4, 124.7, 75.3, 23.1, 19.2, 13.5. Tetrabutyl Ammonium Salt of Trimesic Acid (ATMA). 1H NMR (500 MHz, DMSO-d6), δ 8.11 (s, 3H), 3.18 (t, 24H), 1.57 (m, 24H). 13C NMR (100 MHz, DMSO-d6), δ 169.9, 139.5, 129.8, 57.5, 23.1, 19.2, 13.5. Tetrabutyl Ammonium Salt of Hexahydropyrene-1,4,5,8-Pentatetraenecarboxylic Acid (AP ppm). 1H NMR (500 MHz, DMSO-d6), δ 6.90 (s, 2H), 3.18 (t, 32H), 1.56 (m, 32H). 13C NMR (100 MHz, DMSO-d6), δ 173.56, 139.49, 126.02, 57.44, 23.05, 19.17, 13.45. PolymORIZATION. 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.
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. 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 hydroxide. The choice of tetrabutylammonium hydroxide. The choice of tetrabutylammonium hydroxide 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—actual anate complex—for 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 nucelophilic 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. 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 carbonate 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 × 58.1 + 23, 102.09n + 62 + 2 × 58.1 + 23, 102.09n + 62 + 4 × 58.1 + 23, where 102.09, 62, 58.1, and 30 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...
contain one and two additional PO units, respectively. To further con
firm 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-mPhA) 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 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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>[M]:[I]:[A]</th>
<th>Selectivity(T) (%)</th>
<th>PC (%)</th>
<th>Yield(%)</th>
<th>M&lt;sub&gt;n(NMR)&lt;/sub&gt; (kg/mol)</th>
<th>M&lt;sub&gt;n(GPC)&lt;/sub&gt; (kg/mol)/Đ</th>
<th>D</th>
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<tbody>
<tr>
<td>1</td>
<td>ABA</td>
<td>500:1:2</td>
<td>&gt;99</td>
<td>95</td>
<td>43</td>
<td>19.0</td>
<td>16.8/1.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>TBAC</td>
<td>40:1:2.8</td>
<td>95</td>
<td>91</td>
<td>93</td>
<td>-</td>
<td>4.1/1.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TBAC</td>
<td>10:1:2.8</td>
<td>&gt;99</td>
<td>90</td>
<td>95</td>
<td>-</td>
<td>1.1/1.4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TBAC</td>
<td>20:1:2.8</td>
<td>&gt;99</td>
<td>93</td>
<td>96</td>
<td>-</td>
<td>2.1/1.2</td>
<td></td>
</tr>
<tr>
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<td>TBAC</td>
<td>80:1:2.8</td>
<td>93</td>
<td>96</td>
<td>95</td>
<td>-</td>
<td>7.3/1.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>TBAC</td>
<td>100:1:2.8</td>
<td>95</td>
<td>99</td>
<td>90</td>
<td>-</td>
<td>9.2/1.1</td>
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<tr>
<td>7&lt;sup&gt;g&lt;/sup&gt;</td>
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<td>86</td>
<td>92</td>
<td>-</td>
<td>3.6/1.1</td>
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<td>90</td>
<td>-</td>
<td>3.4/1.1</td>
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<td>63</td>
<td>92</td>
<td>3.6</td>
<td>3.5/1.2</td>
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<tr>
<td>10</td>
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<td>92</td>
<td>80</td>
<td>90</td>
<td>3.7</td>
<td>3.9/1.1</td>
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<tr>
<td>11</td>
<td>ASA</td>
<td>40:1:2.0</td>
<td>92</td>
<td>98</td>
<td>95</td>
<td>3.9</td>
<td>4.3/1.1</td>
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<tr>
<td>12</td>
<td>A-mPhA</td>
<td>40:1:2.0</td>
<td>98</td>
<td>98</td>
<td>96</td>
<td>4.2</td>
<td>5.0/1.1</td>
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<tr>
<td>13</td>
<td>ATMA</td>
<td>40:1:3.0</td>
<td>&gt;99</td>
<td>99</td>
<td>96</td>
<td>4.3</td>
<td>4.6/1.1</td>
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<tr>
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<td>ATMA</td>
<td>60:1:3.0</td>
<td>95</td>
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<td>5.5</td>
<td>6.6/1.1</td>
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<td>15</td>
<td>ATMA</td>
<td>100:1:3.0</td>
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<td>99</td>
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<td>9.3</td>
<td>9.3/1.0</td>
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<tr>
<td>16</td>
<td>APMA</td>
<td>40:1:3.6</td>
<td>98</td>
<td>97</td>
<td>95</td>
<td>4.8</td>
<td>4.2/1.1</td>
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<td>94</td>
<td>6.2</td>
<td>5.6/1.1</td>
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<sup>a</sup>Polymerizations were carried out in 50 mL Parr reactor under 10 bar CO2 with stirring at 40 °C. The ratio of linear to cyclic carbonate was determined by 1H NMR of crude product. Determined from 1H NMR. Calculated by gravimetry. M<sub>n(NMR)</sub> was calculated based NMR data (due to lack of initiating protons of initiator TBAC, no values were provided for entries 2–8). Determined by GPC with THF as eluent and calibrated by polystyrene standard. Under 2 bar of CO2. Under 1 bar of CO2 in glass reactor.

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Macromolecules XXXX, XXX, XXX − XXX

Macromolecules XXXX, XXX, XXX − XXX
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 quantitative analysis of hydroxyl functions in polymers. 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 (a) to (e) and (d) are found close to 1:1:5 and 1:2:10 (Figure 4B,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...
Indoubtedly an economic advantage. TBAC serves as an example for our recyclability study. After polymerization, the poly(propylene carbonate) chains that are formed and carry Bu₄N⁺ cation at their ends are treated with water, leading to the formation of Bu₄NOH which readily migrate to the aqueous phase. Upon neutralization the latter phase with CO₂, 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, quite comparable to those generated from the fresh initiators; 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 CO₂ 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 tetrafuctional 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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### Table 2. Recyclability of TBAC for the preparation PPC-diol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator TBAC</th>
<th>[M]:[I]:[A]</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>Mₙ(thero) (kg/mol)</th>
<th>Mₙ(GPC) (kg/mol)/Đ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fresh</td>
<td>50:1:2.8</td>
<td>93</td>
<td>95</td>
<td>66</td>
<td>3.3</td>
</tr>
<tr>
<td>2</td>
<td>cycle- I</td>
<td>50:1:2.8</td>
<td>94</td>
<td>91</td>
<td>59</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>cycle- II</td>
<td>50:1:2.8</td>
<td>98</td>
<td>90</td>
<td>52</td>
<td>2.6</td>
</tr>
<tr>
<td>4</td>
<td>Fresh</td>
<td>20:1:2.8</td>
<td>95</td>
<td>93</td>
<td>69</td>
<td>1.4</td>
</tr>
<tr>
<td>5</td>
<td>cycle- I</td>
<td>20:1:2.8</td>
<td>98</td>
<td>96</td>
<td>71</td>
<td>1.4</td>
</tr>
<tr>
<td>6</td>
<td>cycle- II</td>
<td>20:1:2.8</td>
<td>91</td>
<td>99</td>
<td>73</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>cycle- III</td>
<td>20:1:2.8</td>
<td>95</td>
<td>86</td>
<td>74</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Polymerizations were carried out in 50 mL Parr reactor under 10 bar CO₂ with stirring at 40 °C. †Ratio of linear to cyclic carbonate was determined by 'H NMR of crude product. ‡Determined from 'H NMR. §Calculated by gravimetry. ‖Calculated based on the formula: \( M_{n(thero)} = 102 \times D P_{target} \times \text{yield} \times \% \). Determined by GPC with THF as eluent and calibrated by polystyrene standard.


