Polymer Chemistry

Cs2CO3-Promoted Polycondensation of CO2 with Diols and Dihalides for the Synthesis of Miscellaneous Polycarbonates

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Cs₂CO₃-Promoted Polycondensation of CO₂ with Diols and Dihalides for the Synthesis of Miscellaneous Polycarbonates

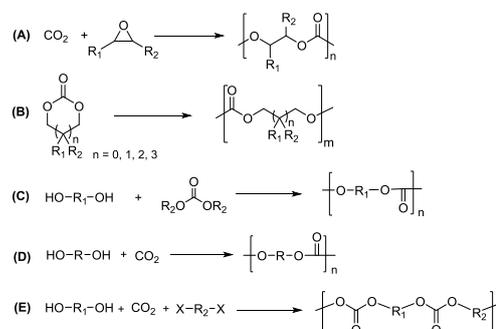Zuliang Chen,[a] Nikos Hadjichristidis,[b] Xiaoshuang Feng[a*] and Yves Gnanou [a*]

A one-pot protocol for the direct synthesis of polycarbonates through polycondensation of diols, dihalides and CO_2 in the presence of Cs_2CO_3 is described. The conditions were optimized by studying the polycondensation of CO_2 with 1,4-phenylenedimethanol and 1,4-dibromobutane as model monomers. Then, diols and dihalides with different spacers between the reactive groups including aliphatic, aromatic and poly(ethylene glycol) were tested under optimal conditions. Miscellaneous polycarbonates exhibiting molar masses in the range of 43,000 g/mol (GPC) and conversion higher than 96% could be obtained. The proposed mechanism rules out the possibility of ether linkage formation during polycondensation and accounts for the creation of carbonate linkages by two different ways. The thermal properties of the synthesized polycarbonates were unveiled by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

Introduction

The continuously rising level of carbon dioxide (CO_2) in the atmosphere makes it one of the major contributors to the so-called greenhouse effect.[1] Besides efforts at reducing its emission or its trapping, attempts have also been made to chemically transform CO_2 and use it as precursors for commodity chemicals such as urea, carbonates, methanol, salicylic acid, etc.[2] In the area of polymers, the synthesis of polycarbonates by copolymerization of CO_2 with epoxides is one well known example (Scheme 1A) but the volumes of such CO_2-made polycarbonates are still modest.[3] On the other hand, polycarbonates are one of the most important engineering thermoplastics and are employed in a wide range of applications[4] with a production of 1.5 million tons per year.[5] Industrial polycarbonates are generally produced from a process involving bisphenol-A and haloformates such as phosgene, a very toxic reagent that tends nowadays to be avoided.[4b,c] The anionic ring opening polymerization of cyclic carbonates (Scheme 1B) is another option that gives access to aliphatic polycarbonates but it requires the prior synthesis of cyclic carbonates; however this approach which is expensive works satisfactorily essentially with trimethylene carbonate.[6] As an alternative to phosgene-based processes, polycarbonates could also be obtained by carbonate interchange reaction between diols and dialkyl carbonates in the presence of appropriate catalysts: dialkylcarbonates such as dimethylcarbonate which were previously prepared using phosgene could be now generated using CO_2,[7] which adds credit to this approach (Scheme

1C).[4a,8] The latter can indeed afford high molar mass aliphatic polycarbonates in generally two steps: the first step consists in partly end-capping diol chain-ends with alkylcarbonates and the second in reacting the latter with the remaining hydroxyls, while removing the methanol formed as by-product. In addition to the interchange with carbonates, polycarbonates could also be synthesized more directly from diols through two-component polycondensations with CO_2 (Scheme 1D)[9], and three-component polycondensation with CO_2 and dihalides (Scheme 1E).[10] In 1998, Kadokawa and co-workers[9a,b] first developed a direct polycondensation of CO_2 with alkanediols in the presence of trisubstituted phosphines, carbon tetrahalides and an organic base which afforded the corresponding polycarbonates; however, the yields were low (from 8% to 75%) and only low molecular weight samples (less than 5000) could be obtained. Recently, the Tomishige group[9c] utilized CeO_2 as catalyst and 2-cyanopyridine as dehydrating agent to obtain polycarbonates with high conversion (40-99%), but still rather low molecular weight (from 500 to 1700). In comparison with the two-component polycondensation where the water formed has to be removed to drive the reaction, the three-component polycondensation carried out in the presence of added bases, so far has received little attention. Indeed very few papers have described the access to

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Scheme 1 General methods for the synthesis of aliphatic polycarbonates.

polycarbonates by this pathway.[10] Mild bases were used in order to avoid possible transcarbonation scrambling reactions but the polycarbonates produced exhibited low conversion and low molar mass (≈ 6000 g/mol, GPC)[10a], which prevented any industrial interest and application.

The goal of this investigation is to revisit this method of polycarbonate synthesis and to find the conditions the most appropriate for an efficient polycondensation of diols with dihalides and CO_2. Towards this end a one-pot protocol using Cs_2CO_3 as base is investigated. This methodology is applied not only for the synthesis of purely aliphatic polycarbonates arising from aliphatic diols and dihalides but it also opens the possibility of generating miscellaneous polycarbonates from both aliphatic and aromatic dihalides and diols. The proposed methodology has been successfully applied for the synthesis of organic carbonates for biological and medicinal applications.[11]

Experimental Section

General Methods. All reactions were carried out under dry and oxygen-free argon atmosphere in a Braun Labmaster glovebox. Anhydrous 1-methyl-2-pyrrolidinone (Sigma-aldrich, 99.5%) was used as received. 1, 1-dibromomethane (>99%), 1,2-dibromoethane (>99%) 1,3-dibromopropane and 1,4-dibromobutane (>99%) were purchased from Alfa Aesar and distilled over CaH_2 prior to use. 1,4-bis(chloromethyl) benzene (Aldrich, 98%) was used as received. For solid diols, 1,4-phenylenedimethanol (Alfa Aesar, 99%), 1,3-phenylenedimethanol (Alfa Aesar, 98%), 1,2-phenylenedimethanol (Alfa Aesar, 98%), 1,6-hexanediol (Pfaltz, 99%), 1,8-octanediol (Alfa Aesar, 98%), 1,10-decanediol (Aldrich, 98%), isosorbide (Aldrich, 98%) and PEG_{2000} (Alfa Aesar) were used as received. For liquid diols, glycol (Aldrich, 99%), 1,4-butanediol (Pfaltz, 99%) and diethylene glycol (Pfaltz, 99%) were dried over acitivated 4 Å molecular sieves before use. 1,3-propanediol (Pfaltz, 99%) was distilled under vacuum before use.

Instruments and Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer in deuterated chloroform at room temperature. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Infrared (IR) spectra were obtained using a Thermo Nicolet iS10 infrared spectrometer. Gel permeation chromatography measurements were carried out on a Viscoteck GPC instrument with styragel ® HR 2 THF and styragel ® HR 4 THF as columns at 35 °C calibrated with polystyrene (PS) standards. Chloroform was used as eluent at a flow rate of 1.0 mL/min. MALDI-TOF MS experiments were carried out by using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix in THF at a loading of 1:5 with NaOAc as ionizing agent. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC1/TC100 in an inert atmosphere (nitrogen). The samples were tested by two methods. The first method was heated from − 50 °C to 100 °C, and cooled to − 50 °C and finally heated again to 100 °C with a heating/cooling rate of 10 °C/min. The second method was heated from 25 °C to 150 °C, and cooled to − 100 °C and finally heated again. The second heating curve was used to determine the glass

transition temperature (Tg), melting temperature (Tm) and degree of crystallinity. Thermogravimetric analysis (TGA) were performed on a Mettler Toledo DSC1/TC100 between 25 °C 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 polycondensation of 1,4-phenylenedimethanol, 1,4-dibromobutane and CO_2 (Table 1, Entry 11) was performed as following: Inside a Braun Labmaster glovebox, to a 100 mL stainless autoclave vessel including a triangular stirring bar (size: 35 × 9 mm). 1,4-phenylenedimethanol (138.2 mg, 1.0 mmol), 1,4-dibromobutane (226.7 mg, 1.05 mmol), 1-methyl-2-pyrrolidinone (NMP, 2 mL) and Cs_2CO_3 (1.303 g, 4.0 mmol) were successively added, then the autoclave was sealed. Outside of the glovebox, the autoclave was pressurized with CO_2 to 10 bar. The resulting reaction mixture was gently stirred (450 rpm) at 100 °C for 48 hours (the stirring rate should be controlled to assure the mixing and minimize the splashing). After the reaction, the stainless autoclave was cooled to room temperature, CO_2 was released gently. After a trace amount of mixture was sampled out for ^{1}H NMR characterization to determine the conversion of 1,4-phenylenedimethanol, the remaining reaction mixture was poured into water (15 mL), to remove the salts and solvents. The collected precipitate was again dissolved in THF, and precipitated in water. The polycarbonate **2a** collected was dried under vacuum overnight. IR (neat): 1737 cm^{-1} (carbonyl group, C=O) and 1232 cm^{-1} (oxycarbonyl group, C-O). ^{1}H NMR (CDCl$_3$, 400M): δ = 7.37, 5.13, 4.16, 1.76; ^{13}C NMR (CDCl$_3$, 100M): δ = 155.02, 135.56, 128.48, 69.08, 67.46, 25.08. Number average molecular weight (Mn) = 22000, polydispersity index (PDI) = 3.63.

Results and Discussion

For the sake of an easy and straightforward identification of the products formed by NMR (see supporting information part I for calculation details), we chose 1,4-phenylenedimethanol, 1,4-dibromobutane as model monomers for the condensation with CO_2. The polymers obtained were purified through precipitation in water to eliminate the salts, all the screened reaction conditions and results obtained are shown in Table 1. For purpose of comparison, the first reaction was performed at 80 °C with 10 bar of CO_2 pressure (1 bar = 10^5 Pa), in the
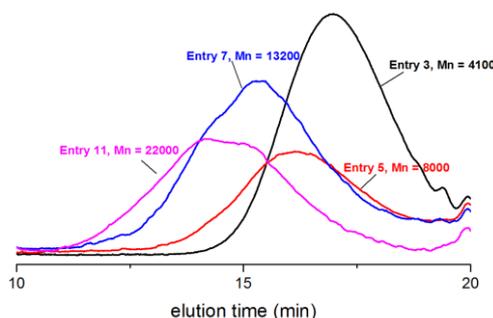

Figure 1. Selected GPC curves of polycarbonates obtained in different reaction conditions with same substrates (Table 1, Entry 3, 5, 7 and 11)

Table 1. Screening polycondensation reaction conditions. [a]

polycarbonate **2a**

Entry	X equiv.	Y	Base	Temperature	Time	Conversion[b]	$M_{n,GPC}$(g/mol)[c]	PDI[c]
1	1.0	10 bar	K_2CO_3	80 °C	24 h	46%	660	1.52
2	1.0	10 bar	DBU	80 °C	24 h	55%	1000	1.53
3	1.0	10 bar	Cs_2CO_3	80 °C	24 h	87%	4100	1.95
4	1.0	10 bar	Li_2CO_3	80 °C	24 h	10%	-	-
5	1.0	10 bar	Cs_2CO_3	80 °C	48 h	89%	8000	1.94
6	1.0	1 bar	Cs_2CO_3	80 °C	48 h	86%	2600	2.14
7	1.05	10 bar	Cs_2CO_3	80 °C	48 h	90%	13200	2.78
8	1.10	10 bar	Cs_2CO_3	80 °C	48 h	92%	13900	2.36
9	1.0	10 bar	Cs_2CO_3	100 °C	48 h	94%	17900	3.40
10	1.0	10 bar	Cs_2CO_3	120 °C	48 h	95%	18600	6.14
11	1.05	10 bar	Cs_2CO_3	100 °C	48 h	97%	22000	3.63
12[d]	1.05	10 bar	Cs_2CO_3	100 °C	48 h	97%	17000	3.90

[a] All the reactions were conducted on 1 mmol scale, 2 mL of NMP, NMP = 1-methyl-2-pyrrolidinone, DBU = 1,8-Diazabicyclo[5,4,0]-undec-7-ene. [b] conversion was measured by ^{1}H NMR of the crude reaction mixture, and calculation based on remaining hydroxyl groups of diols. [c] Mn and polydispersity index (PDI) data were obtained after precipitating from H_2O, and measured by GPC with $CHCl_3$ as eluent (based on polystyrene standards). [d] 3.0 equiv. of Cs_2CO_3 was used.

presence of 4.0 equiv. of K_2CO_3 for 24 hours, a base previously used by Inoue.[10a] Only 46% conversion of 1,4-phenylenedimethanol could be achieved and the number average molecular weight (M_n) was unsurprisingly very low (Table 1, Entry 1). Inoue reported the synthesis of the same polycarbonate (Mn=6400/1.98) and obtained higher yield using more active 1,4-bis(chloromethyl) benzene as dihalide.[10a] Inspired by the efficient synthesis of carbonates/carbamates involving the condensation with CO_2 and alcohols/amines in the presence of 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU)[12] or Cs_2CO_3,[11] we tried DBU or Cs_2CO_3 as base instead of K_2CO_3. A
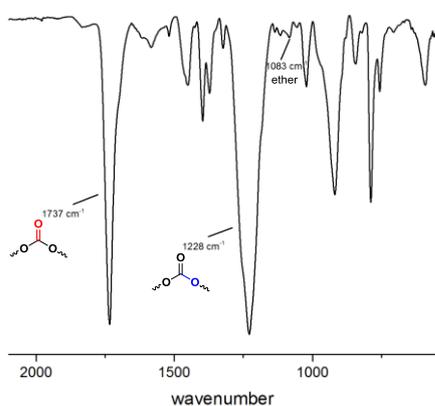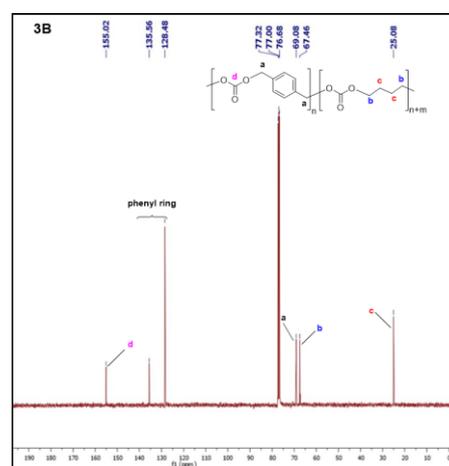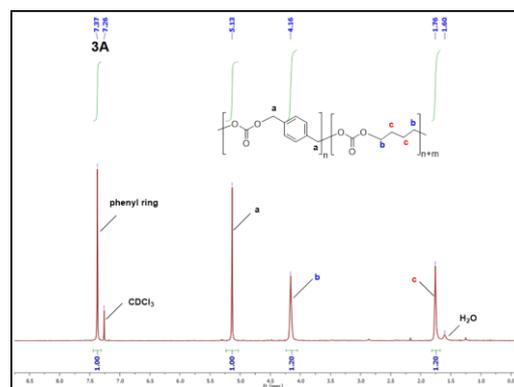

Figure 2. The IR spectra of obtained polycarbonate **2a** in Table 1, Entry 12

Figure 3. The ^{1}HNMR (3A) and ^{13}CNMR (3B) spectrum of polycarbonate **2a**

Table 2. Polycondensation of CO_2, various diols and dihalides. [a]

$$HO-R_1-OH \quad + \quad X-R_2-X \quad + \quad CO_2 \xrightarrow[\text{NMP, 100°C , 48 h}]{Cs_2CO_3 \ (4.0 \ \text{equiv.})} \left[\begin{array}{c} O\ O \\ \| \\ O \end{array} R_1\right]_n \left[\begin{array}{c} O\ O \\ \| \\ O \end{array} R_2\right]_{n+m}$$

1.0 equiv. 　　　1.05 equiv. 　　10 bar

| Entry	HO—R₁—OH	X—R₂—X	Polymer 2 / Conversion[b]	$M_{n,GPC}$ (g/mol) / PDI[c]	T_g (°C)	Integral ratio of a/b[d]
1	HOH₂C—⟨benzene⟩—CH₂OH	Br— (CH₂)₄—Br	**2a** / 97%	22000 / 3.63	- 0.5	1/1.2
2	HOH₂C—⟨benzene⟩—CH₂OH	Br—CH₂—Br	**2b** / 24%	700 / 1.88	–	–
3	HOH₂C—⟨benzene⟩—CH₂OH	Br— (CH₂)₂—Br	**2c** / 40%	900 / 3.78	–	–
4[e]	HOH₂C—⟨benzene⟩—CH₂OH	Br— (CH₂)₃—Br	**2d** / 90%	6000 / 2.34	–	–
5	⟨benzene⟩—CH₂OH / HOH₂C (meta)	Br— (CH₂)₄—Br	**2e** / 96%	24400 / 3.22	-5.4	1/1.09
6[f]	⟨benzene⟩—CH₂OH / CH₂OH (ortho)	Br— (CH₂)₄—Br	**2f** / 94%	11100 / 1.90	-1.2	1/1.07
7[g]	HO— (CH₂)₂—OH	Br— (CH₂)₄—Br	**2g** / 75%	4000 / 2.78	–	–
8[h]	HO— (CH₂)₃—OH	Br— (CH₂)₄—Br	**2h** / 98%	24500 / 1.94	-27	–
9	HO— (CH₂)₄—OH	Br— (CH₂)₄—Br	**2i** / 99%	27000/ 1.84	-34.3	–
10	HO — (CH₂)₆—OH	Br— (CH₂)₄—Br	**2j** / 98%	27600 / 1.81	-42	–
11[j]	HO — (CH₂)₆—OH	Br— (CH₂)₄—Br	26%	5600 / 1.46		–
12	HO — (CH₂)₈—OH	Br— (CH₂)₄—Br	**2k** / 96%	11200 / 1.80	–	–
13	HO — (CH₂)₁₀—OH	Br— (CH₂)₄—Br	**2l** / 96%	11300 / 1.98	–	–
14	Diethylene glycol	Br— (CH₂)₄—Br	**2m** / 95%	10000 / 2.32	-28	–
15	isosorbide	Br— (CH₂)₄—Br	**2n** / 92%	18100 / 2.26	48.4	–
16[i]	PEG₂₀₀₀	Br— (CH₂)₄—Br	**2o** / 90%	21000 / 14.85	–	–
17	HO — (CH₂)₆—OH	Cl—H₂C—⟨benzene⟩—CH₂—Cl	**2p** / 96%	43200 / 2.31	-5.2	1/1.05
18[j]	HO — (CH₂)₆—OH	Cl—H₂C—⟨benzene⟩—CH₂—Cl	87%	7900 / 2.21		–

[a] All the reactions were conducted on 1 mmol scale, 2 mL of NMP, NMP = 1-methyl-2-pyrrolidinone. [b] conversion was measured by HNMR of crude reaction mixture, and calculation based on remaining hydroxyl groups of diols. [c] Mn data was obtained after precipitating from H_2O, and measured by GPC with $CHCl_3$ as eluent (based on polystyrene standards). [d] a = integral intensity of $OCOOCH_2$ derived from diol, b = integral intensity of $OCOOCH_2$ derived from dihalide, determined by ^{1}HNMR. [e] 10% of 1,3-dioxan-2-one was detected by ^{1}HNMR of crude reaction mixture. [f] 7% of ether was detected by ^{1}HNMR of crude reaction mixture. [g] 6% of 1,3-dioxolan-2-one was detected by ^{1}HNMR of crude reaction mixture. [h] 2% of 1,3-dioxan-2-one was detected by ^{1}HNMR of crude reaction mixture. [i] Polymer was precipitated from diethyl ether. [j] Inoue group reported experiment results (Mn was measured by GPC with $CHCl_3$ as eluent, based on polystyrene standards), see reference 10a.

modest increase of conversion was observed in the latter case with DBU as base (Table 1, Entry 2). In contrast, with Cs_2CO_3 as base, strikingly different results could be obtained (4100/1.95) and a conversion of diol up to 87% (Table 1, Entry 3) achieved. Li_2CO_3 was also tried as a base, but the conversion was extremely low, only 10% diol conversion could be obtained (Table 1, Entry 4).Cesium carbonate thus seems to be the most effective base in this three-component polycondensation reaction since the use of other bases including other alkali carbonates and amine bases proved much less efficient. This may be due to the fact that the cesium cation, given its size,

exhibits the weakest association capability with the anions, enhancing thus the nucleophilicities of the corresponding alkoxide and carbonate species which in turn are more prone to the nucleophilic attack to the relatively inert carbon dioxide and halides, unlike other alkali metal alkoxides,[11a,f,h] this is in agreement with other reports of the successful use of cesium carbonate in organic synthesis.[11] For the rest of the study it was thus decided to use Cs_2CO_3 as the base promoting the reaction between diols, dihalides and CO_2. With a longer reaction time, the molar mass of polymer obtained could be increased up to 8000 g/mol and a higher conversion achieved (Table 1, Entry 5).

An increase of the reaction temperature to 100 -120 °C pushed further up the conversion of diols to 94% and 95%, allowing the synthesis of polycarbonates in the range of 18,000 g/mol molar mass (Table 1, entry 9, 10).

We also studied the stoichiometric factor between diols and dihalides: theoretically, for the obtainment of the highest possible molar mass polymer, 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 helped to remarkably increase both the conversion of diols to 97% and the molar mass of polymer formed (Table 1, entry 7, 8, 11). Due to the limited solubility of Cs_2CO_3 in NMP, an excess of latter base was systematically used for the polycondensation reactions (Table 1, entry 11 vs entry 12). Figure 1 exhibits the representative GPC traces of polycarbonates prepared under different reaction conditions (For other GPC curves, see supporting information, part II and III), the molar mass of the polycarbonate **2a** after optimization finally increasing from 4.1K/1.95 to 22K/3.63 with the same substrates. Besides the analysis by GPC, the structures of the
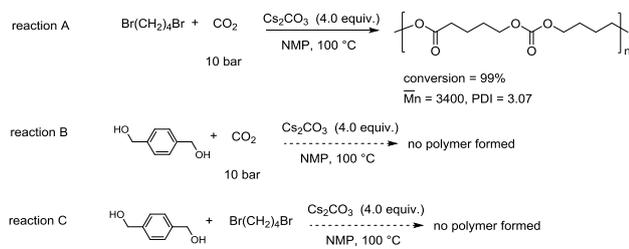
Scheme 2. (A) Control experiment without diol under standard reaction conditions. (B) Experiment without dibromide under standard reaction conditions. (C) Experiment without CO_2 under standard reaction conditions.

precipitated polymer were also characterized by IR spectroscopy. The strong absorption peaks at 1737 and 1228 cm^{-1} shown in the representative IR spectrum (Figure 2) and respectively attributable to the stretching of carbonyl and oxycarbonyl groups of linear carbonate linkages indicate the formation of carbonate functions. The weak absorption at 1083 cm^{-1} assignable to C-O-C ether linkages suggests that the polycarbonate may contain a trace amount of polyether unit. However, no signal due to two methylene protons of ether linkages could be seen at 4.50 and 3.48 ppm in ^{1}H NMR spectrum (Figure 3A).[13] The two peaks at δ = 5.13 (a) and 4.16 (b) are thus assigned to the two methylene protons of benzyl and butyl groups connected to the carbonate linkages. A close examination of the intensity of peaks a and b indicates that they are not equal, the intensity of peak b (1.20) being slightly higher than that of peak a (1.00). Such difference thus reveals the occurrence of the self-polycondensation of dibromobutane in addition to the alternating polycondensation between 1,4-phenylenedimethanol and 1,4-dibromobutane. The characterization by ^{13}C NMR further confirms the totally carbonate nature of the polycondensate formed (Figure 3B). No ether carbons supposed to appear at 72.79[13] could be detected,

the peak seen at 155.02 ppm (d) and at 135.56, 128.48, 69.08, 67.46, 25.08 ppm being due to the carbonate linkages which confirms that the polycondenssate formed only includes carbonate linkages.

From these results, all polycondensation reactions carried out thereafter were performed under these optimized conditions that are at 100 °C for 48 hours under 10 bar of CO_2 with a feeding ratio of diol : dihalide: Cs_2CO_3 (1 : 1.05 : 4.0 eq.). Diols and dihalides of different structures were thus tried to check the versatility of the base used, the results obtained are being shown in Table 2. From the listed results, firstly, one can observe that the size of the dihalide influences the polycondensation results. Only 24% and 40% conversion of diol could be achieved when 1,1-dibromomethane or 1,2-dibromoethane were used as dihalide (Table 2, Entry 2-3). Similar results were observed in the case of Entry 7, which involved a diol with two carbon spacer. These results indicate that the formation of 5-membered (entry 7) or 6-membered (entry 4) cyclic carbonates by back biting is strongly favored. For diols that include either less (entry 8) or more than 4 carbons (entry 9-10, 12-17, Table 2), the formation of the cyclocarbonate is no longer favorable and thus all the polycondensation reactions could be carried out efficiently. With the increase of the spacer between two hydroxyls, both the conversion and the molar masses of the polymers obtained increase consistently (Table 2, Entry 8-10, 12-14). This experiment carried out under conditions described by Inoue[10a] yielded 26% conversion of diols and only 6000 g/mol for the average molar mass of the polycarbonate. Our methodology also works for polymeric diol such as PEG_{2000} which could be incorporated into the block forming poly(ethylene glycol-b-carbonate) (Table 2, Entry 16). To our surprise, bioresourced isosorbide[14] carrying two secondary hydroxyl groups afforded polycarbonate with rather high molar mass despite unfavorable steric hindrance (Table 2, Entry 15). Whether the halide is carried by an aliphatic or an aromatic reagent has little impact on the overall conversion of the polycondensation reaction. As it will be discussed in the next section the only repercussion of
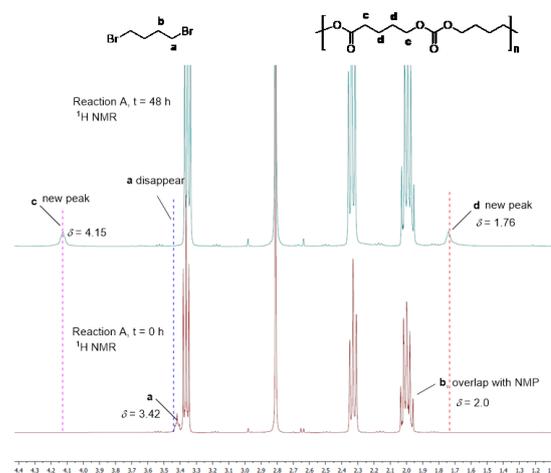

Figure 4. The crude reaction mixture ^{1}HNMR spectrum of condensation of 1,4-dibromobutane with CO_2 or without CO_2. (t = 0 hour vs. t = 48 hour).

the types of dihalide used is reflected on the Tg of the polycondendate formed, those generated from aromatic dihalide exhibiting a higher Tg. For purpose of comparison as listed in this Table (Entry 10 vs. Entry 11; Entry 17 vs. Entry18), the characteristics of polycarbonates synthesized under the same conditions as those described by Inoue,[10a] as shown in this Table, the methodology described in the present work leads to polycarbonate samples of conversion higher than 95% and even equal to 99% and of molar masses (>28,000 g/mol, GPC) that would make that suitable for industrial applications.

As discussed in the previous section dedicated to the optimization of polycondensation, the presence of 5% (mol) excess of dihalide with respect to diol affords higher diol conversion and molar masses than in the case of stoichiometric conditions. Control experiments using dibromobutane and CO_2 without any diol under standard reaction conditions were thus investigated (Scheme 2, reaction A). Interestingly, a polycarbonate with structure similar to **2i** with Mn up to 3400 g/mol under 10 bar CO_2 could be produced (reaction A). However, no polymer was formed when the reaction was carried out under standard conditions without dibromide or without CO_2, respectively (Scheme 2, reaction B and C). These results could indicate that the carbonate linkages mainly come from CO_2. Figure 4 shows the ¹H NMR spectra of the reaction mixture at t = 0 and of the resulting product at t = 48 hour, respectively. Initially, peaks characteristics of dibromobutane could be detected although overlapping with those of the solvents used (peak a and b at δ = 3.42, 2.0 ppm). After the reaction was run for 48 hours, the peaks a and b due to dibromobutane almost vanish, and two new peaks c and d at 4.15 and δ = 1.76 ppm arise attributable to methylene protons in α- and β-positions to the carbonates. As proposed (dashline) in Scheme 3, Cs_2CO_3 acts here as a carbonate source[11i] and as a pure nucleophile that attacks 1, 4-dibromobutane to form a carbonate intermediate, that in turn attacks another 1,4-dibromobutane molecule, the repetition of these two reactions producing the polycarbonate of **2i** structure. Since these reactions certainly also occur during the three component polycondensation, and since no polymer was formed when using the diol with Cs_2CO_3 in the presence of CO_2 (reaction B in Scheme 2), the formation of carbonate linkages thus results from 1) the nucleophilic attack of CO_2 by alkoxides deprotonated by Cs_2CO_3; 2) direct substitution of halides by Cs_2CO_3. Since some of the halides are consumed by direct attack by Cs_2CO_3, the reaction medium runs into an excess of diols, a limitation of the diol conversion and thus of the overall molar mass of the polycarbonate formed. The presence of a slight excess of dihalides helps to drive the reaction towards higher diol conversion and polycarbonates of higher molar mass.

The polycarbonate **2k** synthesized from 1,8-octanediol and 1,4-dibromide and CO_2 was analyzed by MALDI-TOF spectrometry. Its characterization and interpretation results are shown in Figure 5. No terminal bromide group remained after polycondensation, which is in agreement with the results of the control experiments. The presence of alkene groups can be also observed due to the occurrence of an elimination reaction under polycondensation conditions. It should be noted that besides linear polycarbonates

with different terminal groups, some cyclic polymers were also formed, following Jacobson-Stockmayer polycondensation theory.[15]

On the basis of the above experimental results, the mechanism that likely occurs is proposed in Scheme 3. The alcohol functions are first deprotonated by Cs_2CO_3 generating alkoxides that react with CO_2 to produce carbonate anions. The latter then react with halides
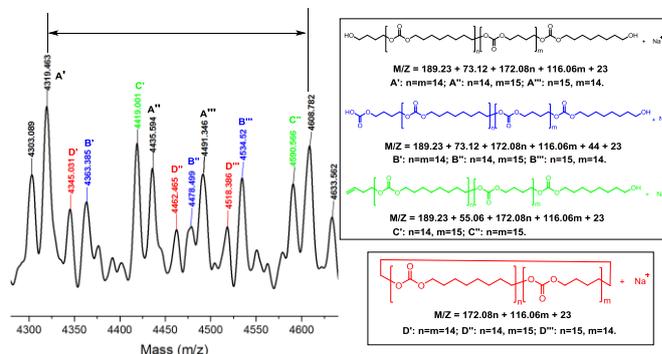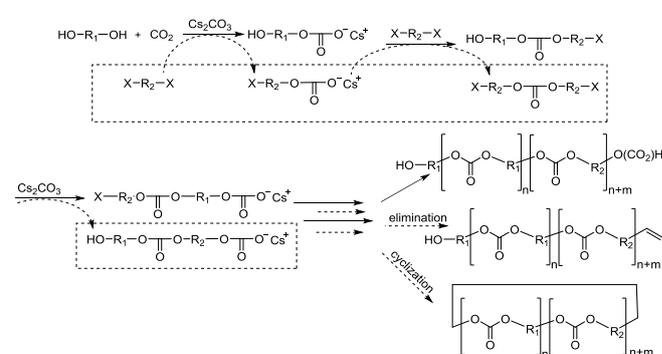

Figure 5. Zoomed MALDI-TOF mass spectrum of Polycarbonate **2k**

Scheme 3. Proposed mechanism of formation of polycarbonate from diols, CO_2 and dihalides with different structures. Dashed parts correspond to the side reactions.

in a nucleophilic substitution that bring about carbonate formation. The repetition of these steps afford linear polycarbonates as a major product from CO_2 as carbonate source. Concomitantly carbonate anions can also be generated by direct replacement of halides by Cs_2CO_3, which further react with halides to generate carbonate linkages. In this case, more of these carbonate linkages would be incorporated into the polycondensates through self-polycondensation. This is clearly indicated by the higher intensity of either aromatic (**2p**) or aliphatic (**2a**, **2e**, **2f**) methylene group connected to carbonate function in the NMR spectra of aromatic-aliphatic polycarbonates (see Table 2, Entry 1 for **2a**, Entry 5-6 for **2e** and **2f**, Entry 17 for **2p**) as shown in Figure 3A. In addition, cyclization and terminal bromide elimination can also occur as side reactions as demonstrated by MALDI-tof characterization (Figure 5). As for the determination of molar masses of these samples, they were deduced from GPC analysis as reported by other studies in the literatures.[9-10]

Besides their molecular characterization, the thermal properties of polycarbonates synthesized (except polycarbonates **2b**-**2d**, **2g** and **2o**) were also investigated by
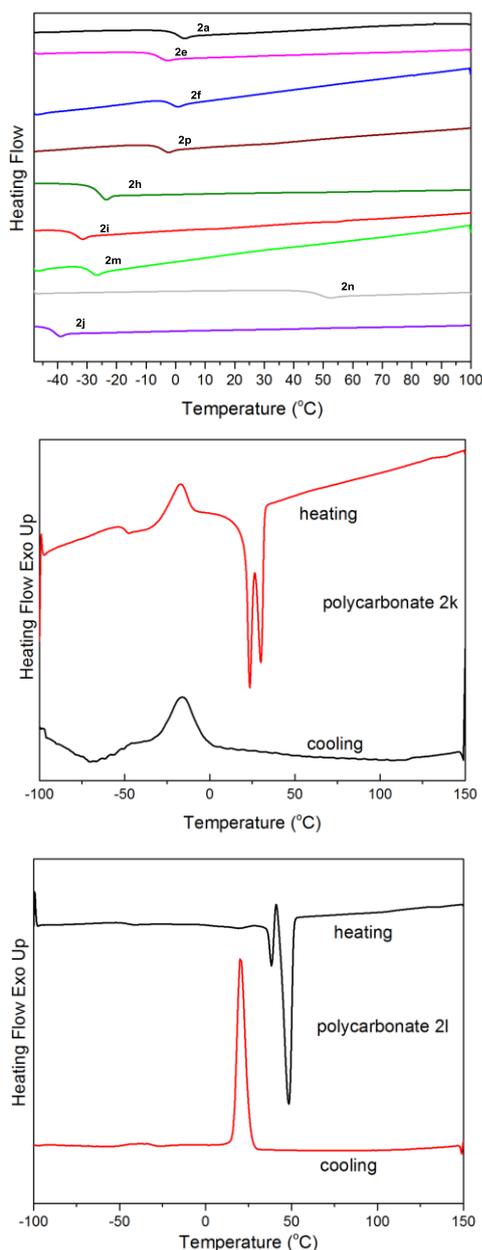
Figure 6. DSC curves of polycarbonates obtained in Table 2.

differential scanning calorimetry (DSC). (Figure 6 for DSC curves). The glass transition temperature (T_g) values of the aromatic-aliphatic polycarbonates **2a**, **2e**, **2f** and **2p** were in the range of -5.4 °C to -0.5 °C, and generally higher than those of aliphatic-aliphatic polycarbonates **2h**, **2i**, **2j** and **2m** whose T_g values range from -27°C, to -34.3 °C, -42.0 °C and -28 °C, respectively. The polycarbonates **2n** derived from secondary diol (isosorbide) exhibited higher T_g value at 48.4 °C due to the rigidity of the isosorbide unit. Specific thermal behaviours were observed for the polycarbonates **2k** and **2l** (see, Figure 6). For polycarbonate **2k**, during the heating cycle, a distinct glass transition (T_g = -50 °C) and one exothermic and two endothermic peaks were found. For polycarbonate **2l**, during heating cycle, one endothermic peak followed immediately by an exothermic peak, and then another endothermic peak were

found. Upon cooling, both polycarbonates **2k** and **2l** exhibited only one exothermic peak. The increase of the spacer size between two carbonate linkages obviously helped the chain-folding and an orderly arrangement, thus promoting the regular crystallized structure. Similar phenomena such as multiple endotherms and exotherms were also observed for the polyurethanes when long carbon chain monomers were used.[16]
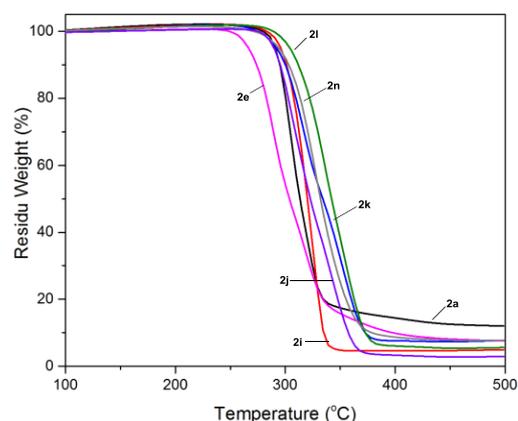

Figure 7. Selected TGA traces of polycarbonates obtained in Table 2 (Entry 1, 5, 9, 10, 12, 13 and 15).

The thermal stability of polycarbonate was then studied by thermal gravimetric analysis (TGA) in a nitrogen atmosphere (see Figure 7 for selected TGA traces, other TGA curves, see supporting information). All the polycarbonates analysed are stable up to 250 °C and start degrading between 250 and 300 °C. Their decomposition behaviour displays a single-step thermal decomposition process. Except for the polycarbonate sample **2f**, the aromatic-aliphatic polycarbonates **2a**, **2e** and **2p** have higher residue mass percentages than aliphatic-aliphatic polycarbonates **2h**, **2i**, and **2j**. Because of the rigidity of the isosorbide unit, the polycarbonates **2n** showed higher stability than other types of polycarbonates. In addition, the crystallized structure (**2k**, **2l**) improves the thermal stability of polycarbonates (Figure 7).

Conclusions

In summary, we have demonstrated that the use of Cs_2CO_3 as a base brings about a highly selective synthesis of polycarbonates by a one-pot protocol from the condensation between diols, CO_2 and dihalides. The structure of the precursors plays an important role on the polycondensation results. Dihalides with a spacer length higher than 4 carbons and diols with spacer length different from 4 afford polycarbonates with high conversion (>96%) and rather high molar mass (43,000 g/mol, GPC). The characterization of the obtained polycarbonates indicates the occurrence of self polycondensation of dihalides with CO_2; a slight excess of dihalides with respect to diols thus improves the polycondensation efficiency. Although not generating polycarbonates of so high molar mass as would do the carbonate interchange methodology, the process described in this investigation is general enough to be successfully applied
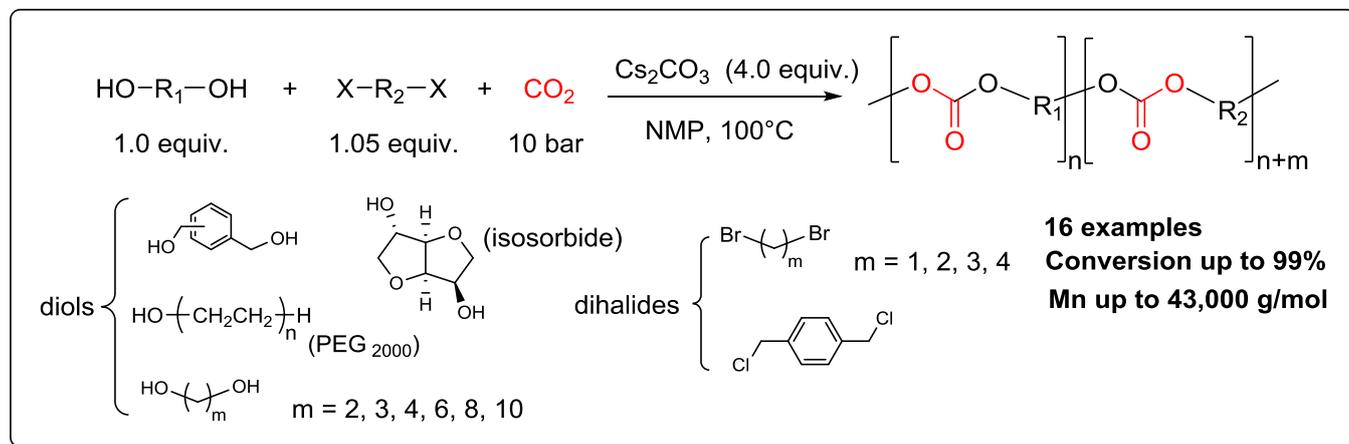
to the preparation of aliphatic-aliphatic, aliphatic-aromatic polycarbonates and polycarbonate-containing block copolymers. Further studies of the utilization of CO_2 for synthesis of aromatic polycarbonates and other polymers through direct polycondensation methodology are ongoing in our laboratory.

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Table of Contents Graphic

Cs₂CO₃-Promoted Polycondensation of CO₂ with Diols and Dihalides for the Synthesis of Miscellaneous Polycarbonates