Poly(urethane–carbonate)s from Carbon Dioxide

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Supporting Information

ABSTRACT: A one-pot, two-step protocol for the direct synthesis of polyurethanes containing few carbonate linkages through polycondensation of diamines, dihalides, and CO₂ in the presence of Cs₂CO₃ and tetrabutylammonium bromide is described. The conditions were optimized by studying the polycondensation of CO₂ with 1,6-hexanediame and 1,4-dibromobutane as model monomers. Then, various diamines and dihalides were tested under optimal conditions. Miscellaneous samples of such carbonate-containing polyurethanes exhibiting molar masses from 6000 to 22 000 g/mol (GPC) and yields higher than 85% were obtained. The thermal properties of such polyurethanes were unveiled by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA): they were found very similar to those of traditional polyurethanes obtained by diisocyanates + diols polycondensation.

INTRODUCTION

The continuously rising level of carbon dioxide (CO₂) in the atmosphere makes it one of the major contributors to the so-called greenhouse effect.1-3 Besides efforts of reducing its emission and capturing it, attempts have also been made to chemically transform CO₂ to commodity chemicals such as urea, carbonates, methanol, salicylic acid, etc.4-10

In the area of polymers, polyurethanes are one of the most important industrial family of polymers, which have been widely used in our daily life, ranging from flexible foams for bed mattresses to rigid foams for thermal insulation, corrosion resistant coatings, elastomers, and components of adhesives.11-13 Traditionally, the preparation of polyurethanes involved the polycondensation of disocyanates and diols, in which great caution has to be taken to deal with the highly toxic and water-sensitive nature of isocyanate monomers (Scheme 1A).12-15 The cationic ring-opening polymerization of aliphatic cyclic urethanes (Scheme 1B) is another option that gives access to aliphatic polyurethanes, but it requires the prior synthesis of cyclic urethanes from α,ω-amino acids and phosgene.16,17 As an alternative to phosgene-based processes, polyurethanes could be synthesized more directly from aziridines through copolymerization with CO₂ (Scheme 1C).18 At present, the two most studied and promising synthetic routes toward polyurethanes are (i) the polycondensation of dicarbonates with diamines or of dicarbamates with diols (Scheme 1D)19-21 and (ii) the ring-opening polymerization of bicyclic carbonates by diamines in a step-growth mode producing the so-called poly(hydroxyurethane)s (Scheme 1E).22,23 These two methods also require the prior phosgene-based synthesis of carbonates but can now be generated using CO₂, which adds credit to these approaches.

However, to the best of our knowledge, the direct synthesis of polyurethane from CO₂ and diamines has not been reported so far. Similarly to the case of carbonates, urethanes or carbamates can be synthesized using CO₂ as starting material in a three-component coupling reaction involving amines or alcohols and halides.24-34 In a previous communication, we reported the synthesis of polycarbonates through direct polycondensation of CO₂ with diols and dihalides in the presence of an appropriate base.35 Our experimental results indicated that Cs₂CO₃ is the most effective base for the polycondensation of CO₂ with diols and dihalides, allowing the synthesis of polycarbonates of high molar masses. In continuation of our efforts to promote the utilization of CO₂, we report here the direct synthesis of polyurethanes from CO₂, diamines, and dihalides as shown in Scheme 1H. This methodology can not only be applied to the synthesis of aliphatic polyurethanes from aliphatic diamines and dihalides but also open the possibility of generating miscella-
neous polyurethanes having all possible combinations between aliphatic/aromatic dihalides and diamines.

**EXPERIMENTAL SECTION**

**Materials.** All reactions were carried out using a dry stainless autoclave vessel (50 mL). 1,4-Dibromobutane (>99%) was purchased from Alfa Aesar and distilled over CaH₂ prior to use. Anhydrous 1-methyl-2-pyrrolidinone (Sigma-Aldrich, 99.5%), 1,4-bis(chloromethyl)benzene (Aldrich, 98%), 1,6-hexanediame (Aldrich, 99%), 1,4-butanediame (Aldrich, 99%), 1,8-octanediame (Aldrich, 98%), 1,10-decanediame (Aldrich, 97%), 1,12-dodecanediame (Aldrich, 98%), 4,4′-diaminodicyclohexylmethane (Aldrich, 98%), and 1,4-

Table 1. Screening Polycondensation Reaction Conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>X (equiv)</th>
<th>Y (bar)</th>
<th>temp (°C)</th>
<th>ammonium salt</th>
<th>isolated yield (%)</th>
<th>(M_n) (g/mol)</th>
<th>(\bar{D})</th>
<th>PU/PC</th>
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All reactions were conducted on 1 mmol scale, 2 mL of NMP, NMP = 1-methyl-2-pyrrolidinone. \(^M_n\) and polydispersity index (\(\bar{D}\)) data were obtained after chemical modification using trifluoroacetic anhydride and then analysis by GPC with CHCl₃ as eluent (based on polystyrene standards). \(^{1}H\) NMR of the polymer at 120 °C. PU = polyurethane, PC = polycarbonate. \(^K_2CO_3\) was used. \(^3\)0 equiv of \(\text{Cs}_2\text{CO}_3\) was used. \(^0.5\) equiv of \(\text{Bu}_4\text{N}^+\text{Cl}^-\) was used. \(^1.5\) equiv of \(\text{Bu}_4\text{N}^+\text{HSO}_4^-\) was used. \(^h\) The reaction time was 48 h.
phenylenedimethanamine (Aldrich, 99%) were used as received. Cs2CO3 and K2CO3 (Alfa Aesar) were used as received.

**Instruments and Measurements.** 1H and 13C NMR spectra were recorded on a Bruker AV600 (FT, 600 MHz for 1H; 150 MHz for 13C) spectrometer in deuterated DMSO at 20 °C. All signals are reported in ppm. Infrared (IR) spectra were obtained using a Thermo Nicolet iS10 infrared spectrometer. Gel permeation chromatography measurements were carried out on a Viscotec GPC instrument with styragel HR 2 THF and styragel HR 4 THF columns at 35 °C calibrated with polystyrene (PS) standards. Chloroform was used as eluent at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 in an inert atmosphere (nitrogen). The sample was heated from 25 to 230 °C, cooled to 25 °C, and finally heated again to 230 °C with a heating/cooling rate of 10 °C/min. The second heating curve was used to determine the glass transition temperature (Tg), melting temperature (Tm), and degree of crystallinity. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo DSC1/TC100 between 25 and 500 °C with a heating rate of 10 °C/min and in nitrogen with a flow rate of 20 mL/min.

**Polymerization Procedure.** A typical procedure for the polycondensation of 1,6-hexanediol, 1,4-dibromobutane, and CO2 (Table 1, entry 1) was performed as follows: To a dried 50 mL stainless autoclave vessel equipped with a triangular stirring bar (size: 35 x 9 mm), 1,6-hexanediol (116.2 mg, 1.0 mmol), 1-methyl-2-pyrrolidinone (NMP, 2 mL), Cs2CO3 (1.303 g, 4.0 mmol), and tetrabutylammonium bromide (TBAB) were successively added, and then the autoclave was sealed. The autoclave was charged to react with CO2 to 10 bar. The reaction mixture was gently stirred (400 rpm) at room temperature for 3 h (the stirring rate should be controlled to ensure good mixing and minimize the splashing). After 3 h, the stainless autoclave was opened, CO2 was released gently, 1,4-dibromobutane (105 Pa), in the presence of 4.0 equiv of Cs2CO3 and 1 equiv of TBAC for 24 h (Table 1, entry 1); an insoluble white solid was obtained after purification through precipitation in water to eliminate the salts. This solid could not be dissolved in any common organic solvent at room temperature. The infrared spectrum of the solid showed absorptions attributable to N=O bond and C=O double-bond stretching vibrations at around 3317 and 1682 cm⁻¹, which are the corresponding characteristic absorptions of urethane functions (Figure 1).

![Figure 1. IR spectrum of obtained poly(urethane-carbonate) 2a in Table 1, entry 1.](image)

**RESULTS AND DISCUSSION**

For the successful synthesis of carbamates via three-component coupling involving CO2, alkylamines, and alkyl halides, it is essential that side reactions, such as N-alkylation of amines or alkylolation of carbamates by alkyl halides, be avoided or suppressed as shown in Scheme 2. Especially, in the synthesis of polyurethanes from difunctional monomers, such alkylolation side reactions would result not only in the formation of cross-linked products but also in the elimination of amide hydrogen. The absence of the hydrogen bond forming amide hydrogen would dramatically affect the properties of the polyurethanes. It was reported that the presence of tetrabutylammonium halide could effectively prevent direct N-alkylations or overalkylation of the formed carbamates.

To start, we chose 1,6-hexanediol and 1,4-dibromobutane as model monomers for the condensation with CO2 in the presence of Cs2CO3 and tetrabutylammonium chloride (TBAC). To effectively avoid N-alkylation, CO2 was first charged to react with diamine before 1,4-dibromobutane was added. The reaction was first performed at 80 °C with 10 bar of CO2 pressure (1 bar = 105 Pa), in the presence of 4.0 equiv of Cs2CO3 and 1 equiv of TBAC for 24 h (Table 1, entry 1); an insoluble white solid was obtained after purification through precipitation in water to eliminate the salts. This solid could not be dissolved in any common organic solvent at room temperature. The infrared spectrum of the solid showed absorptions attributable to N=O bond and C=O double-bond stretching vibrations at around 3317 and 1682 cm⁻¹, which are the corresponding characteristic adsorptions of urethane functions (Figure 1).

![Figure 2. IR spectrum of obtained poly(urethane-carbonate) 2a in Table 1, entry 1.](image)

**Scheme 2. Carbamate Formation and Side Reactions**

![Scheme 2](image)
methylene protons are detected respectively at 1.62 (c) (\(\beta\) position of butyl group) and 1.44 (d) and 1.29 ppm (e) (\(\beta\) - and \(\gamma\) positions of the hexyl group connected to the carbamate). Especially, the ratio of peaks f to b, d, e in both polyurethane 2a and 2a’ cases is close to 1:2:2:2, indicating the presence and integrity of NH proton and thus the absence of an overalkylation of the produced polyurethane. A close look at the area next to peaks a and c in Figure 2 indicates the presence of two small signals appearing at \(\delta = 4.12\) (a’) and \(\delta = 1.68\) ppm (c’), attributable to the butylene groups linking carbonate groups. Our previous investigation on the polycondensation between diols, CO\(_2\), and dihalides \(\text{35}\) revealed that 1,4-dibromobutane could self-polycondense. Under similar conditions, such self-polycondensation of dihalides also occurred during the polycondensation of diamines with CO\(_2\) and dihalides, giving rise to some carbonate linkages (for comparison, please see Figure S2 for \(^1\)H NMR of poly(urethane−carbonate) 2a and polycarbonate). From the integration ratio between the methylene signal at \(\delta = 3.98\) (a) and the one at \(\delta = 4.12\) (a’), the ratio of polyurethane (PU) to polycarbonate (PC) linkages in the polymer formed could be calculated (for Table 1, entry 1, PU/PC = 6.8/1). The characterization by \(^{13}\)C NMR further confirms the polyurethane structure (see Figure S3 for \(^{13}\)C NMR spectrum of polyurethane 2a). The peaks at \(\delta = 155.88\) (f), 62.93 (a), 39.98 (c), 28.85 (b), 25.54 (d), and 25.03 (e) ppm are due to the carbamate linkages. Further derivatization of sample with trifluoroacetic anhydride gave more information about the terminal functional groups. As shown in Figure S4, only hydroxyl groups could be detected in polyurethane 2a’ prepared through conventional diisocyanate + diol polycondensation. In this investigation, both hydroxyl and amine terminal groups could be detected by the presence of peaks at 4.40 and 3.38 ppm attributable to the methylene groups connected respectively to the terminal esters and amides formed after reaction of the hydroxyls and amines with TFA. Using these two peaks as reference, the molar mass could be estimated (see Supporting Information III for details). Because of the insolubility of the prepared polyurethane in common organic solvent, special modification had to be carried out to break the strong hydrogen bonding before GPC analysis. As demonstrated for the NMR characterization, a chemical modification by TFA could significantly improve the PU solubility, and such modified PU polymer could well be analyzed by the GPC. This technique was already reported for the GPC analysis of polyamides and polyurethanes. \(\text{37–41}\) The molar mass of polyurethane 2a’ synthesized from 1,4-butanediol and 1,6-diisocyanatohexane was determined, and a \(M_{n(GPC)}\) value equal to 7000 g/mol (Table 2, entry 0) was obtained: this result is in the range of those reported in the literature, \(\text{15,36}\) but one has to keep in mind that \(M_{n(GPC)}\) value includes the contribution of TFA moieties. Some representative GPC traces of poly(urethane−carbonate)s prepared under different reaction conditions are shown in Figure 3.
218 Then different polycondensation conditions were tried, and 219 the related results are summarized in Table 1. As expected, 220 Cs₂CO₃ led to better results and yields than K₂CO₃. In the case of 221 K₂CO₃ used as a base, only a 4% yield could be obtained (Table 2, entry 2). This is in agreement with other results reported in 222 organic synthesis which also observed the effectiveness of cesium 223 carbonate. Given its size, this cation exhibits a weak 224 association with anions, thus enhancing the nucleophilicities of 225 the corresponding amide anion and carbamate species which in 226 turn are more reactive toward the relatively inert carbon dioxide 227 and halides. For the rest of the study it was thus decided to use 228 Cs₂CO₃ as the base promoting the reaction between diamines, 229 dihalides, and CO₂. When the reaction was performed at 60 or 230 100 °C, poly(urethane—carbonate) samples 2a were isolated in a 232 58–65% yield with a PU/PC ratio around 6/1, and molar masses 233 ranging from 2500 to 4000 g/mol (Table 1, entries 3 and 4), 234 results which were not as good as those obtained at 80 °C. We also studied the stoichiometric factor between diamines 236 and dihalides: theoretically, for obtaining the polymer of highest 237 possible molar mass, the stoichiometry between the various 238 functional groups involved in the polycondensation must be kept 239 equal to 1. But in this case we observed that using a slightly excess 240 of dibromide (1.05 equiv) helped to increase both the yield of 241 polymer and the molar mass (around 6000 g/mol) of the 242 polymer formed (Table 1, entries 5 and 6). As one can see from 243 the NMR characterization of the obtained poly(urethane— 244 carbonate) 2a (Figure 2), a slight excess of dibromide could 245 compensate for its consumption by self-polycondensation. The 246 effect of the pressure of CO₂ was also investigated: both the yield 246

<table>
<thead>
<tr>
<th>Entry</th>
<th>H₂N—R₁—NH₂</th>
<th>X—R₂—X</th>
<th>Polymer 2 / Isolated yield</th>
<th>Mₙ,GPC (g/mol) /</th>
<th>Mₙ,NMR</th>
<th>Tₑ (°C)</th>
<th>Tᵢₙ / Tᵢₘ (°C)</th>
<th>PU/PC</th>
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Table 2. Polycondensation of CO₂ with Various Diamines and Dihalides

*All the reactions were conducted on 1 mmol scale, 2 mL of NMP, NMP = 1-methyl-2-pyrrolidinone, TBAB = tetrabutylammonium bromide. Yield was obtained after precipitation from H₂O and dried at 50 °C under vacuum overnight. Mₙ and polydispersity index (Đ) data were obtained after chemical modification using trifluoroacetic anhydride and then analysis by GPC with CHCl₃ as eluent (based on polystyrene standards). Mₙ were calculated by NMR at room temperature after chemical modification by trifluoroacetic anhydride (see Supporting Information for details). Measured by ¹H NMR of the polymer at 120 °C, PU = polyurethane, PC = polycarbonate. Polyurethane synthesized from 1,4-butanediol and 1,6-diisocyanatothexane (according to the method of ref 11).
(45–65%) and the molar mass of obtained polymer tend to decrease but the extent of urethane linkages tend to increase when the reaction was performed under 1.0 and 20 bar (Table 1, entries 7 and 8). Extending the reaction time did not help to increase the yield and molar mass of the obtained polymer (Table 1, entry 12). Because of the limited solubility of Cs₂CO₃ in NMP, more of this base was necessary to increase the molar mass of the polymer, but the content of urethane linkages as well (Table 1, entry 5 vs entry 9). Ammonium salts were also found crucial to the structure of produced polymer. Only ammonium halides could significantly and efficiently push polycondensation reactions. In the presence of tetrabutylammonium hydrogen-sulfate (Bu₄N⁺HSO₄⁻) and tetrabutylammonium acetate (Bu₄N⁺OAc⁻) less polymer was produced, similarly to the experiment carried out in the absence of any salts (Table 1, entries 13–15). With a 50% equivalent of TBAC the PU sample isolated exhibited only a molar mass of 14 000 g/mol and a very low urethane content (PU/PC = 4.0/1) (Table 1, entry 10). Bromide salts (TBAB) brought about similar results to the chloride salts (Table 1, entry 14). On the other hand, the iodide salt led to a polymer with high molar mass but with low content in urethane linkages (Table 1, entry 17). The activation of dibromobutane through the exchange with iodide might have promoted its self-condensation to form carbonate linkages. Based on the above optimization experiments, all polycondensation reactions were carried out thereafter under the following conditions: 80 °C for 24 h under 10 bar of CO₂ with the following feeding ratio of diamine:TBAB:dihalide:Cs₂CO₃ (1:1:0.5:4.0 equiv.). Diamines and dihalides of different structures were then tried to check the versatility of this synthetic method, the results obtained being summarized in Table 2. When carrying out the polycondensation of 1,4-butanediamine with 1,4-dibromobutane in the presence of CO₂, poly(urethane−carbonate) 2b was obtained with a ratio of PU/PC (5/1) in 60% yield (Table 2, entry 2). With the increase of the distance between amino groups, the yield of the polymers obtained increased accordingly; however, the ratio of PU/PC (around 3.5/1) decreased concomitantly (Table 2, entries 4 and 5). 1,4-Phenylenedimethanamine as monomer also worked well to afford corresponding poly(urethane−carbonate) 2f with high ratio of PU/PC (15/1) in 88% yield (Table 2, entry 6). To our surprise, 4,4′-diaminocyclohexylmethane carrying two secondary amino groups afforded a poly(urethane−carbonate) sample with 87% yield and a high PU/PC ratio (10/1) and high molar mass (22 400 g/mol) despite unfavorable steric hindrance (Table 2, entry 7). When 1,4-dibromobutane was replaced by 1,4-bis(chloromethyl)benzene to react with the different diamines used above under the same conditions, poly(urethane−carbonate)s 2h−2n with Mₙ up to 5900 in 66−90% yield could be isolated (Table 2, entries 8−14).

To better understand this three-component polycondensation, control experiments were carried out under different conditions as shown in Scheme 3. Indeed, similarly to our previously reported results on the synthesis of polycarbonates, dibromobutane was also found here to self-condense, the presence of TBAB being unable to totally suppress this side reaction: a polycarbonate with Mₙ up to 2300 under 10 bar of CO₂ was produced (Scheme 3, reaction A, see Figure S5). However, no self-condensation reaction occurred in the case of diamine and CO₂. No polymer was generated in the absence of CO₂.
CO$_2$, indicating that Cs$_2$CO$_3$ is not a source of CO$_2$ and that carbamate linkages only come from CO$_2$ gas (Scheme 2, reactions B and C).

On the basis of the above experimental results poly(urethane–carbonate)s are thus formed from the sequence of reactions shown in Scheme 4. The amine functions are first deprotonated by Cs$_2$CO$_3$ and then react with CO$_2$ to produce carbamate salts. Ion exchange reaction takes place between the carbamate salt and tetrabutylammonium bromide. As a result, the carbamate anions are activated by tetrabutylammonium ions and readily react with halides in a nucleophilic substitution that bring about the formation of carbamate. The repetition of these steps afford polyurethanes. Concomitantly, trace amount of carbonate anions can be generated by direct replacement of halides by Cs$_2$CO$_3$, which would further react with halides to generate carbonate linkages. In this case, these carbonate linkages would be incorporated into the polyurethanes through self-polycondensation of halides. This is clearly indicated by the small signals appear at $\delta = 4.12$ ($a'$) and $\delta = 1.68$ ($c'$) in the $^1$H NMR spectra of poly(urethane–carbonate) 2a (Figure 2).

The thermal properties of synthesized poly(urethane–carbonate)s were investigated by differential scanning calorimetry (DSC) (Figure 4 and Table 2). Poly(urethane–carbonate) 2a produced through this three-component polycondensation exhibits similar properties to those of polyurethane 2a$'$ prepared from conventional polycondensation process (Figure 4, PU 2a vs 2a$'$). PUs with different thermal behaviors were observed depending on the monomers used. As expected, the polymers exhibit decreasing melting points as the size of methylene units (from C$_4$ to C$_{12}$) between two amino groups increases (Table 2, entries 1–5; Figure 4, PU 2a$-$2e and entries 8–12; Figure 4, PU 2h$-$2l, $T_m$ values). When the aromatic diamine (1,4-phenylenedimethanamine) was used as monomer, poly(urethane–carbonate) 2f showed a melting transition at 227 °C (Table 2, entry 4, $T_m$ value), whereas the $T_g$ of poly(urethane–carbonate) 2m was found equal to 83 °C (Table 2, entry 13, $T_g$ value). Poly(urethane–carbonate)s 2g and 2n derived from secondary diamine (4,4$'$-diaminodicyclohexylmethane) exhibited higher $T_g$ values at 108 and 140 °C (Table 2, entries 7 and 14, $T_g$ value), and no melting points were found.

The thermal stability of poly(urethane–carbonate) was then studied by thermal gravimetric analysis (TGA) in a nitrogen atmosphere (see Figure 5 for TGA traces). Poly(urethane–carbonate) 2a synthesized from this three-component polycondensation and polyurethane 2a$'$ prepared from conventional polycondensation process were both stable up to 280 °C, while...
polyurethane 2a’ had a higher residue mass percentages than poly(urethane–carbonate) 2a (see Figure S6, PU 2a vs 2a’). Except for poly(urethane–carbonate)s 2d and 21 (the ratio of PU/PC is around 3.5/1), all the poly(urethane–carbonate)s analyzed were stable up to 280 °C and start to undergo degradation between 280 and 400 °C. The decomposition behavior of some poly(urethane–carbonate)s (2b, 2h, 2i, 2j, 2k, 2m, and 2n) displays a single-step process, while other poly(urethane–carbonate)s showed more than a two-step process. Aromatic–aliphatic poly(urethane–carbonate)s 2f, 2h, and 2m exhibited higher residue mass percentages than other aromatic–aliphatic or aliphatic–aliphatic poly(urethane–carbonate) (Figure 5).

■ CONCLUSIONS

In summary, we have demonstrated that the use of Cs₂CO₃ as a base brings about a highly selective synthesis of poly(urethane–carbonate)s through a one-pot, two-step protocol for the polycondensation of diamines with CO₂ and dihalides. N-alkylation of amines and over-alkylation of urethanes could be avoided. A slight excess of dihalides with respect to diamines was necessary to improve the polycondensation efficiency. The molar mass of the polymers obtained reached up to 22 400 g/mol and the ratio of PU to PC up to 10/1. The thermal tests indicate that the polymers produced through this three-component polycondensation possess similar properties to those prepared from conventional polycondensation process involving diisocyanates and diols. This investigation is general enough to be successfully applied to the preparation of aliphatic–aliphatic and aliphatic–aromatic poly(urethane–carbonate)s. Further studies on the utilization of CO₂ for thesis of other polymers through direct polycondensation methodology are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b00142.

Additional experimental data, IR, NMR, TGA characterization, and molar mass estimation by NMR, Figures S1–S6 (PDF)

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