1 Poly(urethane–carbonate)s from Carbon Dioxide

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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-hexanediamine 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.

14 ■ INTRODUCTION

15 The continuously rising level of carbon dioxide (CO₂) in the
16 atmosphere makes it one of the major contributors to the so-
17 called greenhouse effect.¹ Besides efforts of reducing its emission
18 and capturing it, attempts have also been made to chemically
19 transform CO₂ to commodity chemicals such as urea, carbonates,
20 methanol, salicylic acid, etc.^{2–10}

21 In the area of polymers, polyurethanes are one of the most
22 important industrial family of polymers, which have been widely
23 used in our daily life, ranging from flexible foams for bed
24 mattresses to rigid foams for thermal insulation, corrosion
25 resistant coatings, elastomers, and components of adhesives.¹¹
26 Traditionally, the preparation of polyurethanes involved the
27 polycondensation of diisocyanates and diols, in which great
28 caution has to be taken to deal with the highly toxic and water-
29 sensitive nature of isocyanate monomers (Scheme 1A).^{12–15} The
30 cationic ring-opening polymerization of aliphatic cyclic ure-
31 thanes (Scheme 1B) is another option that gives access to
32 aliphatic polyurethanes, but it requires the prior synthesis of
33 cyclic urethanes from α,ω -amino acids and phosgene.^{16,17} As an
34 alternative to phosgene-based processes, polyurethanes could be
35 synthesized more directly from aziridines through copolymeriza-
36 tion with CO₂ (Scheme 1C).¹⁸ At present, the two most studied
37 and promising synthetic routes toward polyurethanes are (i) the
38 polycondensation of dicarbonates with diamines or of
39 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(hydroxy-
urethane)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 1F. 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-

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Scheme 1. General Methods for the Synthesis of Aliphatic Polyurethanes

Table 1. Screening Polycondensation Reaction Conditions^a

entry	<i>X</i> (equiv)	<i>Y</i> (bar)	temp (°C)	ammonium salt	isolated yield (%)	<i>M</i> _n (GPC) (g/mol) ^{<i>b</i>}	<i>Đ</i> ^{<i>b</i>}	PU/PC ^{<i>c</i>}
1	1.0	10	80	Bu ₄ N ⁺ Cl [−]	70	4900	1.58	6.8/1
2 ^{<i>d</i>}	1.0	10	80	Bu ₄ N ⁺ Cl [−]	4			
3	1.0	10	60	Bu ₄ N ⁺ Cl [−]	58	2500	2.58	5.9/1
4	1.0	10	100	Bu ₄ N ⁺ Cl [−]	65	4000	1.48	5.8/1
5	1.05	10	80	Bu ₄ N ⁺ Cl [−]	77	5900	1.72	8.0/1
6	1.1	10	80	Bu ₄ N ⁺ Cl [−]	73	5700	1.77	5.8/1
7	1.05	1	80	Bu ₄ N ⁺ Cl [−]	45	1400	1.69	6.4/1
8	1.05	20	80	Bu ₄ N ⁺ Cl [−]	58	2800	1.65	7.0/1
9 ^{<i>e</i>}	1.05	10	80	Bu ₄ N ⁺ Cl [−]	70	4700	1.75	7.3/1
10 ^{<i>f</i>}	1.05	10	80	Bu ₄ N ⁺ Cl [−]	62	14000	2.40	4.0/1
11 ^{<i>g</i>}	1.05	10	80	Bu ₄ N ⁺ Cl [−]	69	4000	1.60	8.3/1
12 ^{<i>h</i>}	1.05	10	80	Bu ₄ N ⁺ Cl [−]	72	4400	1.42	7.9/1
13	1.05	10	80	Bu ₄ N ⁺ HSO ₄ [−]	23			
14	1.05	10	80	Bu ₄ N ⁺ OAc [−]	10			
15	1.05	10	80	no salt	20			
16	1.05	10	80	Bu ₄ N ⁺ Br [−]	79	6000	1.71	9.0/1
17	1.05	10	80	Bu ₄ N ⁺ I [−]	76	28800	5.40	5.0/1

^aAll reactions were conducted on 1 mmol scale, 2 mL of NMP, NMP = 1-methyl-2-pyrrolidinone. ^b*M_n* 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). ^cMeasured by ¹H NMR of the polymer at 120 °C, PU = polyurethane, PC = polycarbonate. ^dK₂CO₃ was used. ^e3.0 equiv of Cs₂CO₃ was used. ^f0.5 equiv of Bu₄N⁺Cl⁻ was used. ^g1.5 equiv of Bu₄N⁺Cl⁻ was used. ^hThe reaction time was 48 h.

neous polyurethanes having all possible combinations between aliphatic/aromatic dihalides and diamines.

64 ■ 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 CaH_2 prior to use. Anhydrous 1-methyl-2-pyrrolidinone (Sigma-Aldrich, 99.5%), 1,4-bis(chloromethyl)benzene (Aldrich, 98%), 1,6-hexanediamine (Aldrich, 99%), 1,4-butanediamine (Aldrich, 99%), 1,8-octanediamine (Aldrich, 98%), 1,10-decanediamine (Aldrich, 97%), 1,12-dodecanediamine (Aldrich, 98%), 4,4'-diaminodicyclohexylmethane (Aldrich, 98%), and 1,4-

phenylenedimethanamine (Aldrich, 99%) were used as received. Cs_2CO_3 and K_2CO_3 (Alfa Aesar) were used as received.

Instruments and Measurements. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV600 (FT, 600 MHz for ^1H ; 150 MHz for ^{13}C) spectrometer in deuterated DMSO at 120 °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 Viscotek 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 (T_g), melting temperature (T_m), 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-hexanediamine, 1,4-dibromobutane, and CO_2 (Table 1, entry 16) was performed as follows: To a dried 50 mL stainless autoclave vessel equipped with a triangular stirring bar (size: 35 × 9 mm), 1,6-hexanediamine (116.2 mg, 1.0 mmol), 1-methyl-2-pyrrolidinone (NMP, 2 mL), Cs_2CO_3 (1.303 g, 4.0 mmol), and tetrabutylammonium bromide (TBAB) were successively added, and then the autoclave was sealed. The autoclave was pressurized with CO_2 to 10 bar. The resulting 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, CO_2 was released gently, 1,4-dibromobutane (226.7 mg, 1.05 mmol) was added, and the autoclave was sealed again and pressurized with CO_2 to 10 bar. The reaction mixture was stirred at 80 °C for another 24 h. After the completion of the reaction, the stainless autoclave was cooled to room temperature, CO_2 was released gently, and the reaction mixture was poured into water (30 mL) to remove the salts and solvents. The collected precipitate was washed with water and methanol. The poly(urethane-carbonate) **2a** was dried at 50 °C under vacuum overnight. Isolated yield = 79%, PU/PC = 8.7/1. IR (neat): 3317 cm^{-1} (NH group), 1682 cm^{-1} (urethane group, C=O). ^1H NMR (DMSO- d_6 , 600M, 120 °C): δ = 6.38 (NH), 3.98, 3.00, 1.62, 1.44, 1.29. ^{13}C NMR (DMSO- d_6 , 150M, 120 °C): δ = 155.88, 62.93, 39.98, 28.85, 25.42, 25.03. Number-average molecular weight ($M_{n,\text{GPC}}$) = 6000; polydispersity index ($\bar{D}$) = 1.71.

RESULTS AND DISCUSSION

For the successful synthesis of carbamates via three-component coupling involving CO_2 , alkylamines, and alkyl halides, it is essential that side reactions, such as N-alkylation of amines or alkylation of carbamates by alkyl halides, be avoided or suppressed as shown in Scheme 2. Especially, in the synthesis

of polyurethanes from difunctional monomers, such alkylation 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.^{24–26,34}

To start, we chose 1,6-hexanediamine and 1,4-dibromobutane as model monomers for the condensation with CO_2 in the presence of Cs_2CO_3 and tetrabutylammonium chloride (TBAC). To effectively avoid N-alkylation, CO_2 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 CO_2 pressure (1 bar = 10^5 Pa), in the presence of 4.0 equiv of Cs_2CO_3 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–H 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 1. IR spectrum of obtained poly(urethane-carbonate) **2a** in Table 1, entry 1.

To confirm the structure of the polymer produced, we synthesized polyurethane **2a'** as a benchmark following a reported conventional polycondensation procedure³⁶ using 1,4-butanediol and 1,6-diisocyanatohexane as precursor monomers and triethylenediamine (DABCO) as catalyst, at 80 °C in NMP; the obtained polymer **2a'** exhibited similar solubility properties to the one described above: it could not be dissolved in common organic solvent at room temperature and showed the same IR absorptions at around 3317 and 1682 cm^{-1} (see Supporting Information, Figure S1A,B). Both polymers could be well dissolved in DMSO at 120 °C and then submitted to NMR characterization in DMSO- d_6 at this temperature.

As shown in Figure 2, the same main signals were detected in both cases, confirming the formation of polyurethane from the three-component polycondensation investigated in this study. The peak (f) at δ = 6.38 can be assigned to the NH protons; as to the two peaks at δ = 3.98 (a) and 3.00 ppm (b), they are attributable to the two methylene protons of butyl and hexyl groups connected to carbamate linkages. The other six

Scheme 2. Carbamate Formation and Side Reactions

Figure 2. ^1H NMR spectra of polyurethanes **2a** and **2a'**.

166 methylene protons are detected respectively at 1.62 (c) (β -
 167 position of butyl group) and 1.44 (d) and 1.29 ppm (e) (β - and γ -
 168 positions of the hexyl group connected to the carbamate).
 169 Especially, the ratio of peaks f to b, d, e in both polyurethane **2a**
 170 and **2a'** cases is close to 1:2:2:2, indicating the presence and
 171 integrity of NH proton and thus the absence of an overalkylation
 172 of the produced polyurethane. A close look at the area next to
 173 peaks a and c in Figure 2 indicates the presence of two small
 174 signals appearing at $\delta = 4.12$ (a') and $\delta = 1.68$ ppm (c'),
 175 attributable to the butylene groups linking carbonate groups. Our
 176 previous investigation on the polycondensation between diols,
 177 CO_2 , and dihalides³⁵ revealed that 1,4-dibromobutane could self-
 178 polycondense. Under similar conditions, such self-polyconden-
 179 sation of dihalides also occurred during the polycondensation of
 180 diamines with CO_2 and dihalides, giving rise to some carbonate
 181 linkages (for comparison, please see Figure S2 for ^1H NMR of
 182 poly(urethane-carbonate) **2a** and polycarbonate). From the
 183 integration ratio between the methylene signal at $\delta = 3.98$ (a) and
 184 the one at $\delta = 4.12$ (a'), the ratio of polyurethane (PU) to
 185 polycarbonate (PC) linkages in the polymer formed could be
 186 calculated (for Table 1, entry 1, PU/PC = 6.8/1). The
 187 characterization by ^{13}C NMR further confirms the polyurethane
 188 structure (see Figure S3 for ^{13}C NMR spectrum of polyurethane
 189 **2a**). The peaks at $\delta = 155.88$ (f), 62.93 (a), 39.98 (c), 28.85 (b),
 190 25.54 (d), and 25.03 (e) ppm are due to the carbamate linkages.
 191 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.^{37–41} The molar mass of polyurethane **2a'**
 synthesized from 1,4-butanediol and 1,6-diisocyanatohexane
 was determined, and a $M_{\text{n(GPC)}}$ value equal to 7000 g/mol (Table
 2, entry 0) was obtained; this result is in the range of those
 reported in the literature,^{15,36} but one has to keep in mind that
 $M_{\text{n(GPC)}}$ 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.

Table 2. Polycondensation of CO₂ with Various Diamines and Dihalides^a

$\text{H}_2\text{N}-\text{R}_1-\text{NH}_2 \quad + \quad \text{X}-\text{R}_2-\text{X} \quad + \quad \text{CO}_2 \xrightarrow[\text{NMP, 80 } ^\circ\text{C, 24 h}]{\text{Cs}_2\text{CO}_3 \text{ (4 equiv.)}, \text{TBAB (1 equiv.)}} \left[\text{O}-\text{C}(=\text{O})-\text{NH}-\text{R}_1-\text{NH}-\text{C}(=\text{O})-\text{O}-\text{R}_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{R}_2 \right]_m$								
Entry	H ₂ N—R ₁ —NH ₂	X—R ₂ —X	Polymer 2 / Isolated yield ^b	M _{n,GPC} (g/mol) / Đ ^c	M _{n,NMR} ^d	T _g (°C)	T _m ¹ / T _m ² (°C)	PU/PC ^e
0 ^f	OCN—(CH ₂) ₆ —NCO	HO—(CH ₂) ₄ —OH	2a' / 84%	7000/1.79	4500	-	168/178	1/0
1	H ₂ N—(CH ₂) ₆ —NH ₂	Br—(CH ₂) ₄ —Br	2a / 79%	6000/1.71	3100	-	164/172	9/1
2	H ₂ N—(CH ₂) ₄ —NH ₂	Br—(CH ₂) ₄ —Br	2b / 60%	2400/1.40	1500	-	185/-	5/1
3	H ₂ N—(CH ₂) ₈ —NH ₂	Br—(CH ₂) ₄ —Br	2c / 85%	3600/1.62	1700	-	155/-	8/1
4	H ₂ N—(CH ₂) ₁₀ —NH ₂	Br—(CH ₂) ₄ —Br	2d / 88%	23000/1.30	9500	-	153/-	3.5/1
5	H ₂ N—(CH ₂) ₁₂ —NH ₂	Br—(CH ₂) ₄ —Br	2e / 85%	3700/1.76	1600	-	144/-	3.3/1
6		Br—(CH ₂) ₄ —Br	2f / 88%	insoluble	-	-	227/-	15/1
7		Br—(CH ₂) ₄ —Br	2g / 87%	22400/2.33	7900	108	-	10/1
8	H ₂ N—(CH ₂) ₄ —NH ₂		2h / 66%	1000/1.65	600	-	181/208	5/1
9	H ₂ N—(CH ₂) ₆ —NH ₂		2i / 79%	1800/1.82	1100	-	157/184	6/1
10	H ₂ N—(CH ₂) ₈ —NH ₂		2j / 76%	2200/2.10	1300	-	153/-	8/1
11	H ₂ N—(CH ₂) ₁₀ —NH ₂		2k / 89%	3100/1.76	2000	-	157/175	7/1
12	H ₂ N—(CH ₂) ₁₂ —NH ₂		2l / 90%	2000/1.72	1100	36	145/-	3.4/1
13			2m / 81%	2600/1.62	1500	83	-	5/1
14			2n / 89%	5900/2.33	2600	140	-	14/1

^aAll the reactions were conducted on 1 mmol scale, 2 mL of NMP, NMP = 1-methyl-2-pyrrolidinone, TBAB = tetrabutylammonium bromide. ^bYield was obtained after precipitation from H₂O and dried at 50 °C under vacuum overnight. ^cM_n 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). ^dM_n were calculated by NMR at room temperature after chemical modification by trifluoroacetic anhydride (see Supporting Information for details). ^eMeasured by ¹H NMR of the polymer at 120 °C, PU = polyurethane, PC = polycarbonate. ^fPolyurethane synthesized from 1,4-butanediol and 1,6-diisocyanatohexane (according to the method of ref 11).

Figure 3. Selected GPC traces of poly(urethane-carbonate)s obtained under different reaction conditions (Table 1, entries 3, 8, 11, and 16).

1, entry 2). This is in agreement with other results reported in organic synthesis which also observed the effectiveness of cesium carbonate.^{24–34} Given its size, this cation exhibits a weak association with anions, thus enhancing the nucleophilicities of the corresponding amide anion and carbamate species which in turn are more reactive toward the relatively inert carbon dioxide and halides. For the rest of the study it was thus decided to use Cs₂CO₃ as the base promoting the reaction between diamines, dihalides, and CO₂. When the reaction was performed at 60 or 100 °C, poly(urethane-carbonate) samples **2a** were isolated in a 58–65% yield with a PU/PC ratio around 6/1, and molar masses ranging from 2500 to 4000 g/mol (Table 1, entries 3 and 4), results which were not as good as those obtained at 80 °C.

We also studied the stoichiometric factor between diamines and dihalides: theoretically, for obtaining the polymer of highest possible molar mass, the stoichiometry between the various functional groups involved in the polycondensation must be kept equal to 1. But in this case we observed that using a slightly excess of dibromide (1.05 equiv) helped to increase both the yield of polymer and the molar mass (around 6000 g/mol) of the polymer formed (Table 1, entries 5 and 6). As one can see from the NMR characterization of the obtained poly(urethane-carbonate) **2a** (Figure 2), a slight excess of dibromide could compensate for its consumption by self-polycondensation. The effect of the pressure of CO₂ was also investigated: both the yield

Scheme 3. (A) Control Experiment without Diamine under Standard Reaction Conditions; (B) Experiment without Dibromide under Standard Reaction Conditions; (C) Experiment without CO₂ under Standard Reaction Conditions

Scheme 4. Proposed Mechanism of Formation of Poly(urethane-carbonate)s from Diamines, CO₂, and Dihalides^a

^aDashed parts correspond to side reactions.

(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 16). 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 (1:1:1.05:4.0 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'-diaminodicyclohexylmethane 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 $\bar{M}_n$ 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,³⁵ dibromobutane was also found here to self-condense, the presence of TBAB being unable to totally suppress this side reaction: a polycarbonate with $\bar{M}_n$ up to 2300 g/mol 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

Figure 4. DSC curves of poly(urethane-carbonate)s described in Table 2.

Figure 5. TGA traces of poly(urethane-carbonate)s described in Table 2.

CO₂, indicating that Cs₂CO₃ is not a source of CO₂ and that carbamate linkages only come from CO₂ 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 Cs₂CO₃ and then react with CO₂ 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 Cs₂CO₃, 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 ¹HNMR 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 C4 to C12) 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 **2l** (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)s (Figure 5).

CONCLUSIONS

In summary, we have demonstrated that the use of Cs_2CO_3 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 CO_2 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 CO_2 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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Notes

The authors declare no competing financial interest.

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