A Chitosan Derivative Containing Both Carboxylic Acid and Quaternary Ammonium Moieties for the Synthesis of Cyclic Carbonates

Vincent Besse,^[a, b] Nicolas Illy,^[a, c] Ghislain David,^[a] Sylvain Caillol,^{*[a]} and Bernard Boutevin^[a]

1

Chitosan, a renewable feedstock, is modified and used as a catalytic support in the presence of potassium iodide. The system is highly efficient towards the incorporation of carbon dioxide (CO_2) into epoxides. It demonstrates very good thermal stability and is recyclable more than five times without loss of activity. The optimal reaction conditions were determined using allylglycidyl ether as a model and extended to a wide range of other epoxides. Cyclic carbonates were obtained with very high yield in a few hours under mild conditions (2–7 bar \approx 0.2–0.7 MPa, 80 °C) and no solvent.

Introduction

Cyclic carbonates were first described in the early 1930s by Carothers et al.^[1a,b,c] They are gaining a great deal of attention in both scientific and industrial communities because they are very versatile; for example, they can be used as synthons in organic synthesis, as high boiling polar solvents, or as electrolytes. In the field of materials chemistry, they have long been used for the preparation of polycarbonates but they are also especially promising for the synthesis of non-isocyanate polyurethanes (NIPUs).^[2a-g]

Scheme 1 shows the conventional routes used to synthesize five-membered cyclic carbonates. 1,2-diols can react with phosgene to form cyclic carbonates with high yields. But the toxicity of phosgene is the main drawback. Greener alternatives have been developed recently, whereby diols are reacted with ethylene carbonate, urea, or carbon dioxide.^[3] Carbon dioxide is of particular interest as this reagent is cheap, environmentally friendly and a green source of chemical carbon to substitute the phosgene. A wide range of CO₂ incorporation reactions has been developed for the synthesis of cyclic carbonates from dioxolane derivatives, olefins, or epoxides. Currently, cyclocarbonates are industrially produced from the 100% atom eco-

```
[a] Dr. V. Besse, Dr. N. Illy, Dr. G. David, Dr. S. Caillol, Prof. B. Boutevin
   Institut Charles Gerhardt Montpellier UMR 5253
    CNRS, Université de Montpellier
   l'Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM)
   8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5 (France)
   E-mail: sylvain.caillol@enscm.fr
[b] Dr. V. Besse
   COLAS S.A.
   7 place René Clair, 92653 Boulogne-Billancourt (France)
[c] Dr. N. Illy
   Sorbonne Universités
   UPMC Univ Paris 06, CNRS
   Institut Parisien de Chimie Moléculaire
   Equipe Chimie des Polymères
   4 place Jussieu, 75005, Paris (France)
   Supporting Information and the ORCID identification number(s) for the
   author(s) of this article can be found under http://dx.doi.org/10.1002/
   cssc 201600499
```



Scheme 1. Conventional routes for the synthesis of five membered cyclic carbonates.

nomic reaction between carbon dioxide and epoxides.^[4] However, CO_2 has a low reactivity and this reaction needs a high activation energy.^[5] To reduce the energy input required to transform CO_2 and to overcome the high reaction barrier, the development of high-performance catalysts is a key technology.

The attractiveness of a catalyst could be evaluated in accordance with the following criteria: its catalytic activity, the required reaction conditions (temperature, pressure, and time), the achieved yields and selectivities, its price and availability, its reusability and recycling abilities, and its environmental sustainability.^[6] A large variety of catalytic systems has been developed to perform the carbonation reaction. Different metalbased systems have proven to be very efficient and allow the cycloaddition under mild conditions (atmospheric pressure and room temperature).^[4] Nevertheless, organocatalysts are a promising alternative because they provide potential economic, environmental, and scientific benefits. They are often less sensitive to air and moisture allowing an easier experimental procedure, less expensive, and less toxic than metal-based systems.^[7] Recent reviews have summarized the large variety of organocatalysts that have been developed for this purpose.^[6,8] To the



best of our knowledge, no organocatalyst currently fulfills all the above criteria.

Supported organocatalysts are the easiest way to perform solvent-free heterogeneous phase reactions and to facilitate the reusability of the catalyst. Inorganic supports (e.g., silica^[9a-f]) as well as organic supports such as synthetic polymers^[9b, f, 10a-i] have been reported. However, immobilized catalysts require harsh conditions (T > 100 °C, P > 12 bar \approx 1.2 MPa, and/ or long reaction times) to reach high conversions and high yields. These restrictive conditions are an obstacle for their development of industrial use. Milder conditions with these catalysts inevitably result in a loss of activity. Bio-based platforms are even more interesting to increase the sustainability of the process.^[6, 11]

Chitosan is the deacetylation product obtained from chitin, which is the second most abundant natural polysaccharide (10¹³ kg/year) and can be extracted from shells of crustaceans and the cells walls of fungi and insects.^[12] Although only 24 kilotons were produced in 2015, the potential production capacity of chitosan could raise to 250 kilotons. This polymer is known to be biodegradable,^[13] biocompatible,^[14] and nontoxic.^[15] In addition, chitosan offers numerous possibilities for modification such as alkylation, acylation, quaternization, hydroxyalkylation, thiolation, sulfation, and phosphorylation.^[16a-h] The resulting chitosan derivatives are promising high-value materials; for example, chitosan has been widely used for tissue engineering,^[17] cosmetics,^[18] food,^[19] or wastewater treatment technologies.^[20] Several chitosan-based systems are efficient organocatalysts for the synthesis of cyclic carbonates.^[21a-c] Quaternary ammonium salt-functionalized chitosan derivatives are active catalyst under conventional heating^[22a-b] or microwave irradiation.^[23] Sun et al.^[24] developed a chitosan-supported ionic liquid catalyst. However, harsh conditions are required to reach quantitative conversion even under microwave irradiation (P > 12 bar; $T > 120 \degree C$).^[22a, 23] In the case of quaternary ammonium bearing chitosan, several authors underlined the role of chitosan hydroxyl groups.^[22b] Carboxylic acid groups are also known to enhance the catalytic activity^[11,25] but this effect has never been combined with quaternary ammonium groups supported on chitosan derivatives.

In this paper, we report on the synthesis of a chitosan-based catalytic system that shows high activity even at a temperature of 80 °C and under a CO_2 pressure of 7 bar. To the best of our knowledge, such mild pressure and temperature conditions have never been reported for supported organocatalysts. Chitosan was functionalized by both quaternary ammonium and a carboxylic group and used as a catalyst in combination with potassium iodide in solvent-free conditions. The optimal conditions in terms of concentration, temperature, and pressure were determined with allyl glycidyl ether prior to the carbonation of various epoxides.

Results and Discussion

First, the modification of chitosan and its characterization will be described. Then, the obtained chitosan derivative will be evaluated as a carbonation catalyst under different reaction conditions. Finally, its efficiency to achieve the synthesis of structurally different cyclic carbonates will be assessed.

Chitosan catalyst synthesis

According to the work of Song et al. on lecithin,^[26] the chitosan was modified in a way that the resulting structure is likely to dissociate KI. Thus, ammonium and carboxylic acid functions were introduced in two steps as shown in Scheme 2. Numerous papers have reported the modification of the primary amine of chitosan with epoxides in a water medium. $^{\scriptscriptstyle [16d,f]}$ Thus, in a first step, allyl and trimethylammonium moieties were introduced along the chitosan backbone through epoxideamine reactions with allyl glycidyl ether (AGE) and glycidyl trimethylammonium (GTA) chloride. The reaction was performed in water at 85 °C. Notably, the hydroxyl groups of chitosan are not sufficiently nucleophilic to induce ring opening of glycidyl trimethylammonium chloride or AGE, whereas the amine group of chitosan is nucleophilic enough to do $so.^{\scriptscriptstyle [16e,27]}$ The epoxidized chitosan is water-soluble. The ¹H NMR spectrum shows signals corresponding to the introduction of the allyl and quaternary ammonium substituents (Figure S1, Supporting Information). Two multiplets at 5.92 ppm ($CH_2 = CHCH_2O$) and 5.20–5.40 (CH₂=CHCH₂O) and a doublet at 4.04 ppm (CH₂= CHCH₂O) are typical of the allyl protons. The methyl groups of the quaternary ammonium group are observed as a very strong peak at 3.22 ppm. The degrees of substitution were calculated from the comparisons between the signal intensities of the $-CH=CH_2$ protons and the $-C(CH_3)_3^+$ protons with the signal of acetyl groups and were found to be approximately 0.70 and 0.30, respectively. The functionalization with glycidyl trimethylammonium chloride seems to be more difficult probably owing to the charge repulsion between quaternary ammonium moieties. The allyl-group-containing compound 1 (see Scheme 3 for structure of compounds 1 and 2) was then functionalized with 3-mercaptopropionic acid using a thiol-ene addition reaction to afford compound 2 according to a procedure reported by Illy et al. [16f] ¹H NMR analysis of compound 2 demonstrated that the addition of the thiol to the allyl groups occurred in 100% yield, with data consistent with that expected for the modified side chain groups (Figure S2).

The resulting polymer contains both quaternary ammonium and carboxylic acid groups with a ratio of 30/70 and is, therefore, zwitterionic. Chitosan was also functionalized with glycidyl trimethylammonium chloride only (compound **3**, see Figure S3 and Supporting Information for its synthesis). Its degree of substitution was approximately equal to 0.75.

Thermal characterization of the catalyst

Thermogravimetric analysis (TGa) of compound **2** (see Figure S4 and S5) shows that its thermal degradation starts at approximately 220 °C. This value is similar to the degradation temperature of unmodified chitosan. The stability of compound **2** at 80 °C was assessed by a 64 h isothermal TGA experiment. We observed a relatively rapid weight decrease of 8.9% after which a plateau was reached. This mass loss is only



Scheme 2. Modification of chitosan with AGE and GTA followed by thiol-ene addition with 3-mercaptopropionic acid.

owing to the moisture content of compound **2**, which shows a very high stability at this temperature.

Catalytic properties of compound 2

Table 1 shows the poor catalytic effects of chitosan as well as KI when they are used separately for the carbonation of propylene oxide (PO). Different polymer-supported ammoniumbased catalytic systems have been developed and reported for the carbonation of PO. Very recently, polystyrene-supported triethanolammonium iodide displayed a high activity and was CHEMSUSCHEM Full Papers

the most efficient in terms of energy consumption for this type of catalyst. Compound **2** was designed to induce the greatest possible dissociation of KI, thus the quantity of compound **2** is related to the functionalization of chitosan. As shown in Table 1 (Entry 14), compound **2** associated with KI displayed a remarkable activity to catalyze the propylene oxide carbonation. A quantitative yield was achieved with half the amount of catalyst and under milder conditions compared to the previously published ammonium-supported catalytic systems. In particular, the required pressure is below the pressures previously used in the literature. This outcome is very promising and additional studies were performed using allyl glycidyl ether (AGE) as a model substrate.

AGE carbonation using compound 2

Table 2 summarizes the results obtained for the carbonation reaction of AGE. Runs 1-3 were performed without KI as a control. A preliminary experiment was conducted without any catalyst (Entry 1). As expected, no reaction took place. The second entry was performed with only native chitosan (Entry 2) and no conversion was observed. Tharun et al.^[22b] have demonstrated the efficiency of a chitosan quaternized with methyl iodide (CH₃I) for the carbonation reaction of propylene oxide. The conditions described remain harsh as the best carbonation conditions were obtained at 11.7 bar at 120 °C and the conversion was not quantitative (87%). As a consequence, we decided to proceed to an experiment with compound 3, which contains quaternary ammonium moieties thanks to glycidyl trimethylammonium (see synthesis in Supporting Information). In that case, we clearly see that the use of compound 3 without KI results in low yield (15%). This could be explained by the presence of chlorine anions, which are known to show a lower activity compared to iodide for the synthesis of cyclic carbonates. Nevertheless, Zhao et al.^[22a] have shown that a similar chitosan derivative with I⁻ as a counterion required a temperature of 140°C and a CO₂ pressure of 40 bar to perform the carbonation (Table 1, Entry 6). The subsequent tests were then conducted using Compound 2 and KI as the catalytic system (Entries 4-11). The conversion

was completed after 4 h at 80 °C and under 7 bar (Entry 4), thus confirming the preliminary result obtained with propylene oxide. The concentration of the catalytic system was then reduced to 0.125 mol% (Entry 5) and 0.06 mol% (Entry 6) and the reactions were stopped after 4 h; the yields were still quantitative according to AGE conversion. This clearly demonstrates a synergistic effect between the synthesized compound **2** and KI.



Scheme 3. Proposed carbonation mechanism using the chitosan-based catalytic system.

Table 1. Comparison of the activity of different ammonium-supported catalytic systems toward carbonation of propylene oxide.

Entry	Catalyst	Cat. amt. [mol%]	t [h]	P [bars]	<i>Т</i> [°С]	Yield [%]
1	chitosan	1	4	20	120	2[24]
2	KI	1	2	20	120	3 ^[28]
3	PS Me ₃ N ⁺ Cl [−]	5	12	80	100	97 ^[10a]
4	PS EtN(CH ₂ CH ₂ OH) ⁺ Br ⁻	2	3	20	110	92 ^[10g]
5	PS-hexyl-NMe ₃ ⁺ l ⁻	0.6	6	12	120	98 ^[29]
6	chitosan-N ⁺ Me₃Cl ⁻	1.7	6	40	140	73 ^[22a]
7	chitosan-N ⁺ Me₃I ⁻	1.7	6	40	140	100 ^[22a]
8	CH ₃ I-quaternized chitosan	1.6	6	11.7	120	89 ^[23]
9	bis-ammonium PS	0.75	2.5	12	130	99 ^[30]
10	PS-MeN(CH ₂ CH ₂ OH) ₃ ⁺ I ⁻	2	4	10	90	93 ^[9f]
11	chitosan-functionalized	1	4	20	120	96 ^[24]
	1-ethyl-3-methyl imidazolium Br					
12	chitosan-grafted quaternary	-	4	25	120	99 ^[31]
	phosphonium ionic liquid					
13	carboxymethyl cellulose/ionic liquid	1.2	2	18	110	98 ^[11]
14	2+KI [this work]	0.38	3	7	80	97

Effect of the temperature, reaction time, and pressure on the catalytic system efficiency

An important aspect of such a carbonation reaction is the temperature needed to obtain complete conversion of the epoxide reactants. To investigate the effect of the temperature we performed three experiments at room temperature ($25 \,^{\circ}$ C), $50 \,^{\circ}$ C, and $80 \,^{\circ}$ C (Entries 7–9). The carbonation does not occur at

room temperature and remains slow at 50 $^\circ\text{C}$ (6%) compared to the quantitative conversion reached at 80 $^\circ\text{C}$ after only 2 h.

In addition, the sample of compound **2** that was subjected to a 64 h TGA experiment at 80 °C was used to evaluate its stability over time. No loss of activity was noticed as AGE was converted into the corresponding cyclic carbonate quantitatively after 3 h (P=7 bars, T=80 °C, [compound **2**]=[KI]= 0.125 mmol).

The effect of the reaction time on the conversion of AGE was also investigated. Tests were performed in the presence of 0.125 mmol of chitosan and 0.125 mmol KI under a CO₂ pressure of 7 bars and a temperature of 80 °C. The reaction proceeds very fast as 50% of the initial AGE was converted into its carbonation product after 30 min. The reaction is almost finished after only 2 h with a conversion of 98%. As a consequence, under these conditions, a reaction time of 2 h is sufficient for this system. Notably, under milder conditions and a lower concentration of the catalytic system, this system is twice as efficient as any other catalytic systems described in the literature. Carbonation experiments were also performed under different pressure conditions (Entries 9-11). After 4 h, the conversion increased with a carbon dioxide pressure rising to 7 bars and then reached up to 98% over 7 bar. However, an increase of the pressure led to a decrease of the conversion; the yield was only 86% after 4 h under 12 bar. A widely accepted interpretation is that the pressure of carbon dioxide affects the mass transfer during the reaction. Two phases exist under the reaction condition: a gas phase (carbon dioxide-rich) and a liquid phase (AGE-rich). The concentrations of both CO₂ and AGE in the two phases changes with CO₂ pressure. At a lower CO₂ pressure range the concentration of carbon dioxide in the liquid phase increases with CO₂ pressure, which is favorable for the reaction because the catalyst is located in the liquid phase and CO₂ is a reactant. However, the solubility of AGE in CO₂ increases with increasing CO₂ pressure and thus leads to a dilution effect in the liquid phase at a higher CO₂ pressure range, which might hinder the adsorption of AGE on the surface of the catalyst. These two competing factors resulted in a maximum reaction activity at approximately 7 bar.

Proposed mechanism of the coupling reaction

The best activity of KI is found if the interaction between K⁺ and I⁻ is low, meaning that the anion is free to react with electrophilic species. As a result, the presence of a well-defined support in the medium allows for better dissociation. Song et al. described a mechanism for the lecithin/potassium halide system.^[26] In this mechanism, KI dissociates owing to the car-



Table 2. Carbonation reactions performed with 32.2 mmol AGE as sub- strate.							
Run	Catalyst	Support	KI [mol]	T I°Cl	t [b]	P [bar]	Conv.
	system		[IIIOI]	[]	[11]	[Dai]	[/0]
1	-	0	0	80	24	7	0
2	chitosan	0.25	0	80	24	7	0
3	3	0.25	0	80	24	7	15
4	2 /KI	0.25	0.25	80	4	7	100
5	2 /KI	0.125	0.125	80	4	7	98
6	2 /KI	0.06	0.06	80	4	7	98
7	2 /KI	0.125	0.125	25	4	7	0
8	2 /KI	0.125	0.125	50	4	7	6
9	2 /KI	0.125	0.125	80	2	7	97
10	2 /KI	0.125	0.125	80	2	2	41
11	2 /Kl	0.125	0.125	80	2	12	86

boxylic acid function and the ammonium moiety, which leads to better activity of the iodide anion.

The formation of the cyclic carbonate is typical and can be described as follow. The first step is the dissociation of KI. Secondly, the I^- anion attacks the less hindered carbon of the epoxy ring, prior to a ring opening reaction step. The next step is the introduction of CO₂ to form an alkyl carbonate anion. The last step is an intramolecular cyclic step to form the desired cyclic carbonate and at the same time regenerate the catalytic system.

Nevertheless, it should be underlined that chloride anions are also present in our catalytic system as the initial counter-ions of the ammonium groups. Cl⁻ and l⁻ act as competitors. When it comes to nucleophilic attack in such reaction media, iodide ions are way more reactive toward ring opening compared to chloride ions.^[32] The iodide based catalysts are about 8–10 times more reactive than those based on chloride anion. Therefore, by interacting with the ammonium group, Cl⁻ might decrease the dissociation of Kl and reduce the catalytic activity of our system. Thus, our system might not be fully optimized and the elimination of the Cl⁻ anions might result in an improvement of our system.

Reusability of compound 2

The reusability of compound **2** was investigated following a procedure similar to that described by Tharun et al.^[22b] Chitosan (0.125 mmol) and KI (0.125 mmol) were used for the carbonation of AGE at 7 bar and 80 °C. The reactor was opened after 4 h. Compound **2** was regenerated by washing with acetone, which allows for the complete removal of KI. It was then filtered and dried at 40 °C for 18 h. The regenerated compound **2** was then used for the carbonation of AGE under similar conditions. The catalytic system was perfectly stable even after 5 cycles as no loss of activity was observed.

This result can be explained by the excellent thermal stability of the modified chitosan at 80 °C according to the isothermal TGA experiments (see Figure S5).

Synthesis of a library of cyclic carbonates from CO_2 and epoxides

The effectiveness of a good carbonation catalyst is not only measured by its ability to selectively yield a product in a short time but even more so, its ability to efficiently catalyze a wide range of epoxides. Therefore, we investigated the synthesis of different cyclic carbonates using the corresponding epoxides, KI, and compound **2** in a stainless steel autoclave (50 mL) equipped with a mechanical stirrer. Table 3 summarizes the results obtained, which show that the catalytic system is highly efficient for the synthesis of all the mono-substituted terminal epoxides we investigated (Entries 1–6). After 4 h of reaction, AGE showed the highest yield (100%) whereas epichlorohydrin, containing an electron withdrawing group (CH₂–CI),

Table 3. Various carbonates obtained by epoxide carbonation catalyzed by KI in the presence of compound 2 (P=7 bar, 32.2 mmol epoxide, 0.125 mmol KI, 0.125 mmol compound 2, 80 °C).

Entry	Epoxide	Products	<i>t</i> [h]	Yield [%]	TOF [h ⁻¹]	TON
1	Å		4	89	57.3	229.2
2			4 (2)	100 (98)	63.9	255.6
3	$\bigcirc \bigcirc $		4	89	57.3	229.2
4	\sim		4	100	62.6	250.2
5	Lo~^		4	91	58.6	234.4
6	cı 🗸		4	81	52.2	208.8
7	Ч	ОСОН	4	0	0	0

showed the lowest yield (81%). The turnover frequency (TOF) and turnover number (TON) correlated with the reaction yields. As an example, the best TOF of 63.9 h^{-1} (TON = 255.6) was obtained for the quantitative conversion of AGE (Table 3, Entry 2), whereas the lowest TOF of 52.2 h^{-1} (TON = 208.8) was obtained with epichlorohydrin, which had a conversion of 81% (Table 3, Entry 6). This can be explained by a reduced electron density of the epoxide oxygen atom in the latter.^[26] We tried to obtain a 6-membered cyclic carbonate (6-CC) from 3-methyl-3-oxetanemethanol but the reaction did not succeed. The synthesis of six-membered heterocycles based on the direct coupling between oxetanes and CO₂ is generally more difficult than the carbonation of epoxides. Carbon dioxide insertion into a heterocyclic ring requires a high-energy substrate to favor the reaction. Epoxides have higher ring-strain and are therefore easier to ring-open. Recently, several papers have been able to design transition metal based bi-component catalysts that



allow the conversion of oxetanes into 6-membered cyclocarbonates.^[8,33a-c] They required the use of an organometallic catalyst and a nucleophilic compound under carbon dioxide pressure above 10 bar.^[34] The metal complex serves as a Lewis acid to form an adduct with the heterocycle to activate the oxetane by increasing its electrophilicity. In a second step, the activated oxetane is ring-opened by the nucleophilic compound. Our catalytic system does not rely on Lewis acid metals and is, therefore, unsuitable for oxetanes.

Conclusions

The first part of this work was dedicated to the modification of chitosan to improve the dissociation of potassium iodide. This work demonstrates the convenience of the chitosan-based catalytic system, which allows the synthesis of 5-membered cyclic carbonates under low pressure (7 bar or less), low temperature (80 $^\circ\text{C})\text{,}$ with a low amount of potassium iodide (compound 2/KI, 1:1, 0.125 mmol) and without solvent. Our study provides proof of the stability of the chitosan-based system even after 5 cycles. Moreover, compound 2 is stable after 64 h at 80 °C as it can be reused without any noticeable deterioration in its performance. Chitosan derivative 2 and potassium iodide have an excellent synergetic effect. As a consequence, chitosan has the potential to be an abundant, greener, and active catalyst for the synthesis of cyclic carbonates from CO₂ and epoxides. Notably, this system is not active toward 3-methyl-3-oxetanemethanol. Oxetane carbonation requires an increase in the electrophilicity of the heterocycle. However, our catalytic system does not rely on a heterocycle activation process and is therefore not suitable for 6-CC synthesis.

Experimental Section

Materials and methods

Chitosan 652 (Chitine, France) is an ivory white powder originating from shrimp shells. Its degree of deacetylation is 90% (supplier data), its molecular weight is approximately 150000 g mol⁻¹ and its hydration degree is 10 w% (TGA). Sodium iodide (KI, 99.5%), sodium hydroxide (97%), and 1-methyl-2-pyrrolidinone (99%) were purchased from Sigma–Aldrich and used without further purification. Allyl glycidyl ether (97%, AGE) and other epoxides were also obtained from Sigma–Aldrich and used as received. Glycidyltrimethylammonium chloride (>90%), 4,4'-azobis(4-cyanovaleric acid) (>75%), 3-mercaptopropionic acid (>99%) were purchased from Sigma–Aldrich and used as received. Glycidyltrimethylammonium chloride as received. CO₂ of 99.999% purity was used without further purification. CH₂Cl₂ was obtained from SK Chemicals, Korea, and used as received. Deuterated solvents (D₂O, CDCl₃, and [D₆]DMSO) were purchased from Eurisotop (Saint-Aubin, France).

Characterization

All ¹H NMR measurements were recorded on Bruker 250 MHz and AC-400 MHz spectrometers at room temperature in deuterium oxide (D₂O), deuterated chloroform (CDCl₃) or deuterated dimethyl-sulfoxide ([D₆]DMSO). The chemical shifts are reported in parts per million relative to tetramethylsilane. Thermogravimetric analyses

(TGA) were obtained on a TA Instruments Q50 apparatus. The initial weight of each sample tested was approximately 15 mg. Data were collected using the following temperature programs: a 10° Cmin⁻¹ ramp between 35 and 600 °C or a 64 h isotherm at 80 °C. All experiments were performed under a stream of air.

Synthesis of compound 1

Chitosan (2.0 g, 10.9 mmol of primary amine groups, 1 eqiuv.) was dispersed in 100 mL of deionized water at 85 °C. Glycidyltrimethylammonium chloride (1.65 g, 9.79 mmol, 0.9 eqiuv.) and AGE (0.60 g, 5.26 mmol, 0.48 eqiuv.) were added dropwise to the reaction mixture under vigorous stirring. Subsequently, the same amounts of the reactants were added dropwise after 24 and 48 h of reaction. The reaction was stopped after 72 h. The polymer was recovered by precipitation in acetone. The precipitate was washed several times with acetone and dried under vacuum at 45 $^\circ\text{C}$ for 48 h to obtain compound 1 as a white powder (2.55 g). ¹H NMR (D₂O, 400 MHz): $\delta = 5.92$ (m, 0.70 H, CH₂CH=CH₂), 5.20–5.40 (m, 1.36 H, CH₂CH=CH₂), 4.40-4.80 (m, H-1, HDO), 4.25 (m, 0.5 H, CH₂CH(OH)CH₂N), 3.32-4.16 (m, 7.8 H, CH₂CH=CH₂, CH₂N(CH₃)³⁺, CH₂CH(OH)CH₂O, CH₂OCH₂CH=CH₂, H-3, H-4, H-5, H-6), 3.19 (s, 2.88 H, $CH_2N(CH_3)^{3+}$), 2.35–3.08 (m, 2.5 H, $NHCH_2$, H-2), 2.05 ppm (s, 0.3 H, C(O)CH₃).

Synthesis of compound 2

Compound 1 (0.5 g, 1 eqiuv. of allyl groups) was dissolved in 20 mL of deionized water at 50 °C. After complete dissolution and cooling of the solution to room temperature, 3-mercaptopropionic acid (2.0 g, \approx 15 eqiuv.) and 4,4'-azobis(4-cyanovaleric acid) (0.1 g, \approx 0.2 eqiuv.) dissolved in 2.0 mL of methanol were added. After 20 min of argon bubbling, the stirred homogeneous reaction mixture was heated at 70 °C and stirred for 20 h. The pH of the solution was adjusted to 5.5 by the addition of a NaOH solution. The polymer was recovered by precipitation in acetone, dissolved de novo in deionized water, precipitated again in acetone, and finally dried under vacuum at 45 °C for 48 h to obtain compound 2. 0.47 g of slightly yellow powder are obtained. ¹H NMR (D₂O, 400 MHz): δ = 4.20–5.15 (m, H-1, CH₂CH(OH)CH₂N, HDO), 3.03–4.32 (m, 13.51 H, $CH_2CH(OH)CH_2O$, $CH_2N(CH_3)^{3+}$, $CH_2OCH_2CH=CH_2$, OCH₂CH₂CH₂S, CH₂N(CH₃)³⁺, H-3, H-4, H-5, H-6), 2.33-3.03 (m, 6.74H, NHCH₂, CH₂SCH₂CH₂COOH, H-2), 2.07 (s, 0.3 H, C(O)CH₃), 1.89 ppm (m, 1.43 H, OCH₂CH₂CH₂S).

Synthesis of cyclic carbonates

Carbonation reactions of the epoxide reactants were typically performed according to the following procedure. The epoxide (32.2 mmol), modified chitosan (0.125 mmol), and potassium iodide (KI, 0.125 mmol) were introduced in an autoclave (50 mL). The carbon dioxide was then added (7 bar) and the reaction proceeded at 80°C during 2 h. The conversion was determined using 1H NMR for all the monomers using the specific chemical shifts of the oxirane and carbonate protons. The crude material was filtered off and distilled to remove chitosan and KI.



Acknowledgements

The authors would like to thank the ChemSud foundation (Chemistry for Sustainable Development) for financial support and Marion Medinilla for her help during her training period.

Keywords: chitosan · cyclic carbonates · epoxides heterogeneous catalysis · supported catalyst

- [1] a) J. W. Hill, W. H. Carothers, J. Am. Chem. Soc. 1933, 55, 5031-5039;
 b) W. H. Carothers, J. W. Hill, W. H. Carothers, J. Am. Chem. Soc. 1933, 55, 5043-5052; c) E. W. Spanagel, W. H. Carothers, J. Am. Chem. Soc. 1935, 57, 929-934.
- [2] a) V. Besse, F. Camara, C. Voirin, R. Auvergne, S. Caillol, B. Boutevin, *Polym. Chem.* 2013, 4, 4545–4561; b) V. Besse, R. Auvergne, S. Carlotti, G. Boutevin, B. Otazaghine, S. Caillol, J.-P. Pascault, B. Boutevin, *React. Funct. Polym.* 2013, 73, 588–594; c) M. Fache, E. Darroman, V. Besse, R. Auvergne, S. Caillol, B. Boutevin, *Green Chem.* 2014, 16, 1987–1998; d) M. Desroches, S. Benyahya, V. Besse, R. Auvergne, B. Boutevin, S. Caillol, *Lipid Technol.* 2014, 26, 35–38; e) V. Besse, F. Camara, F. Méchin, E. Fleury, S. Caillol, J.-P. Pascault, B. Boutevin, *Eur. Polym. J.* 2015, 71, 1–11; f) D. C. Webster, *Prog. Org. Coat.* 2003, 47, 77–86; g) M. Calle, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, *J. Polym. Sci. Part A* 2014, *52*, 3017–3025.
- [3] J. A. Castro-Osma, M. North, Curr. Green Chem. 2014, 1, 257-272.
- [4] J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, Green Chem. 2015, 17, 1966–1987.
- [5] M. Aresta, A. Dibenedetto, Dalton Trans. 2007, 2975-2992.
- [6] M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann, F. E. Kühn, ChemSusChem 2015, 8, 2436–2454.
- [7] D. W. C. MacMillan, Nature 2008, 455, 304-308.
- [8] G. Fiorani, W. Guo, A. W. Kleij, Green Chem. 2015, 17, 1375-1389.
- [9] a) C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona, M. Gruttadauria, *ChemSusChem* 2011, *4*, 1830–1837; b) J. Wang, J. Leong, Y. Zhang, *Green Chem.* 2014, *16*, 4515–4519; c) K. Motokura, S. Itagaki, Y. Iwasawa, A. Miyaji, T. Baba, *Green Chem.* 2009, *11*, 1876–1880; d) T. Sakai, Y. Tsutsumi, T. Ema, *Green Chem.* 2008, *10*, 337–341; e) T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda, T. Sakakura, *Chem. Commun.* 2006, 1664–1666; f) C. Kohrt, T. Werner, *ChemSusChem* 2015, *8*, 2031–2034.
- [10] a) Y. Du, F. Cai, D.-L. Kong, L.-N. He, Green Chem. 2005, 7, 518–523;
 b) H. Kawanami, Y. Ikushima, Chem. Commun. 2000, 2089–2090; c) Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu, K. Ding, Angew. Chem. Int. Ed. 2007, 46, 7255–7258; Angew. Chem. 2007, 119, 7393–7396; d) Q.-W. Song, L.-N. He, J.-Q. Wang, H. Yasuda, T. Sakakura, Green Chem. 2013, 15, 110–115; e) C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij, M. A. Pericas, Green Chem. 2014, 16, 1552–1559; f) A. J. R. Amaral, J. F. J. Coelho, A. C. Serra, Tetrahedron Lett. 2013, 54, 5518–5522; g) X. Chen, J. Sun, J. Wang, W. Cheng, Tetrahedron Lett. 2012, 53, 2684–2688; h) Y. Du, J.-Q. Wang, J.-Y. Chen, F. Cai, J.-S. Tian, D.-L. Kong, L-N. He, Tetrahedron Lett. 2006, 47, 1271–1275; j) J. He, T. Wu, Z. Zhang, K. Ding, B. Han, Y. Xie, T. Jiang, Z. Liu, Chem. Eur. J. 2007, 13, 6992–6997.
- [11] K. R. Roshan, G. Mathai, J. Kim, J. Tharun, G.-A. Park, D.-W. Park, Green Chem. 2012, 14, 2933–2940.
- [12] P. Jolles, R. A. A. Muzzarelli, Chitin and Chitinases, Springer, Basel, 1999.
- [13] Y. Shigemasa, K. Saito, H. Sashiwa, H. Saimoto, Int. J. Biol. Macromol. 1994, 16, 43-49.

CHEMSUSCHEM Full Papers

- [14] P. J. VandeVord, H. W. T. Matthew, S. P. DeSilva, L. Mayton, B. Wu, P. H. Wooley, J. Biomed. Mater. Res. 2002, 59, 585-590.
- [15] M. Rinaudo, Prog. Polym. Sci. 2006, 31, 603–632.
- [16] a) N. M. Alves, J. F. Mano, Int. J. Biol. Macromol. 2008, 43, 401-414;
 b) V. K. Mourya, N. N. Inamdar, React. Funct. Polym. 2008, 68, 1013-1051; c) N. Illy, S. Benyahya, N. Durand, R. Auvergne, S. Caillol, G. David, B. Boutevin, Polym. Int. 2014, 63, 420-426; d) N. Illy, G. Couture, R. Auvergne, S. Caillol, G. David, B. Boutevin, RSC Adv. 2014, 4, 24042-24052;
 e) N. Illy, M. Fache, R. Menard, C. Negrell, S. Caillol, G. David, Polym. Chem. 2015, 6, 6257-6291; f) N. Illy, M. Robitzer, R. Auvergne, S. Caillol, G. David, P. Menard, C. Negrell, S. Caillol, G. David, Polym. Chem. 2015, 6, 6257-6291; f) N. Illy, M. Robitzer, R. Auvergne, S. Caillol, G. David, P. Menard, C. Negrell, S. Caillol, G. David, Polym. Chem. 2015, 6, 6257-6291; f) N. Illy, M. Robitzer, R. Auvergne, S. Caillol, G. David, B. Boutevin, J. Polym. Sci. Part A 2014, 52, 39-48; g) J. Ji, L. Wang, H. Yu, Y. Chen, Y. Zhao, H. Zhang, W. A. Amer, Y. Sun, L. Huang, M. Saleem, Polym.-Plast. Technol. Eng. 2014, 53, 1494-1505; h) G. Z. Kyzas, D. N. Bikiaris, Mar. Drugs 2015, 13, 312-337.
- [17] M. Gingras, I. Paradis, F. Berthod, Biomaterials 2003, 24, 1653-1661.
- [18] S.-K. Kim, Y. D. Ravichandran, S. B. Khan, Y. T. Kim, *Biotechnol. Bioprocess Eng.* 2008, 13, 511–523.
- [19] H. K. No, S. P. Meyers, W. Prinyawiwatkul, Z. Xu, J. Food Sci. 2007, 72, R87-R100.
- [20] I. G. Lalov, I. I. Guerginov, M. A. Krysteva, K. Fartsov, Water Res. 2000, 34, 1503 – 1506.
- [21] a) H. Xie, S. Zhang, S. Li, Green Chem. 2006, 8, 630-633; b) L.-F. Xiao, F.-W. Li, C.-G. Xia, Appl. Catal. A 2005, 279, 125-129; c) A. El Kadib, Chem-SusChem 2015, 8, 217-244.
- [22] a) Y. Zhao, J.-S. Tian, X.-H. Qi, Z.-N. Han, Y.-Y. Zhuang, L.-N. He, J. Mol. Catal. A 2007, 271, 284–289; b) J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A. C. Kathalikkattil, D.-W. Park, Catal. Sci. Technol. 2012, 2, 1674–1680.
- [23] J. Tharun, D. W. Kim, R. Roshan, Y. Hwang, D.-W. Park, Catal. Commun. 2013, 31, 62–65.
- [24] J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang, Y. She, Green Chem. 2012, 14, 654–660.
- [25] L. Han, H.-J. Choi, S.-J. Choi, B. Liu, D.-W. Park, Green Chem. 2011, 13, 1023 – 1028.
- [26] J. Song, B. Zhang, P. Zhang, J. Ma, J. Liu, H. Fan, T. Jiang, B. Han, Catal. Today 2012, 183, 130–135.
- [27] S.-H. Lim, S. M. Hudson, *Carbohydr. Res.* 2004, 339, 313-319.
- [28] Y.-B. Sun, C.-Y. Cao, S.-L. Yang, P.-P. Huang, C.-R. Wang, W.-G. Song, *Chem. Commun.* 2014, 50, 10307 – 10310.
- [29] S.-D. Lee, B.-M. Kim, D.-W. Kim, M.-I. Kim, K. R. Roshan, M.-K. Kim, Y.-S. Won, D.-W. Park, Appl. Catal. A 2014, 486, 69–76.
- [30] Q. Deng, G. He, Y. Pan, X. Ruan, W. Zheng, X. Yan, RSC Adv. 2016, 6, 2217–2224.
- [31] J.-X. Chen, B. Jin, W.-L. Dai, S.-L. Deng, L.-R. Cao, Z.-J. Cao, S.-L. Luo, X.-B. Luo, X.-M. Tu, C.-T. Au, *Appl. Catal. A* 2014, 484, 26–32.
- [32] K. R. Roshan, A. C. Kathalikkattil, J. Tharun, D. W. Kim, Y. S. Won, D. W. Park, *Dalton Trans.* 2014, 43, 2023–2031.
- [33] a) D. J. Darensbourg, A. I. Moncada, *Macromolecules* 2010, 43, 5996–6003; b) C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Adv. Synth. Catal.* 2012, 354, 469–476; c) J. Rintjema, W. Guo, E. Martin, E. C. Escudero-Adán, A. W. Kleij, *Chem. Eur. J.* 2015, 21, 10754–10762.
- [34] D. J. Darensbourg, A. Horn Jr, A. I. Moncada, Green Chem. 2010, 12, 1376-1379.

Received: April 17, 2016 Revised: June 6, 2016 Published online on

7

www.chemsuschem.org

ChemSusChem 2016, 9, 1-8

FULL PAPERS

V. Besse, N. Illy, G. David, S. Caillol,* B. Boutevin

A Chitosan Derivative Containing Both Carboxylic Acid and Quaternary Ammonium Moieties for the Synthesis of Cyclic Carbonates



Renewable catalysis: A chitosan-based catalyst for epoxide carbonation is described. The catalyst is efficient for the synthesis of a wide range of compounds under significantly milder operating conditions (pressure and temperature) compared to previously reported bio-based supported catalysts. It is also recyclable more than five times without loss of activity.