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Par Antoine Brège

CO2-based synthons, from the synthesis to the elaboration of low carbon footprint polycarbonates

Sous la direction de Dr. Thierry Tassaing et de Prof. Christine Jérôme

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Membres du jury :

Mme. DE OLIVEIRA-VIGIER, Karine	Professeure, Université de Poitiers, France	Président
M. BUCHARD, Antoine	Reader, University of Bath, United Kingdom	Rapporteur
Mme. MARTIN-VACA, Blanca	Professeure, Université Paul Sabatier, France	Rapporteur
Mme. MEDINA-GONZALEZ, Yaocihuatl	Chargée de Recherche, Université de Bordeaux, France	Examinateur
M. TASSAING, Thierry	Directeur de Recherche, CNRS, France	Directeur de thèse
Mme. JEROME, Christine	Professeure, Université de Liège, Belgique	Directrice de thèse
M. DETREMBLEUR, Christophe	Directeur de Recherche, FNRS, Belgique	Invité,Secrétaire
M. MEREAU, Raphaël	Ingénieur de Recherche, Université de Bordeaux, France	Invité

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RESUMÉ EN FRANÇAIS

La raréfaction des ressources fossiles, l'augmentation de leur prix au fil du temps ainsi que les problèmes environnementaux que leur extraction et utilisation en tant que matière première génèrent, poussent le chimiste à s'intéresser à de nouvelles sources de carbone peu coûteuses, abondantes, faiblement toxiques et écologiques. Aujourd'hui perçu comme un déchet, le CO_2 est paradoxalement un candidat de choix pour remplir ces critères exigeants. Avec près de 40 GT de CO_2 relâchées dans l'atmosphère chaque année par les activités humaines, c'est autant de carbone qui reste inutilisé et malgré tout accessible. Combiné avec l'utilisation de la biomasse comme ressources renouvelables, ce gaz à effet de serre pourrait devenir une des nouvelles sources carbonées C1 pour le développement de molécules organiques et de matériaux polymères à faible empreinte carbone. En raison de sa grande stabilité thermodynamique, de nombreuses voies de synthèse ont été proposées et développées afin de valoriser le CO_2 comme réactif pour l'obtention de produits chimiques couramment utilisés. Notamment, une des voies les plus abouties aujourd'hui reste son couplage avec les époxydes ou oxétanes afin de produire des carbonates cycliques à 5 ou 6 chaînons, ou encore des polycarbonates. Avec des résultats prometteurs en voie d'industrialisation, cette dernière reste néanmoins limitée en termes de substrats accessibles ce qui réduit considérablement son champ d'application. De plus, la toxicité accrue des époxydes et oxétanes rend leur utilisation à l'échelle industrielle problématique, ce qui pousse la communauté scientifique à s'intéresser à d'autres substrats. Notamment, les alcools présentent l'avantage d'être, pour la plupart, non-toxiques avec une gamme de structures chimiques accessible considérable et pouvant être issus de la biomasse. Dès lors, combiner la valorisation du CO_2 et des alcools biosourcés constitue une piste prometteuse pour l'obtention de composés ou matériaux organiques. Dans ce contexte, le travail de cette thèse a pour but d'étudier en détails le couplage entre le CO_2 et les diols pour l'obtention de carbonates (a)cycliques et polycarbonates (voir Schéma 1).

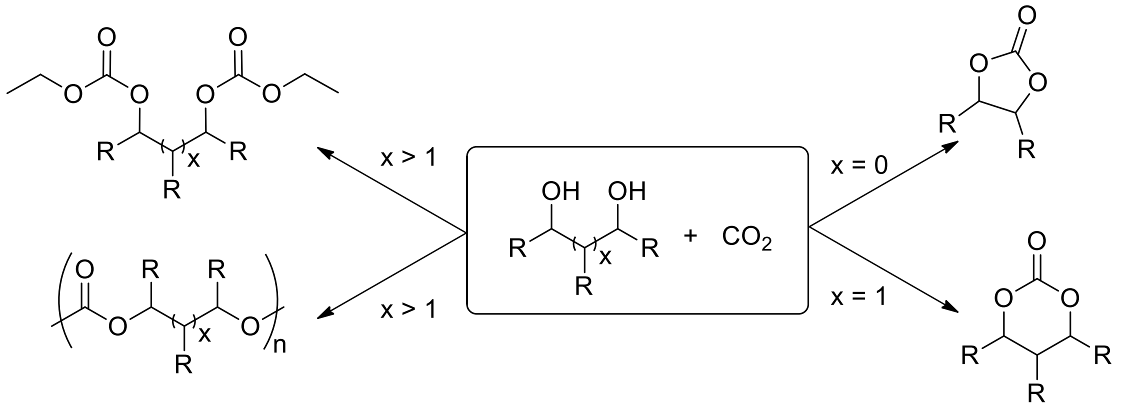

Schéma 1 : Le couplage diol/CO_2 pour la synthèse de carbonate (a)cycliques ou polycarbonates

Comme déjà décrit dans la littérature, le couplage CO_2/diol en carbonate (a)cyclique est limité par un équilibre (voir Schéma 2). Comme il s'accompagne de la formation quantitative d'une molécule d'eau par lien carbonate formé, de nombreuses stratégies de synthèse ont été employées pour éliminer l'eau lors de la réaction, déplaçant ainsi l'équilibre vers la formation de carbonates. Allant de systèmes déshydratants à l'utilisation de co-réactifs pour outrepasser cette formation d'eau, les systèmes proposés dans la littérature sont généralement lourds, leur mécanisme peu compris et manquent de répétabilité.

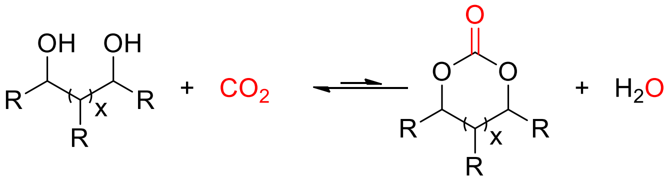

Schéma 2 : Formation d'eau comme co-produit du couplage diol/CO_2 pour l'obtention de carbonates cycliques

Dans ce contexte, un des premiers travaux de cette thèse est d'étudier en détails le couplage diol/CO_2 pour la synthèse de carbonate (a)cycliques en utilisant des systèmes organiques duaux (base organique et composé halogéné) visant d'une part à activer la réaction dans des conditions douces et d'autre part à éviter la formation d'eau. A l'aide d'outils puissants comme la spectroscopie ATR-IR *in-situ* en combinaison avec la modélisation moléculaire par calculs DFT, une première réaction modèle sur le propylène glycol pour l'obtention du carbonate de propylène a été réalisée en utilisant le système DBU/EtBr. Un mécanisme de la réaction a été proposé en se basant sur l'évolution de l'intensité de différentes bandes caractéristiques en ATR-IR tout au long de la réaction (voir Figure 1). Notamment, un des premiers résultats consiste en l'étape de carbonatation de l'alcool qui passe par un mécanisme trimoléculaire faisant intervenir la base, le CO_2 et l'alcool. En l'absence d'une de ces trois espèces, aucune réaction ne se passe, pas même la déprotonation du propylène glycol par le DBU. Le mécanisme qui ressort de cette étude est présenté en Schéma 3. L'étude de l'influence de divers paramètres expérimentaux comme la température, la pression, le solvant ou encore la nature de l'halogénure d'alkyle (EtBr, EtCl, BuBr, CH_3I …) sur les cinétiques et rendements de la réaction est proposée. Une attention particulière sur le choix de l'halogénure d'alkyle en fonction de la base afin d'éviter une réaction secondaire (quaternisation de la base) a permis d'identifier les principales limitations de ce système. De plus, un phénomène de double carbonatation (chaque alcool est carbonaté puis alkylé) rentre en compétition avec la réaction de cyclisation désirée, produisant ainsi des carbonates d'alkyles linéaires comme sous-produits. Un autre système organique dual fut étudié en détails de la même manière, comprenant la TEA comme base et le chlorure de tosyle (TsCl) comme agent halogéné. En raison du caractère moins basique de la TEA, aucun problème de quaternisation n'a été observé bien que le TsCl soit hautement réactif. De ce fait, des cinétiques beaucoup plus rapides furent obtenues en utilisant ce système pour la synthèse de carbonate de propylène au départ de propylène glycol et de CO_2. Dans ce cas, une des réactions secondaires à considérer est la tosylation des alcools plutôt que leur carbonatation. Ces deux systèmes organiques activateurs de la réaction, utilisés en quantité stœchiométriques pour outrepasser la formation d'eau, furent ensuite appliqués à une banque de substrats comprenant des diols 1,2 ; des diols 1,3 ; un diol 1,4 et l'isosorbide, un diol à la structure bicyclique (deux furanes fusionnés) dérivé de l'amidon. Une attention particulière sur la sélectivité vers le produit cyclique ou le sous-produit fut portée.

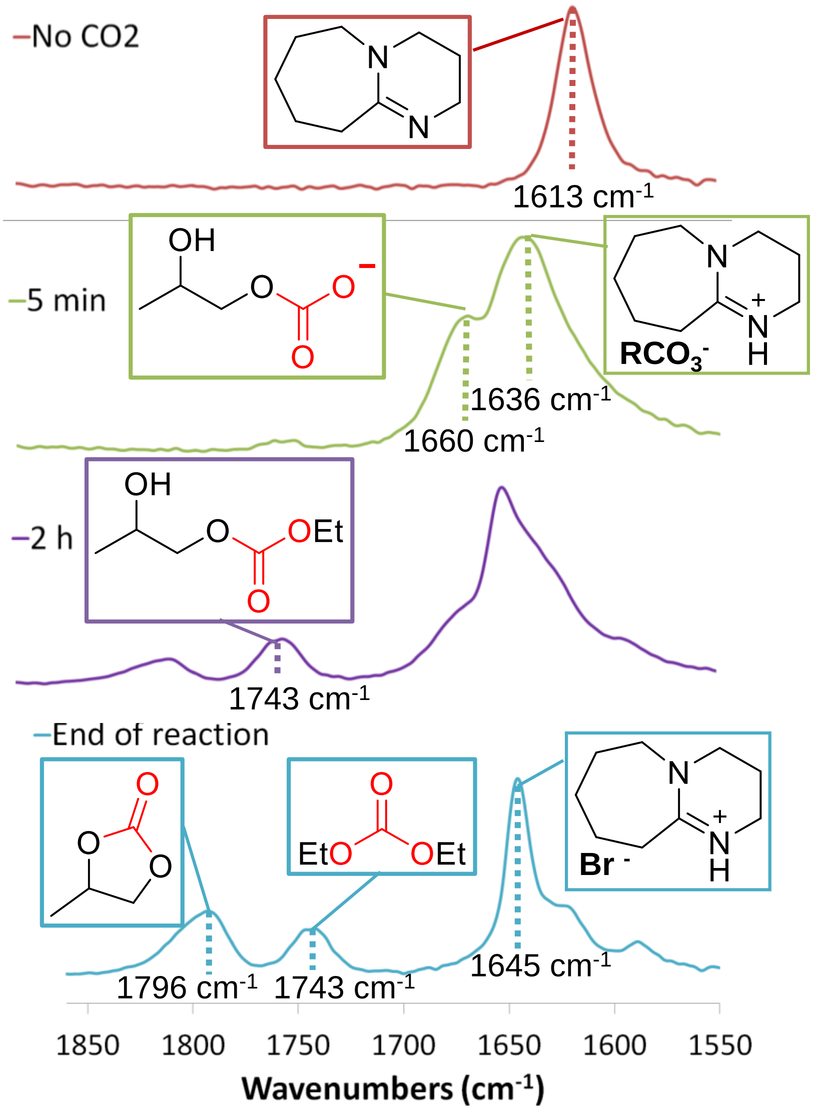

Figure 1 : Sélection de spectres ATR-IR au cours de la réaction montrant l'apparition et disparition de bandes caractéristiques, permettant d'identifier des intermédiaires réactionnels

D'une manière générale, le système DBU/EtBr tend à favoriser la double carbonatation pour les diols 1,2 et 1,3, à l'exception du glycérol et du pinacol dont la formation de carbonate cyclique est exclusive. Concernant le système TEA/TsCl, les carbonates à 5 et 6 chaînons sont obtenus avec des rendements relativement plus élevés. Comme attendu, les diols 1,4 et l'isosorbide ne produisent pas de carbonates cycliques en raison de leur structure peu propice à la cyclisation. Dans le cas DBU/EtBr, les carbonates linéaires sont obtenus. Dans le cas TEA/TsCl, des traces d'oligomères ont été détectées.

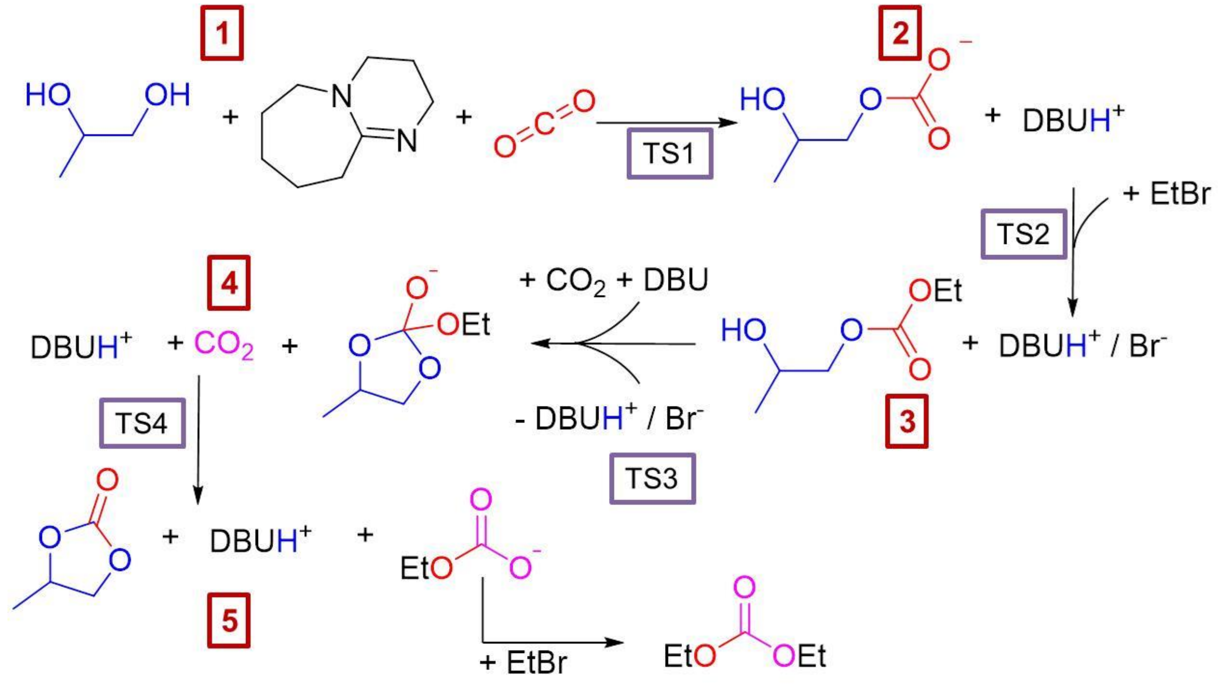

Schéma 3 : Mécanisme proposé pour la formation de carbonate de propylène au départ de propylène glycol et de CO_2 utilisant le système dual DBU/EtBr, confirmé par la modélisation moléculaire (calculs DFT).

A la lumière des précédents résultats, notamment sur le couplage isosorbide/CO_2 avec le système TEA/TsCl, une stratégie de synthèse pour l'obtention de polycarbonate d'isosorbide par copolymérisation directe avec le CO_2 a été étudiée dans un second temps. Notamment, la carbonatation de l'isosorbide en présence de CO_2 et de TEA laisse suggérer la formation d'un adduit RCO_3Ts très réactif qui, en présence d'une autre fonction alcool, est propice à la transcarbonatation. En choisissant une stœchiométrie adéquate, soit 2 fonctions alcools pour une fonction TsCl, le système est alors enclin à une oligomérisation pour la production de polycarbonates d'isosorbide (voir Schéma 4).

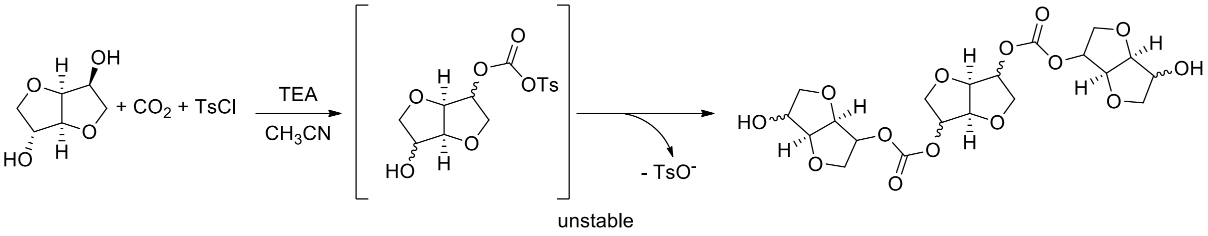

Schéma 4 : Stratégie de synthèse d'oligocarbonates par polycondensation directe entre l'isosorbide et le CO_2, activée par le système organique dual TEA/TsCl

De par leur structure bicyclique apportant de la rigidité au polymère final, les polycarbonates d'isosorbide présentent des propriétés thermomécaniques analogues aux polycarbonates conventionnels synthétisés au départ de Bisphénol A. Cette stratégie qui permet de remplacer le Bisphénol A, toxique et pétrosourcé, par l'isosorbide biosourcé est donc une alternative durable qu'il convient d'étudier plus en détails. Un premier suivi cinétique par spectroscopie ATR-IR *in-situ* avec comme milieu réactionnel l'isosorbide (1 eq), la TEA (2 eq) et le TsCl (1 eq) à 70 °C dans l'acétonitrile sous 1.5 MPa de pression de CO_2 a permis de mettre en évidence la formation de liens carbonates avec la disparition concomitante des espèces TsCl, suggérant une première oligomérisation par copolymérisation directe (voir Figure 2). Une analyse du milieu réactionnel brut obtenu en fin de réaction (1 h) par spectroscopie RMN ^{1}H a permis d'identifier les espèces suivantes : Isosorbide non réagi, TsCl non réagi, motifs isosorbide liés par lien carbonates, alcools des isosorbides tosylés, et sels de TEA protonnée et TsO^-, comme présenté en Figure 3.

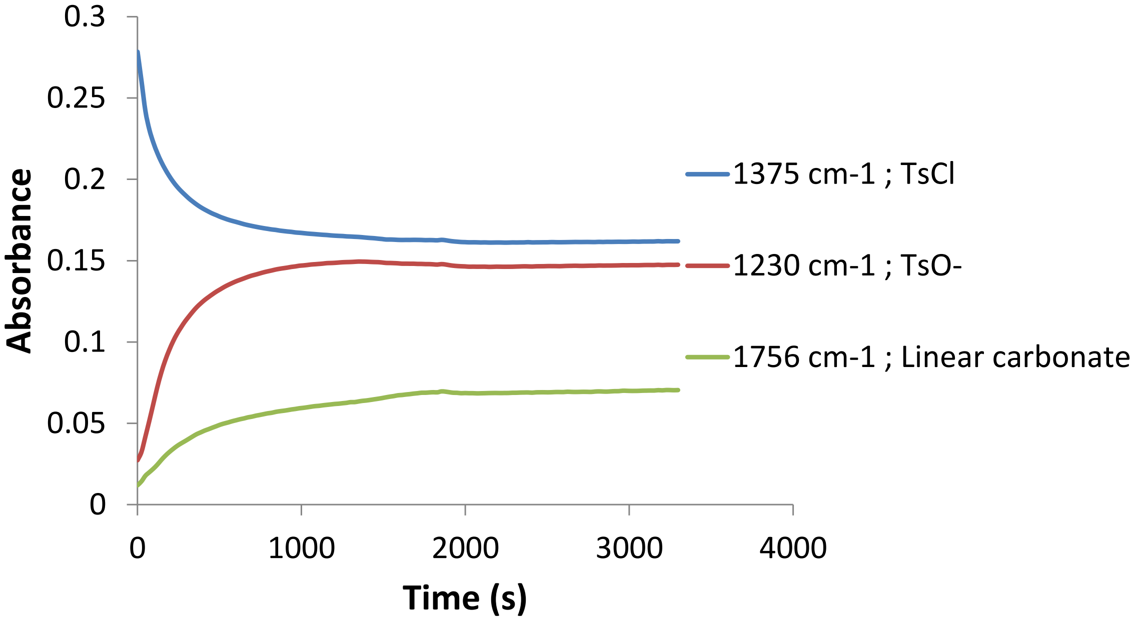

Figure 2 : Suivi cinétique par ATR-IR *in-situ* des bandes d'absorption caractéristiques des espèces TsCl, TsO^- et de la fonction carbonate linéaire.

Une analyse GPC du mélange réactionnel brut (voir Figure 4) révèle la présence de dimères et trimères. La limitation en prise de masse molaire s'explique par une conversion en isosorbide relativement faible (43 %) ainsi que par la présence de réactions secondaires (tosylation des alcools) en quantité non négligeable (sélectivité de 23 % pour la tosylation contre 77 % pour la formation de liens carbonates). Une optimisation des paramètres expérimentaux comme la température, la concentration, la pression, le solvant ou encore l'ajout de co-catalyseurs tels que le TBD, le TBA/PhO^- ou le LiCl a permis d'orienter la sélectivité vers la formation exclusive de liens carbonates. Cependant, les conversions restent faibles et donc les masses molaires limitées : des dimères et trimères sont obtenus principalement. Il est important de rappeler que le système organique dual est ici utilisé en quantité stœchiométrique, voire en excès, et qu'il n'est pas régénéré en fin de réaction, puisqu'on le retrouve principalement sous la forme de sels de $TEAH^+/Cl^-$ et $TEAH^+/TsO^-$. Au vu des limitations de ce protocole expérimental lourd ne permettant d'atteindre que des masses molaires limitées, notre équipe de recherche s'est intéressée à d'autres stratégies de synthèse que la copolymérisation directe qui reste très difficile à mettre en place.

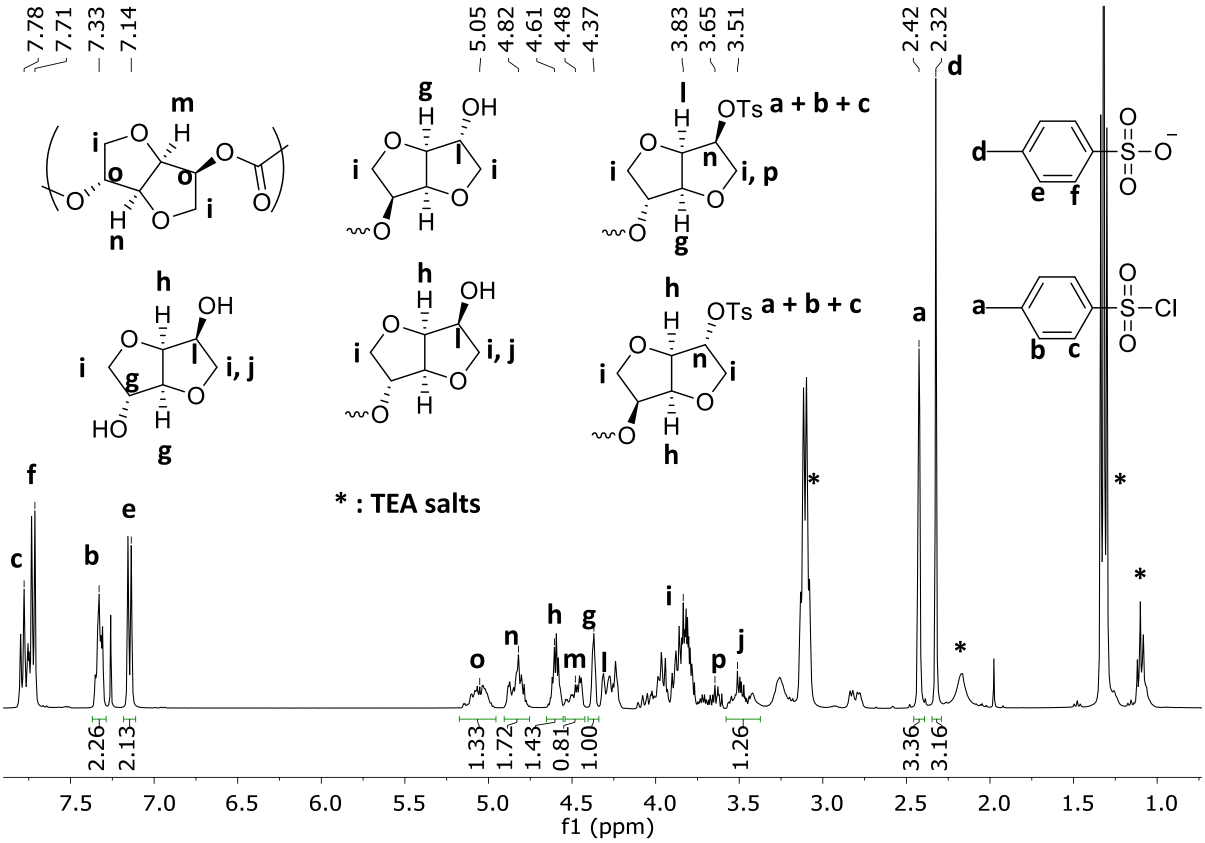

Figure 3 : Spectre RMN ^{1}H du mélange brut réactionnel obtenu en fin de réaction. Conditions expérimentales : Isosorbide (1 eq), TEA (2 eq), TsCl (1 eq), Acétonitrile, 70 °C, 1.5 MPa CO_2

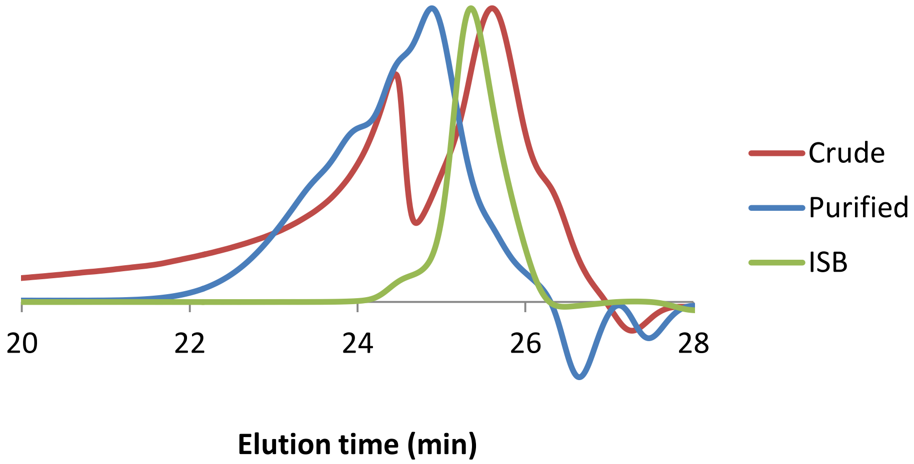

Figure 4 : Chromatogrammes GPC du mélange réactionnel brut (courbe rouge), d'un oligomère purifié et isolé (courbe bleue) et du monomère isosorbide (courbe verte)

La synthèse de polycarbonates d'isosorbide est aujourd'hui principalement décrite dans la littérature via des procédés de polycondensation classiques entre l'isosorbide et le carbonate de diméthyle ou de diphényle. Dans ce contexte, nous avons proposé l'élaboration de nouveaux monomères CO_2- et bio-sourcés comme agents de carbonatation propices à la polycondensation à l'état fondu en présence de diols. La stratégie de synthèse adoptée est la suivante : i) synthèse et purification de carbonates cycliques d'α-alkylidène (αCC) au départ de CO_2 et d'alcools propargyliques suivi de ii) la synthèse et purification de monomères carbonates linéaires bifonctionnels (bisLC) par ouverture de cycle régio-sélective de ces αCC par des diols ainsi que iii) leur polycondensation à l'état fondu par la même gamme de diols ayant servi à la synthèse de bisLC (voir Schéma 5). Dans un premier temps, une étude mécanistique sur la synthèse de ces nouveaux monomères bisLC est proposée par suivi cinétique ATR-IR *in-situ* supporté par des calculs DFT. Catalysée par le DBU, cette synthèse donne lieu à des rendements isolés de l'ordre de 75 % en 2 h dans l'acétonitrile à 25 °C pour les diols utilisés, soit le 1,4-butanediol (bisLC1), l'isosorbide (bisLC2), l'isomannide (bisLC3) et le benzène-1,4-diméthanol (bisLC4). Leur purification consiste simplement en une extraction liquide-liquide avec l'eau après solubilisation du milieu réactionnel dans le dichlorométhane.

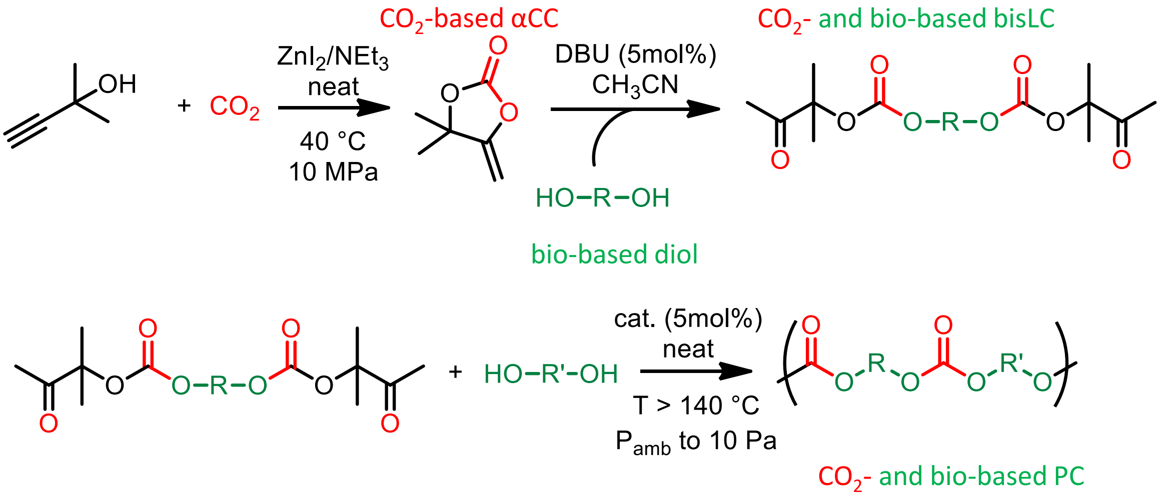

Schéma 5 : Stratégie de synthèse pour l'obtention de polycarbonates CO_2- et bio-sourcés par procédé de polycondensation à l'état fondu.

Par la suite, la polycondensation à l'état fondu fut mise en œuvre en respectant deux étapes distinctes mais réalisées sans étape de purification intermédiaire : une étape d'oligomérisation sous atmosphère d'azote pour permettre une première transcarbonatation entre le diol et le bisLC avec départ d'hydroxycétone (sous-produit de la polycondensaton), puis une étape d'extension de chaîne où le vide est appliqué pour enlever quantitativement l'hydroxycétone du milieu réactionnel, déplaçant ainsi l'équilibre vers la formation de polycarbonates. Une étude approfondie sur les étapes d'oligomérisation et d'extension de chaîne du bisLC1 avec le 1,4-butanediol pour l'obtention de polycarbonate de butylène est proposée en testant différents catalyseurs de type acides de Lewis (LiCl, $AlCl_3$,

$ZnCl_2$, $Sn(Oct)_2$) ou de type bases organiques (DBU, TBD, DMAP, TBA/PhO^-) à différentes températures. Pour chaque condition expérimentale donnant lieu à l'obtention d'oligomères ou de polymères, l'apparition de réactions secondaires générant des carbonates cycliques à 5 chaînons (5CC) a pu être mise en évidence par spectroscopie ATR-IR et par spectroscopie RMN. Notamment, l'attaque d'un alcool sur la fonction cétone du bisLC rentre en compétition avec la transcarbonatation désirée et vient alors perturber la stœchiométrie entre les fonctions alcools et carbonates, limitant ainsi la masse molaire des chaînes. Dans de telles conditions de température, il est raisonnable de penser que ces 5CC sont sujets à une ouverture par la présence d'alcools, donnant lieu à des alcools trifonctionnels présentant une fonction cétal que l'on retrouve dans le squelette polymère. Cependant, des résultats prometteurs furent obtenus en utilisant LiCl comme catalyseur à 140 °C avec une étape d'oligomérisation de 24 h (atmosphère N_2) suivi d'une étape d'extension de chaîne de 24 h (vide : 10 Pa). Après reprécipitation dans le méthanol, le polymère obtenu aune M_n de 11,000 g/mol (voir Figure 5) et une T_g de – 39 °C. La caractérisation par RMN ^1H des polymères précipités a pu mettre en évidence la présence de défauts générés par les réactions secondaires, et l'attribution de certains pics reste encore en suspens à ce jour.

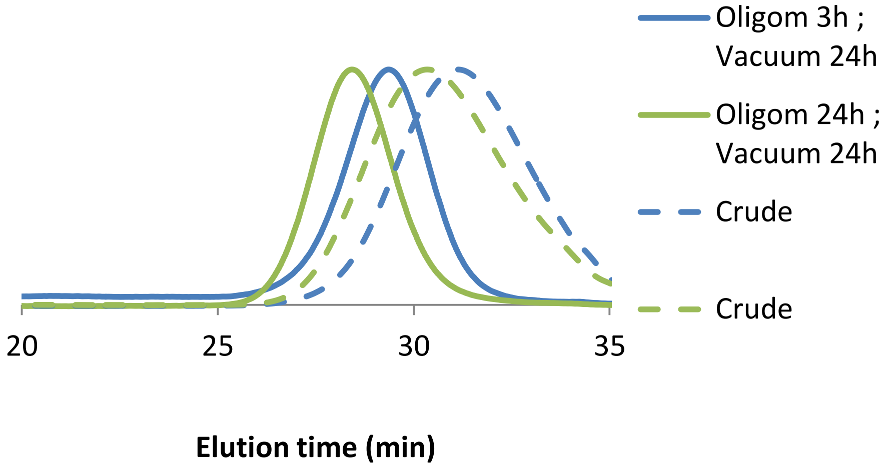

Figure 5 : Chromatogrammes GPC des polycarbonates de butylène synthétisés à 140 °C avec LiCl pour différents temps d'oligomérisation en comparant le milieu brut réactionnel (traits pointillés) et le polymère obtenu après reprécipitation dans le méthanol (traits pleins).

Cette étude est par la suite étendue à la synthèse de polycarbonates d'isosorbide au départ d'isosorbide et du bisLC2. De façon analogue à la synthèse de polycarbonates de butylène, les réactions secondaires (présence de 5CC) furent observées pour toutes conditions expérimentales donnant lieu à la formation de polycarbonates ou oligocarbonates d'isosorbide. Les meilleurs résultats furent également obtenus avec LiCl comme catalyseur en appliquant une température d'oligomérisation de 140 °C pendant 3 h et une température d'extension de chaîne de 180 °C pendant 20 h (M_n = 2,100 g/mol pour le polymère précipité, T_g = 132 °C). Contrairement aux polycarbonates de butylène dont la structure aliphatique permet une fusion à basse température, l'état fondu est difficilement maintenu à une température de 140 °C dans le cas des polycarbonates d'isosorbide, d'où la nécessité de monter en température lors de la prise en masse moléculaire des chaînes, afin de pallier les limitations de mobilité des chaînes et maintenir une agitation satisfaisante. Cependant, l'équipement disponible ne permettant pas de monter au-delà de 180 °C (bain d'huile, réacteurs de type ballon en verre), de longs temps de réaction sont nécessaires pour compenser le manque d'agitation en fin de réaction. Dès lors, une collaboration avec des partenaires de l'Université de Mons (laboratoire CIRMAP) a été mise en place afin d'utiliser des réacteurs de polycondensation classiques permettant une montée en température et une agitation contrôlée. Avec une température finale de 240 °C (rampe de 40 °C / h), un polycarbonate d'isosorbide de M_n = 3,000 g/mol fut obtenu pour une oligomérisation et une extension de chaine de 3 h, mettant en évidence la nécessité d'augmenter la température lors de la croissance des chaînes pour maintenir l'état fondu. De façon générale, les polycarbonates d'isosorbide obtenus par cette voie de synthèse présentent des problèmes de solubilité dans les solvants organiques communs, soulignant la présence de défauts ou de potentiels branchements ou réticulation dans le polymère due aux réactions secondaires qui ne peuvent être évitées. Après caractérisation par spectroscopie RMN (voir Figure 6), des pics autour de 1.2 ppm furent difficilement attribuables à une structure chimique spécifique, bien que la présence de polycarbonates d'isosorbide fût mise en évidence. Tout comme les polycarbonates de butylène, il apparait que les chaînes des polymères synthétisés soient quasi-exclusivement terminées par des fonctions OH, avec l'absence de signaux relatifs aux motifs oxo des bisLC dans les spectres RMN ^{1}H.

Dès lors, nous pouvons considérer ces matériaux comme étant des polymères téléchéliques hydroxyles sujets à une extension de chaîne avec des diisocyanates pour l'obtention de poly(carbonates-*co*-uréthanes). Le couplage entre un polycarbonate d'isosorbide préalablement synthétisé et purifié avec le 4,4'-diisocyanate de diphénylméthylène (MDI) fut réalisé dans du DMF sec à 80 °C catalysé par du dilaurate de dibutylétain. Une rapide augmentation de la masse molaire fut observée. L'obtention d'un matériau de type « gel » gonflé par le DMF et insoluble dans les solvants organiques communs conforte notre hypothèse de branchements ou réticulation sur les polycarbonates synthétisés. Une analyse GPC de la fraction soluble a pu être réalisée (voir Figure 7), mettant en évidence l'augmentation de la masse molaire.

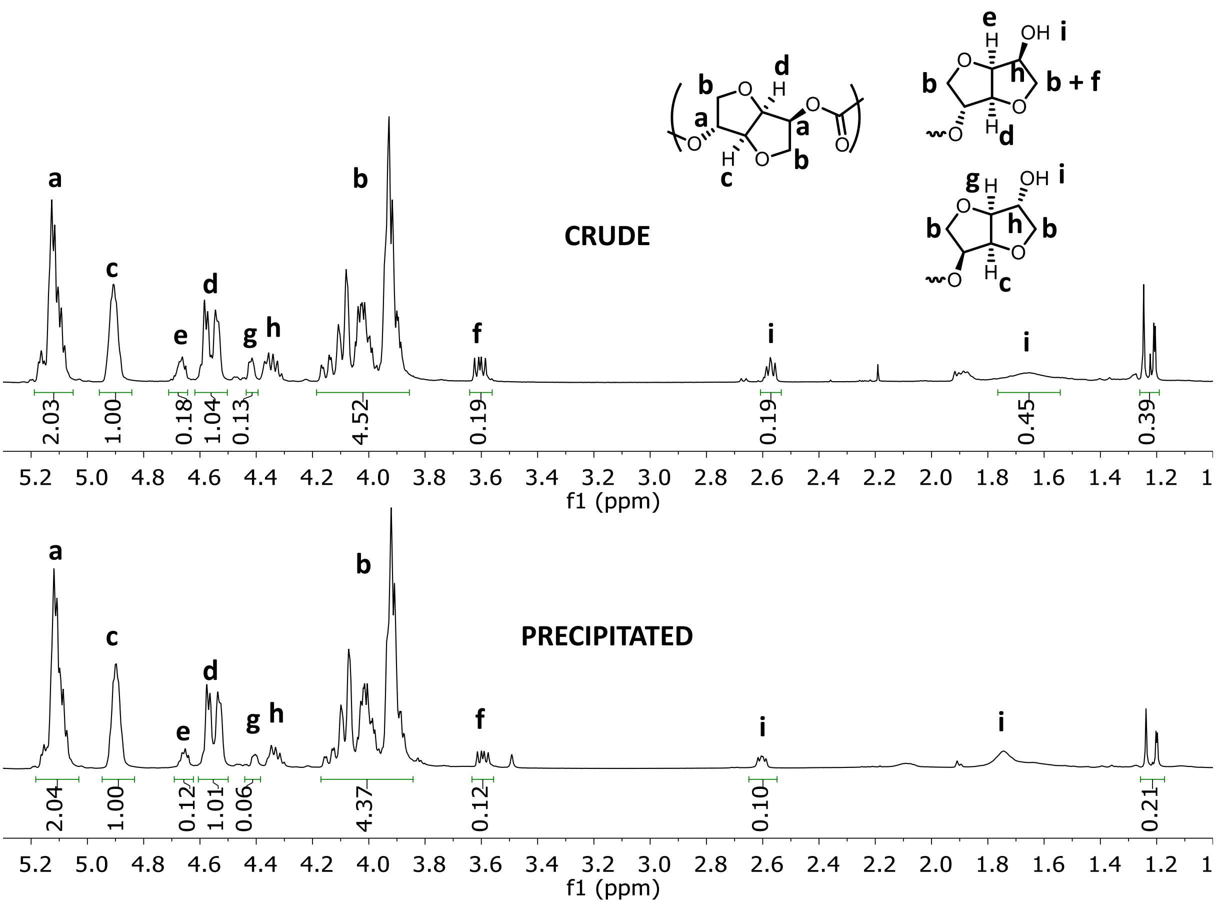

Figure 6 : Caractérisation RMN ^{1}H d'un polycarbonate d'isosorbide avant et après purification.

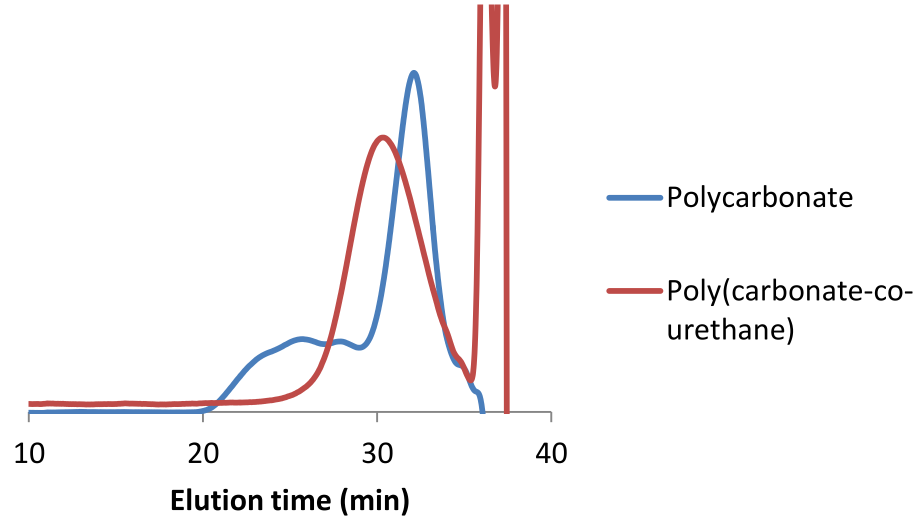

Figure 7 : Chromatogrammes GPC du polycarbonate d'isosorbide précurseur du couplage avec le MDI (courbe bleue) et du poly(carbonate-co-urethane) obtenu après couplage.

Afin d'étendre l'applicabilité des nouveaux monomères bisLC synthétisés et de prouver leur versatilité, des copolycarbonates au départ d'isosorbide et des bisLC1 ; bisLC3 et bisLC4 furent synthétisés en utilisant les conditions optimisées précédemment (oligomérisation à 140 °C pendant 3 h ; extension de chaîne à 140 °C ou 180 °C pendant 20 h). Ainsi, des copolymères alternés isosorbide/butylene ; isosorbide/isomannide et isosorbide/benzène-1,4-diméthanol furent obtenus. La nature de ces copolymères alternés fut confirmée par caractérisation RMN et leurs propriétés thermiques furent évaluées par DSC et TGA. L'observation d'une T_g unique pour ces copolymères (voir Figure 8) met en évidence leur caractère alterné. Dès lors, la polycondensation à l'état fondu de ces nouveaux monomères permet le contrôle de l'incorporation de différents motifs dans le squelette polymère et ouvre ainsi la voie à des matériaux alternatifs à ceux obtenus par polycondensation classique utilisant le carbonate de diméthyle ou de diphényle. Cependant, des recherches approfondies, notamment sur le développement d'un catalyseur plus performant permettant d'éviter la formation de réaction secondaires, devraient être poursuivies afin de proposer un procédé compétitif en termes de masses molaires accessibles.

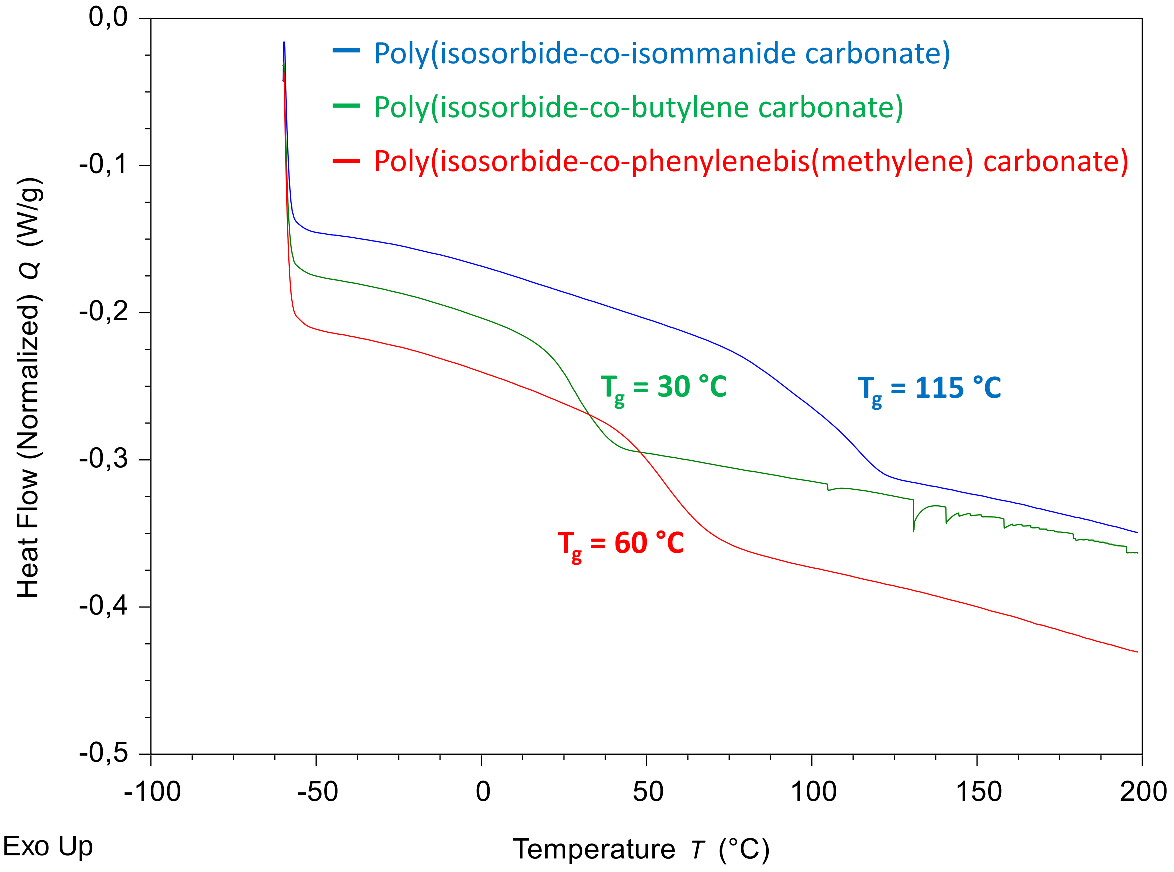

Figure 8 : Courbes DSC obtenues pour les copolycarbonates synthétisés.

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LIST OF ABBREVIATIONS:

- αCC (α-alkylidene cyclic carbonate)

- 5CC (5-membered cyclic carbonate)

- ACN (Acetonitrile)

- ATR-IR (Attenuated Total Reflectance Infrared spectroscopy)

- bisLC (Bifunctional Linear Carbonate)

- BPA (Bisphenol A)

- BuBr (Butyl bromide)

- DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene)

- DEC (Diethyl Carbonate)

- DFT (Density Functional Theory)

- DMACC (4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one ; Dimethyl α-Alkylidene Cyclic Carbonate)

- DMAP (4-(Dimethylamino)pyridine)

- DMC (Dimethyl Carbonate)

- DMF (*N,N*-Dimethylformamide)

- DPC (Diphenyl Carbonate)

- DSC (Differential Scanning Calorimetry)

- GPC (Gel Permeation Chromatography)

- ISB (Isosorbide)

- ISM (Isomannide)

- MDI (4,4'-methylene diphenyl diisocyanate)

- MTBD (7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene)

- NHC (*N*-heterocyclic carbene)

- NHO (*N*-heterocyclic olefin)

- NMP (*N*-Methyl-2-pyrrolidone)

- NMR (Nuclear Magnetic Resonance)

- PC (Polycarbonate)

- ROP (Ring Opening Polymerization)

- SEC (Size-exclusion Chromatography)

- TBAI (Tetrabutylammonium iodide)

- TBA/PhO (Tetrabutylammonium phenolate)

- TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene)

- $T_d^{5\%}$ (Degradation Temperature where the sample has lost 5 % of its mass)

- TEA (Triethylamine)

- T_g (Glass transition temperature)

- TGA (Thermogravimetric Analysis)

- THF (Tetrahydrofuran)

- T_m (Melting temperature)

- TMP (2,2,6,6-Tetramethylpiperidine)

- TS (Transition State)

- TsCl (Tosyl Chloride)

General introduction

Environmental concerns related to climate change is now well established and widely known in our modern society, bringing new challenges for the scientific community to overcome. Among these challenges, changing our carbon feedstock from fossil resources to greener and more sustainable alternative sources has become a priority. To date, around 40 GT of CO_2 is released in the atmosphere every year due to anthropogenic activities, which represents a tremendous amount of carbon that remains unused. Today seen as a waste, CO_2 could play a major role in the carbon feedstock of tomorrow as it is cheap, abundant and non-toxic in addition of being an atmospheric pollutant that causes greenhouse effect and ocean acidifications. Thus, utilizing CO_2 as a C1 carbon feedstock and valorizing it into valuable organic chemicals or materials is now on the board of many scientific studies and industrial developments. Due to its thermodynamic stability, synthetic strategies combining CO_2 and other substrates have to be imagined to overcome its poor reactivity. A known way to valorize CO_2 is to obtain cyclic carbonates or polycarbonates by the coupling of oxiranes with CO_2. Although promising results have emerged, opening the way for further industrialization, the toxicity of these substrates as well as the lack of affordable diversified chemical structures push the chemists to find other substrates for the fabrication of these chemicals. Among others, diols are candidates of choice for such coupling with CO_2 to obtain (a)cyclic carbonates and polycarbonates as they are usually easy to handle with low toxicity, and present a large variety of chemical structures. Moreover, bio-based diols derived from the biomass are now accessible on a commercial scale, which is of high interest for the production of chemicals and materials with low carbon footprint. In this context, this thesis aims at synthesizing CO_2-based synthons such as (a)cyclic carbonates and CO_2-based polycarbonates by studying in details the coupling of CO_2 with diols (Figure 1).

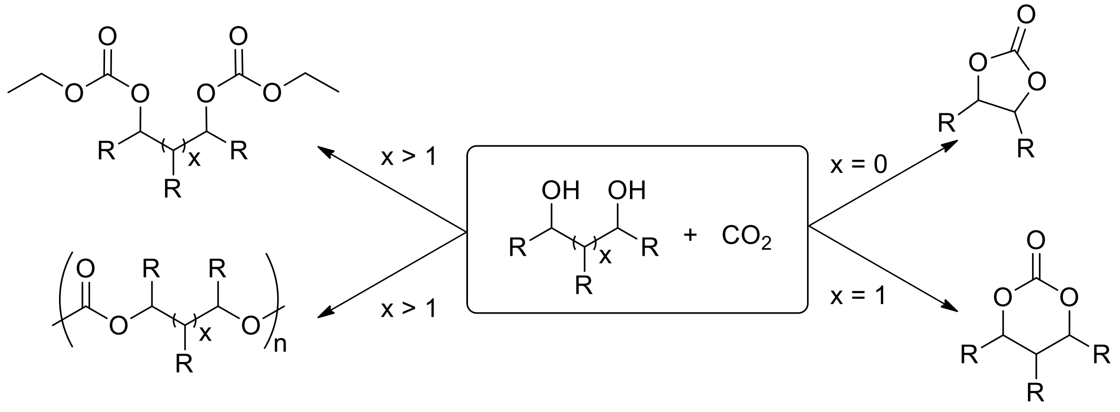

Figure 1: The coupling of CO_2 with diols for the synthesis of (a)cyclic carbonates and polycarbonates

To achieve this purpose, the Institute of Molecular Sciences (ISM) from the University of Bordeaux and the Center of Education and Research on Macromolecules (CERM) from the University of Liège have joined their respective expertise in i) the development of analytical tool such as ATR-IR *in-situ* spectroscopy for the establishment of kinetic profiles and identification of reaction intermediates, in combination with DFT calculations to provide consistent mechanisms from experiment and molecular modelling investigations and ii) monomers synthesis and characterization with emphasis on CO_2 valorization and their polymerization into organic materials. The first 18 months of this research project were conducted at the ISM for the exclusive synthesis of organic synthons such as (a)cyclic carbonates. The next 24 months were dedicated to the fabrication of CO_2- and bio-based polycarbonates at the CERM.

This thesis is composed of 4 chapters, where chapter 2 was published as an article in the Journal of CO_2 Utilization.

The first chapter is dedicated to a detailed background and literature review on the coupling of CO_2 with alcohols for the formation of (a)cyclic carbonates and polycarbonates. After a brief discussion on general aspects of CO_2 valorization, the first part reviews the synthesis of organic carbonates such as dialkyl carbonates or cyclic carbonates from the carbonation of alcohols. Many different synthetic strategies were reported (dehydrative condensation, alkylation route, “leaving group” strategy, carbodiimides route, protected alcohols route…) with various substrates (mono-alcohols, diols, allyl alcohols, halohydrins, propargylic alcohols…). The second part reviews the formation of polycarbonates, with an emphasis on the direct copolymerization of CO_2 with diols. The main advantages and limitations of the ring-opening polymerization route is also briefly discussed. Finally, polycondensation processes involving CO_2-based dimethyl and diphenyl carbonates with aliphatic or aromatic and cycloaliphatic diols are described.

The second chapter deals with the synthesis of (a)cyclic carbonates from CO_2 and diols using organic dual systems in mild conditions. A detailed investigation on the model reaction with propylene glycol led to proposition of a mechanism supported by ATR-IR *in-situ* kinetic monitoring in combination with DFT calculations. Then, comparison of two dual activating systems, namely DBU/EtBr and TEA/TsCl was achieved with particular attention on reactivity and selectivity disparities toward the formation of cyclic or linear carbonates depending on the nature of the diol.

The third chapter focuses on the direct copolymerization of Isosorbide, a bio-based diol derived from starch, and CO_2 for the fabrication of poly(isosorbide carbonate) using the TEA/TsCl dual activating system. The influence of different parameters such as the temperature, pressure, concentration and addition of co-catalysts was evaluated on the diol conversion and selectivity toward the formation of carbonate linkages and the obtained final molar mass. Due to thermodynamic limitations, only dimers or trimers were afforded with no significant improvement regarding any experimental parameter evaluated. Thus, a different scientific strategy was adopted for the synthesis of CO_2-based polycarbonates, as proposed in the next chapter.

The fourth chapter is dedicated to the synthesis of new CO_2- and bio-based monomers and their later melt polycondensation to obtain polycarbonates with low carbon footprint. An innovative strategy was proposed to replace the conventionally used dimethyl or diphenyl carbonate as carbonylating agents by introducing monomers with tunable structures, so that a large range of affordable thermo-mechanical properties could be achieved. A detailed investigation on the reactivity of these new monomers with diols during melt polycondensation processes was conducted to better understand the occurrence of side reactions that would limit the molar mass. Synthesis and characterization of poly(isosorbide carbonate) and poly(butylene carbonate), as well as copolycarbonate with moderate M_n was achieved.

General conclusions and outlooks are proposed at the end of this manuscript to summarize the main results obtained and their respective limitations.

Chapter I:

Background and literature review:

The coupling of CO_2 and alcohols for the formation of (a)cyclic carbonates and polycarbonates

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    III-3-b) Polycondensation between bis(α-alkylidene cyclic carbonates) and diols 62

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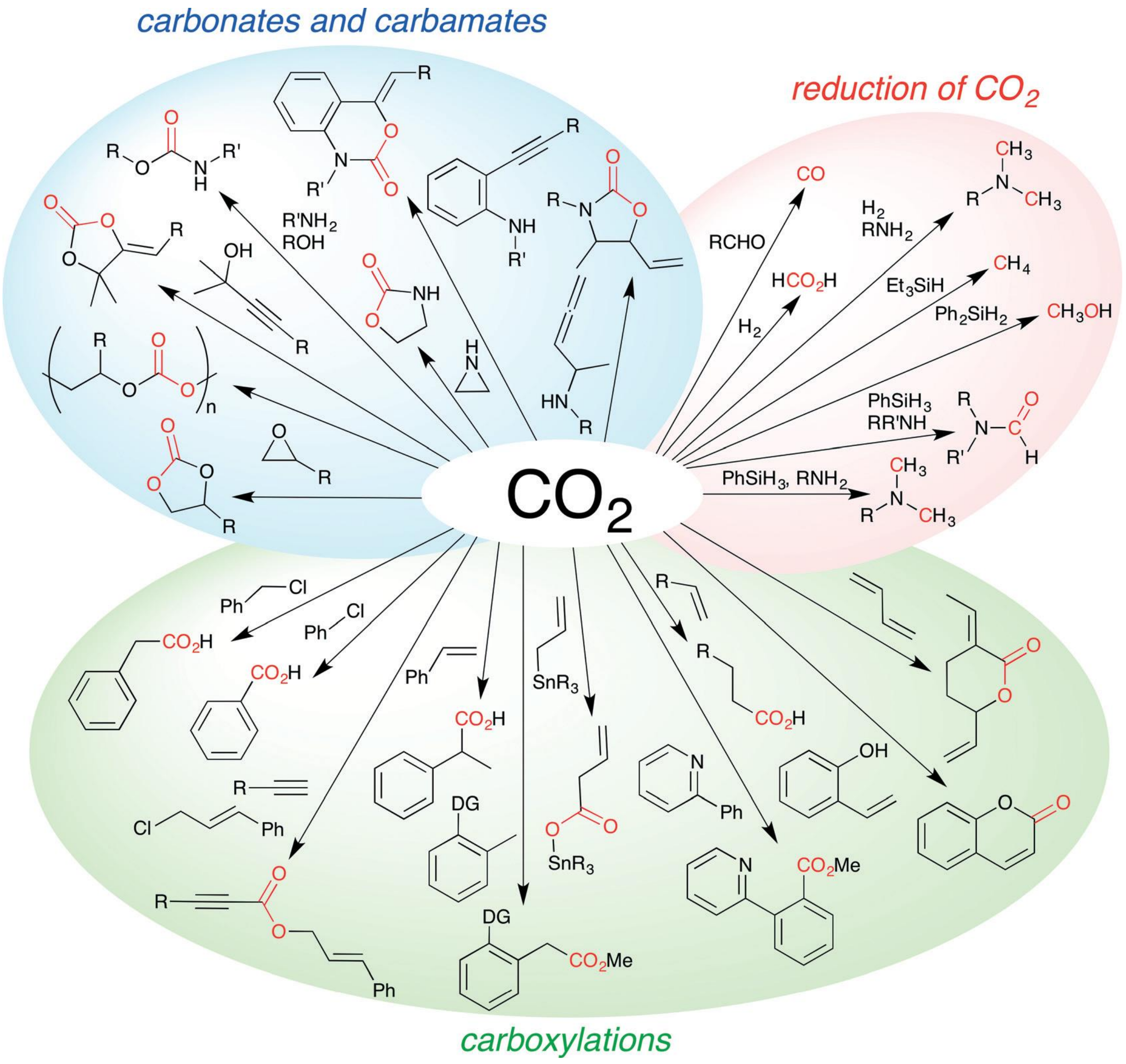
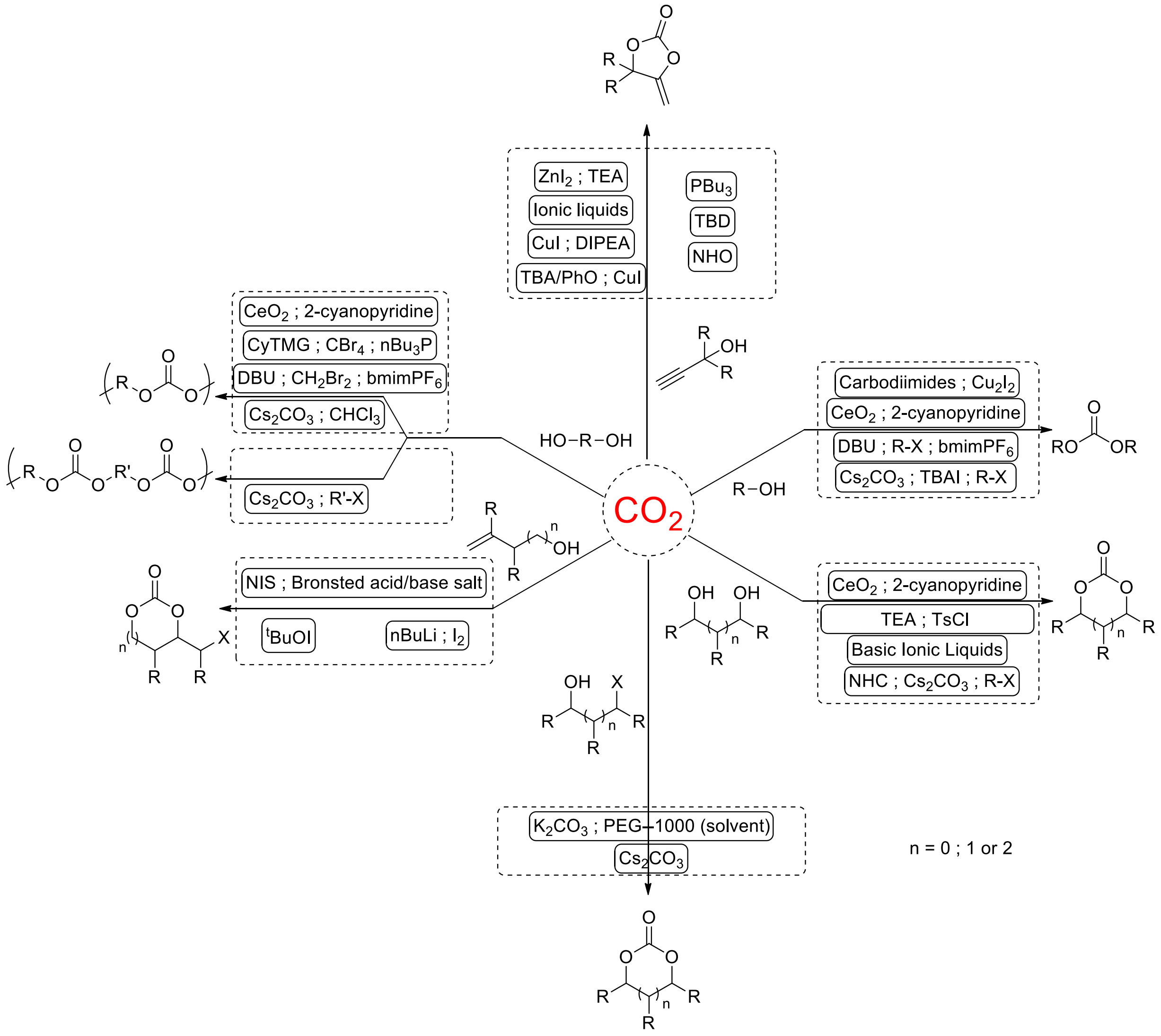
I) Chemical conversion of CO2: general aspects

Today, our modern society is facing the climate change and oceans acidification caused by the continuous increase of the CO_2 level within the atmosphere. Our annual anthropogenic emissions are now approaching 40 Gt/year and it is recognized that, alongside other gases including water vapour, methane, fluoro-compounds…, CO_2 has become a major contributing factor to the greenhouse effect[1-3]. Legally binding obligations, governmental incentives and/or demands from the industrial stakeholders are now strong drivers to fight the global warming and to shift our societal paradigm based on fossil resources towards a more sustainable and circular vision, including CO_2 utilization. Being seen as a waste, CO_2 may become paradoxically the key to green our economy. Unlike biomass which growth is inter-seasonal and requires multi-step post-treatment (extraction, fractionation, fermentation…) prior valorization, CO_2 is a cheap and renewable carbon source regenerated instantaneously and locally. This resource may enter within numerous chemical processes and syntheses to design existing commodity organic molecules/polymers or new (sophisticated) ones[4-6]. However, the main thermodynamic barrier to the large scale utilization of CO_2 as C1-buiding block lies on its stability with a standard enthalpy of formation of $\Delta_f H^{\circ} = -394$ kJ/mol[7]. To surpass this chemical inertness, the use of high energy (co)reactants, the development of new catalytic methods and external energetic inputs are required to turn CO_2 into value. The production of salicylic acid via the Kolbe-Schmitt process, urea from ammonia and CO_2 or polyols by ring-opening copolymerization of oxiranes with CO_2 are just few examples of competitive products already trademarked by the chemical industry. CO_2 also serves now to fabricate the next generation of fuels or store renewable energy via the so-called power-to-fuel technology. Its electrochemical reduction provides carbon monoxide, a key molecule in the Fischer-Tropsch process to produce alkanes. Plethora of works revisits the Sabatier's reaction, known from more than a century, to fabricate synthetic methane from renewable H_2 while partial hydrogenation of CO_2 provides methanol. Myriad of sophisticated molecules are also accessible by the chemical conversion CO_2 via C-O or C-N bond formation (Scheme 1). This route, reviewed by others, is very promising as (highly) reactive organic precursors counter-balance the low reactivity of CO_2. (Photo)catalytic carboxylation of alkanes, alkenes or alkynes provides a diversified portfolio of carboxylic acids. The methylation of primary amines or the formylation of secondary ones are conducted with CO_2 and a reductant (H_2, $PhSiH_3$…). (a)Cyclic organic carbonates and carbamates with ample structural diversity are fabricated with a high level of selectivity and a 100% atom economy pathway by non-reductive catalytic transformations of CO_2 with oxiranes [8-11], aziridines[12], and amines[13]. Among them, the insertion of CO_2 within epoxides is by far the most largely explored transformation of CO_2 as it provides 5-membered cyclic carbonates used as solvent, electrolyte for Li-ion batteries or intermediate in fine organic chemistry and polymer sciences. Despite being very attractive and easily producible by facile oxidation of olefins, including natural ones derived from vegetable oils or terpenes, epoxides display acute toxicity as they act as alkylating agent capable to bind with DNA[14,15]. In this context, replacing epoxides by safer and easy to handle (renewable) substrates to synthesize organic carbonates and polycarbonates is now deserving huge interest in the scientific community. Alcohols are ubiquitous scaffolds with low toxicity made from multiple synthetic or natural sources. This makes them ideal candidates within the field of CO_2 transformation to replace epoxides. This review provides an overview of the recent progresses made in the synthesis of (a)cyclic and polymeric carbonates from alcohols substrates. The first section is dedicated to the main pathways that are engineered to upgrade CO_2 with mono-, di- or polyols, haloalcohols, allylic or propargylic alcohols into organic scaffolds and is complemented by mechanistic guidelines. The second section makes emphasis to the synthesis of polycarbonates either by direct polycondensation of CO_2 with alcohols or via the polymerization of CO_2-sourced monomers through ring-opening or step-growth methods. An overview of the most relevant routes discussed in this review for the direct coupling of CO_2 with alcohols to produce (a)cyclic carbonates and polycarbonates is presented in Scheme 2.



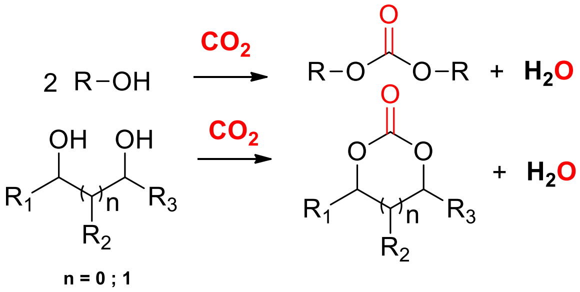
Scheme 1: Chemical transformation of CO_2 into organic scaffolds (reprinted from ref [5])



Scheme 2: Main strategies to afford (a)cyclic carbonates and polycarbonates from the coupling of alcohols and CO_2.

II) CO_2-based synthons: organic carbonates synthesis from the carbonation of alcohols

Industrially, oxidative carbonylation of alcohols by phosgenation is the most facile and economically viable route to fabricate (a)cyclic organic carbonates. However, the toxicity of phosgene, the protective measures for its safe transportation, storage and handling, and the large volume of chlorinated waste generated during the reaction are strong limitations that support the development of a more sustainable carbonation process. In this context, forming carbonates by coupling of alcohols and CO_2 looks very attractive but remains an elusive endeavour as this approach faces two severe limitations linked to i) the difficulties to identify ways to properly activate CO_2 as it won't spontaneously react with alcohols and ii) the formation of water as a by-product that affects the reaction equilibrium (Scheme 3).



Scheme 3: The CO_2/alcohol coupling to synthetize organic carbonates

To surpass these hurdles, three main strategies have been envisioned, i.e.:

i) The “dehydrative condensation” combining the utilization in synergy of a catalyst, which facilitates the CO_2 fixation onto the alcohol moiety, with physical or reactive dehydrating agents trapping/consuming water

ii) The “alkylation” strategy involving the activation of CO_2 under the form of a hemi-carbonate ion in the presence of an excess of base prior further reacting with an alkyl halide via nucleophilic substitution. As a variant, the “leaving group” approach proposes the *in-situ* formation of highly reactive carbonate intermediate from the ter-reaction between CO_2, an alcohol and a dihalide that undergoes facile transcarbonation into an acyclic carbonate

iii) The “protected alcohols” route that generates *in-situ* alcohols from ketals, trimethyl phosphates or orthoesters via water consumption prior reaction with CO_2

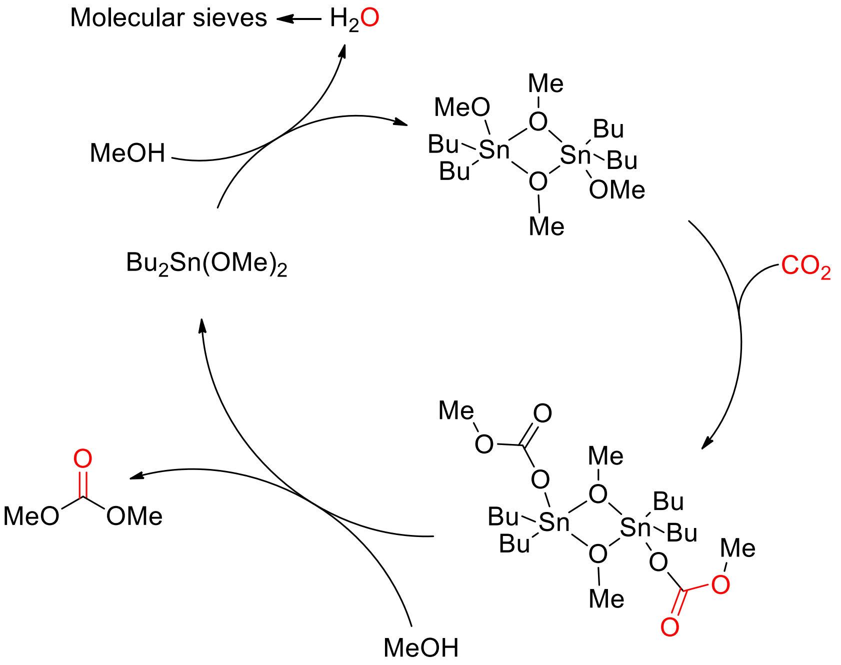
II-1) Synthesis of dialkyl carbonates

The synthesis of dimethyl carbonate (DMC) is by far the most widely studied pathway to illustrate the conversion of alcohols and CO_2 into useful organic scaffolds. However, the high standard Gibbs-free energy of DMC formation from methanol and CO2 ($\Delta^R G \approx +37$ kJ/mol) indicates that the reaction is thermodynamically unfavourable limiting the yield of the overall reaction below 1 %[16-18]. Various approaches have then been proposed and optimized to produce DMC with good yields and selectivity.

II-1-a) DMC synthesis by dehydrative condensation

Since the pioneer works of Kizlink[19,20] who demonstrated the low yield but selective formation of DMC from CO_2 and MeOH using organotin catalysts, a tremendous number of metal alkoxide catalysts have been developed. Titanium- ($Ti(OEt)_4$, $Ti(OBu)_4$…)[21], nickel- ($Ni(OAc)_2.4H_2O$)[22], niobium- ($[Nb(OMe)_5]_2$)[23] and magnesium-based catalysts[24] are just examples of homogenous systems that have proven their utility to drive the formation of the acyclic organic carbonates. Heterogeneous amphoteric metal oxides systems combining acid and basic sites such as ZrO_2[25-27] or ZrO_2/phosphoric acid dual catalysts [28,29], ceria oxides[30,31] and other mixed oxides[32-34] or Cu-Fe, Cu-Ni… bimetallic oxides immobilized onto graphite oxide and graphene nanosheets[35-37] also displayed some catalytic activity. However, for all systems, the formation of water as a by-product limited severely the reaction yields (up to 5 % for the $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ system[38]). Some catalysts also faced selectivity issues with the high temperature concomitant formation of formaldehyde and carbon monoxide from CO_2 and methanol. To push away these boundaries, the utilization of metal-based catalysts that operate in synergy with "physical" or reactive desiccants/dehydration system emerged as a valuable option to push the reaction manifold toward high yield and selective formation of DMC.

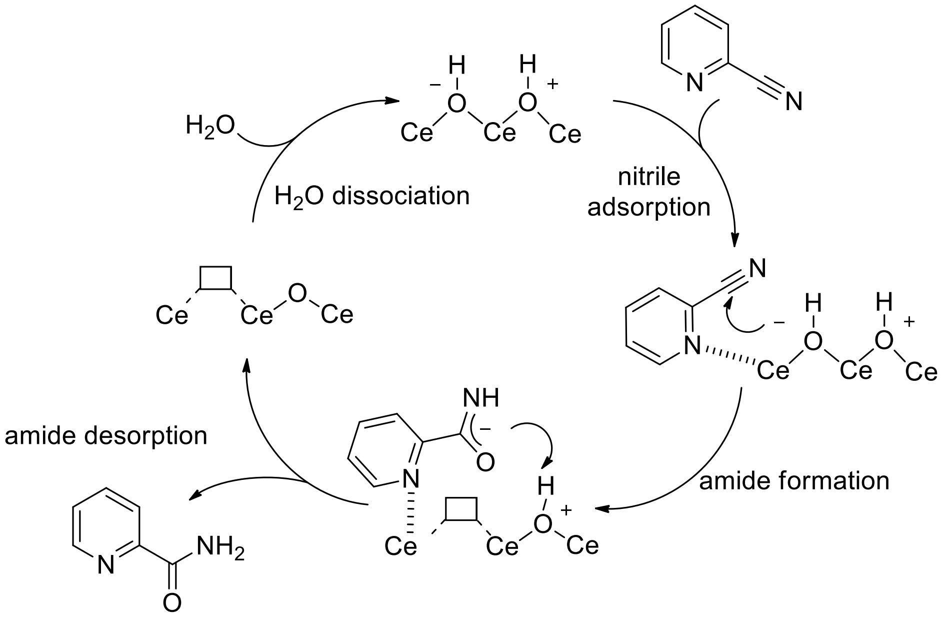
Physical drying systems: Membrane catalytic reactors combing a Cu catalyst immobilized onto mixed oxide carrier ($MgO-SiO_2$) with hydrophilic polyimide-silica or polyimide-titania hybrid separating membranes[39], or the dual use of inorganic absorbents such as molecular sieves or zeolites with organotin catalysts[40,41] were engineered to get rid of water and displace the reaction equilibrium towards the DMC formation. Among them, the $Bu_2Sn(OMe)_2$/molecular sieves 3A furnished the best DMC yields (45 %) under operative conditions of 180 °C and 30 MPa of CO_2 in 80 h. This system highlights the benefits of the desiccant on the carbonylation of methanol with a 10-fold increase of the DMC yield [40,42]. The catalytic cycle of $Bu_2Sn(OMe)_2$ is shown in Scheme 4.



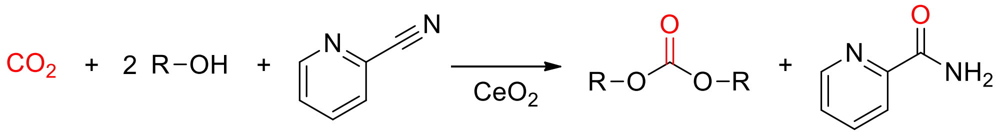
Scheme 4: Catalytic cycle for the formation of DMC using $BU_2Sn(OMe)_2$. Adapted from[40]

Reactive dehydrative system: To tackle the water issue and push the reaction equilibrium towards the DMC formation, two scenarios involving stoichiometric or excess of reactive dehydrative systems were developed. In the first one, DMC was synthesized from CO_2 and methanol (P_{CO2} = 15 MPa, T = 180 °C, t = 2-10 h) using $(Bu)_2SnO$ in combination with CaC_2 that spontaneously consumed water to form acetylene as a by-product. DMC was formed with a yield up to 11 % with 13 mol% of CaC_2[43]. In the second scenario, a single catalyst was used to drive simultaneously the alcohol carbonation and hydration of the desiccant, for example, the catalytic hydration of nitriles into amides. This elegant concept was pioneered by Tomishige who used in synergy CeO_2 as metal oxide catalyst and nitriles as reactive desiccant[44,45]. Alike zirconia-based catalysts[26,29], amphoteric CeO_2 displays simultaneously active acidic and basic sites that activates CO_2 and methanol. These acid and base sites were characterized by Lavalley *et al* where they differentiate low-coordinated Ce cations due to oxygen defects as acid sites, and oxygen atoms adjacent to these low-coordinated Ce cations as basic sites[46,47] that can properly fix alcohols and CO_2[48]. Interestingly, these acid-base properties can efficiently catalyse nitriles hydration into amides. Among nitriles, acetonitrile was firstly considered. *In-situ* FT-IR studies revealed the presence of CH_3CN adsorbed over CeO_2. When water is added to the system, simultaneous decrease of CH_3CN species with increase of acetamide anion CH_3CONH^- and amide CH_3CONH_2 can be observed, meaning that CeO_2 successfully catalyses this reaction[44]. Mechanistic insights revealed that water is dissociated over CeO_2 and the OH^- species generated on the acid sites react with the adsorbed CH_3CN to form the acetamide anion. Reprotonation occurs thanks to the H^+ species generated on basic sites from H_2O dissociation over CeO_2.

When applied to the synthesis of acyclic alkyl carbonates from alcohol and CO_2, the CeO_2/Acetonitrile system effectively increased the yield of carbonate[49,50]. DMC was obtained with a 8.9 % yield and a 64 % selectivity, and diethyl carbonate (DEC) with a 7.5 % yield and a 94 % selectivity under relatively mild conditions (150 °C and 0.2-0.5 MPa). The low selectivity for DMC formation arose from side reactions driven by the by-produced amide. The latest can react with alcohols such as methanol to form esters with the release of ammonia. NH_3 further reacts with DMC to form methyl carbamate. To overcome these problems, the generated amide has to be more stable than acetamide. Benzonitrile was thus tested since the phenolate ring would increase the stability of the benzamide and possibly prevent side reactions. At 150 °C and 1 MPa CO_2 pressure, the dual system CeO_2/benzonitrile afforded DMC in 47 % yield with a 78 % selectivity[51]. To increase the yield, efforts were made to better understand the hydration reaction of nitriles over CeO_2. Tamura *et al*. successfully demonstrated that an heteroatom in β-position of the nitrile function would considerably increase its adsorption over CeO_2 by coordinating this heteroatom, as it was demonstrated for pyridine[52]. Combining all these aspects, 2-furonitrile and 2-cyanopyridine were selected as best candidates and showed excellent hydration yields at mild temperatures (90 % at 80 °C after 7 h and 100 % at 30 °C after 1 h respectively[44]). A proposed mechanism by the authors is presented in Scheme 5. The best result was obtained with 2-cyanopyridine: DMC could be formed at a 94 % yield with 96 % selectivity after 12 h at 120 °C and 5 MPa CO_2 pressure. A methanol:2-cyanopyridine ratio of 2:1 was needed, highlighting the need of stoichiometric amount of dehydration agents. It should be noted that enhancement of the catalytic activity by increasing the amount of low-coordinated Ce sites was achieved by preheating at 600 °C under air atmosphere for 3 h[53]. The protocol was extended to other alcohols and successfully demonstrated its versatility to afford a huge library of linear carbonates[54], see Scheme 6.



Scheme 5: Catalytic cycle for the reaction of water with 2-cyanopyridine over CeO_2. Adapted from [44]



R = C_2H_5
yield : 91 %

R = C_3H_7
yield : 91 %

R = C_4H_9
yield : 87 %

R = C_5H_{11}
yield : 86 %

R = C_6C_{13}
yield : 85 %

R = C_8C_{17}
yield : 87 %

R = $C_{10}C_{21}$
yield : 90 %

R = isobutyl
yield : 69 %

R = C_7H_{14}
yield : 49 %

R = Benzyl
yield : 74 %

Scheme 6: Library of linear carbonates afforded via the CeO_2/2-cyanopyridine route. Reprinted from[54]

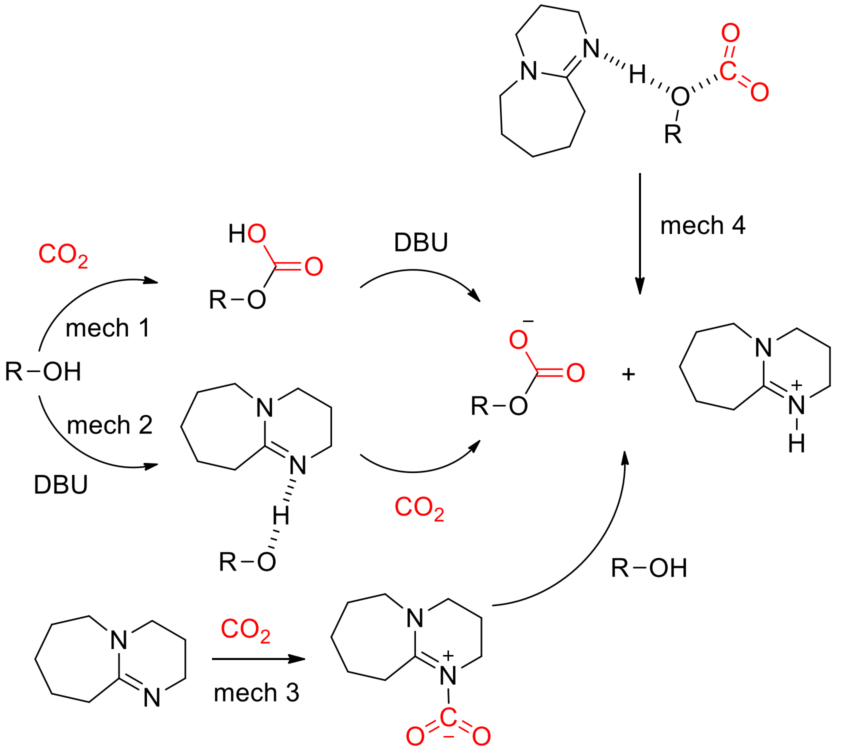
II-1-b) Synthesis of acyclic carbonates by the alkylation route

Another way to promote the formation of linear carbonates from the coupling of alcohols and CO_2 is to use co-reagents in stoichiometric amounts that will bypass the formation of water. Conceptually, alcohols can be activated, or even deprotonated, by bases to generate a methoxy species that can bind spontaneously with CO_2 to form the corresponding $ROC(O)O^-$ hemi-carbonate. This nucleophilic anion further reacts with a halide reagent R'-X that undergoes a nucleophilic substitution to produce the envisioned ROC(O)OR' specie.

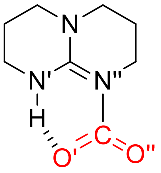
Inorganic bases: Inorganic carbonates have been studied for the three-component coupling of CO_2, alcohols and alkyl or benzyl halides. Jung et al. proposed a comparative study of different inorganic carbonates with tetrabutylammonium iodide (TBAI) as additive and n-butyl bromide as co-reagent on the model carbonation of 4-phenyl-1-butanol with CO_2 [55].

Interestingly, Na_2CO_3, Rb_2CO_3, K_2CO_3 and Cs_2CO_3 successfully demonstrated their activity in mild conditions (23 °C, atmospheric pressure of CO_2 bubbling). No reaction was observed with Li_2CO_3. The yield remained low for sodium and potassium based carbonates (2 %) as well as for Rb_2CO_3 (10 %). Excellent yield was displayed for Cs_2CO_3 (85 %) in only 6 h. Good enhancement of the base activity was attributed to the known “cesium effect”. Due to its larger ionic radius, the cesium cation weakly bonds to the methoxy species generated through alcohol deprotonation. TBAI plays its role on stabilizing the carbonate anion generated after CO_2 insertion and prevents from non-desired alkylations. The scope was then extended to other alcohols and alkyl or benzyl halides more sterically hindered, affording a wide variety of linear carbonates. By using excess of base (5 eq), TBAI (5 eq) and R-X (5 eq), cheaper base K_2CO_3 could afford linear carbonates from various substrates (up to 82 % with benzyl alcohol and benzyl bromide) at 60 °C[56]. The utilization of other additives such as crown ethers, KI or tetrabutylammonium bromide was found detrimental on the reaction yields.

Organic bases: Alike inorganic bases, organic superbases drove the synthesis of acyclic carbonate from alcohols, CO_2 and alkyl halides. With KI or KI/crown ethers as additives added in a catalytic amount (10 mol% regarding the alcohol) dibenzyl carbonate was successfully synthetized in moderate yields (25 % and 30 % respectively), demonstrating the efficiency of DBU for the CO_2 fixation onto alcohols[56]. It should be noted that in this case, benzyl chloride was used instead of benzyl bromide to prevent possible side quaternization of DBU[57]. Bicyclic guanidines were thus tested as bases for the coupling of alcohols and CO_2. Merging computational and experimental studies allowed elucidating the reaction mechanism. Computational insights (conducted at a B3LYP level using the 6-31g(d) basis set) aided to comprehend the mechanism of the carbonate formation using DBU as a base. Wang *et al.* suggested 4 possible mechanisms shown in Scheme 7[58]. Considering thermodynamic and kinetic aspects ($\Delta G = -16.20$ kJ/mol and $\Delta G^{\ddagger} = 30.47$ kJ/mol, rate constant of 2.9×10^7 s^{-1}) the plausible mechanism involves a one-step trimolecular reaction between CO_2 the alcohol and DBU (mechanism 4 in Scheme 7) even though activation of CO_2 by DBU (mechanism 3 in Scheme 7) is theoretically feasible prior formation of the acyclic carbonate by addition onto the alkyl halide. However, it should not be generalized to other amidines and guanidines. Indeed, when using TBD, the zwitterionic adduct with CO_2 was still observed under strictly anhydrous conditions[59]. Thanks to the presence of both sp^2 amine and secondary sp^3 amine functions, the adduct is stabilized and could be isolated and well characterized by X-Ray diffraction to determine the crystal structure (see Scheme 8). In this case, the adduct is more stable than in the case of DBU thanks to the hydrogen bonding between secondary amine of the N’ labelled atom with the O’ atom of CO_2 bounded to TBD. Although, when applied to the alcohol/CO_2 system, propanediol in this case, the synthesis of the corresponding carbonate is more likely to happen with activation of the alcohol rather than CO_2 [60].



Scheme 7: Mechanisms considered for the computational studies of the CO_2 fixation onto alcohols via organic superbase DBU. Mechanism 4 displays the most favoured pathway in terms of kinetics and thermodynamics. Adapted from [58]



Scheme 8: TBD-CO_2 stabilized adduct isolated and characterized by X-Ray diffraction. Adapted from [59]

Ionic liquids derived from Hünig's base-type cations were used as recyclable base in replacement of DBU or TDB for the fixation of CO_2 onto alcohols with benzyl bromide as co-reagent[61]. Due to their non-nucleophilic characters, no side reaction between the base and the benzyl halide was detected. The high basicity of the ionic liquids allowed the spontaneous deprotonation of the alcohol moiety. The methoxy species generated is able to attack CO_2, and S_N2 on benzyl bromide will generate the corresponding unsymmetrical linear carbonate. At 25 °C and under 1 MPa CO_2 pressure after 72 h, good yields were obtained for ethanol (82 %), allyl alcohol (80 %), benzyl alcohol (83 %), phenol (78 %), propargylic alcohol (76 %) and 2-butanol (67 %), with an alcohol:halide:IL molar ratio of 1:0.5:0.6. The ionic liquid could successfully be recycled by distillation or extraction, with no loss of activity when reused.

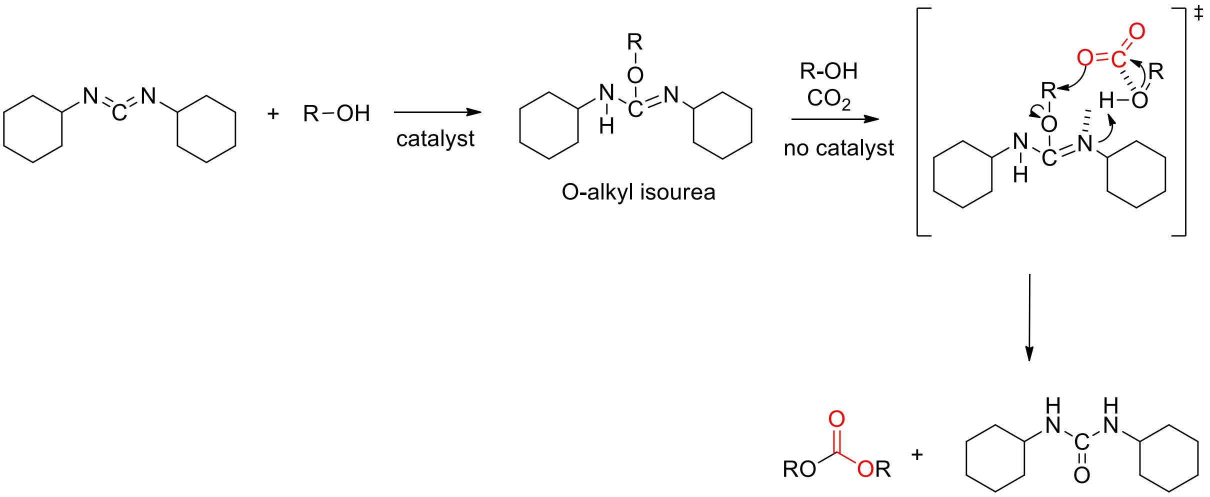
II-1-c) Synthesis of acyclic carbonates by the "leaving group" strategy

The acyclic carbonate formation by the leaving group strategy shares conceptual similarities with the alkylation route. The hemi-carbonate ion resulting from the trimolecular reaction between the alcohol, the base and CO_2 attacks through a nucleophilic substitution a dihalide species such as CH_2X_2 to produce the corresponding acyclic carbonate. This highly reactive $ROC(O)OCH_2X$ further undergoes a transcarbonation reaction with a second alcohol providing the desired ROC(O)OR carbonate.

This concept was applied to fabrication of dibenzyl carbonate from CO_2 and benzyl alcohol using DBU with ionic liquid $bmimPF_6$ as additive in CH_2Br_2 at 70 °C under 1 MPa CO_2 pressure [62]. Dibenzyl carbonate was obtained in 69 % yield with 2 equivalents of DBU and 0.1 mL of $bmimPF_6$ for 0.5 mmol of benzyl alcohol. Equimolar amounts of [DBUH]Br salt and $BrCH_2OH$ were concomitantly generated as by-product. The authors do not mention any particular role of the ionic liquid in the mechanism itself, but as a promotor for CO_2 solubilisation in the reaction media. When $bmimPF_6$ was not added to the system, the yield decreased from 69 % to 25 %. Similarly, when CH_2Cl_2 was used instead of CH_2Br_2, the yield decreased to 25 %, supporting the SN_2 mechanism that is more favourable with bromine regarding its reactivity versus chlorine. No carbonate was produced with more reactive halides such as CH_3I, supposedly due to quaternization of DBU. The optimized protocol was applied to other benzyl alcohols derivatives and could afford the corresponding carbonates in moderate to good yields (from 47 % to 73 %). DMC was also synthetized with 48 % yield.

II-1-d) Synthesis of acyclic carbonates from the carbodiimide route

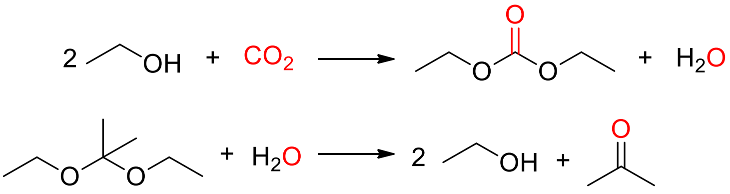
Aresta *et al.* engineered an elegant methodology to synthesize acyclic carbonates using carbodiimides acting both as a co-reagent and a base[63]. Carbodiimides react with the alcohol to produce an isolable O-alkyl isourea intermediate[64]. This reaction can be catalysed by transition metal-based complexes (mostly Copper-based) such as CuCl, Cu_2I_2, CuO, $Cu(OAc)_2$ and ZnO_2, organic superbases such as TBD, or alkali-metal TBD complexes[65]. Then, the O-alkyl isourea participates in a trimolecular interaction between the alcohol and CO_2 via its remaining basic iminoether moiety, leading to an isourea-hemicarbonate adduct that allows for the carbonation of a second alcohol molecule. The latter will react with the alkyl part fixed on the O-alkyl isourea to generate the corresponding linear alkyl carbonate (see Scheme 9). Following this approach, DMC was synthetized with yields up to 62 % in 6 h at 65 °C with 5 MPa of CO_2. Allyl alcohol successfully gave the corresponding carbonates as well, with best yield of 93 % using alcohol:DCC ratio of 15:1 and DCC:Cu_2I_2 ratio of 500 at 65 °C and 5 MPa CO_2 pressure after only 4 h.



Scheme 9: Reaction mechanism proposed for the synthesis of acyclic carbonates from alcohols, CO_2 and carbodiimides. Adapted from [63].

II-1-e) Synthesis of acyclic carbonates from the "protected alcohols" route

Ketals undergo reversible hydrolysis to form alcohols and ketones. Thus, they can be seen as the protected form of dehydrated alcohols. Upon water release, the ketal decomposes *in-situ* into the former ketone and an alcohol that is subsequently involved in a cascade coupling reaction with CO_2 to afford the acyclic carbonate (Scheme 10). Notably, systems merging the utilization of 2,2-dimethoxypropane or 2,2-diethoxypropane with CeO_2 or CeO_2-ZrO (mixte) oxide catalysts and CO_2[66,67] gave access to DMC with yields of 13.8-59.3 mmol.gcat^{-1} in 2h at 110-140 °C and 5-6 MPa of CO_2. However, the main bottleneck of these systems arose from the slow hydration rate of the 2,2-dialkoxypropane. To improve the performances, acidic co-catalysts were used as additives to boost the ketals hydration. Heterogeneous acids such as zeolites (H-FAU zeolite with SiO_2/Al_2O_3=5.5) used in combination with 2,2-diethoxypropane and CeO_2 catalyst remarkably increased the DEC yields up to 72 % based on 2,2-diethoxypropane (T = 120 °C and 9.5 MPa of CO_2)[68].



Scheme 10: Cascade reaction for the formation of DEC from 2,2-diethoxypropane, initiated by ethanol. Adapted from [68]

Alike ketals, the structural features of orthoesters make them also sensitive to hydrolysis and decompose into esters and alcohols. Orthoesters are then good candidates to consume water while releasing *in-situ* the alcohols entering in the fabrication of the acyclic carbonates. As representative example, DMC was synthesized by combining trimethyl orthoacetate with supercritical CO_2 using binary catalysts made of organotin complexes and ammonium or phosphonium salts additives[69] or ceria-zirconia mixte oxides catalysts[70]. The highest DMC yield of 70 % was obtained after 72 h at 180 °C, under 30 MPa of CO_2 pressure using the $Bu_2Sn(OMe)_2/Bu_4PI$ catalytic system while lower DMC yields of 1.8-10.4 % were obtained at 12 MPa after 34 h when 1,1,1-trimethyl orthoformiate was combined to ceria-zirconia oxides. Recently, Fukaya revisited this conceptual route by using water sensitive alkoxysilane, i.e. tetraethyl orthosilicates, as alcohol precursor and $Zr(OEt)_4$ catalyst that favours the ethoxylation of CO_2[71]. The DEC yield reached 58 % after 24 h at 180 °C under 5 MPa of CO_2. As last method, trimethylphosphate was tested as water scavenger to synthesize DMC from in-situ generated methanol. The transformation of CO_2 into the acyclic carbonate was performed at 180 °C for 20 h under 2.8 MPa of CO_2 using catalytic amounts of $Bu_2Sn(OBu)_2$ and provided DMC with moderate yield of 47 %[19].

II-2) Synthesis of cyclic organic carbonates

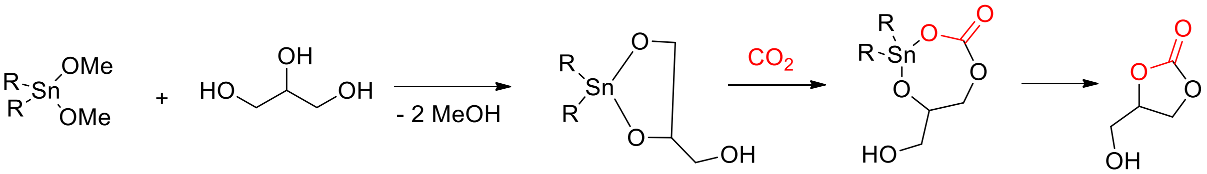
Cyclic carbonates are useful chemicals deserving huge interest as green solvent, electrolyte for batteries, or monomers to design polycarbonate or isocyanate-free polyurethanes. Most of them are easily produced from vicinal or 1,3-diols and highly reactive phosgene derivatives, diphenyl carbonate (DPC) or DMC[72-74] which can be CO_2-based as demonstrated previously in this review. Finding efficient routes to convert alcohols directly into their corresponding cyclic carbonate has become a challenge in CO_2 chemistry. This section is then fully dedicated to the various strategies that have been engineered to synthesize these heterocycles from various alcohols substrates, including vicinal or 1,3-diols, allylic or propargylic alcohols or halohydrins. One has to keep in mind that 5-membered and 6-membered cyclic carbonates will be exclusively discussed in this section since their formation is thermodynamically or kinetically more favourable than smaller or larger rings.

II-2-a) Synthesis of cyclic carbonates from diols

Diols are ubiquitous scaffolds largely available from biomass making them attractive substrates for the synthesis of cyclic carbonates[75,76]. However the direct carbonation of vicinal or 1,3-diols suffers from the same thermodynamic limitation as the one observed for the synthesis of acyclic carbonates from monoalcohols, i.e. the formation of water by-product[77]. Therefore, most of the strategies proposed for the fabrication of acyclic carbonates may be transposed to diols substrates. However, the large diversity of substrates investigated in the scientific literature to produce cyclic carbonates from diols made the finding of guidelines difficult to summarize and rationalize the results. This may confer to the reader of the following sections the perception of a lack of coherence in the manuscript.

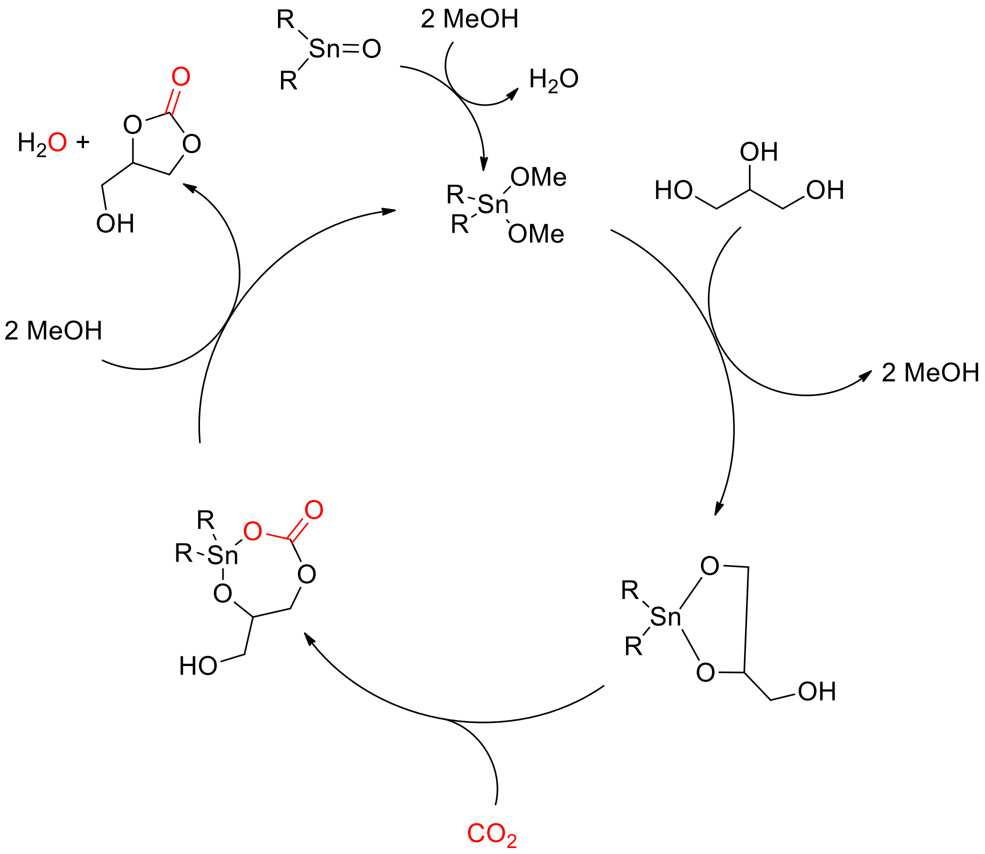
II-2-a-i) Dehydrative condensation

Physical drying systems: Glycerol, a waste bio-based polyol from the production of biodiesel, was converted by Aresta *et al.* into glycerol carbonate with CO_2 via the dehydrative condensation approach. By using n-$Bu_2Sn(OCH_3)_2$ in combination with molecular sieves at 180 °C under 5 MPa CO_2 pressure, the cyclic carbonate was produced with a low yield of ~7 % in 15 h (see Scheme 11)[78].



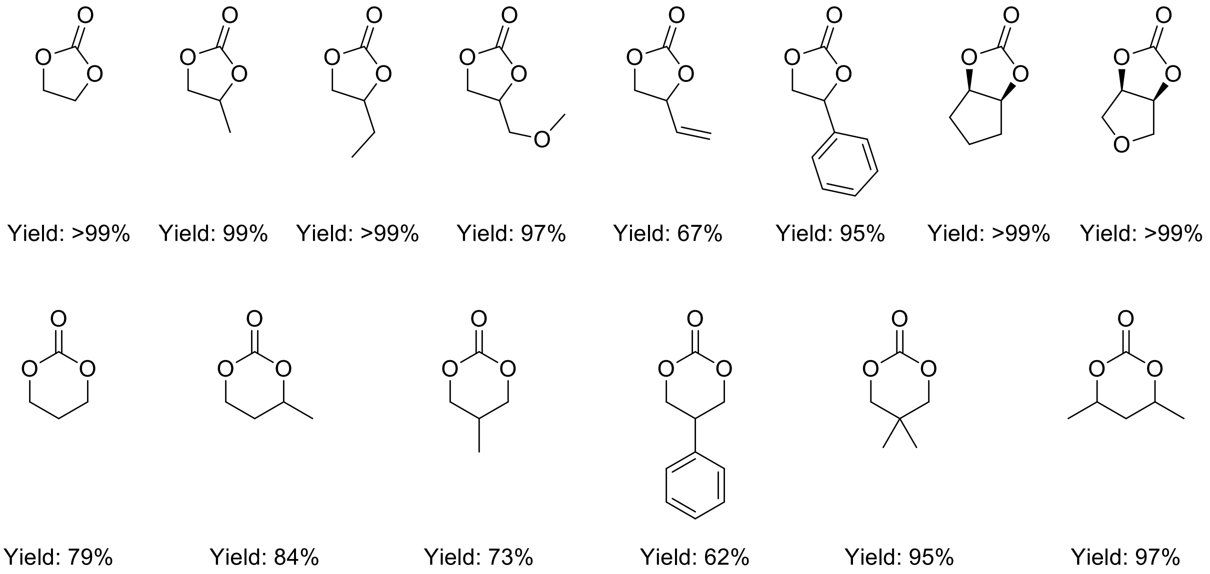
Scheme 11: Synthetic pathway for the synthesis of glycerol carbonate from glycerol catalysed by n-$Bu_2Sn(OCH_3)_2$. Adapted from [78].

Switching to n-Bu_2SnO was detrimental with glycerol carbonate yields that felt down to ~3 %. The catalytic activity of n-Bu_2SnO could be enhanced by the addition of methanol[41]. Glycerol carbonate was obtained selectively with a yield of 35 % in 4 h with 13X Zeolite as the dehydration agent, at 120 °C under 13.5 MPa CO_2. It was postulated that methanol played a dual role. It acted as a solvent providing a homogeneous reaction mixture. Methanol also transformed *in-situ* Bu_2SnO into the more active n-$Bu_2Sn(OCH_3)_2$ catalyst. The catalytic cycle involved is presented in Scheme 12. This protocol was extended to the selective synthesis of ethylene carbonate and propylene carbonate from ethylene glycol and propylene glycol, respectively, in good yields (61 % and 42 % respectively), using zeolite as drying system[79].



Scheme 12: Catalytic cycle for the synthesis of glycerol carbonate from glycerol and CO_2 using n-$Bu_2Sn(OCH_3)_2$ as catalyst. Adapted from [41]

Reactive dehydrative systems: The activity of dual catalysts mixing a metal oxide (ZrO_2, Al_2O_3, TiO_2, polyhedral CeO_2 or ZnO) with 2-cyanopyridine was evaluated for the synthesis of glycerol carbonate from glycerol and CO_2 (T = 170 °C, 10 MPa of CO_2 for 12 h). Benchmarking of the glycerol carbonate yields evolving from ~ 10.4 to 14.2 % enabled to classify the catalysts regarding their activity in the order ZrO_2 ~ Al_2O_3 < TiO_2 < ZnO < CeO_2. In the quest for the optimization of the glycerol carbonate production, the influence of the reactive desiccant on the reaction was evaluated with polyhedral CeO_2 and revealed that replacing 2-cyanopyridine by 3- or 4-cyanopyridine and acetonitrile was detrimental with yield below ~1-5 %. The crucial role of the CeO_2 crystallinity[30] on the catalytic performances was also highlighted. Mesoporous CeO_2 or nanocubes displayed the lowest efficiency with similar glycerol carbonate yields of ~ 10.3 %. CeO_2 nanorod and nanowires increased the cyclic carbonate yields to ~ 13 %. Then, CeO_2 with polyhedral crystallinity remained the most effective catalyst[80]. Tomishige *et al.* further extended the substrate scope to other mono- or di-substituted vicinal or 1,3-diols using the CeO_2/2-cyanopyridine catalytic system (T = 130-150 °C, P_{CO2} = 5 MPa, t = 1-8 h). Remarkably, the corresponding substituted 5-membered and 6-membered cyclic carbonates were synthesized in good to excellent yields (from 62 % to 99 % for 14 examples)[81], demonstrating the versatility of such systems (see Scheme 13).

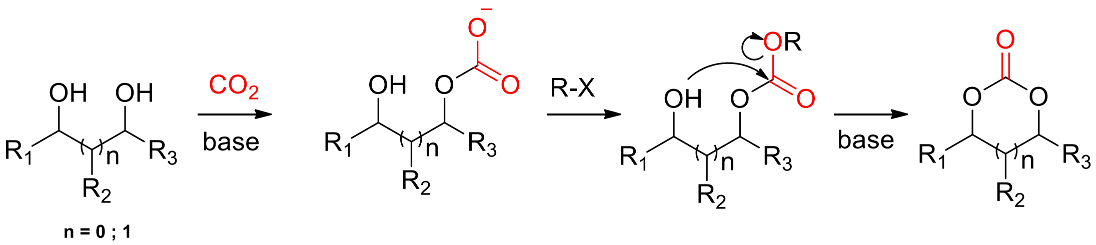


Scheme 13: Library of affordable 5- and 6-membered cyclic carbonates obtain with the dual CeO_2/2-cyanopyridine system. Adapted from [81]

As 2-cyanopyridine is rather expensive and used in large excess, acetonitrile was also considered as a more affordable solvent and dehydration agent. In combination with organic base such as TBD (2.5 mol%), propylene carbonate could be synthetized with yields up to 22.5 % but with a low selectivity of 60.3 %[82], due to side-reaction of propylene glycol with the hydrolysis product of acetonitrile, namely acetic acid (ammonia is also generated). Ammonium carbonate $(NH_4)_2CO_3$ was found to considerably increase the selectivity toward propylene carbonate, by preventing the decomposition of acetamide into ammonia and acetic acid. However, the yield was lowered to 15.6 %, due to decomposition of $(NH_4)_2CO_3$ into NH_4^+ which inhibits the hydrolysis of acetonitrile.

II-2-a-ii) Cyclic carbonates synthesis by the leaving group strategy or alkylation route

Alike acyclic carbonates (Section II-1-b) and II-1-c)), strategies utilizing bases and alkyl or aryl halides R-X as co-reagents to bypass the formation of water were extended to the CO_2 fixation onto vicinal or 1,3-diols. Mechanistically, the hemi-carbonate ion formed by fixation of CO_2 onto one OH moiety undergoes an alkylation by SN_2 substitution with an alkyl halide. Then, the second OH group is involved in an intramolecular transcarbonation reaction promoting the ring closure of the molecule (see Scheme 14).

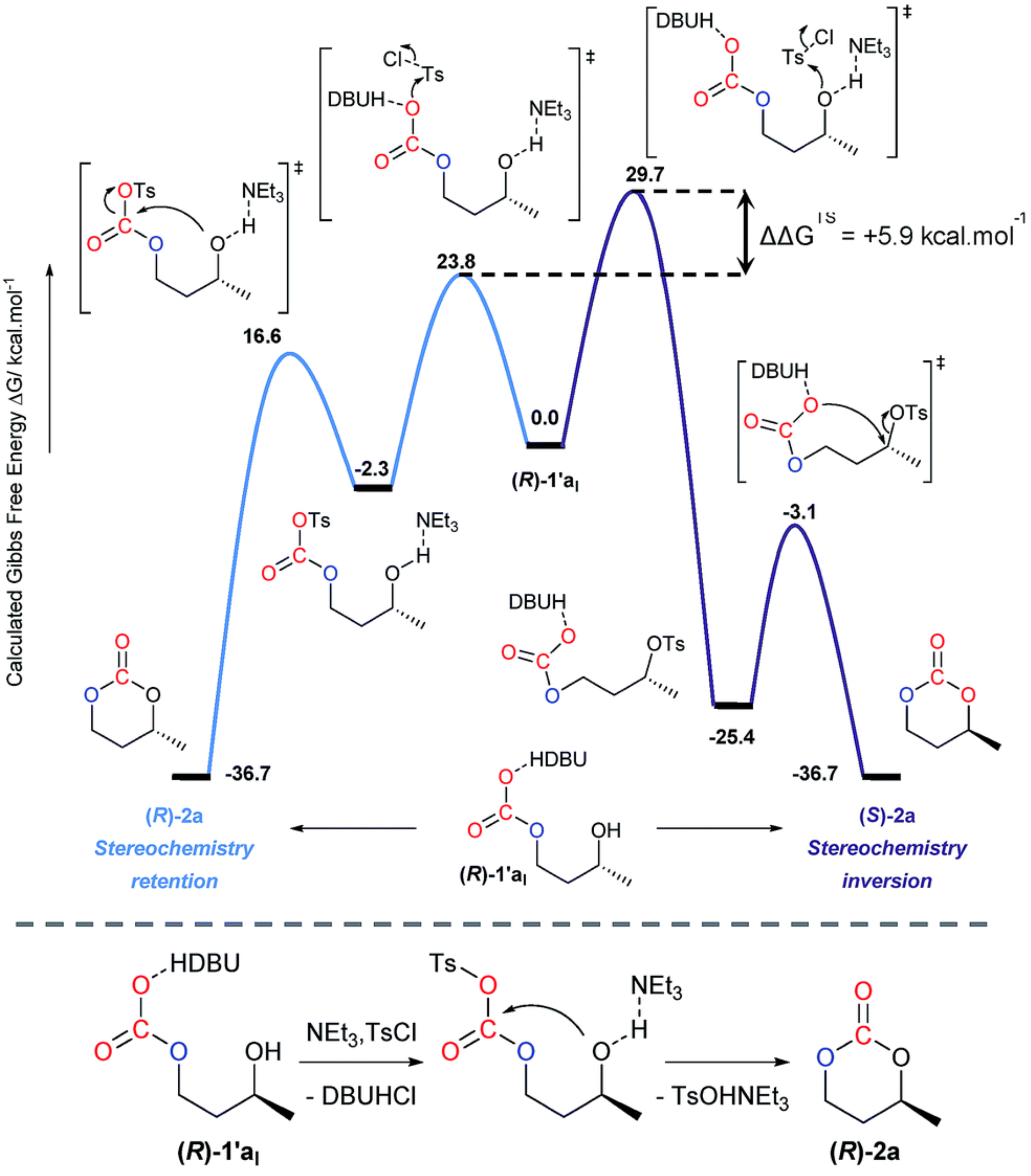


Scheme 14: General “leaving group” or “alkylation” strategy to obtain cyclic carbonates from diols

Organic systems combining DBU with CH_2Br_2 or BuBr as alkylation agent and ionic liquid bmimPF_6 or CH_2Cl_2 as solvents promoted the formation of a large diversity of (substituted) 5- and/or 6-membered cyclic carbonates (glycerol, styrene, propylene, *cis*-cyclohexene, trimethylene… carbonates) under mild operative conditions (T = 25-70 °C, P_{CO2} = 0.1-1 MPa, t = 18-24 h)[62,83] and yields ranging from 60 to 90 %.Unfortunately, when diols are chosen as substrates to fix CO_2, the carbonation of both alcohols moiety followed by double alkylation drives the concomitant formation of an acyclic bis-carbonate by-product. The competition between the mono- and double carbonations seems dependant on both the substrate and the nature of the base. A second difficulty lies in the formation of a second type of acyclic carbonates. Upon cyclisation, an alcoholate group is released in the reaction medium. This species is then capable to fix one molecule of CO_2 and react via SN_2 with the alkyl halide co-reagent to form a (reactive) linear dialkyl carbonate. Inspired by these works, Buchard *et al.* introduced the utilization of highly reactive tosyl chloride (TsCl) as co-reagent in combination with organic bases to promote the fixation of CO_2 onto 1,3-diols[84]. TsCl reacts easily with *O*-nucleophiles to form a tosylate known to be a very good leaving group[85]. However, TsCl is not compatible with DBU and spontaneously form a [DBUTs]Cl salt so that a sequential procedure was engineered to fabricate the 6-membered cyclic carbonates. Firstly, the carbonation of one of the 2 alcohol moieties by CO_2 fixation was promoted by using 1 equivalent of DBU. Once all the DBU was reacted, TsCl and TEA were introduced to perform the intramolecular cyclisation. A mechanistic proposal was proposed by DFT calculations and supported by carbonation experiments of optically active diols. Similarly to what was proposed with alkyl or aryl halides, TsCl reacted preferentially with the generated anionic carbonate than with the remaining alcohol moiety, with stereochemistry retention exclusively (see Scheme 15). Such approach enabled the synthesis of up to ten 6-membered cyclic carbonates from substituted 1,3-diols with moderate to good isolated yields at room temperature with atmospheric pressure of CO_2 in chloroform.

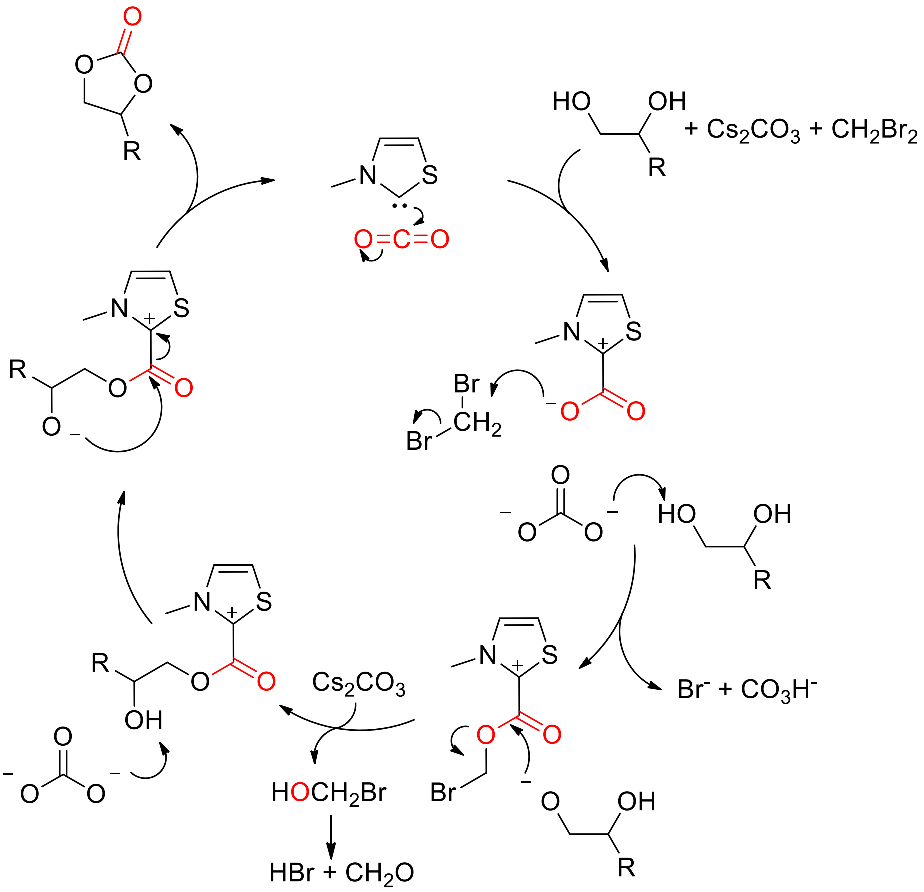
Later, the same group decoupled the reaction and investigated in details the influence of various tertiary amines and the solvent on the carbonation step of neopentyl glycol[86]. With less-toxic acetonitrile instead of chloroform, 1 eq of DBU afforded 85 % of CO_2 insertion with a mono:double carbonation ratio of 59:41. 2,2,6,6-Tetramethylpiperidine (TMP) and TEA showed very low CO_2 insertion of 2 % and 4 % respectively, but with a 100 % selectivity toward monoinsertion. No carbonation was observed with pyridine.

In accordance with these results, they adapted their synthetic procedure in a one-pot/one-step fashion by utilizing TsCl (1eq) with TEA or TMP as the base (2eq) for the carbonation of 1,x-diols (with x= 2-4) including challenging tri- or tetrasubstituted substrates. The non-nucleophilic character of these organic bases allowed the simultaneous addition of TsCl and the base without undesirable side quaternization of the amine. 5-, 6- or even 7-membered cyclic carbonates were fabricated with excellent isolated yields by this simple approach, with similar or even better yields than those reported by the phosgene route. Nevertheless, with 1,4-diols, non-negligible amount of oligomers were noted, possibly due to the poor stability of 7-membered cyclic carbonates in basic conditions or a competition between the cyclization and the polymerization.

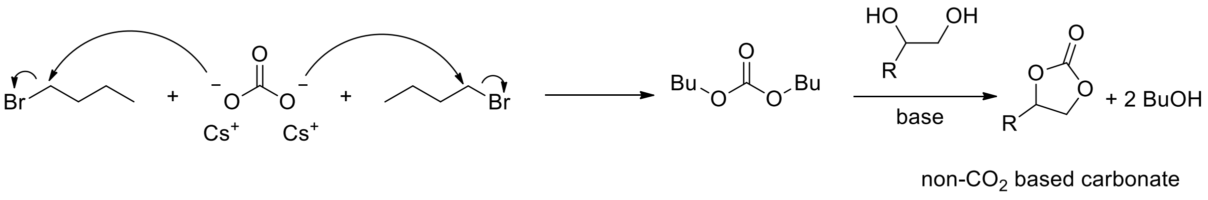


Scheme 15: Computational study for the synthesis of 6-membered cyclic carbonate from a diol using the DBU/TsCl system. G. L. Gregory, M. Ulmann and A. Buchard, *RSC Adv.*, 2015, **5**, 39404 - Published by The Royal Society of Chemistry.[84]

N-heterocyclic carbenes (NHC) are known to activate CO_2 under the form of imidazolium carboxylates[87,88] and can be used in combination with a base and an alkylating agent to form cyclic carbonates from diols. Dyson *et al.* illustrated how thiazolium carbene (20 mol%) generated *in-situ* by Cs_2CO_3 (3 eq) promoted the formation of styrene carbonate (yield of 61%) when used in combination with 2 eq. of BuBr (T = 90°C, 0.1 MPa of CO_2 in DMF)[89]. The authors suggested two competitive mechanisms leading both to cyclic carbonates. In the first one, CO_2 was activated via the formation of thiazolium carboxylate diadduct that attacked the alkyl halide R-X through nucleophilic substitution forming a carbonate ion. Deprotonation of an alcohol moiety by the base allows transesterification on this carboxylate with RO^- as the leaving group. The cyclisation is promoted with a second equivalent of base (Scheme 16). In the second plausible mechanism, dibutyl carbonate could be formed from the reaction of CO_3^{2-} with BuBr. Then, an oxidative carboxylation occurs by reaction between the diol and dibutyl carbonate to produce the cyclic carbonate. In this case, CO_2 did not participate to the carbonation of the diol (Scheme 17). The validity of this hypothesis was supported by the formation of the cyclic carbonate even in the absence of CO_2 as the cyclic carbonate yield considerably decreased, but was still significant (25 %).



Scheme 16: Mechanism proposed for the formation of cyclic carbonates from diols catalysed by ionic liquids and Cs2CO3 in the presence of alkyl halides. Adapted from [89].

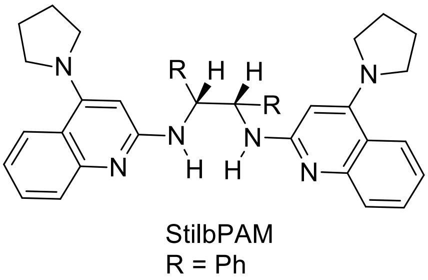


Scheme 17: Competitive pathway for the formation of carbonate linkages leading to non-CO_2 based cyclic carbonates. Adapted from [89]

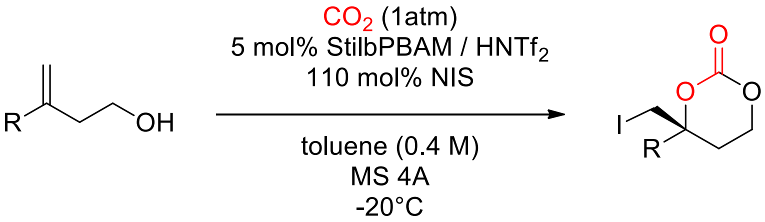
II-2-b) Synthesis of cyclic carbonates from allyl alcohols

Pioneer work by Cardillo *et al.* in 1981 demonstrated the efficiency of allyl alcohols as valuable substrates for the formation of cyclic carbonates with CO_2[90]. In their study, various 5- and 6-membered cyclic iodocarbonates were synthetized from allylic and homoallylic alcohols and CO_2, using n-butyllithium as a base and I_2 as a promotor for cyclisation. Functionalization of the double bond by I_2 is highly regioselective, which allows the formation of the product in very good yields under mild conditions (CO_2 bubbling in THF ; T = 25 °C, t = 12 h). With an alcohol/iodine/base molar ratio of 10/20/6.6, various 5-membered cyclic iodocarbonates were obtained from primary, secondary and even tertiary allylic alcohols in moderate to good yields (60 - 90 %). 6-membered cyclic iodocarbonates were also obtained from primary and secondary homoallylic alcohols in yields ranging from 72 % to 80 %. The generated iodocarbonate could be converted into iodine-free carbonate by treatment with Bu_3SnH. Conversion of homoallylic alcohols into 6-membered cyclic iodocarbonates was also investigated using N-iodosuccinimide as the iodine agent (1.1 eq with regard to the alcohol)[91]. The catalytic system used relies on a Brønsted acid/base bifunctional salt with best results using pyrrolidine-substituted bis(amidine) incorporating *trans*-stilbene diamine (StilbPBAM, see Scheme 18) as the base and triflimidic acid $HNTf_2$ as the acid. Good to excellent yields were obtained for a large substrate scope of primary homoallylic alcohols in toluene at -20 °C with CO_2 bubbling (Scheme 19). High enantiomeric excess were observed in most of the cases. Molecular sieves were added to prevent deactivation of the catalyst in presence of water and CO_2. The use of an acid is assumed to stabilize the CO_2-alcohol adduct.

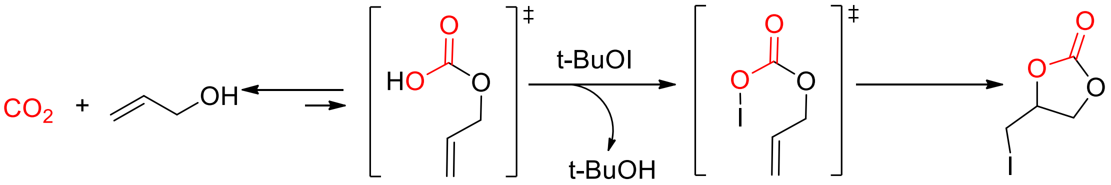
To overcome the use of toxic or expensive iodinating agents, Minakata *et al.* proposed the use of ^tBuOI, which can be generated *in-situ* from ^tBuOCl and NaI, for the conversion of allylic and homoallylic alcohols into 5 and 6-membered iodocarbonates[92]. In this case, ^tBuOI abstracts the proton of a weak acid that is replaced by an iodine atom. The thermodynamically disfavoured synthesis of alkylcarbonic acid from the CO_2/alcohol coupling can then be turned into highly reactive iodinated intermediate which cyclisation is promoted by the presence of the double bond (Scheme 20). Thus, if the alkylcarbonic acid could be trapped in some way, the equilibrium should be displaced toward the formation of cyclic iodocarbonates. This proposed mechanism should be consolidated with more theoretical and experimental studies. The substrate scope proved the efficiency of this non-catalytic method, affording cyclic carbonate scaffolds with good yields (from 57 % to 93 %) when 2eq of ^{t}BuOI are used at -20 °C with CO_2 bubbling.



Scheme 18: StilbPAM structure as the base for Brønsted acid/base bifunctional salt used in the synthesis of iodocarbonates from allyl alcohols.



Scheme 19: Example of iodocarbonate synthesis from allyl alcohol using Brønsted acid/base bifunctional salt catalysts and N-iodosuccinimide as the iodinating agent. Adapted from [91].

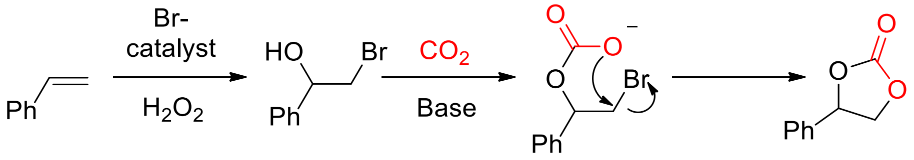


Scheme 20: Proposed mechanism for the formation of iodocarbonate from allyl alcohol using t-BuOI as iodinating agent. Adapted from [92]

II-2-c) Synthesis of cyclic carbonates from halohydrin

A more direct route for the synthesis of 5- and 6-membered cyclic carbonates is the use of β- and γ-halohydrins in combination with a base (1.1 eq) and CO_2. Ethylene carbonate and trimethylene carbonate are examples of scaffolds obtained from 2-chloroethanol and 3-chloropropanol by this approach providing excellent yields (> 95 % yield by simple bubbling of CO_2 at 40 °C)[85]. The proposed mechanism is quite simple. Cs_2CO_3 deprotonates the alcohol to form an alcoholate that fixes CO_2. Then, the ring-closure occurs by intramolecular nucleophilic substitution with Cl^- as the leaving group. Less reactive base such as K_2CO_3 afforded a lower carbonate yield (54 %), as well as the more reactive KO^tBu (20 %), once again highlighting the excellent properties of cesium for these reactions. Slightly lower yields were obtained when replacing 2-chloroethanol with 2-bromo or 2-iodoethanol. Interestingly, when tosylate OTs substituent was used instead of an halide, the corresponding cyclic carbonate was also obtained in very good yields for a range of substrates (from 65 % to 95 %). When (±)-3-chloro-1,2-propanediol was used as the substrate, exclusive formation of glycerol carbonate was observed, demonstrating the excellent selectivity of this reaction. As K_2CO_3 is a cheaper and more affordable base than Cs_2CO_3, Wang *et al.* investigated the effect of additives on the formation of cyclic carbonate from halohydrins and CO_2 with K_2CO_3[93]. With Poly(ethylene glycol) of M_n = 400 g/mol (PEG-400), styrene carbonate, propylene carbonate, ethylene carbonate and chloromethyl-ethylene carbonate were formed quantitatively after 3 h at 50 °C under 2 MPa CO_2 pressure using 0.5 eq of K_2CO_3. The more challenging cyclohexene carbonate was obtained with 72 % yield in the same conditions. The role of the additive was assumed to coordinate potassium cations favouring the salt dissociation in the medium and thus increasing the basicity of K_2CO_3. Non-nucleophilic basic ionic liquids tested for the synthesis of linear carbonates by Goodrich *et al.* were also tested on 3-bromopropanol and 2-chloroethanol, successfully producing ethylene carbonate and trimethylene carbonate in good yields (> 90 %) with excellent selectivity toward cyclic products[61].

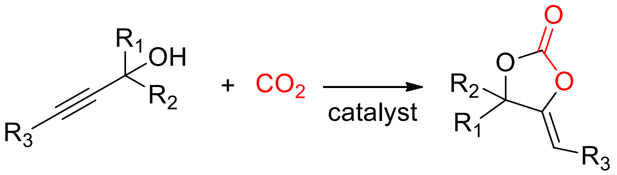
As halohydrins are not widely available and are generally synthetized from oxidation of olefins, a one-step synthesis from terminal alkenes was proposed by Li *et al*[94] (Scheme 21). This method relies on the *in-situ* generation of bromohydrin using water as both the solvent and oxidation agent, N-bromosuccinimide as the bromination agent (1 eq) and DBU as the base (2 eq) for the CO_2 fixation onto the generated alcohol. 5-membered cyclic carbonates could be obtained in moderate to excellent yields after few hours of reaction at 60 °C under 2 MPa CO_2 pressure. From these results, a catalytic process was then envisioned since bromide ion can be oxidised back to bromination agents under oxidative conditions, thus being able to perform a catalytic cycle for the *in-situ* generation of bromohydrin from olefins [95]. Hydrogen peroxide was used to regenerate the bromination agent. Several bromination agents were tested, and the best results were obtained with tetrabutylammonium bromide or NaBr. Styrene carbonate could be obtained at 70 % yield using an olefin/base/bromination agent molar ration of 1.5/0.2/0.15 after 15 h at 50 °C under 2 MPa of CO_2 pressure.



Scheme 21: Synthetic strategy to obtain cyclic carbonates from terminal alkenes via *in-situ* generation of halohydrin. Adapted from [96]

II-2-d) Synthesis of cyclic carbonate from propargylic alcohols

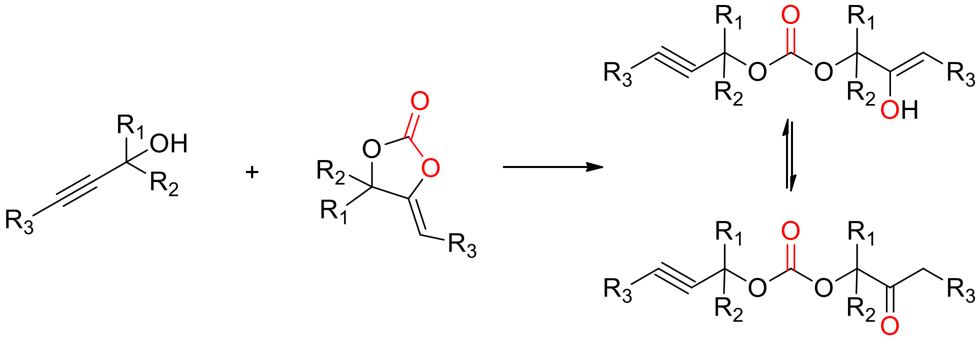
The carboxylation coupling of propargylic alcohols with CO_2 is highly attractive. This 100% atom economy synthetic pathway provides organic cyclic carbonates that slightly differ from conventional cyclocarbonate scaffolds by the presence of an additional exovinylene moiety (Scheme 22). A large diversity of catalysts has been reported to promote this reaction. These catalysts have to fulfil a dual role: the activation of the alcohol moiety or CO_2 activation to facilitate the carbonation step, and the activation of the triple bond to drive the intramolecular cyclisation and ring formation. The chemical structure of the substrate also strongly influences the formation of the cyclic scaffold. The carboxylative cyclization of tertiary propargylic alcohols is driven by the presence of 2 alkyl groups that facilitate the ring closure via the Thorpe Ingold effect. Until now, the carbonation of secondary or primary propargylic alcohols remains very challenging.



Scheme 22: Synthesis of exovinylene cyclic carbonates from the coupling of propargylic alcohols and CO_2.

Organocatalysts like organophosphorous compounds such as trialkyl- or triphenyl-phosphine can catalyse the carboxylation of propargylic alcohols in supercritical CO_2 (P_{CO2} = 10 MPa and T = 100 °C). With low $(nBu)_3P$ loading of 5 mol% which appears to be the most efficient phosphine, internal and terminal tertiary propargylic alcohols were converted into the corresponding exovinylene cyclic carbonate (also called α-alkylidene cyclic carbonate) in very good yields (up to 11 examples in the range of 64-99 % yield)[97]. For internal propargylic alcohols, products with olefins of (Z)-configuration were observed exclusively. The plausible mechanism suggested by the authors proposed a possible phosphine-CO_2 adduct formation in supercritical conditions that would help CO_2 insertion. Attempts to obtain optically active cyclic carbonates with chiral phosphine proved its efficiency[98]. Phosphorous ylides were also investigated as they are known to form an adduct with CO_2 thanks to the work of Matthews *et al*[99]. Internal tertiary propargylic alcohols could be converted into exovinylene cyclic carbonates in good yields at 80 °C under atmospheric pressure of CO_2.

N-heterocyclic carbenes (NHC) also catalyse successfully the carboxylation of propargylic alcohols in a similar manner, with typical imidazolium-2-carboxylates as intermediate in the CO_2 fixation. Exovinylene cyclic carbonates were obtained under supercritical conditions or milder conditions (P_{CO2} = 4.5 MPa, T = 60 °C) in good yields[100]. To enhance the CO_2 activation, N-heterocyclic olefins (NHO) such as ketene aminals are good candidates since they display a highly polarized C=C bond that can act as a nucleophile, while stabilizing a positive charge due to electron delocalisation via the heterocycle. After kinetic considerations, terminal and internal tertiary propargylic alcohols were successfully converted into the corresponding exovinylene cyclic carbonate in good yields (from 50 % to 98 % for 7 examples) using 5 mol% of NHO at 60 °C under 2 MPa of CO_2 pressure in neat conditions. Although NHO/CO_2 adduct occurs, increasing CO_2 solubility in the reaction media via its fast sequestration, computational studies suggest a mechanism based on OH activation (hemi-carbonate ion formation) rather than nucleophilic attack of the alcohol moiety on the NHO/CO_2 adduct[101,102]. In this case, the *in-situ* generated $[NHOH]^+[RCO_3^-]$ species is more reactive compared to the analogue when NHC are used. Moreover, NHO are less basic than NHC, which limits possible side reactions such as ring-opening of the exovinylene cyclic carbonate by the unreacted propargylic alcohols (see Scheme 23) which is promoted by formation of a $[NHO]^+[RO]^-$ ionic pair[103].



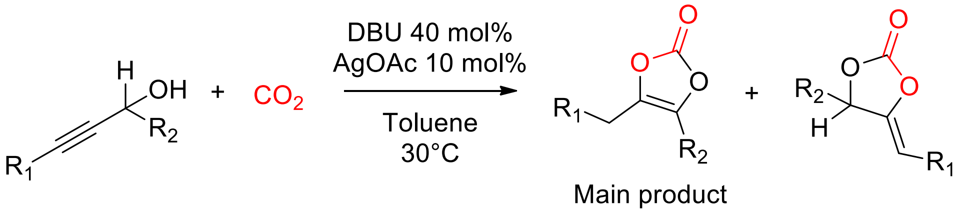
Scheme 23: Undesired side-reactions of ring-opening of exovinylene cyclic carbonates by unreacted propargylic alcohols.

Amidines and guanidines are efficient promotors for the carboxylation of CO_2 onto alcohols. These organic superbases have been tested with propargylic alcohols by our group [104]. Mechanistic and kinetic studies were conducted to better understand side reactions (see Scheme 23) and disparities in selectivies. Optimal conditions of 100 °C and 3 MPa CO_2 pressure in acetonitrile led to quantitative conversion of terminal tertiary propargylic alcohol with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) as catalyst (5 mol%). By tuning the reaction time, the best selectivity of 80 % toward the exovinylene cyclic carbonate was observed. Replacing MTBD by TBD led to the formation of an oxo-alkyl carbonate (resulting from the ring-opening of the exovinylene carbonate by unreacted propargylic alcohol) with a selectivity above 85 %. This arose from the capability of TBD to act both as a base and a proton donor, as justified by DFT calculations.

Basic organic salts and ionic liquids with easy tunable structure and basicity by changing both the anion and the cation structure were then investigated as cheap catalysts to selectively design exovinylene cyclic carbonates. The use of ionic liquid also offer the benefit of increasing the CO_2 solubility within the reaction medium, which is favourable for the fast and selective coupling of CO_2 with propargylic alcohols substrates. Excellent results were obtained with alkylammonium salts displaying basic counter anions such as acetate, azide, phenolate, isocyanate… with almost quantitative formation of exovinylene cyclic carbonate after 8 h at 80 °C and 3 MPa CO_2 pressure in neat conditions [105]. Deeper investigations on the influence of the cation-anion pair of the organic salts were later described by our group. Within the range of tested catalysts, the optimum activity was found for a controlled ionic pair separation made of sterically hindered cations (ideally ammonium or phosphonium cations tetrabutyl chains), and basic anions with pKa of ~ 4.5 -9 to promote the reaction without detrimental effects on the selectivity[106]. Several terminal tertiary propargylic alcohols were successfully converted, as well as bifunctional alkynols to produce quantitatively bis-cyclic carbonates that are useful monomer entering in the fabrication of world-class relevant polymers, i.e. poly(thio)carbonates and polyurethanes[107]. Azole-anion based aprotic ionic liquids such as tetrabutylphosphonium/2-methyl Imidazole, tetrabutylammonium phenolate, phosphonium levulinate… are just few examples of ionic liquid that proved their efficiency to convert various terminal tertiary propargylic alcohols into their corresponding cyclic carbonate, generally under non-demanding conditions (P_{CO2} = 0.1-5 MPa, T = 25 – 80 °C, t = 1 to 24 h)[108,109].

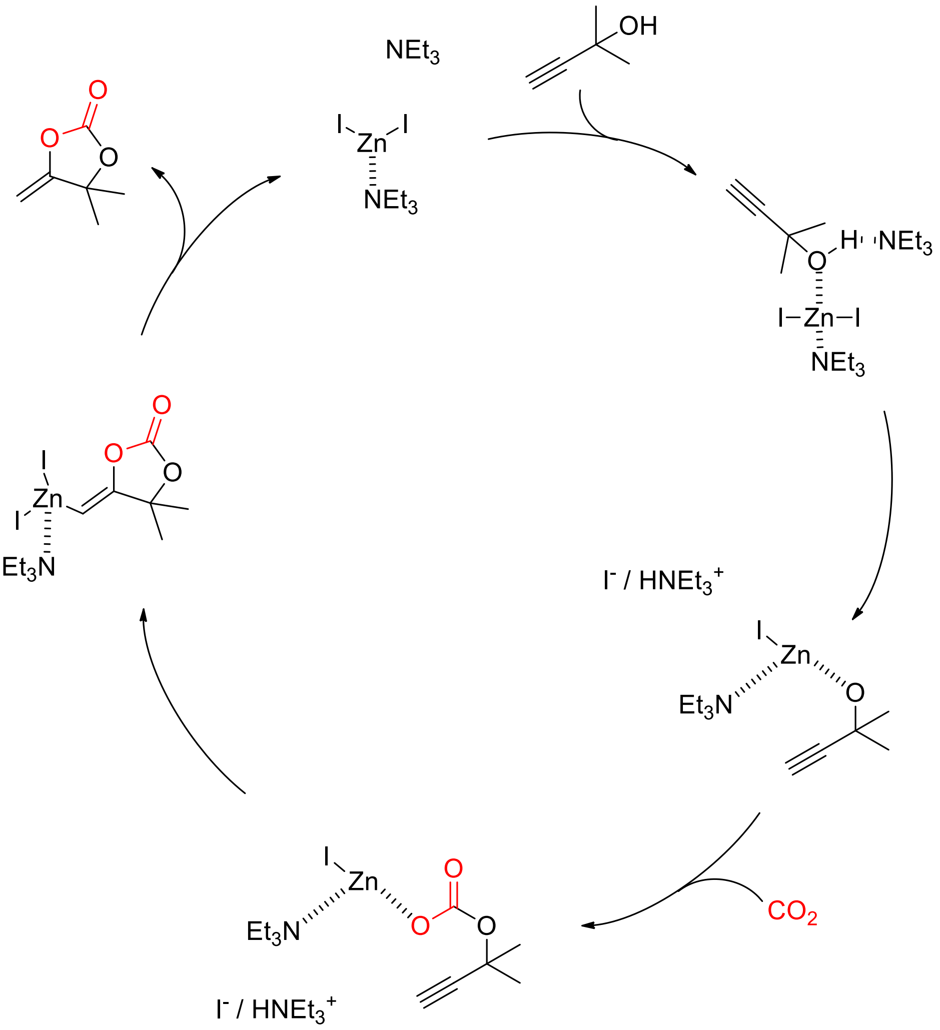
Copper-based catalysts. The use in synergy of metal salt with a base or basic ionic liquids/salts represents an elegant method to boost the catalytic performances while providing the selective formation of exovinylene cyclic carbonates. The benefits of using these binary catalyst is assigned to the dual activation of the alcohol substrate, i.e. the OH activation by the base, ionic liquid or organic salt which facilitate the formation of a carbonate ion and the triple bond activation by interaction with the metal cation to favour the ring closure of the molecule. As selected examples, an ionic liquid with bio-derived levulinate anions combined to CuI provided series of exovinylene cyclic carbonates from terminal tertiary propargylic alcohols[110] with excellent yields from 80 % to 99 % just at 25°C and 1 MPa of CO_2 in 4 h. CuI also operate in synergy with N,N-diisopropylethylamine at temperatures between 80-120 °C under 4 MPa CO_2 to provide series of cyclic carbonates with internal exocyclic olefin in Z configuration with yields from 43 % to 96 %[111]. Remarkably, this dual catalyst system also enable the conversion of a challenging terminal secondary alcohol (R_1 = H ; R_2 = isopropyl) with 95 % yield.

Silver-based catalysts. Alike copper salts, Ag salts which are by far the most widely used metal salts in the literature, have proven their utility in enhancing the efficiency of the catalyst. The pioneer work of Kikuchi *et al.* illustrated that terminal and internal tertiary propargylic alcohols were converted to cyclic carbonates in very good yields (up to 14 examples) using AgOAc as catalyst (10 mol%) and DBU (1 eq) as the base just at room temperature, under 1 MPa of CO_2 [112]. A more recent study showed a different selectivity for internal secondary propargylic alcohols by tuning the amount of base[113]. In this particular case, great selectivity toward vinylene carbonate was obtained when lowering the amount of DBU (0.4 eq instead of 1 eq), and presence of exovinylene carbonates was not observed (see Scheme 24). Other examples using silver-based catalysts such as AgI/OAc [114], silver sulfadiazine/Et_4NBr[115], silver oxides with KI and carbenes[116] or silver nanoparticles supported by polymers[117-119] proved their efficiency for terminal or internal tertiary propargylic alcohols. To date, only Schaub *et al.* developed a remarkable dual catalyst combining a silver salt with DavePhos ligand to synthesise exovinylene cyclic carbonate from challenging primary propargylic alcohols at room temperature and 2 MPa of CO_2 in acetonitrile[120]. In this study, the use of a bulky donor ligand (phosphine) provokes an angle compression of the alcohol substrate which mimics the Thorpe Ingold effect[121]. The versatility of this elegant catalytic system afforded a large portfolio of exovinylene cyclic carbonates with external or internal olefin (with exclusively Z configuration) from primary, secondary and tertiary substrates in very good yields from 65 % to 95 %.



Scheme 24: Selective synthesis of vinylene carbonates rather than exovinylene cyclic carbonates using DBU/AgOAc catalytic systems on secondary propargylic alcohols.

Zinc catalyst. Ma et al. reported the only zinc-based catalysts that provided good efficiency when associated to TEA for the carboxylative cyclization of terminal tertiary propargylic alcohols[122,123]. The ZnI_2/NEt_3 binary catalyst operated at low temperature (30 °C) and 1 MPa of CO_2 and provided exclusively the desired cyclic carbonates scaffolds. The major weakness of this system arose from the high content of the Zn salt (20 mol%) and NEt_3 (200 mol%). The mechanistic insights through DFT calculation suggested that OH of the substrate was activated by formation of a propargylic alcohol-ZnI_2-Net_3 complex which drove the formation of a carbonate ion. The Zn salt also took part in the ring closure step by interacting with the alkyne, facilitating the formation of the envisioned cyclic carbonate[124] (see Scheme 25).



Scheme 25: Catalytic cycle of the ZnI$_2$/NEt$_3$ dual system for the carboxylation of tertiary propargylic alcohols to afford exovinylene cyclic carbonates. Adapted from [124]

III) Strategies to afford CO$_2$-based polycarbonates

III-1) Direct polymerization of CO$_2$ with diols

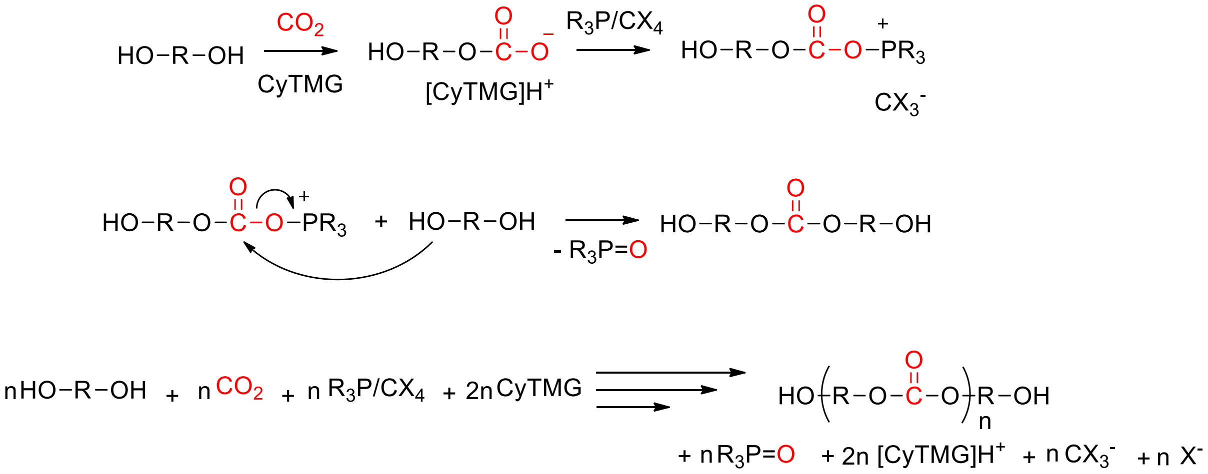
Designing polycarbonates (PC) by direct condensation of diols with CO$_2$ faces the same bottlenecks as the synthesis of (a)cyclic carbonates, i.e. the formation of water as by-product and the proper activation of the OH moieties and/or CO$_2$. A second difficulty lies from the intrinsic structural features of the diols that is involved in the polymerization manifold. Indeed, the length and the nature of the spacer between both alcohol moieties are decisive: 1,2- and 1,3-diols are prone to the thermodynamically favoured formation of 5- and 6-membered cyclic carbonates, whereas longer spacer or vicinal diols inducing the formation of constrained cyclic carbonate substrates would drive the formation of oligomers or even polymers.

III-1-a) Direct copolymerization by dehydrative polycondensation

The only relevant catalytic system to fabricate polycarbonates from the direct carboxylative coupling of diols with CO_2 was proposed by Tomishige *et al*[125]. The synergistic utilization of CeO_2 with excesses of 2-cyanopyridine, that was already good performing in synthesizing cyclic carbonates from 1,2- and 1,3-diols, was naturally extended to the dehydrative polycondensation of various 1,x-diol substrates (with x > 3). Aliphatic C_4–C_{10} α,ω-diols provided the corresponding polycarbonates with microstructures free of ether defects in 8 h at 130 °C and 5 MPa of CO_2. However, the polymer chains displayed low molar masses (M_n ~ 1,650 g/mol). With diols of rigid structure such as 1,4-Cyclohexanedimethanol and 1,4-benzenedimethanol, oligomers with M_n of only 500 – 600 g/mol were obtained, while with the dimethyl-substituted 2,5-Dimethyl-2,5-hexanediol, no polymer was formed. To surpass these bottleneck, the same group evaluated the influence of other nitriles desiccants while, at the same time, deepening the structural characterization of the polymers. Switching from 2-cyanopyridine to 2-furonitrile enabled the fabrication of polycarbonates with M_n up to 3,900 g/mol from 1,6-hexane diol with a ten-fold excess of nitrile (compared to the diol) at 130 °C under 5 MPa CO_2 pressure. The fine microstructural characterization of the polymers highlighted the presence of chain ends defects, causing termination reactions. The amide produced from the hydration of the cyano- derivatives was involved in a “transesterification” reaction with the hydroxyl chain ends to form a polycarbonate (PC) terminated by an unreactive ester moiety. This side reaction is accompanied by the formation of ammonia that provoked a scission of the PC. This released short dead chains end-capped by an unreactive amide moiety and a second hydroxyl-terminated PC fragment that was capable to further growth[126]. The design of the CeO_2 catalyst plays an important role on its activity. In this case, CeO_2 nanorods could enhance its activity toward the formation of polybutylene carbonate as its capacity to uptake CO_2 is increased, as well as its oxygen-vacancy sites[127].

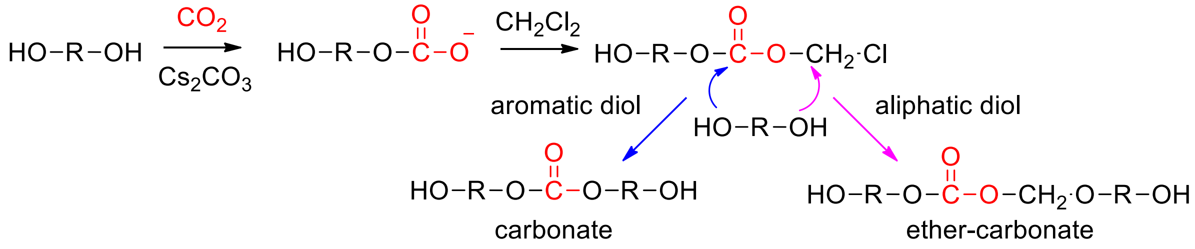
III-1-b) Direct copolymerization via alkylation

The polycondensation of CO_2 with xylylene glycol using a base/CX_4/R_3P activating system is one of the pioneer work on the synthesis of PCs from diols[128]. Polymers with M_w up to 3,800 g/mol were fabricated with CBr_4 and n-Bu_3P as polymerization promotors and N-cyclohexyl-N’,N’,N’’,N’’-tetraethylguanidine (CyTMG) as the base at room temperature in DMF. Remarkably, PCs free of ether linkages defects were synthesized. The scope of diols was further extended to di(ethylene glycol) using Ph_3P and $CBrCl_3$ to deliver the corresponding polycarbonate with M_n up to 6,000 g/mol[129]. Alike the synthesis of (a)cyclic organic carbonates, the polymerization manifold relied first on the CO_2 fixation onto the diol thanks to the OH activation by the base. The $[R_3P\text{-}CX_3]^+[X]^-$ diadduct formed *in-situ* from the R_3P/CX_4 dual system undergoes an ionic exchange with the generated RCO_3^- species, leading to the $[RCO_3\text{-}PR_3]$ intermediate. Then, the chain growth proceeded via successive transcarbonation reactions with another diol molecule thanks to the good leaving group ability of the R_3P^+-O- fragment (see Scheme 26).



Scheme 26: Mechanism for the formation of polycarbonates from the polycondensation of diols and CO_2 promoted by the CyTMG/R_3P/CX_4 system

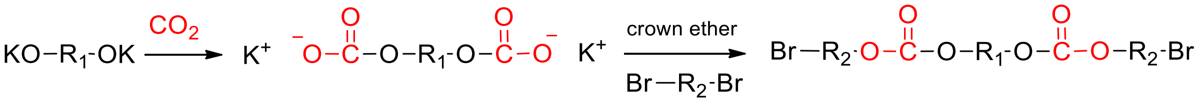
By a similar concept, Du and coworkers proposed a straightforward methodology to copolymerize various diols with CO_2 by using Cs_2CO_3 as the base (4 eq) and dichloromethane as co-reagent (6.2 eq) in NMP[130]. Interestingly, the nature of the diol dictates the microstructural feature of the polymer backbone toward either a polycarbonate or a poly(ether carbonate) which alternates carbonates and ether linkages. For benzylic diols such as 1,4-benzenedimethanol, a high conversion (> 99 %) was observed after 24 h at 100 °C and a polycarbonate with very few ether linkages was obtained (63.7 % yield ; M_n = 1,800 g/mol). With the aliphatic 1,4-cyclohexanediol, the formation of a polymer (M_n = 5,000 g/mol) with a pattern alternating ether and carbonate linkages representing 93 % of the structure was synthesized. The origin of the ether defects arises from side reactions on the chloromethylated intermediate. The polymerization mechanism is analogue to the one described for the cyclic carbonate formation from vicinal diols. An hemi-carbonate anion formed by CO_2 fixation onto one alcohol moiety subsequently undergoes an alkylation reaction with dichloromethane. Then, depending on the diol, the chain growth occurs either via the carbonyl attack to provide a carbonate linkage or via the α-methylene attack forming ether linkages (see Scheme 27). By using the DBU/CH_2Br_2/bmimPF_6 ternary system, Jang and coworkers designed biorenewable PCs by copolymerization of a monosaccharide, i.e. α-methyl D-glucopyranoside (MDG), with CO_2[131]. As most sugars, this polyol possesses both primary and secondary alcohols functions. As both type of alcohols display different reactivity, linear polyglycocarbonates with M_n up to 7,000 g/mol were fabricated without any protection steps of the hydroxyl moieties. The NMR structural characterization highlighted the absence of branching as the carbonate linkages mostly emanated from the C-6 primary alcohol and the C-3 or C-2 secondary hydroxyls.



Scheme 27: Competitive pathways between carbonyl attack (blue) and methylene attack (pink) for the formation of carbonate or ether linkages. Adapted from [130]

III-1-c) Terpolymerization methods

To overcome the limitations brought by the formation of water for the direct diols/CO_2 coupling, the terpolymerization approach utilizing dihalides as comonomers was pioneered by Ikeda *et al*. More precisely, diolate potassium salts generated from diols mixed with α,ω-dibromo compounds and crown ethers led to formation of polycarbonates under CO_2 pressure in dioxane[132,133]. 18-crown-6-ether is believed to promote the ion separations of diolate salts by forming stable complexes with metal cations. The proposed mechanism relies on CO_2 fixation onto the diolate, followed by the nucleophilic substitution of the dihalide by the carboxylate species (see Scheme 28). After experimental investigations, it appears that crown ethers don't play a key role for CO_2 fixation onto the diolate, but they considerably increase the kinetic of nucleophilic substitution on dihalides. Interestingly, this pathway provided selectively polycarbonates chains free of any ether linkages.



Scheme 28: Terpolymerization synthetic pathway for the formation of polycarbonates using diolates and dihalides.

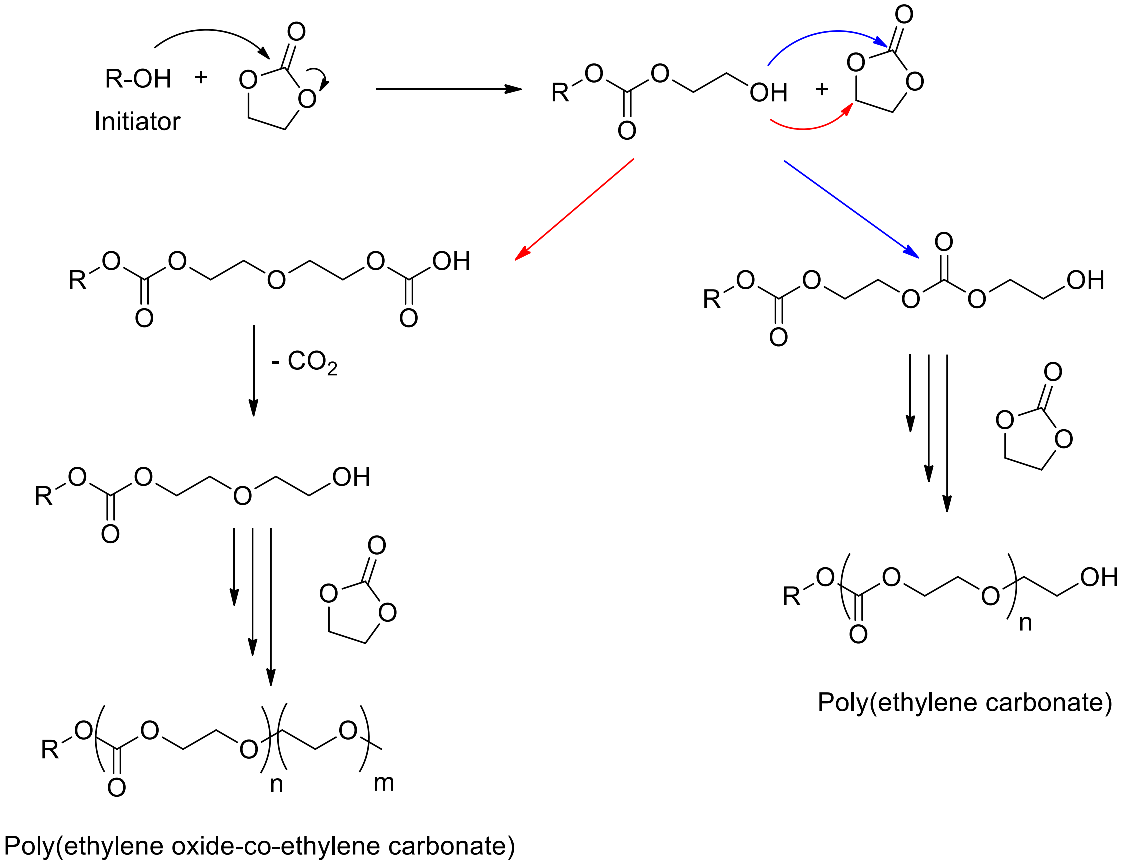
Later, this terpolymerization concept was revisited by Gnanou *et al.* using Cs_2CO_3 as a base to generate the diolate[134]. As mentioned previously, the so-called "cesium effect" allows to increase the nucleophilicity of the reactive diolate anions which facilitates the fixation of CO_2 and the nucleophilic attack of the carbonate ion onto the halide. The protocol was valid for dihalides with spacers of at least 4 carbons to prevent the risks of back-biting reactions causing the formation of cyclic carbonates by-products. Other bases like K_2CO_3, DBU and Li_2CO_3 were found less effective. Under the optimum parameters ($T = 100$ °C, $P_{CO2} = 1$ MPa, $t = 48$ h and a diol:dihalide:Cs_2CO_3 ratio of 1:1.05:4) 97% of diols were converted into polycarbonates of M_n up to 22,000g/mol and PDI of 3.6. PC with excellent M_n up to 43,000 g/mol were design by proper selection of both aliphatic and aromatic diols and dihalides, as it is the case for the couple 1,6-hexanediol/1,4-bis(chloromethyl)benzene. More sterically hindered biorenewable isosorbide bearing two secondary alcohol was also successfully converted into the poly(isosorbide carbonate) (M_n = 18,000 g/mol). Similarly, the terpolymerization of α-methyl-2,3-di-O-methyl D-glucopyranoside (MDMG), a naturally occurating monosaccharide, with dibromobutane or 1,4-bis(chloromethyl)benzene and Cs_2CO_3 furnished PCs with M_n of 8,000 g/mol and 14,000 g/mol, respectively. To get deeper insights on the role of the dihalide structure, Bian *et al.* proposed a comparative study on the use of dihalomethanes and dihaloethanes [135]. As a general result, higher monomer conversions were noted for dihaloethanes than for dihalomethanes. In the case of dihaloethane, alternating polycarbonates incorporating both the diol and dihalide structure is more likely to happen.

III-2) Ring-opening polymerization of cyclic carbonates

As the synthesis of PC by direct copolymerization of alcohols with CO_2 remains an elusive endeavour, one option to surpass these hurdles lies in the fixation of CO_2 into cyclic carbonate structures that undergo facile ring-opening polymerization (ROP). This technique relies on a chain-polymerization mechanism[136] which allegedly brings accurate control of the polymer molar mass, dispersity and properties. Even though most of the studies on the synthesis of polycarbonates via ROP have been made on non-CO_2 based cyclic carbonates, the general principles also apply to CO_2-based cyclic carbonates (see section II-2) as they present identical structural features. Among them, the polymerization enthalpy is one of the key parameters to consider since it heavily depends on the ring size and its ring constraint. The following discussion will focus on the ROP of 5- and 6-membered cyclic carbonates as well as exovinylene cyclic carbonates as these substrates are well described in the literature[137].

III-2-a) 5-membered cyclic carbonates

5-membered cyclic carbonates undergo difficile ROP because of their high positive polymerization enthalpy[138,139]. However, by combining a high temperature of 170 °C with metal alkoxides catalysts such as dibutyltin dimethoxide, titanium tetrapropanolate or zirconium tetrabutanolate, polymers were obtained from ethylene carbonate with yields from 55 % to 100 % and M_n ranging from 3,000 to 22,000 g/mol. The structural elucidation of the polymers showed the typical features of poly(ethylene oxide-*co*-ethylene carbonate). Interestingly, the content of carbonate linkages could be controlled via the choice of the catalysts, and the incorporation of 50 mol% of ethylene carbonate units within the polymer backbone was achieved using dibutyltin dimethoxide (catalytic loading of 2 mol%). A careful investigation on the polymerization enthalpy and entropy to afford homopolycarbonates indicated that the formation of the cyclic monomer was more favoured than the polymerization itself. However, producing poly(ethylene oxide-*co*-ethylene carbonate) is slightly more favoured. In fact, the polymerization mechanism involves a CO_2 loss to afford the ether repeating unit, which compensates the entropy loss and facilitates the formation of an alternating polymer. On the one hand, at 170 °C, an enthalpy of 112.5 kJ/mol was calculated for the formation of pure poly(ethylene carbonate). On the other hand, the same polymerization enthalpy dropped to -11.7 kJ/mol for a random poly(ethylene oxide-*co*-ethylene carbonate). Deeper investigations on the mechanism for the ROP of ethylene carbonate were conducted by Storey and Hoffman[140] who highlighted the role of the catalyst, namely organotin catalysts and sodium stannate trihydrate catalysts. Alike the ROP of lactones[141,142], organotin complexes act both as initiators and catalysts for the ROP of ethylene carbonate. In the case of sodium stannate trihydrate, the use of a diol as an initiator was required. In both cases, the mechanism relies on nucleophilic attack of the initiator on the carbonyl of the cyclic carbonates, generating a reactive alcoholate moiety which will further attack another carbonyl group (Scheme 29, blue pathway). Due to the high polymerization enthalpy of this reaction, a competitive pathway (Scheme 29, red pathway) is also likely to occur, leading to formation of ether linkages driven by the loss of CO_2. More insights were given by Clements[143] on the effect of the initiator's structure. As an example, aromatic alcohols involve a systematic CO_2 loss in the initiation step whereas aliphatic alcohols preferentially favour the formation of a carbonate linkage. Lee *et al*. also described the several hypothetical pathways for the formation of ether linkages in the ROP of ethylene carbonate, as well as possible depolymerisation processes by using KOH as initiator [144]. Other catalysts such as phosphazenes[145] or $ZnEt_2$[146] were tested to design polymers by the ROP of various 5-membered cyclic carbonates. Both catalysts required high polymerization temperature (T = 180 °C) to display sufficient activity and only provided poly(ether-co-carbonates) with low carbonate content of 21 – 54 % and M_n of 4,300 - 14,000 g/mol. With ionic liquids, the ROP of ethylene carbonate proceeded at relatively low temperature (from 80 to 120 °C) but only afforded oligomers with low carbonate contents up to 34 %. Haba or Guillaume introduced an elegant concept based on the increase of their ring strain of 5-membered cyclic carbonates to construct ether-free PCs by direct ROP. A known example is the ROP of ethylene carbonate fused in a trans configuration onto a cyclohexane ring, i.e. *trans*-cyclohexane carbonate[147,148], whereas its *cis*- analogue does not polymerize[149]. The Zn(diphenolate) promoted ROP of this bicyclic monomer provided a pure isotactic poly(cyclohexene carbonate) with a M_n up to 21,000 g/mol at 60 °C. Similarly, 4,6-*O*-benzylidene-2,3-*O*-carbonyl-r-*D*-glucopyranoside, i.e. ethylene carbonate fused onto a biorenewable glucopyranoside, furnished polycarbonates of M_n up to 16,000 g/mol at 25 °C using a superbase organocatalyst.[150].



Scheme 29: Competitive pathways between methylene attack (red) and carbonyl attack (blue) to produce poly(ether-co-carbonates) or homopolycarbonates by ROP of 5-membered cyclic carbonates

III-2-b) 6-membered cyclic carbonates

The ROP of 6-membered cyclic carbonates is thermodynamically much more favoured than their 5-membered analogues due to increased ring strain, yielding in most cases a negative polymerization enthalpy that compensates the positive polymerization entropy. Indeed, the carbonyl group displays a flat geometry, which increases the strain of the 6-membered cyclic compounds[151]. ROP of 6-membered cyclic carbonate was extensively reviewed by others and won't be discussed in detail in this introduction. Cationic polymerization utilizes Brønsted or Lewis acids to activate the monomer and generate species capable to propagate. However, in many cases, propagation is accompanied with decarboxylation which induces ether defects in the polymer skeleton, as well as backbiting termination reactions, as it was first demonstrated by Kricheldorf *et al.* in their attempt to polymerize trimethylene carbonate using methyl triflate as the initiator[137,152]. Efforts to prevent such decarboxylation reactions and obtain pure polycarbonates were successfully conducted with alkyl halides initiators (namely methyl iodide, benzyl bromide and allyl iodide)[153], methanesulfonic- and phosphoric acids [154,155], but only afforded polymers with M_n in the range of 3,000 – 16,000 g/mol.

Anionic ROP provided better polymerization control and enable the synthesis of high molar masses polycarbonates. Alkali metal alcoholates or sec-butyllithium[156] were efficient initiators, yielding ether-free polymer chains. However, backbiting termination reactions could not be supressed and oligomers with cyclic structures were concomitantly formed. Taking advantage of the facile ROP with anionic mechanisms, substituted 6-membered cyclic carbonates with pendant groups such as amino-acid (M_n up to 24,000 g/mol)[157], 2-ethyl-2-hydroxymethyl[158], norbornene[159], aromatic[160] and more[161,162] were polymerized efficiently.

To prevent non-desired side reactions arising from the high reactivity of the ionic active centers in anionic and cationic ROP of 6-membered cyclic carbonates, coordination-insertion mechanisms have been proposed and studied in details by Kricheldorf *et al.* and Darensbourg *et al*. Organometallic complexes containing Al[163], Ca[164-166], Sn[167-170] or lanthanides[171] were engineered and showed great activity for the synthesis of defects-free polycarbonates. The general polymerization mechanism is based on (i) the ring-opening of the cyclic carbonate via addition of a nucleophile initiator to the metal-activated carbonyl of the ester group followed by the (ii) monomer insertion into the oxygen-metal bond generated after initiation, which is then (iii) prone to propagation. The authors mention that in the propagation step, the acyl-oxygen bond is broken rather than the alkyl-oxygen bond for monomer insertion[164]. These coordination-insertion ROP provide a “quasi-living” mechanism, where a linear increase of the polymer M_n with the monomer conversion is observed.

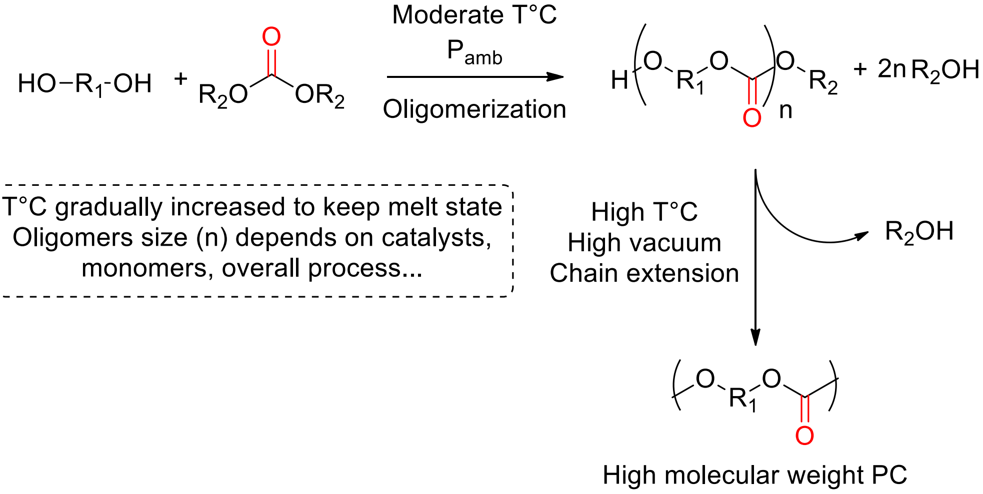
Organo-ROP represents the most attractive route to design metal-free PCs with controlled molecular parameters and architectures. Systems comprising benzyl alcohol as initiators and catalysts derived from amidines, guanidines, n-heterocyclic carbenes or olefins (eventually coupled to hydrogen bond donors such as thioureas) successfully polymerize trimethylene carbonate in a very controlled manner at ambient temperature[172-174]. In an attempt to produce CO_2-sourced polycarbonates, Buchard *et al.* designed 6-membered cyclic carbonates by carbonation of polyol sugars (see section II-2-a-ii)) and further studied their organocatalytic ring-opening polymerization using TBD as catalysts. Promising results were obtained from D-mannose (M_n up to 33,000 g/mol)[175], 2-deoxy-D-ribose (M_n up to 42,000 g/mol) [176], thymidine (M_n up to 17,000 g/mol) [177] and others [178]. Similarly, Gnanou *et al.* also reported the ROP of 6-membered sugar based cyclic carbonates obtained from the coupling of glycosides and CO_2 (based on the DBU/CH_2Br_2 carbonation protocol at 70 °C). Various ROP organocatalysts were selected, i.e TBD/4-methyl benzyl alcohol and DBU/1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea/4-methyl benzyl alcohol, yielding pure polycarbonates of M_n up to 4,300 g/mol [179].

III-3) Polycondensation of alcohols with (a)cyclic carbonates

While ROP is an appealing method to produce polycarbonates in a controlled manner it is limited to a narrow library of aliphatic polymer microstructures, due to the thermodynamic constraints that mostly restricts the polymerization to 6-membered cyclic carbonates. Even though substrates with a large variety of pendant groups have successfully been polymerized by ROP, the urge to develop more diversified architectural structures with cheap and easily scalable processes has brought step-growth polymerization as a practical solution for industries. To date, the mass production of polycarbonates arises from the polycondensation of diols with phosgene. DMC, DEC or DPC, easily accessible from CO_2 (see Section II-1)), are now emerging as valuable alternative to phosgene and their polycondensation with naturally occurring ubiquitous diols offers a route to the design of polycarbonates with reduced carbon footprints. Attempts to valorize 5-membered cyclic carbonates as useful carbonylation synthons for the production of polycarbonates were also reported but remained elusive. As highlighted for ROP, they generally face the same limitations, such as competitive methylene and carbonyl attacks, generating poly(ether-co-carbonates)[180-182].

III-3-a) DMC and DPC as carbonylating agents

The formation of polycarbonates from diols and DMC or DPC by polycondensation responds generally to a two steps approach, usually performed in a one pot fashion and in solvent-free conditions (see Scheme 30). First, oligocarbonates of low molar masses are fabricated via transcarbonation between the diol and the acyclic carbonate (DMC or DPC) at moderate temperatures (high enough to maintain a molten reaction media) and ambient pressure. The so-produced telechelic oligomers end-capped with both alcohol and carbonate moieties are then chain extended by applying a high vacuum shifting the reaction equilibrium (step-growth polymerization mechanism) by elimination of methanol (for DMC) or phenol (for DPC). Temperatures are progressively increased during the process to overcome mass-transfer limitations reflecting the viscosity and molar masses increase. The nature of the initial diol(s) monomer dictates the final polymer microstructure (i.e. aliphatic or non-aliphatic polycarbonates).



Scheme 30: Schematic representation of polycarbonates synthesis via melt polycondensation of diols with DPC or DMC ($R_2 = CH_3$ or C_6H_5)

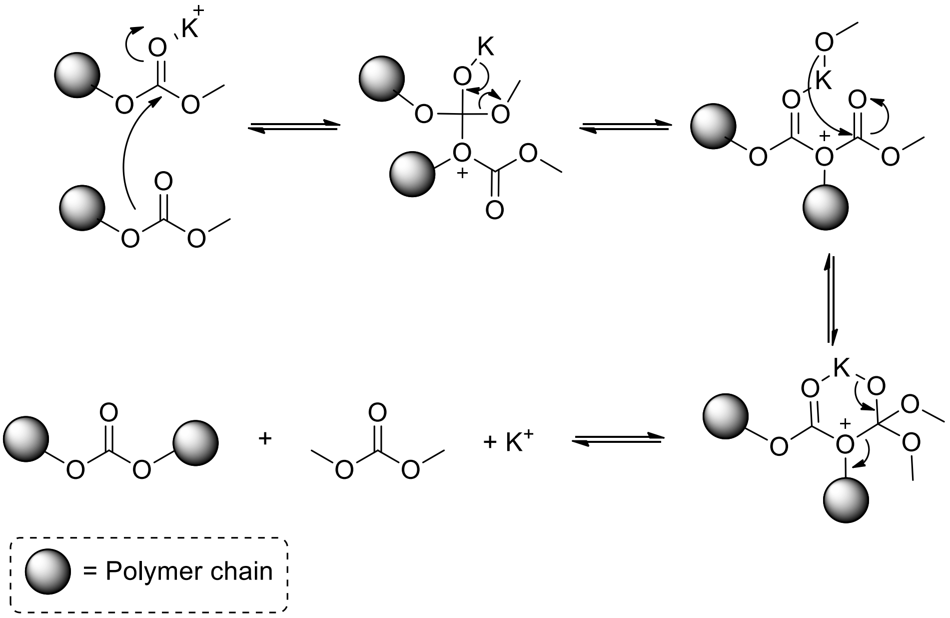
III-3-a-i) Aliphatic PC

Aliphatic PC have recently gained huge interest in research thanks to their properties of biodegradability and biocompatibility, making these materials suitable for the biomedical field[183]. Depending on the structure of the aliphatic diols, the occurrence of side-reactions was highlighted by Xie and coworkers when dialkylcarbonate was used as the carbonylating agent[184], which limit the access to high molar masses aliphatic PCs. However, side alkylation reactions of the alcohol chain-end either by the methylene attacks of DEC or via backbiting side-reactions furnished polycarbonates with unreactive ether chain ends or cyclic by-products causing the death of the chain growth. These side reactions were especially highlighted for poly(ethylene carbonate) or poly(propylene carbonate) made from ethylene glycol and 1,3-propanediol, but were considerably limited or even totally supressed when diol with spacer larger than 3 carbon units were used as monomers. Following this approach, aliphatic PCs with moderate to high molar masses were successfully synthetized from a diversified library of linear alkyl diols with DMC when suitable catalyst were used. For example, the utilization of binary DMAP/thioureas organocatalyst provided poly(butylene carbonate) with a M_n up to 52,000 g/mol[185,186], while imidazolium or TBD furnished respectively poly(hexamethylene-co-trimethylene carbonate) with a M_n up to 7,400 g/mol [187] and poly(hexamethylene carbonate) of M_n up 33,000 g/mol[188].

Metal-based catalysts such as sodium alkoxide Li(Acac), Na(Acac) and K(Acac) were also reported as efficient systems to construct polycarbonates with diversified microstructures and (M_W up to 200,000 g/mol)[189,190] while TiO_2/SiO_2 based catalysts furnished poly(hexamethylene carbonate) with M_w of 160,000g/mol and terpolymers with M_w up to 87,000 g/mol[191,192]. Interestingly, this concept was extended to the fabrication of hyperbranched PC when blends of diols and triols were condensed with DMC using DMAP or Li(Acac) as catalysts[193].

Unlike DMC or DEC, the utilization of DPC enabled supressing the side alkylations of the hydroxyl chain ends of growing PC. Moreover, phenol may be viewed as a better leaving group than methanol of DMC which should facilitated the construction of high molar masses polymers. However, phenol displays a high boiling point so that the polycondensation were generally performed at temperatures over 200 °C. As selected examples, poly(butylene carbonate)s with M_w up to 156,000 g/mol or 202,000 g/mol were synthesized using respectively $Zn(OAc)_2$ or basic solid MgO as catalysts at temperatures of 200-210 °C[194,195].

A different approach was proposed by Miller and Vanderhenst where they first synthetize decane-1,10-diyl dimethyl dicarbonate from 1,10-decanediol and an excess of DMC, catalysed by Na_2CO_3 at 85 °C. The bifunctional carbonate is then subjected to self-polycondensation and aliphatic polycarbonates are obtained via carbonate metathesis polymerization after isolation of these bis-carbonates. Mw up to 88,000 g/mol were observed with $Zn(OAc)_2$ as catalyst and reaction temperature of 150 °C for the oligomerization step (12 h) and 175 °C for the chain extension (1.5 h). A proposed mechanism by the authors is presented in Scheme 31 with K_2CO_3 as the catalyst. A one pot process with the diol and an excess of DMC as starting reagents was proposed to afford aliphatic PC of M_W up to 56,000 g/mol[196].



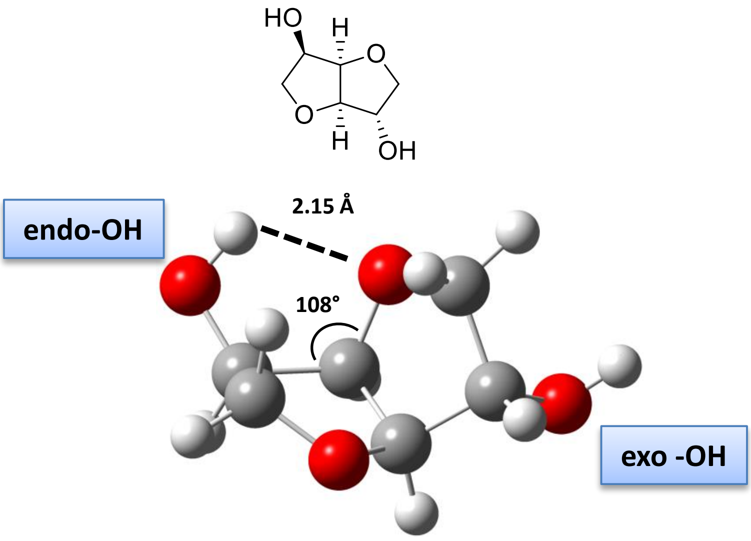
Scheme 31: Carbonate metathesis polymerization principle catalysed by K_2CO_3. DMC is removed under vacuum to displace the equilibrium toward PC formation. Adapted from [196]

III-3-a-ii) Aromatic and cycloaliphatic PC

Aromatic PC displays remarkable thermo-mechanical and optic properties useful for plethora of applications within the construction, automotive, electronics and other sectors. Historically, high molar masses polycarbonates were firstly industrialised by phosgenation of Bisphenol A (BPA). The toxicity and safety issues linked to the utilization of phosgene pushed the scientists to evaluate the potential of DMC or DPC to construct aromatic PCs from BPA. In combination with molecular sieves, a dual DMAP/$(Bu_2SnCl)_2O$ catalytic system afforded PC of high-molecular weight (M_w up to 75,000 g/mol) using BPA and DMC, but very high temperature of 320 °C was needed to maintain a molten reaction medium, leading to poor control of the dispersity (Đ = 3.8)[197]. Lithium- and lanthanum-based catalysts were also reported and proved their efficiency to access to aromatic polycarbonates from BPA [198,199]. The utilization of DPC as carbonylation agent is now emerging at the industrial level (also known as Asahi Kasei process) to construct PC derived from BPA[200]. Briefly, a carbonate source is brought by the coupling reaction between CO_2 and ethylene oxide, affording ethylene carbonate that further undergoes methanolysis to produce DMC. The latter is converted into DPC using phenol. The melt polycondensation responds to a two-step procedure with a first oligomerization between DPC and BPA at 230 °C, followed by a chain extension at 265 °C to design aromatic PCs of molar masses up to 117,000 g/mol.

In the quest for sustainable and less toxic alternatives to BPA-based PC, emerging researches focus now on the utilization of sugar-based bicyclic diols, i.e. 1,4:3,6-Dianhydro-D-sorbitol also known as isosorbide, to construct the new PC generation with thermo-mechanical properties competing with the ones of the aromatic PC.

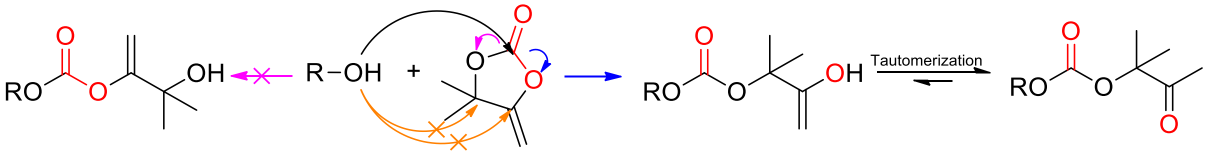
Due to the bicyclic structure (two fused tetrahydrofuran rings) of isosorbide, both alcohol functions are not equivalent. The so-called “endo” OH displays an intramolecular H-bonding with O atom of a tetrahydrofuran ring, inducing disparity in the two OH reactivities (see Scheme 32). In this regard, a large portfolio of catalysts was tested to activate selectively the endo or exo alcohols moieties and to prevent them from reactivity disparities that would considerably limit the molar mass of PC. Among them, metal salts[201], metal alkoxides [202,203], inorganic carbonates [204], ionic liquids [205-212], organic bases[213] and others[214-217] enabled the facile construction of defects-free PCs derived from isosorbide with M_n in the range of 14,000 to 55,000 g/mol.



Scheme 32: 3D structure of Isosorbide with explicit intramolecular H-bond for endo-OH

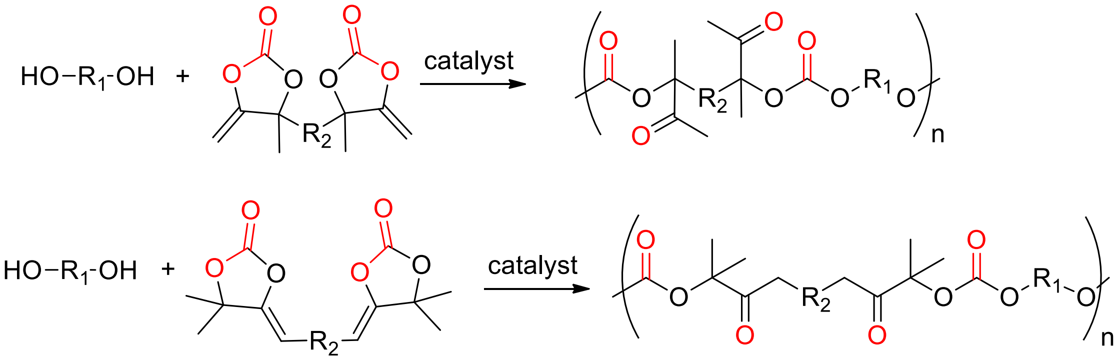
III-3-b) Polycondensation between bis(α-alkylidene cyclic carbonates) and diols

Unlike conventional 5-membered cyclic carbonates that poorly react with alcohol in “soft” experimental conditions, CO_2-based exovinylene cyclic carbonates (see Section II-2-d)) undergo facile and regioselective alcoholysis, even at room temperature. The thermodynamic driving force of the ring opening lies in the formation of a keto-enol equilibrium (see Scheme 33).



Scheme 33: Regioselective alcoholysis of exovinylene cyclic carbonates.

Taking advantage of this concept, new CO_2-based bis(α-alkylidene cyclic carbonates) were designed by our group. Bis(α-alkylidene cyclic carbonates) were either prepared by direct coupling of bis-propagylic alcohols with CO_2 (aliphatic spacer R_2, see Scheme 34) or by heck coupling of two CO_2-based exovinylene cyclic carbonates with 1,4-diiodobenzene (aromatic spacer R_2, see Scheme 34). These new monomers were further copolymerized by step-growth with diols to obtain regioregular PC with microstructures free of any defects [107,218-220]. Indeed, unlike conventional 5-membered cyclic carbonates, the formation of ether linkages (via decarboxylation) was not observed. New poly(β-oxo carbonates) with M_n ranging from 5,500 to 25,000 g/mol were fabricated using DBU as catalyst in DMF or chloroform (see Scheme 34). This concept was extended to the formation of poly(oxo-urethanes) and poly(hydroxyl-oxazolidone)[107]. Aliphatic poly(oxo-carbonates) synthetized with OH-terminated poly(ethylene glycol) and bis(α-alkylidene cyclic carbonates) with M_n up to 60,000 g/mol showed great properties for potential applications as solid electrolytes for solid Li-ion batteries[218]. Attempt to perform the synthesis of poly(β-oxo carbonates) in a one step/one pot strategy directly from the terpolymerization of diols, bis-propargylic alcohols and CO_2 was recently reported. The key of the success lies in the utilization of a single dual system, i.e. tetrabutylammonium phenolate/AgI, capable to catalyse two different reaction, i.e. the carboxylative cyclization of CO_2 with the bispropargylic alcohol to deliver in-situ the bis(α-alkylidene cyclic carbonates) followed by its polymerization in cascade with a primary diol. Even though the results were promising, only oligomers with M_n in the range of 1,000 to 2,700 g/mol were obtained due to the occurrence of side reactions [219].



Scheme 34: Synthetic procedure to access regioregular poly(β-oxo carbonates). Adapted from [107]

IV) Conclusion

This chapter reviews the main strategies to afford (a)cyclic carbonates and polycarbonates from the coupling of alcohols and CO_2, or CO_2-based synthons. Compared to the well-known coupling of CO_2 with epoxides, these systems suffer from limitations in terms of yields and demanding experimental conditions, due to the formation of water as by-product that considerably affects the formation of carbonates. However, the challenging coupling of alcohols and CO_2 is still very interesting as it provides a large manifold of accessible and easy-to-handle substrates, opening views for the formation of carbonates that are hardly affordable with epoxide/CO_2 coupling. Many routes have been proposed to overcome the formation of water, combining dehydration agents with catalysts, or co-reagents with excess of bases to trap water formation. In all cases, synthesis of (a)cyclic carbonates or polycarbonates couldn’t be achieved without the use of stoichiometric or excess amounts of additives, as quantitative removal of water is needed to reach satisfying yields.

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Chapter II:

The coupling of CO_2 with diols promoted by organic dual systems: towards products divergence via benchmarking of the performance metrics

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ABSTRACT

Herein, we propose a critical study balancing two metal-free dual activating systems, namely DBU/EtBr and TEA/TsCl, for the coupling of CO_2 with 1,x-diols to afford (a)cyclic carbonates. *In-situ* ATR-IR monitoring correlated with DFT calculations led to mechanism propositions for the model formation of propylene carbonate from propylene glycol. Kinetics upon various experimental conditions were established for the first time, leading to an optimized synthetic protocol. The substrates scope was then investigated and selectivities toward the formation of cyclic or linear carbonates were correlated to the dual activating system and the diol structure. By choosing the suitable organic dual activating system, one is able to control the product selectivity to substituted ethylene- or trimethylene carbonate and/or acyclic compounds, providing a powerful tool to synthesize CO_2-based precursors that are highly relevant for organic and polymer chemistry from ubiquitous building blocks.

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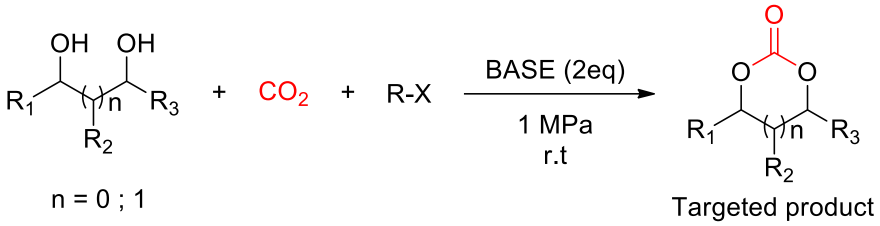
I) Introduction

It is widely known that carbon dioxide concentration in the atmosphere, among other greenhouse gases, keeps increasing every year, partly due to the petrochemical industry and combustion of fossil fuels[1,2]. New scientific challenges have risen to mitigate such anthropogenic emissions and prevent the environmental concerns. Among them, Carbon Dioxide Utilization (CDU) has emerged as a solution to valorise CO_2 as a key intermediate for chemistry[3-12]. In this context, converting CO_2 into organic cyclic carbonates was extensively investigated to design CO_2-based materials with a lower carbon footprint finding wide applications as intermediates in the organic and polymer chemistry[13-21], as well as promising green aprotic polar solvents[22,23]. Various synthetic pathways were developed to access (functional) 5- or 6-membered cyclic carbonates such as the [3+2] coupling of CO_2 with epoxides[24-29] or via the fixation of CO_2 into oxetanes[26,30,31]. Although terminal epoxides are easily converted into 5-membered cyclic carbonates, the conversion of internal di-, tri- and tetra-substituted epoxides or (substituted) oxetanes into their corresponding five- and six-membered cycles still remained very challenging[31]. To broaden the scope and functionality of cyclic carbonates, other substrates such as propargylic alcohols[15,32-37], 1,2 and 1,3-diols[38-41] were subjected to carbonation in order to afford α-alkylidene cyclic carbonates, five- and six-membered cyclic carbonates, respectively. Although the use of diols is a promising alternative, their reaction with CO_2 is kinetically and thermodynamically limited due to the formation of water as a by-product. To surpass these hurdles, catalytic platforms based on both homogeneous and heterogeneous organometallic catalysts (Bu_2SnO, K_2CO_3, CeO_2…) used in combination with dehydrating systems (molecular sieves, zeolites, 2-Cyanopyridine…) were developed[42,43]. To the best of our knowledge, the most efficient system involved CeO_2 as the catalyst and 2-Cyanopyridine as dehydrating agent[43]. The main drawback related to this process is the use of harsh reaction conditions (150 °C, 5 MPa) and an expensive dehydrating agent used in large excess. Alternative protocols have been recently proposed to displace the reaction equilibrium and to overcome the limitation induced by the formation of water by combining the use of an organic base and an alkylating agent under mild conditions. Such strategy has been shown by Zhang et al. [44] and Buchard et al. [45,46] by combining strong Lewis bases and Tosyl chloride (TsCl) as the alkylating agent to promote the synthesis of 6-membered cyclic carbonates with the formation of the TsO- anion as a by-product. A similar protocol has been proposed by Kitamura et al.[47] and Dyson et al. [41] using alkyl halides as the alkylating agents that allow the synthesis of cyclic carbonates in good yields from different substrates. Gnanou et al. also investigated the cyclization or polymerization of glycoside and diols with a larger spacer in a similar fashion[48-50]. Addition of ionic liquids to these systems to promote CO_2 activation to afford cyclic carbonates from diols was also studied[51]. Although plausible mechanisms have been proposed for the carbonation of 1,2-diols promoted by organic bases/alkyl halide dual system, a molecular level understanding of the reaction mechanism and the determination of the key structural parameter of the reactants and the organic activating system that governs the yields and the selectivity of the reaction is still missing.

To this aim, we propose a detailed investigation and comparison of the coupling of CO_2 and various 1,x-diols in a one pot/one step fashion under mild conditions promoted by two different organic dual activating systems (Scheme 1).



Scheme 2: Strategy for the synthesis of 5 to 6 membered cyclic carbonates from diols and CO_2 promoted by organic bases and alkyl halides under mild conditions.

A mechanism of the model carbonation of propylene glycol using DBU and bromoethane is first proposed by correlation of *in-situ* ATR-IR kinetic monitoring and DFT calculations. The effects of the temperature, the pressure, the solvent and the nature of the alkyl halide on the kinetics, the carbonate yields and selectivities were then evaluated. In a similar fashion, the model carbonation of propylene glycol was studied using a second dual activating system with triethylamine (TEA) as a base and TsCl as the alkylating agent. Extension of the synthetic protocols to the carbonation of challenging mono-, di- and tetrasubstituted vicinal diols, to 1,3- and 1,4 diols or isosorbide, a bio-based diol with a two fused furan rings structure, was then investigated using both dual systems. The benchmarking of their performance metrics will guide us opting to the most appropriate activating system regarding the nature of the diol substrate and the desired product selectivity, i.e. a cyclic or a linear carbonate.

II) Material and Methods

II-1) Material

Propylene glycol (PG, Sigma Aldrich), Ethylene glycol (Sigma Aldrich), 2,3-butanediol (Sigma Aldrich), Pinacol (Sigma Aldrich), Glycerol (Sigma Aldrich), 1,3-butanediol (Sigma Aldrich), Hexylene glycol (Arkema), 1,4-butanediol (Sigma Aldrich), Isosorbide (Alfa Aesar), trans-1,2-Cyclohexanediol (Alfa Aesar), Pyrocatechol (Sigma Aldrich), Bromoethane (Sigma Aldrich), Bromobutane (Sigma Aldrich), Chlorobutane (Sigma Aldrich), Benzyl bromide (Sigma Aldrich), Benzyl chloride (Sigma Aldrich), Methyl iodide (Sigma Aldrich), Dichloromethane (CH_2Cl_2, Sigma Aldrich) Acetonitrile (CH_3CN, Sigma Aldrich), Chloroform ($CHCl_3$ Sigma Aldrich), Anisole (Alfa Aesar), Dimethyl sulfoxide (DMSO, Sigma Aldrich) were used without further purification.

II-2) Methods

General procedure for kinetic studies:

The reactions were monitored *in-situ* by IR spectroscopy using a home-made Ge ATR accessory (see Fig. 1) suitable for high-pressure measurements (up to 5 MPa) and high temperature (up to 100 °C).

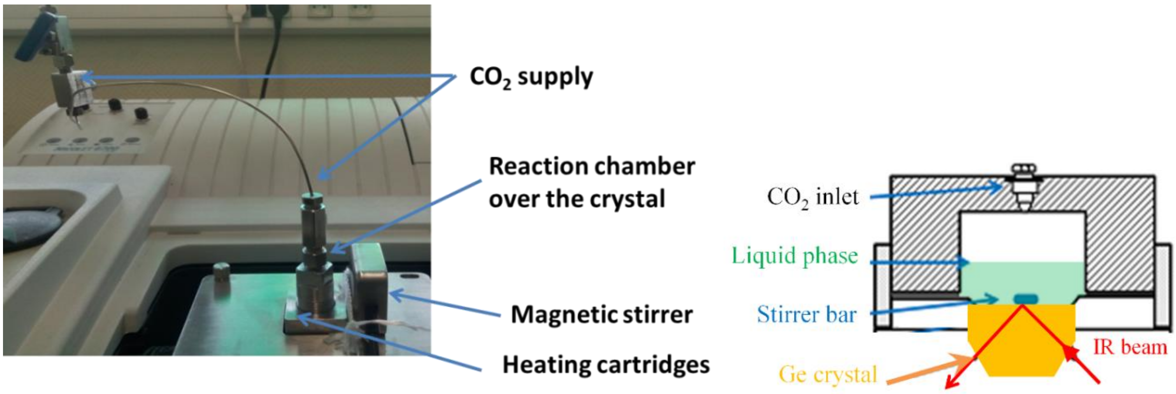


Figure 1: ATR-IR setup for the kinetic studies. The reaction mixture is injected directly in the reaction chamber. When the system is sealed, it can be put under pressure.

It was coupled with a ThermoOptek interferometer (type 6700) equipped with a globar source, a KBr/Ge beamsplitter and a DTGS (Deuterated TriGlycine Sulphate) detector. Single beam spectra recorded in the spectral range (400-4000 cm^{-1}) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 20 accumulated interferograms for the first hundred spectra (one spectra every 75 sec), and then Fourier transformation of 80 accumulated interferograms until the end of reaction time (one spectra every 5 min).

Diol (0.5 mmol) was solubilized in a 2 mL vial with 200 µL of solvent. Organic base (1 mmol) was added to the vial. Alkyl halide (1.2 mmol) was added to the vial. The whole mixture was then transferred to the reaction chamber (volume: 5 mL) which is directly fixed on the Ge crystal of the ATR-IR device. The setup is sealed with the CO_2 feed pipe so it can be put under pressure. To best avoid side reactions between the base and the alkyl halide, it is worth noting that the faster the system is pressurized, the less side reactions are observed. Experiments where cyclic carbonates were obtained in good yields (> 50 %) were carried out again on a larger scale for further purification. Products were purified by column chromatography (100 % Ethyl acetate for glycerol carbonate, 5 % Acetone / 95 % Chloroform for others) and weighted to get the isolated yield.

General procedure for batch reactions:

Diol (0.5 mmol) was solubilized in a 2mL vial with 200 µL of solvent. Organic base (1 mmol) was added to the vial. Alkyl halide (1.2 mmol) was added to the vial. A stir bar was added to the vial. The vial was sealed with a septum cap which was perforated to let CO_2 enter the vial and dissolve in the solution. Up to 8 vials were transferred into the high pressure reacting chamber, placed on a magnetic stirrer. A pressure of 1 MPa CO_2 was initially applied to the chamber, which volume is large enough to keep the pressure quasi constant throughout the reaction (pressure drops as CO_2 dissolves in the media). At the end of the reaction time, the reaction chamber was slowly depressurized and the vials were taken out. Septum caps were replaced by sealed caps. All products were analysed by both ATR-IR spectroscopy and ^1H NMR spectroscopy without further purification. To best avoid side reactions between the base and the alkyl halide, it is worth noting that the faster the system is pressurized, the less side reactions are observed.

Nuclear magnetic resonance spectroscopy (NMR)

^1H and ^{13}C NMR spectra were recorded at 298 K with a Bruker advance DRX 400 spectrometer operating at 400.13 MHz, on the Fourier transform mode. All NMR spectra were phased and baseline-corrected. The samples were prepared by dissolving 15-20 mg of product in 0.7 ml of a deuterated solvent ($CDCl_3$) and were calibrated with the 7.26 ppm residual signal of $CDCl_3$.

Method for the determination of conversion and yields by quantitative ATR-IR and quantitative 1H NMR

All yields were determined by quantitative ^1H NMR using 1,3,5-trimethoxybenzene (TMB) as internal standard, except for the synthesis of propylene carbonate where the yield was determined by both ^1H quantitative NMR and ATR-IR. A known mass of TMB (0.333 equivalent) was added to the reaction mixture before the introduction of CO_2. Here are presented ^1H NMR (Fig. 2) spectrum and ATR-IR (Fig. 3) spectrum of the same sample at the end of reaction time to compare the yields obtained and confirm both methods work as quantitative methods.

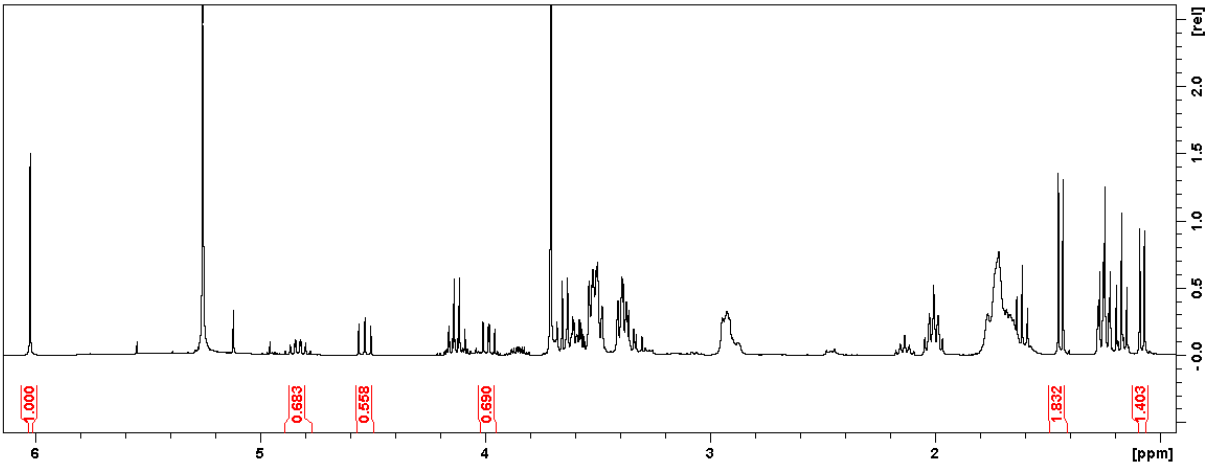


Figure 2: ^1H NMR spectrum of model reaction in $CDCl_3$ (Scheme 2) after 20h for the synthesis of Propylene carbonate. Propylene glycol (0.5mmol ; 36.7µL) ; DBU (1mmol ; 149.2µL) ; EtBr (1.2mmol ; 89.4µL) ; CH_2Cl_2 (200µL) ; 1,3,5-trimethoxybenzene (0.162mmol ; 27.22mg) as internal standard. 50µL of the reaction mixture are mixed with 600µL $CDCl_3$ to perform ^1H NMR analysis.

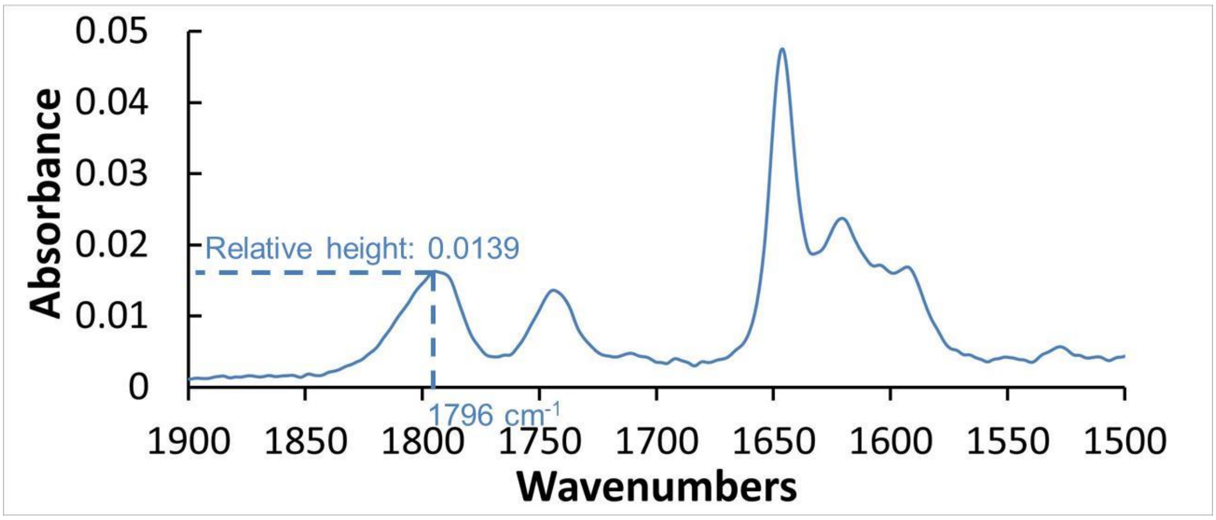


Figure 3: ATR-IR spectra of model reaction (same sample that for ^{1}H NMR spectrum, Fig. S9).

- <u>Yield obtained from ^{1}H NMR analysis :</u>

Propylene carbonate: δ: 4.9 – 4.77 (1 H, m, MeC*H*O), 4.57 – 4.50 (1 H, dd, CH*H*O), 4.02 – 3.95 (1 H, dd, C*H*HO), 1.48 – 1.42 (3 H, d, CH_3CHO).

Propylene glycol: δ: 3.91 – 3.8 (1H, m, MeC*H*OH), 3.63 – 3.55 (1H, m, CH*H*OH), 3.42 – 3.2 (1H, m, C*H*HOH), 1.10 – 1.06 (3H, d, CH_3CHOH)

TMB: δ: 6.02 (3H, Ar*H*), 3.71 (9H, OCH_3)

Proton signals of propylene carbonate were integrated with aromatic protons signal of TMB (3 H) as reference (integration value of 1). As TMB was introduced with a known mass (0.333 equivalent of propylene glycol), one can calculate the exact mole number of propylene carbonate.

$$n(PC) = \frac{\sum_i \frac{\int_i PC}{N_H^i}}{i} * 3 * n_{TMB}$$

$n(PC): Mole\ number\ of\ propylene\ carbonate$

$\int_i PC\ :\ integration\ value\ of\ signal\ "i"\ relative\ to\ propylene\ carbonate$

$N_H^i\ :\ number\ of\ hydrogen\ taken\ into\ account\ for\ signal$ "i"

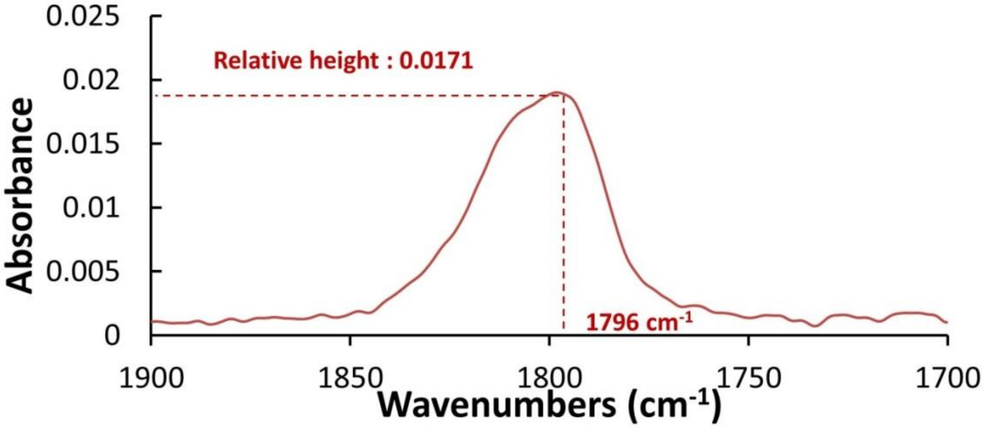
$n_{TMB}\ :\ mole\ number\ of\ TMB\ initially\ introduced\ in\ the\ reaction\ media$

Yield obtained from Fig. 2 is of **62 %**.

- Yield obtained from ATR-IR analysis :

Propylene carbonate: ν(C=O) : 1796cm^{-1}

The experimental determination of the molar attenuation coefficient of PC to calculate yields from kinetic studies is presented in Figure 4 below.



Molecular species	Carbonate concentration	Peak height	ε*l (mL/mmol)
PC ; DBU ; BuBr ; CH_2Cl_2	0.96 mol/L	0.0171	0.0178
PC (pure)	11.85 mol/L	0.227	0.0192

Figure 4: Experimental determination of the molar attenuation coefficient of propylene carbonate by ATR-IR: Propylene carbonate (0.5 mmol ; 42.3 µL) ; DBU (1 mmol ; 149.2 µL) ; BuBr (1.2 mmol ; 130 µL) ; CH_2Cl_2 : (200 µL).

As we calculated the value of ε*l for propylene carbonate, one can calculate the concentration of propylene carbonate in the reaction media using Beer-Lambert law with the absorbance at 1796cm^{-1}.

Yield obtained from Fig. 3 is of **69 %**.

Both methods lead to the same yield with only small differences attributed to experimental factors.

Density Functional Theory (DFT) computational details

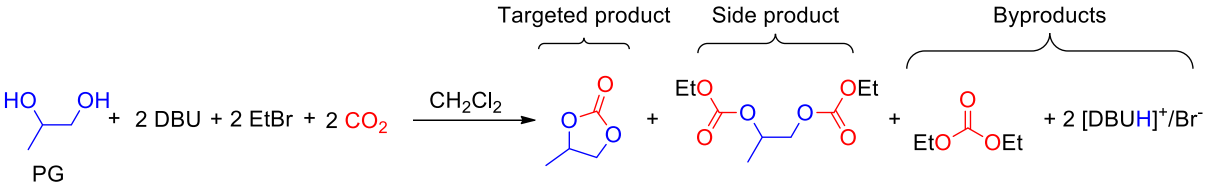
Preliminary calculations of equilibrium structures were performed using a semi-empirical model (AM1-D3H4) to determine the most stable conformations. These semi-empirical calculations were performed using the AMPAC software. The CHAIN algorithm was used for locating intermediates and transition states along the reaction path. The lowest energy structures obtained at the AM1-D3H4 level were further investigated using the Density Functional Theory method (DFT) implemented in the Gaussian 16 package. DFT calculations of geometries, energies, and vibrational frequencies reported in this article were carried out with the M06-2X functional using the 6-311G(d,p) basis set. All frequencies of each structure have also been calculated to verify the presence of a single imaginary frequency for transition states and the absence of imaginary frequency for ground states. The intrinsic reaction coordinate (IRC) method has been used to verify that the obtained transition states were effectively connected to the desired minima. For all activating systems, a wide range of possible configurations and interactions have been modelled and the more stable of them are reported in this work. To consider entropic effects, the energies mentioned in this study correspond to the Gibbs free energy (ΔG).

III) Results and discussion

III-1) Dual system DBU/R-X

III-1-a) Synthesis of propylene carbonate from propylene glycol: mechanistic study

Insights into the mechanisms and the kinetics of the carbonation of 1,x-diols to access (a)cyclic carbonates were first performed for a model reaction between propylene glycol (PG) and CO_2 promoted by a dual system composed of an organic superbase, i.e. 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and an alkylating agent, i.e. bromoethane (EtBr) (Scheme 2).



Scheme 3: One pot/one step model reaction studied for the synthesis of propylene carbonate from PG and CO_2. Diethyl carbonate is obtained as a by-product.

The model reactions were performed in dichloromethane under low CO_2 pressure (0.5 – 4 MPa) and monitored by in-situ ATR-IR spectroscopy. Typical spectra recorded at different reaction times are depicted in Figure 5.

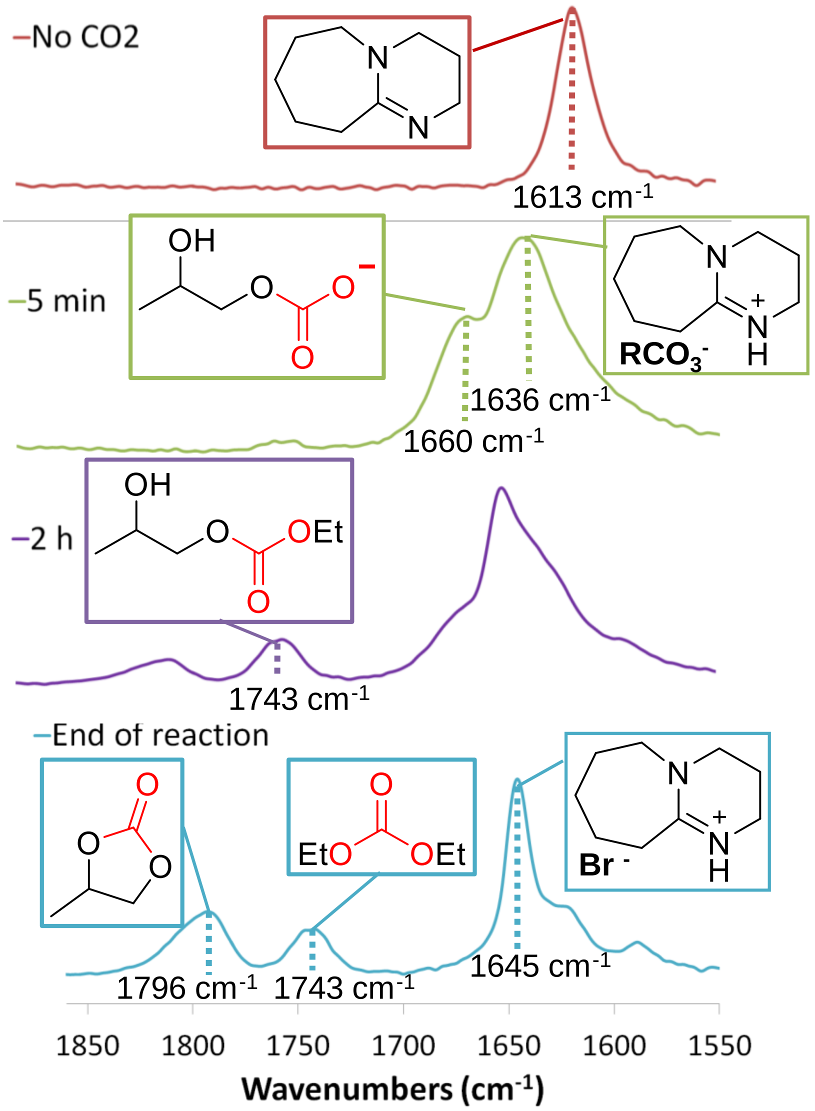


Figure 5: Monitoring of the model reaction between PG and CO_2 promoted by a dual DBU/EtBr system using ATR-IR spectroscopy. Conditions: PG (0.5mmol) ; DBU (1mmol) ; EtBr (1.2mmol) ; CH_2Cl_2 (200µL) ; 1 MPa ; 25°C

Fine interpretation of the spectral footprints enabled us to identify several key intermediates formed at 25 °C under 1 MPa CO_2 pressure. First, before the introduction of CO_2 in the reaction mixture, a well-defined band observed at 1613 cm^{-1} is characteristic of the C=N stretching mode of DBU which indicates that there is no specific interaction and/or reaction between DBU and another reactive species (red curve). In particular, neither spontaneous deprotonation of the alcohol moiety by DBU nor a possible alkylation of DBU by EtBr were observed. Addition of CO_2 to the system at 1 MPa pressure (green curve) induced a DBU absorption band shifts toward 1636 cm^{-1}, which has been assigned to the $C=NH^+$ stretching mode of protonated DBU[52,53]. Concomitantly, a shoulder of this broad peak appears around 1660 cm^{-1} and was attributed to the C=O stretching of the alkyl carbonate anion RCO_3^- species[53-55]. These spectral changes highlight a trimolecular reaction between CO_2, PG and DBU forming the $RCO_3^-/DBUH^+$ organic salt, confirmed by DFT calculations and ATR-IR characterizations (see Fig. 6).

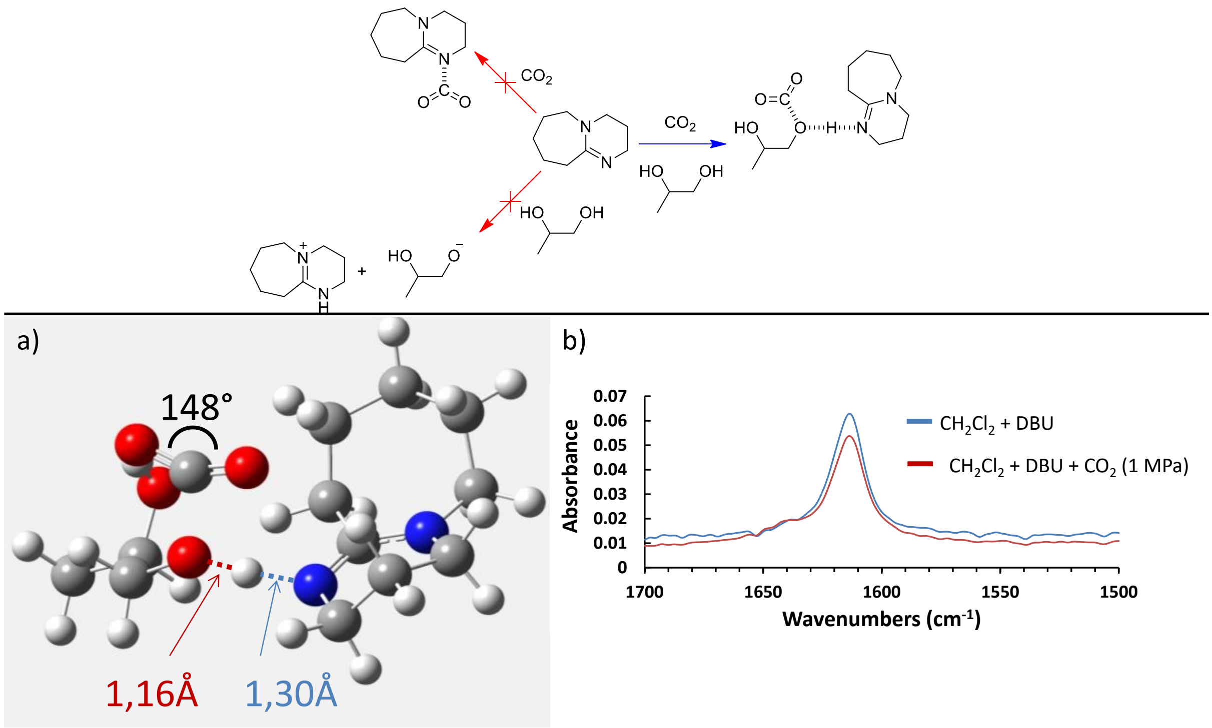
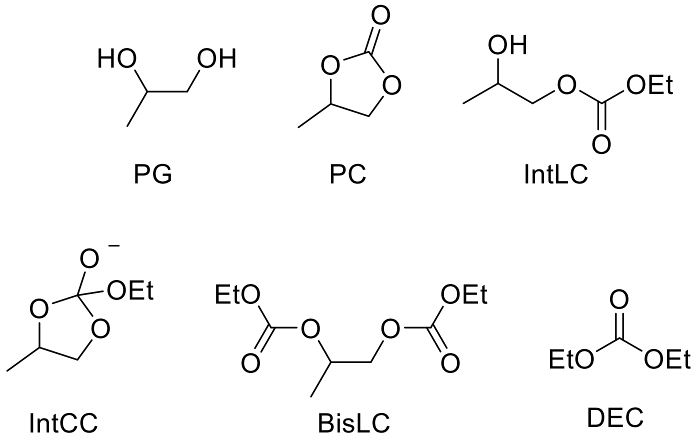


Figure 6: Trimolecular reaction between PG, DBU and CO_2 isolated in DFT calculations (a). No CO_2-DBU adduct could be detected without the presence of PG in ATR-IR as C=N stretching mode of DBU (1613 cm^{-1}) does not shift under 1 MPa CO_2 pressure (b).

Indeed, the hydrogen bonding between sp^2 N atom from DBU and the alcohol moiety of PG will increase the nucleophilicity of the O atom and thus promotes its attack on the C atom of CO_2. It should be noted that the formation of the carbonate salt occurs within 5 minutes and is regulated by the CO_2 solubilisation in the organic phase, which is known to be high in dichloromethane[56,57]. By ATR-IR, it was however not possible to discriminate which of the primary or the secondary alcohol is preferentially involved in the formation of the carbonate salt. When the reaction goes on, around 30 min after introduction of CO_2, the absorption band of protonated DBU starts shifting from 1636 cm^{-1} to higher wavenumbers of 1645 cm^{-1} (purple curve). The peak got thinner and the shoulder tended to disappear. This was attributed to a change in the anionic environment of protonated DBU, due to the time consumption of the RCO_3^- species that are progressively replaced by the bromine anion of EtBr. Concomitantly, two novel absorption bands appeared around 1743 cm^{-1} and 1796 cm^{-1} and were respectively assigned to the C=O stretching mode of a linear alkyl carbonate[58] **IntLC** (see Scheme 3) and to the vibrational stretching of the C=O function of a 5-membered cyclic carbonate[58], i.e. propylene carbonate (PC).



Scheme 3: Substrate (PG), reaction intermediates (IntLC ; IntCC) and products (PC ; BisLC ; DEC) of the model reaction

So far, the ATR-IR analysis could not differentiate **IntLC** from diethyl carbonate (**DEC**) co-produced at the end of the reaction. To get clues about the formation of **DEC** by-product, kinetic profiles were drawn from the time evolution of the intensity of the specific signals of both the linear and the cyclic carbonate (Fig. 7). As a matter of fact, the absorption band $\nu_{C=O}$ = 1743 cm^{-1} of **IntLC** started increasing after only 5 min., i.e. far before the formation of PC ($\nu_{C=O}$ = 1796 cm^{-1}) that appears at t = 60 min, suggesting that PC is produced from **IntLC**. Then, one would expect that the consumption of **IntLC** should be accompanied with a progressive decrease of the intensity of the peak at $\nu_{C=O}$ = 1743cm^{-1}. But, this specific signal reached a quasi-plateau as soon as PC started to be synthesized confirming that each mole of **IntLC** that is consumed produces PC but also one mole of **DEC** co-product, both intermediate **IntLC** and **DEC** having the same absorption band. We believe that the absorbance of the peak at $\nu_{C=O}$ = 1743cm^{-1} keeps increasing very slightly because of the formation of side products (see Scheme 2), namely **BisLC** (Scheme 3). Indeed, a linear biscarbonate **BisLC**, which absorption band of the C=O stretching mode is around 1743 cm^{-1}, is obtained in low yields (~15 %) from carbonation of each alcohol moieties, followed by double alkylation. This study led to consistent proofs for the prior formation of **IntLC** before PC and **DEC**.

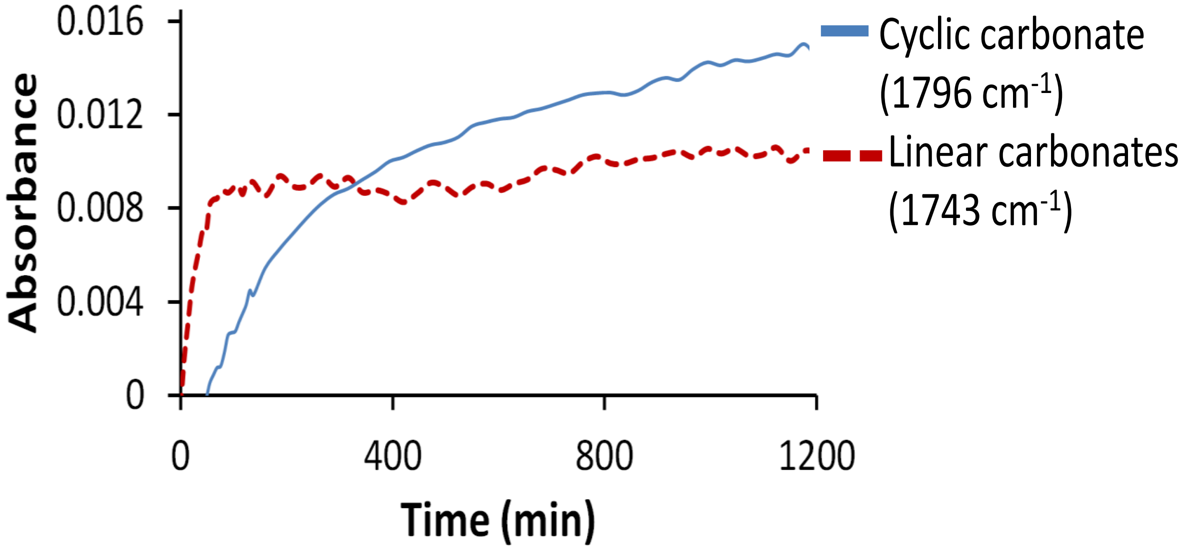


Figure 7: Kinetic study of the carbonation of PG promoted by DBU/EtBr system: time evolution of the absorption bands relative to PC and linear carbonates (**DEC, IntLC** and **BisLC**). Conditions: PG (0.5 mmol) ; DBU (1 mmol) ; EtBr (1.2 mmol) ; CH_2Cl_2 (200 µL) ; 1 MPa ; 25°C

The ^{1}H NMR characterization of the crude reaction medium after 20 h (see Figure 8) confirmed the presence of PC, **DEC** and **BisLC** (yield of PC = 73 %, PC/DEC = 2, yield of biscarbonated products **BisLC** = 15 %).

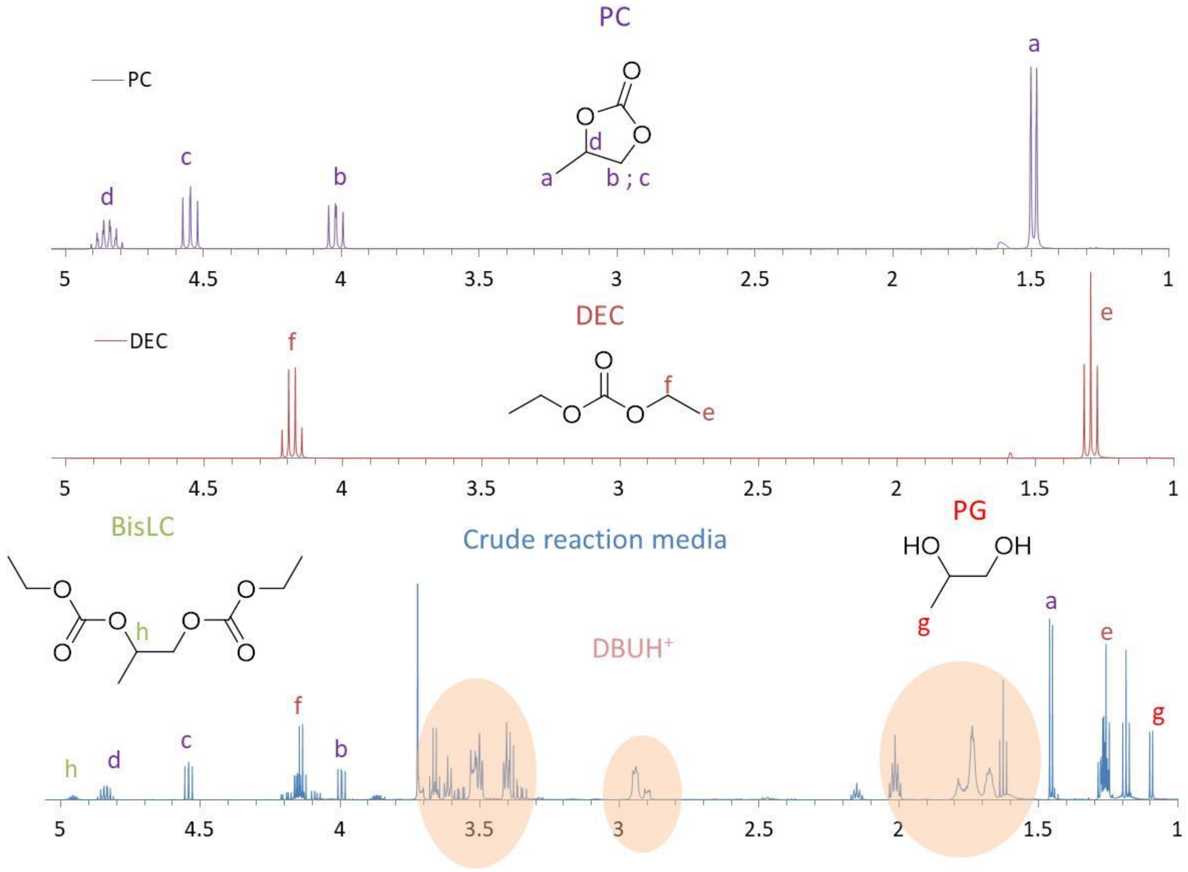
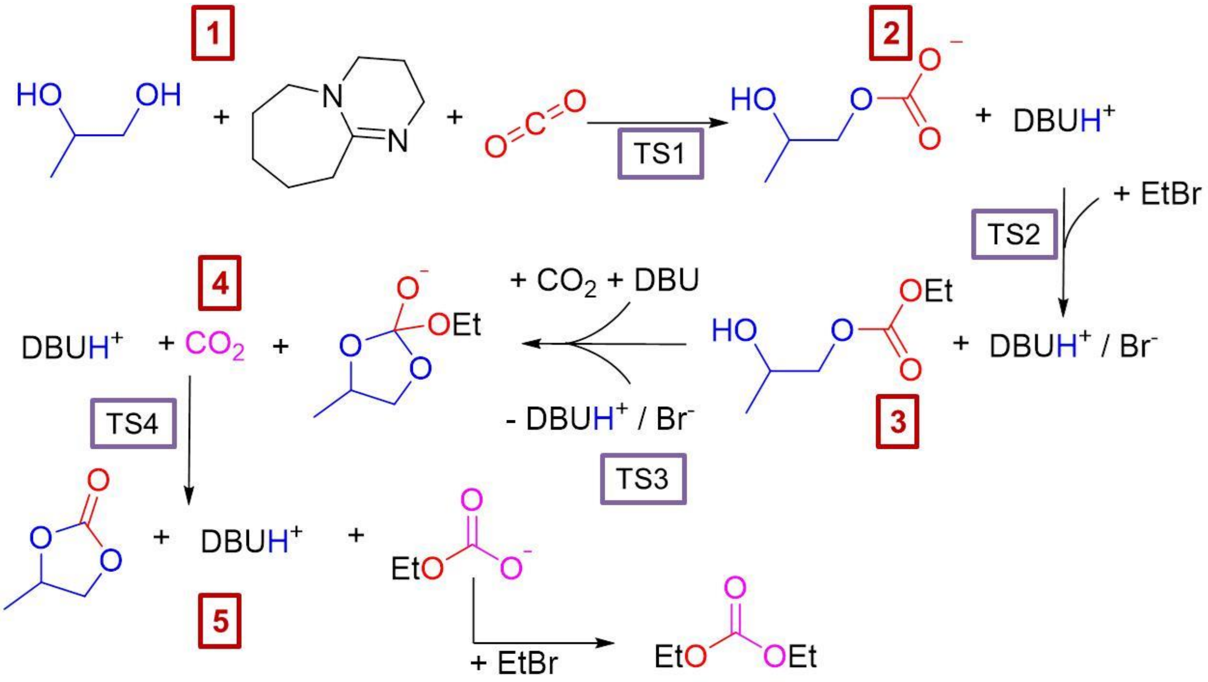


Figure 8: ^{1}H NMR spectra (300MHz, $CDCl_3$) of (a) propylene carbonate (PC), (b) diethyl carbonate (DEC) and (c) the crude reaction mixture (sample entry 1, Table 1)

Control experiment for the synthesis of **DEC** from ethanol and CO_2 promoted by dual system composed of DBU/EtBr in the same experimental conditions was carried out. **DEC** was obtained in 55 % yield after 23 h, which explain the origin of the PC/DEC ratio of 2 at the end of reaction time. The identification of the specific intermediates correlated to the kinetic data obtained through ATR-IR monitoring led to a mechanism proposal (Scheme 4).



Scheme 4: Mechanism proposal for the formation of propylene carbonate from PG, based on reaction intermediates identified from Fig.1. The presence of IntCC was not shown by ATR-IR experiments but was proposed regarding DFT calculations (Fig. 3).

As proposed before, the first step relies on the carbonation of one alcohol moiety of PG to generate an alkyl carbonate ion /$DBUH^+$ adduct. The second step consists of a SN_2 addition of the generated alkyl carbonate ion on EtBr, leading to the linear alkyl carbonate **IntLC**. Then, a second equivalent of DBU creates an hydrogen bonding with the second alcohol moiety rendering the oxygen atom more reactive and capable of an intramolecular attack onto the carbonyl group of the acyclic carbonates. This reaction generates the cyclic intermediate **IntCC** that expelled ethanolate with concomitant formation of propylene carbonate. Ethanolate undergoes a carbonation reaction with the CO_2 dissolved in the medium to generate an anionic alkyl carbonate, which will react with a second equivalent of EtBr through a SN_2 reaction to generate the acyclic diethyl carbonate as a co-product. To confirm our predictions deduced from the experimental ATR-IR results, this mechanism was confronted to molecular modelling through DFT calculations at the M062X/6-311g(d,p) level (Fig. 9). As expected from experimental results, TS1 involves a trimolecular reaction

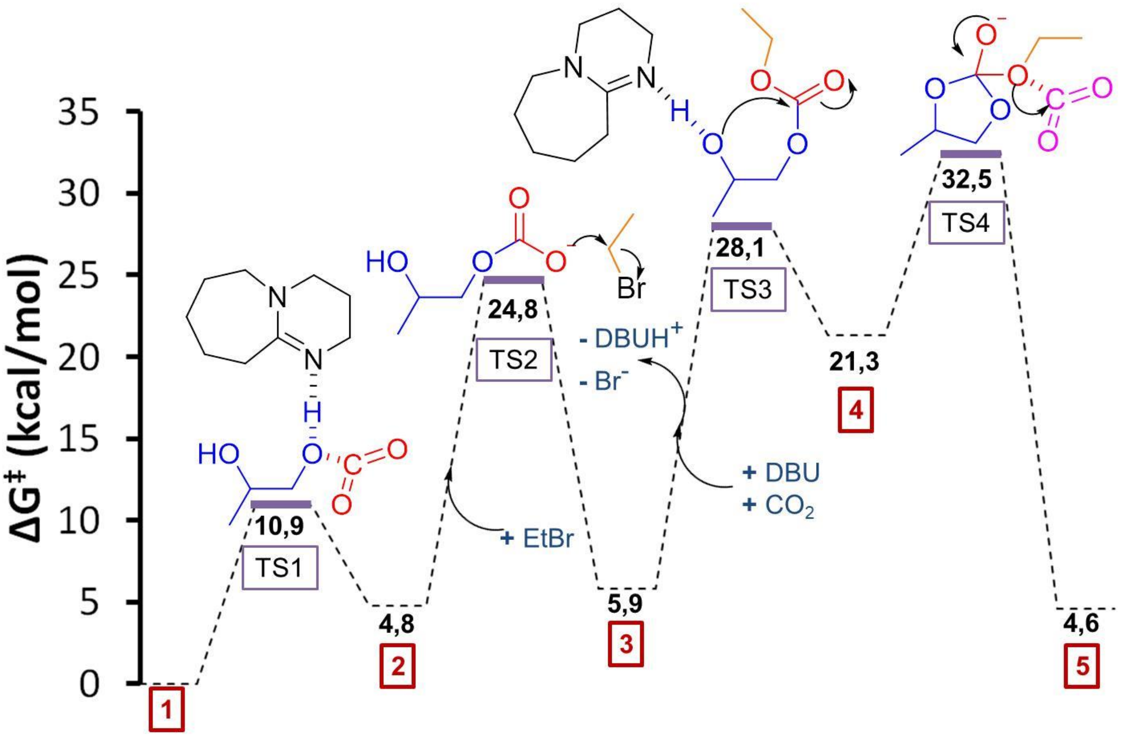


Figure 9: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Scheme 4. Red numbers correspond to optimized reaction intermediates shown in Scheme 4 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates.

through hydrogen bonding which activates the alcohol function and induces angular deformation of CO_2 ($\Delta G_{TS1}{}^{\ddagger}$ = 10.9 kcal/mol). TS2 confirms the SN_2 hypothesis on EtBr with simultaneous addition of RCO_3^- and elimination of Br^- ($\Delta G_{TS2}{}^{\ddagger}$ = 20.0 kcal/mol). TS3 involves another hydrogen bonding to promote the cyclization ($\Delta G_{TS3}{}^{\ddagger}$ = 22.2 kcal/mol). Finally, TS4 is related to the cyclization of propylene carbonate with the release of an ethyl carbonate anion formed from the addition of an excess CO_2 to the released ethanolate. Thus, although DFT calculation results show that the cyclization (TS3) and the formation of the cyclic carbonate (TS4) are two different steps, the intermediate **IntCC** was not identified by ATR-IR spectroscopy probably due to the high Gibbs Free Energy of intermediate 4 and the low activation barrier of TS4 ($\Delta G_{TS4}{}^{\ddagger}$ = 11.2 kcal/mol).

The low activation barrier of $\Delta G_{TS1}{}^{\ddagger}$ is well correlated with the fast formation of the anionic alkyl carbonate RCO_3^- (~ 5min for carbonation of the alcohol moiety). As **IntLC** is very stable (linear alkyl carbonate), $\Delta G_{TS3}{}^{\ddagger}$ has the highest activation barrier and is thus the rate limiting step of the reaction. Once again, it is well correlated with kinetic profiles obtained by ATR-IR, since absorption band of **IntLC** ($\nu_{C=O}$ = 1743 cm^{-1}) appears before and increases faster than absorption band of the cyclic product ($\nu_{C=O}$ = 1796 cm^{-1}).

It should be noted that the DFT energetic profile of Fig. 9 was modelled with (R)-1,2-propanediol and assuming that the carbonation would first occur on the primary alcohol function. Yet, all the possible reaction pathways were modelled for both the (R) and (S) stereoisomers of propylene glycol and by assuming either the carbonation of the primary or secondary alcohol upon CO_2 addition (see Fig. 10). No major differences in the activation barrier of each transition states were found, and we concluded that all paths could occur, with a slight preference over carbonation of primary alcohol of (R)-1,2-propanediol.

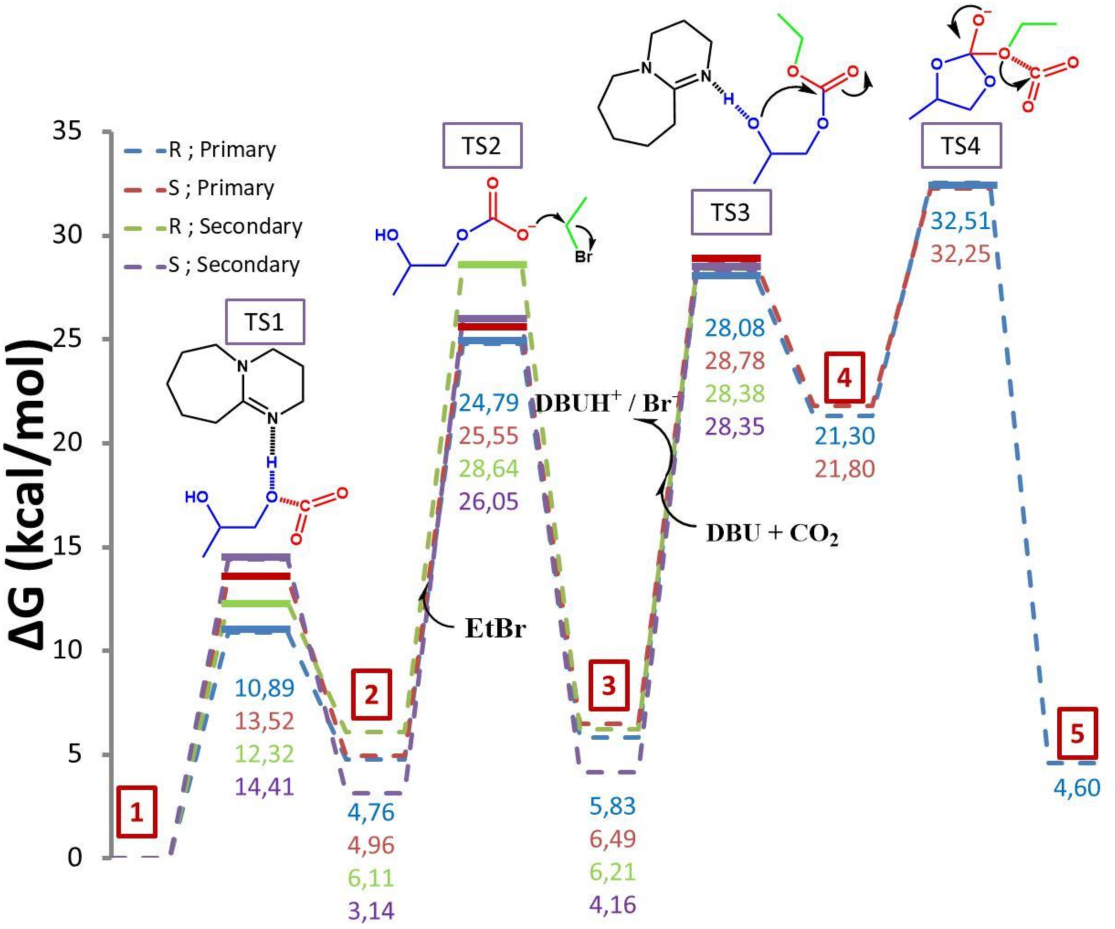


Figure 10: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Scheme 4. All pathways were considered for the monocarbonation of propylene glycol: carbonation on the primary or secondary alcohol moiety, with either (R) or (S) stereochemistry. Red numbers correspond to optimized reaction intermediates shown in Scheme 4 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates.

The optimized structures of the intermediates and transition states for the reaction path calculated with the (R) primary alcohol are reported in Figure 11.

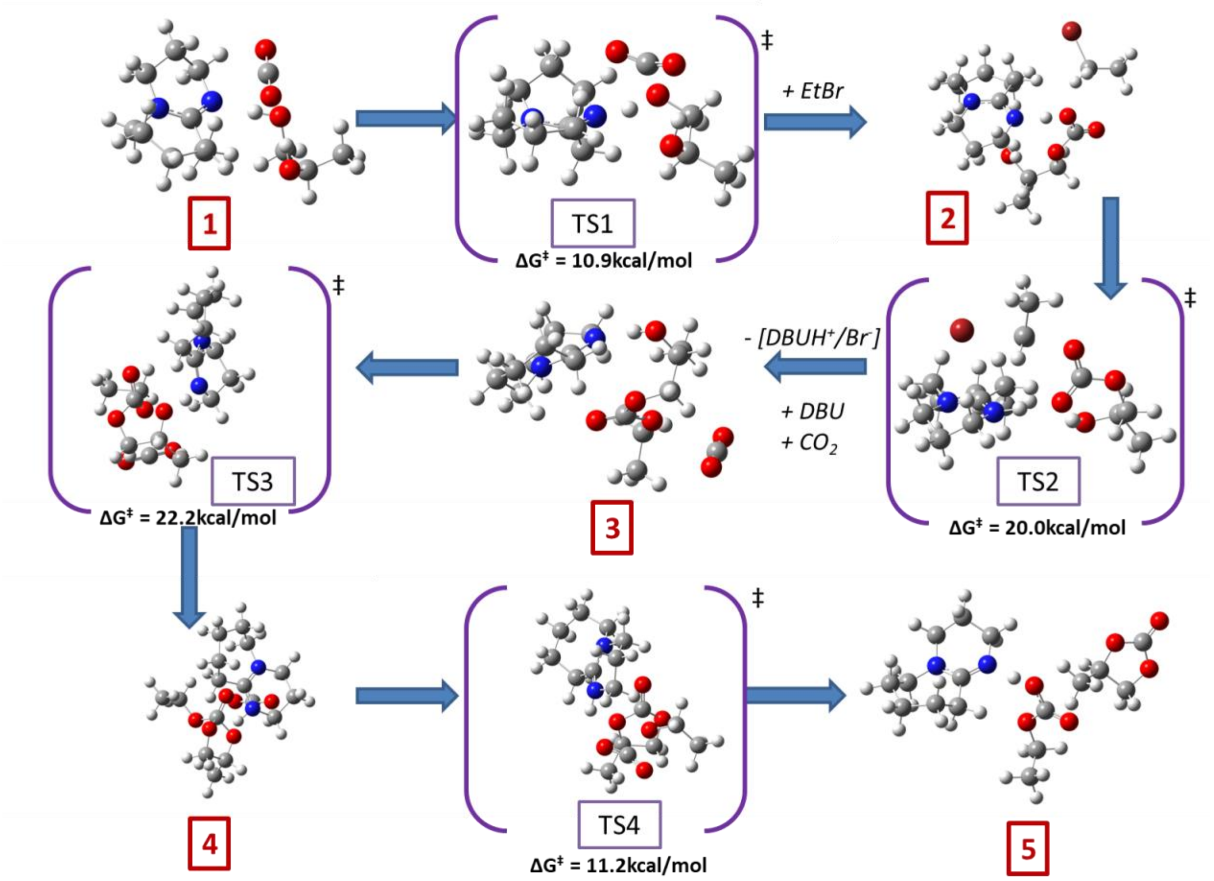


Figure 11: Optimized structures at the M062X/6-311g(d,p) level of the intermediates and transition states for the reaction path of the model reaction with PG, DBU (2eq), EtBr (2eq), CO2 (2eq) calculated with the (R) primary alcohol

To further understand how the experimental parameters may affect the DBU-promoted carbonation of 1,x-diols, the influences of the temperature, the pressure, the solvent, the alkylating agent and the substrate scope were investigated through ATR-IR and results were complemented by quantitative ^{1}H NMR characterization of the crude media. Full conversion of the diol was never observed. In most of the spectra, a small fraction of the intermediate **IntLC** obtained from the corresponding 1,x-diol remained not converted into the cyclic product.

III-1-b) Temperature, pressure and solvent effect on kinetics and yields

Effect of the temperature:

At a fixed pressure of 1 MPa, an increase of the temperature from 25 °C to 50 °C slightly increases the overall yield (from 70 % to 76 % after 20h) but considerably increases the kinetics (Table 1, entries 1-2). Figure 12a (green curve) highlights a two-fold acceleration of the formation of propylene carbonate by simple doubling of the temperature. In contrast, heating up to 70 °C do not increase the kinetic of the reaction but has a detrimental effect on the yield (Table 1, entry 3 ; Fig. 12a, red curve). In both cases, increasing the temperature led to lower yields of **BisLC** biscarbonated side-products (2 % and 5% for 50 °C and 70 °C respectively).

Table 1: Effect of the temperature, pressure and solvent on the reaction of propylene glycol to afford propylene carbonate. Reaction conditions: Propylene glycol (0.5 mmol in 200µL solvent), DBU (1 mmol), EtBr (1.2 mmol).

Entry	P_{CO2} (MPa)	T (°C)	Solvent	PG conv. (%)[1,2]	PC yield (%)[1,3]	Biscarbonate yield (%)[1,4]
1	1	25	CH_2Cl_2	90	73	15
2	1	50	CH_2Cl_2	78	76	2
3	1	70	CH_2Cl_2	70	49	5
4	0.5	25	CH_2Cl_2	74	62	12
5	2	25	CH_2Cl_2	40	35	0
6	3	25	CH_2Cl_2	20	16	2
7	4	25	CH_2Cl_2	41	34	7
8	1	25	neat	87	61	26
9	3	25	neat	56	22	22
10	1	25	anisole	72	46	16
11	1	25	ACN	78	30	19
12	1	25	$CHCl_3$	70	45	10
13	1	25	DMSO	69	15	14

[1] Determined after 20h
[2] Conversion of propylene glycol calculated from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard
[3] PC yield calculated from ATR-IR and from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard
[4] Yield of the biscarbonated product BisLC calculated from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard

Effect of the pressure:

Increasing the pressure from 1 MPa to 4 MPa had a detrimental effect on both the kinetics and PC yields for the model reaction promoted by DBU/EtBr in CH_2Cl_2 at 25°C for 20 h (Figure 12b). While the CO_2 solubility increases with the pressure in CH_2Cl_2 [56], a two-fold decrease of the reaction yield (PC yields from 70 % to 35 %, Table 1, entries 1 and 5) was noticed upon simple doubling the CO_2 pressure from 1 MPa to 2 MPa and the reaction was quasi inhibited at 3 MPa of CO_2. Such experimental observations were assigned to a "salting out effect" presumably caused by the formation of a CO_2-expanded reaction medium provoking the precipitation of the $RCO_3^-/DBUH^+$ organic salt (see Fig. 13). As the system is under pressure, carbonation of the alcohol moiety occurs. Around 4 MPa, large absorption band between 2400 cm^{-1} and 3500 cm^{-1} appears, characteristic of the formation of solid organic salts (here $RCO3^-/DBUH^+$) that interferes with the infrared beam as it deposits on the FT-IR cell window. When the system is depressurized, FT-IR profile is nearly fully recovered from the initial state, indicating organic salts are well solubilized in dichloromethane. Attempts to improve the addition of CO_2 onto PG by decreasing the pressure from 1 MPa to 0.5 MPa also gave mitigated results. If the kinetic is faster during initial course of the reaction (below 500 min) at 0.5 MPa, the PC yield ceiled at 50-60 % after 500-600 min while it continued to increase up to ~ 70 % at 1 MPa (Fig. 12b). Therefore, we set up the optimal pressure and temperature for this reaction in CH_2Cl_2 to 1 MPa and 25°C, respectively. Regarding the formation of **BisLC** side product, lower yields were unexpectedly obtained with higher pressures, which indicate that the CO_2 concentration in the reaction mixture is not decisive for this side reaction.

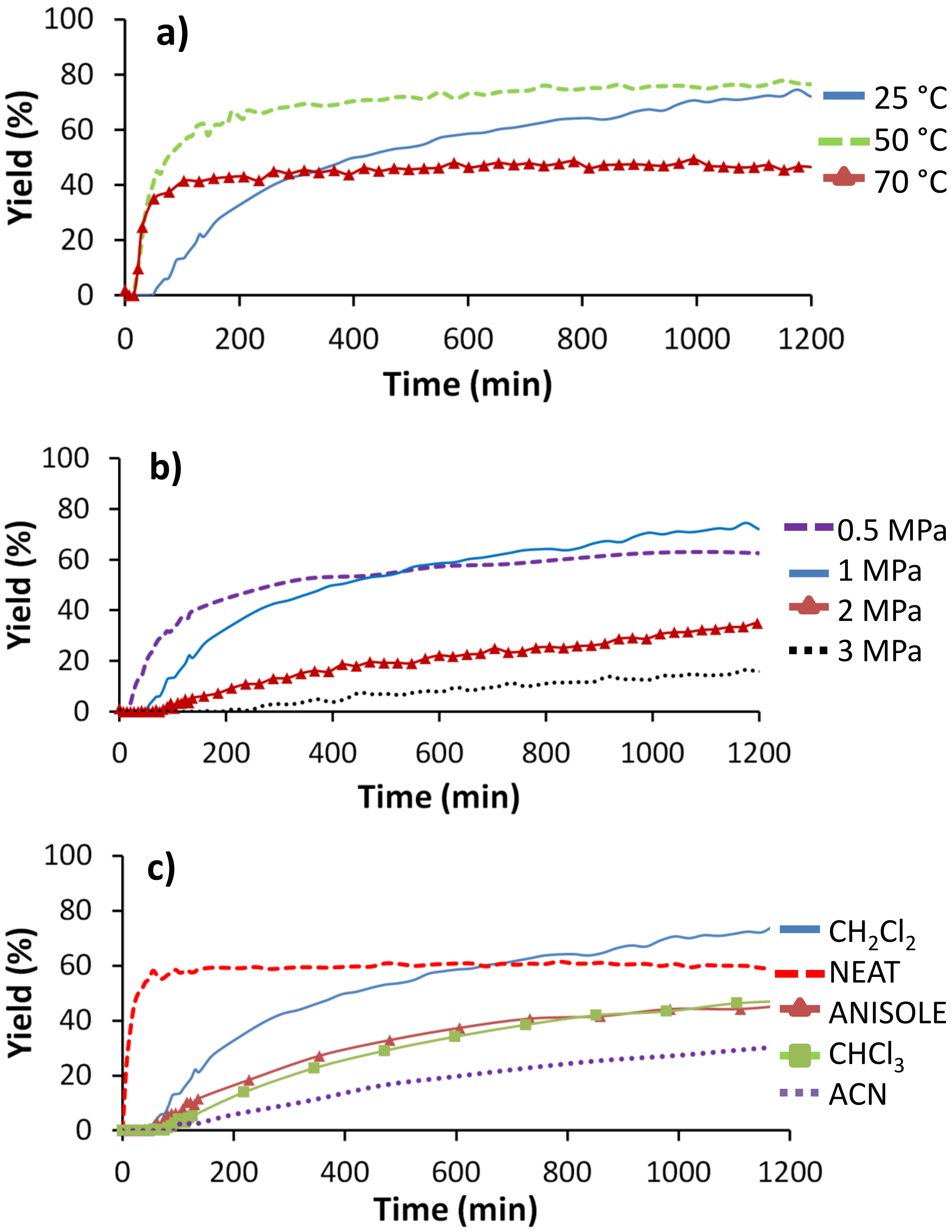


Figure 12: Yield of propylene carbonate (PC) with the reaction time for different (a) temperatures, (b) pressures and (c) solvent conditions. Reaction conditions are described in Table 1.

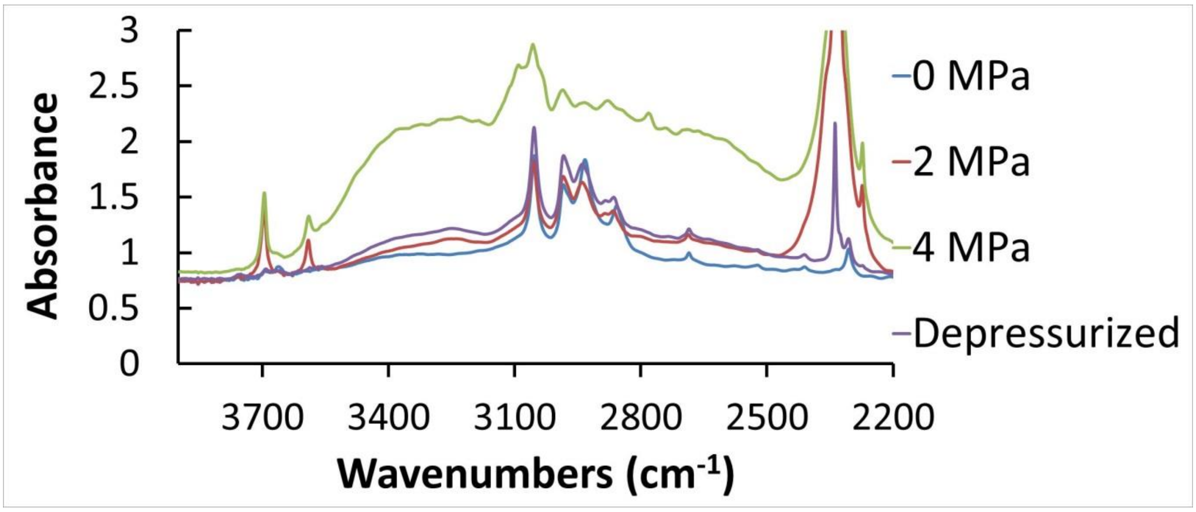


Figure 13: FT-IR (transmission) spectra collected at the equilibrium over different pressure. Purple curve was collected after depressurizing the cell at 4 MPa. Conditions: PG (0.67 mmol ; 49.2 µL), DBU (0.67 mmol ; 100 µL), CH_2Cl_2 (850 µL)

Effect of the solvent:

To study the influence of the solvent on the system, the model reactions were reproduced at 1 MPa and 25°C in neat condition or using anisole, $CHCl_3$, DMSO or acetonitrile (ACN) (Table 1, entries 8-13). Even though CO_2 is poorly soluble in glycols [59], reactions performed under neat conditions at 1 MPa and 25 °C displayed faster kinetics, and PC yields up to 60 % were obtained after only 2 h (Table 1, entry 8, Fig. 12c red curve). Alike the model reactions carried out in CH_2Cl_2, increasing the pressure had a negative impact on both the kinetic and PC yields (Table 1, entries 8-9). Switching from CH_2Cl_2 to other solvents (Table 1, entries 10-13) led systematically to lower/moderate PC yields (from 16 % in DMSO to 46 % in anisole after 20 h). The benchmarking of the kinetic profiles recorded for each solvent clearly highlighted slower reaction rates in solvents other than CH_2Cl_2 (Fig. 12c). Interestingly, when the reaction was carried out in anisole, precipitation of organic salts $DBUH^+/Br^-$ occurred after 30 min of reaction. When DMSO was used instead of CH_2Cl_2, PC was synthesized in very low yield (Table 1, entry 15). We believe the variation of the PC yields in the various solvents was caused by the occurrence of side-reactions (enhanced alkylation of DBU by EtBr), that will be discussed below. Unlike neat conditions that favoured the formation of **BisLC** side-product with a yield up to 27 % (Table 1, entry 8-11), its formation remained limited to ~15 % by switching from CH_2Cl_2 to other solvents.

Influence of the alkylating agent:

As shown by our DFT calculations, the R-X alkylating agent is expected to play an important role on the carbonation of diols. It was expected that the nature of the halide would dictate the reactivity for the alkylation of the carbonate anion (step 2 in Scheme 4) whereas the R motif is expected to trigger the cyclization step prior formation of PC by providing a good RO^- leaving group (TS4 in Scheme 4). To verify this hypothesis, different alkyl halides were screened for the DBU promoted synthesis of PC from PG and CO_2 at 25 °C and 1 MPa in CH_2Cl_2.

When bromobutane replaced bromoethane, a slower kinetic was observed (Fig. 14, dark red curve), resulting in lower PC yield of 50 % after 20 h (Table 2, entry 2).

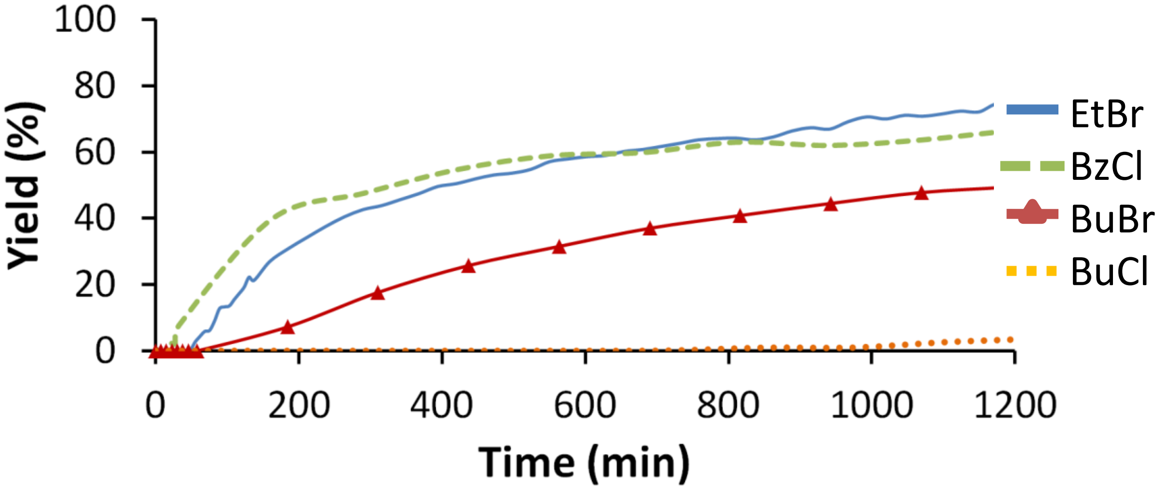


Figure 14: Yield of propylene carbonate (PC) with the reaction time for different alkylating agents. Reaction conditions: Propylene glycol (0.5 mmol in 200 µL CH_2Cl_2), DBU (1 mmol), R-X (1.2 mmol), 1 MPa, 25 °C, 20 h. One pot/one step reactions.

Table 2: Effect of the alkyl halide on the carbonation of propylene glycol under a pressure of 1 MPa CO_2 at 25 °C. Reaction conditions: diol (0.5 mmol in 200 µL CH_2Cl_2), DBU (1 mmol), Alkyl halide R-X (1.2 mmol)

Entry	R-X	PG conv. (%)[1,2]	PC yield (%)[1,3]	Biscarbonate yield (%)[1,4]
1	EtBr	90	73	15
2	BuBr	60	50	10
3	BuCl	3	3	0
4	BzCl	65	65	0
5	BzBr	0	0	0
6	MeI	0	0	0
7[a]	EtBr	28	10	0
8[b]	EtBr	35	32	0
9[c]	/	3	3	0

[1] Determined after 20 h

[2] Conversion of propylene glycol calculated from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard

[3] PC yield calculated from ATR-IR and from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard

[4] Yield of the biscarbonated product BisLC calculated from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard

[a] 0.5 mmol DBU.

[b] 0.5 mmol R-X.

[c] No R-X.

Extending the reaction time to 39 h led to similar yield with regard to bromoethane (76 % yield of PC). Replacing bromobutane by its chlorinated analogue dramatically decreased the reaction rate with a marginal PC yield of only 3 % after 20 h (Table 2, entries 2 and 3, Fig. 14 orange curve). This result is consistent with the proposed mechanism that involved the formation of the intermediate **IntLC** by a SN_2 reaction (step 2, see Scheme 4). Chlorine being a poorer leaving group than bromine, the nucleophilic substitution is disfavoured.

Unlike chlorobutane, a higher PC yield of 65 % was obtained with benzyl chloride. Indeed, the benzyl group displays better leaving group capability in comparison with the butyl group for the cyclization step. Surprisingly, with the more reactive benzyl bromide (BzBr) or methyl iodide (MeI), no PC was formed (Table 2, entries 5-6). We therefore postulate that the possible quaternization of DBU by these alkyl halides might explain this lack of reactivity. This quaternization is typically used for the synthesis of ionic liquids[60]. This hypothesis was further confirmed by ATR-IR and DFT analyses, as presented in Figure 15. The C=N stretching mode at 1613cm^{-1} of DBU shifts toward 1622cm^{-1} upon alkylation (see Fig. 15a) and is favoured with more reactive alkyl halides. From these experiments, BzCl and EtBr are the best candidates in combination with DBU for the synthesis of PC. Still, presence of quaternized DBU salts can be shown at the end of reaction time in Fig. 5 with a shoulder at 1622 cm^{-1} of the protonated-DBU peak, probably due to the presence of an excess of alkylating agent (2.4 eq) and non-reacted base (diol not fully converted). Control experiments (Table 2, entries 7-8) highlighted the need of using 2 equivalents of DBU and 2.4 equivalents of R-X to reach the highest PC high yields, as previously described. [47] In the absence of alkylating agent, only traces of PC (yield of 3 %, Table 2, entry 9) was measured, excluding any role of CH_2Cl_2 as an alkylating agent in promoting the carbonation of PG.

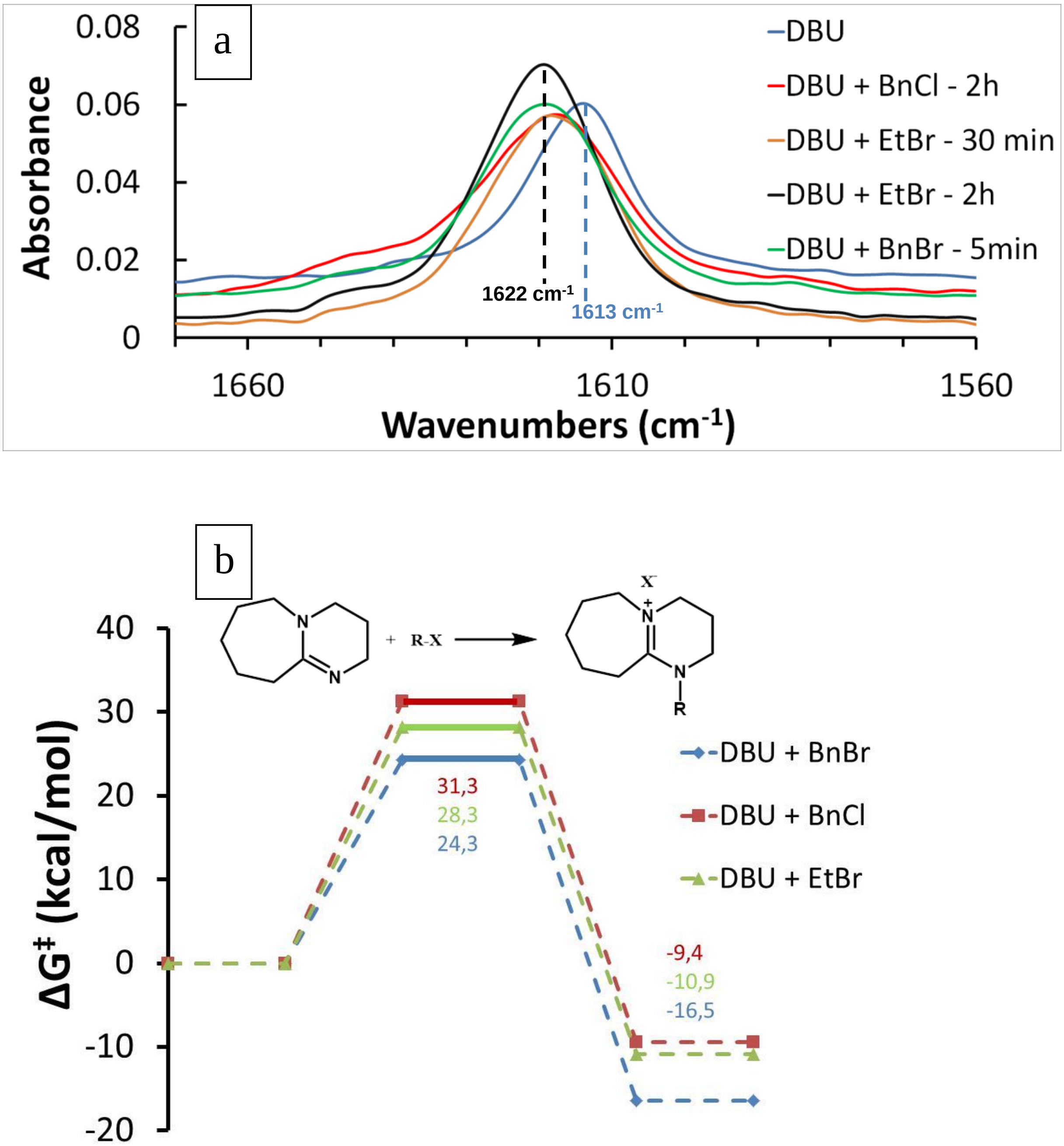


Figure 15: ATR-IR spectra of the DBU/BnCl, DBU/BnBr and DBU/EtBr systems over time. DBU absorption band is shifted from 1613cm^{-1} to 1622cm^{-1} while alkylation occurs (a). DFT computed pathway (*M062X/6-311g(d,p)*) of DBU quaternization with alkyl halides. Energetic barrier increases using less reactive R-X (b).

III-2) Dual system TEA/TsCl

To increase the versatility of the coupling between diols and CO_2 for the synthesis of cyclic carbonates, other tertiary amines than DBU were tested as bases, such as N,N,N′,N′-tetramethylethylenediamine (TMEDA), triethylamine (TEA), N,N-diisopropylethylamine (DIPEA) and N-methyl pyrrolidine. In all cases, carbonation of the alcohol of PG occurred as highlighted by *in-situ* ATR-IR by the formation of RCO_3^- species at 1660 cm^{-1}. But no propylene carbonate was formed when EtBr was used as alkylating agent. Surprisingly, no absorption band could be observed around 1743 cm^{-1}, indicating that step 2 (SN_2 reaction with EtBr) did not occur. Further investigations were carried out with TEA as the model organic base to compare with DBU, using PG as the diol. DFT calculations (Fig. 16) showed that TEA poorly stabilises TS2, rendering the oxygen atom involved in SN_2 less reactive than in the case of DBU (Mulliken charges of -0.451 vs -0.467), highlighting the important role of the base in every step of the reaction and not only for the protonation steps. This leads to a consistent increase of the Gibbs Free Energy of TS2 for TEA (36.5 kcal/mol vs 24.8 kcal/mol) which is now the highest energetic barrier of the overall reaction ($\Delta G_{TS2}^{\ddagger}$ = 27.4 kcal/mol), explaining why SN_2 doesn't occur in the case of TEA and EtBr.

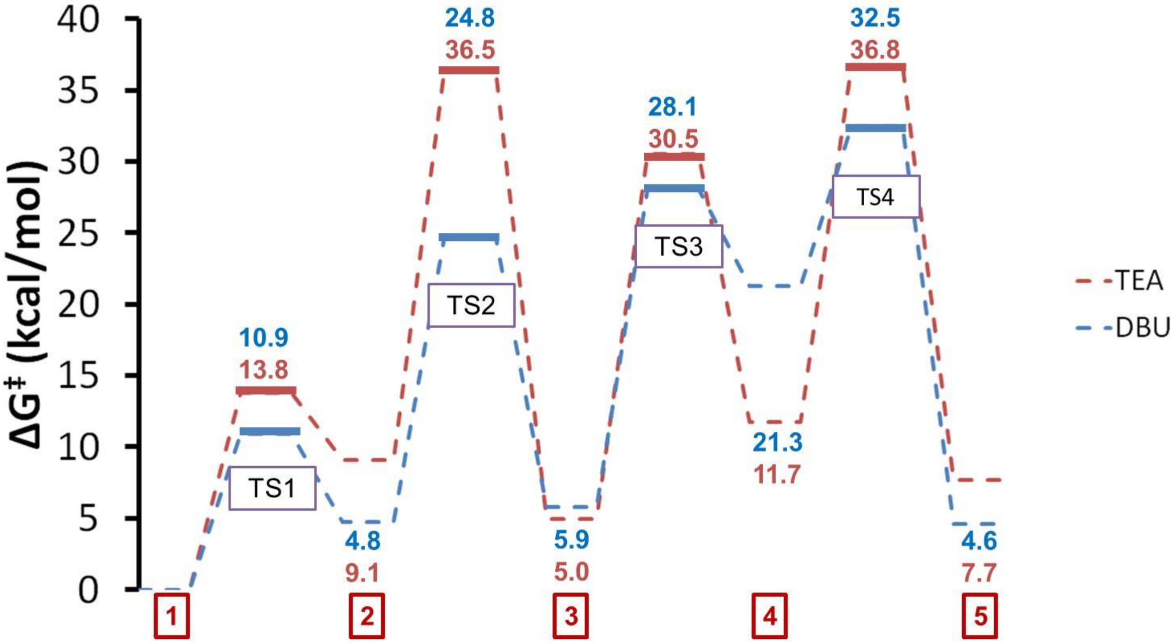


Figure 16: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Scheme 4 with two different organic bases (DBU or TEA). Red squares correspond to optimized reaction intermediates shown in Scheme 4 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates.

TEA being a less nucleophilic base than DBU, other more reactive R-X could be tested while avoiding side reactions mentioned above (quaternization of the base). Tosyl chloride (TsCl) was selected as a good candidate due to previous research [44-46]. Similarly to the synthetic pathway with DBU/EtBr, the model carbonation reaction of propylene glycol into propylene carbonate was studied using the dual system TEA/TsCl. As the mechanism was already demonstrated by Buchard *et al*[45] for the carbonation of 2,2-dimethyl-1,3-propanediol, the experimental confirmation of this mechanism is presented in Figure 17 with propylene glycol. Kinetic studies are reported for the first time by ATR-IR *in-situ* monitoring in pressurized reactors that enabled to identify important reaction intermediates and to confirm the reaction mechanism (see scheme 5).

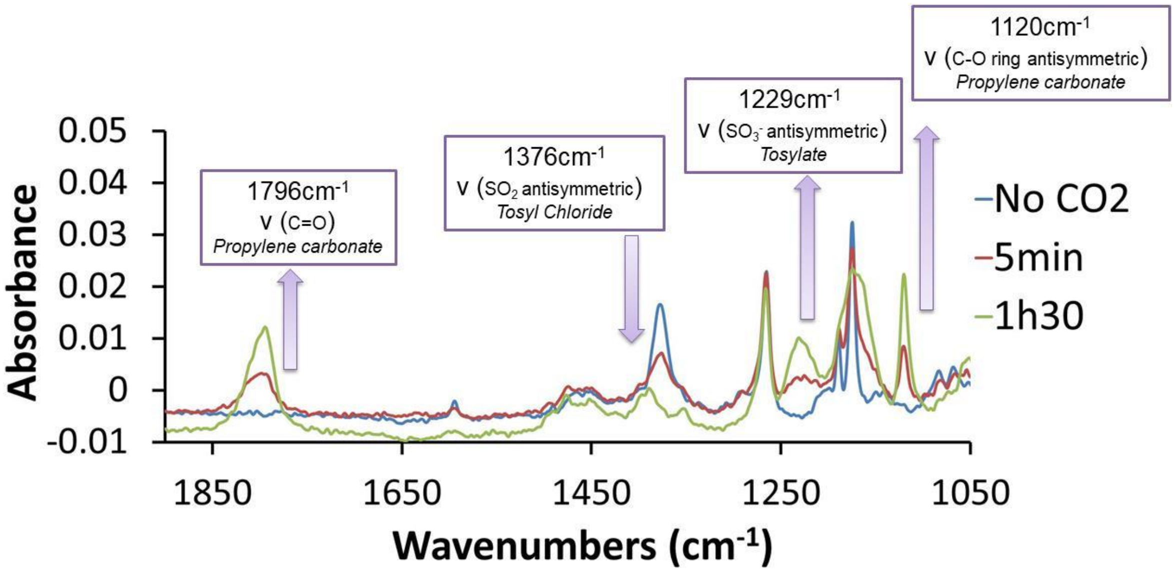
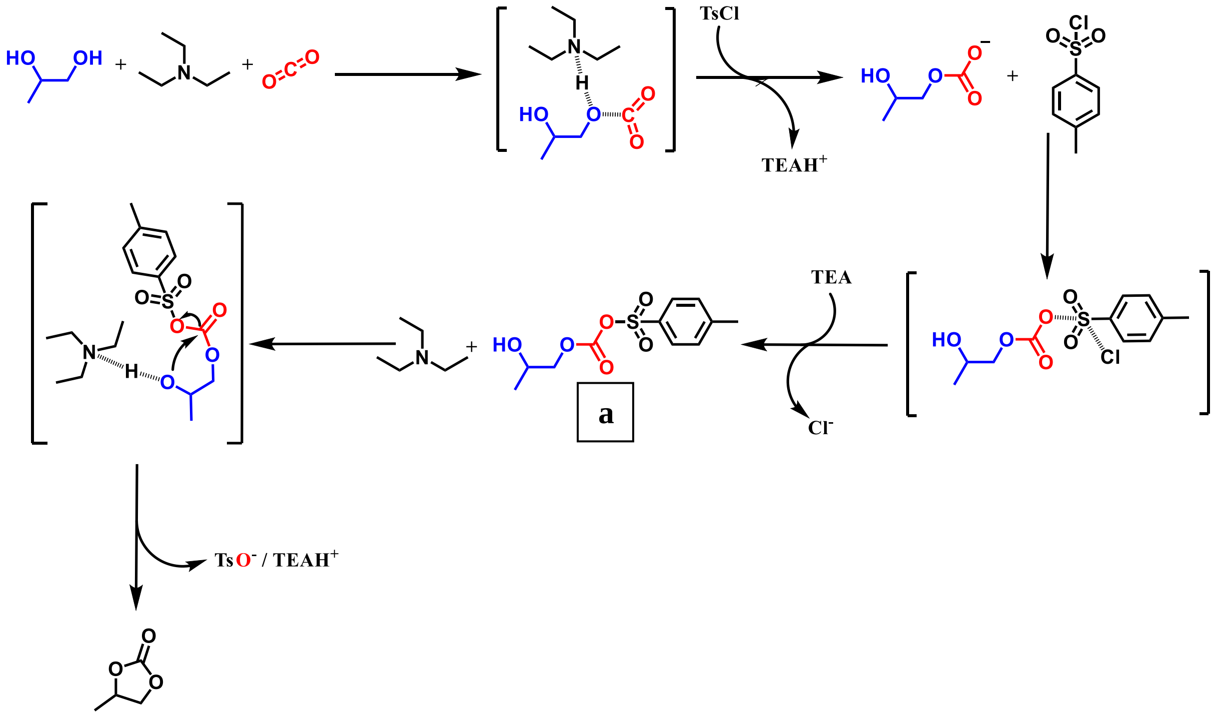


Figure 17: Monitoring of the model reaction between PG and CO2 promoted by a dual TEA/TsCl system using ATR-IR spectroscopy. Conditions: PG (0.5 mmol) ; TEA (1 mmol) ; TsCl (0.5 mmol) ; CH_2Cl_2 (200 µL) ; 1 MPa ; 25°C



Scheme 5 : Mechanism proposal for the formation of propylene carbonate from PG, inspired from Buchard et al[45]. The presence of compound **a** was not shown by ATR-IR experiments but was proposed regarding preliminaries DFT calculations.

At room temperature and a fixed pressure of 1 MPa, a maximum PC yield of 79 % is obtained after only 70 min (Fig. 18a, blue curve). When the reaction media was heated up to 50 °C and 70 °C, the yield decreased to 70 % and 60 % respectively (Table 3, entries 2-3).

Table 3: Effect of the temperature, pressure and solvent on the reaction of propylene glycol to afford propylene carbonate Reaction conditions: Propylene glycol (0.5 mmol in 200µL solvent), TEA (1 mmol), TsCl (0.5 mmol).

Entry	P_{CO2} (MPa)	T (°C)	Solvent	PG conv. (%)[1,2]	PC yield (%)[1,3]
1	1	25	CH_2Cl_2	80	79
2	1	50	CH_2Cl_2	79	70
3	1	70	CH_2Cl_2	62	60
4	0.5	25	CH_2Cl_2	80	62
5	2	25	CH_2Cl_2	66	65
6	3	25	CH_2Cl_2	70	68
7	4	25	CH_2Cl_2	70	55
8	1	25	neat	90	90
9	1	25	anisole	90	85
10	1	25	ACN	80	75
11	1	25	$CHCl_3$	79	60

[1] Determined after 3h

[2] Conversion of propylene glycol calculated from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard

[3] PC yield calculated from ATR-IR and from ^1H NMR with 1,3,5-trimethoxybenzene as internal standard

Regarding pressure effects, at the optimized temperature of 25 °C, an optimum yield for 1 MPa was observed (Table 3, entry 1 and entries 4-7) and increasing the pressure had a detrimental effect on the overall PG conversion and yield. No major differences were observed in terms of kinetics for both heating and increasing the pressure (Fig 18a and 18b), unless for a low pressure of 0.5 MPa (Fig 18b, purple curve) that displayed slow kinetics.

The optimized conditions were applied in neat conditions, which gave the best results so far with 90 % PC yield after only 70 min (Fig 18c, red dashed curve; Table 3, entry 8). Other solvents were tested resulting in a drop of the PC yields to 85 % in anisole (Table 3, entry 9). Switching to acetonitrile or $CHCl_3$ gave PC yields of 75 % and 60 % respectively (Table 3, entries 10-11), with slower kinetics in chloroform (Fig 18c, green curve).

As for the DBU/EtBr dual system, side reactions are expected. In this case, with propylene glycol as a substrate, the main side reaction is the tosylation of one or both alcohol groups, as it is a known reaction for protecting alcohol groups in organic chemistry when a base is involved. Nevertheless, yields of tosylated alcohol never exceeded 3 % for all experiments listed in Table 3.

Other kinetics were performed with tertiary amines such as DIPEA, TMEDA and N-methyl pyrrolidine. Best results were obtained with TEA when dichloromethane was used as solvent. Still, DIPEA could afford propylene carbonate with a yield of 75 % in 150 min (Table 4 entry 2; Fig 19 red curve). TMEDA and N-methyl pyrrolidine displayed lower activity as figured out by lower yields and slower kinetics (Table 4, entries 3-4).

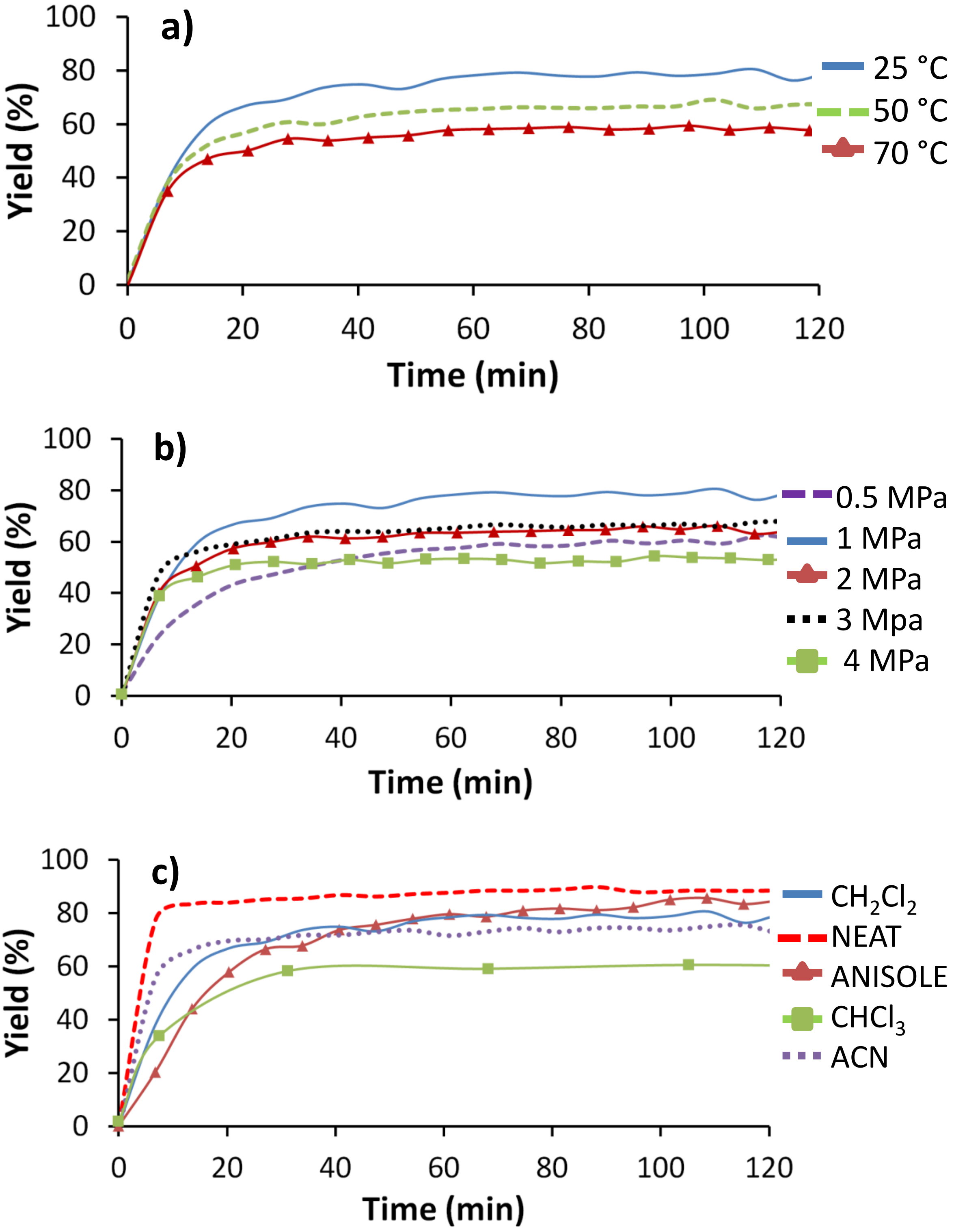


Figure 18: Yield of propylene carbonate (PC) with the reaction time for different (a) temperatures, (b) pressures and (c) solvent conditions. Reaction conditions are described in Table 3.

Table 4: Effect of the organic base for the carbonation reaction of propylene glycol to afford propylene carbonate. Reaction conditions: Propylene glycol (0.5 mmol in 200 µL CH_2Cl_2), base (1 mmol), TsCl (0.5 mmol), 25 °C, 1 MPa.

Entry	Base	PG conv. (%)^{1,2}	PC yield (%)^{1,3}
1	TEA	80	80
2	DIPEA	75	75
3	TMEDA	58	58
4	N-Methyl Pyrrolidine	ND	45

[1] Determined after 3h

[2] Conversion of propylene glycol calculated from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard

[3] PC yield calculated from ATR-IR and from ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard

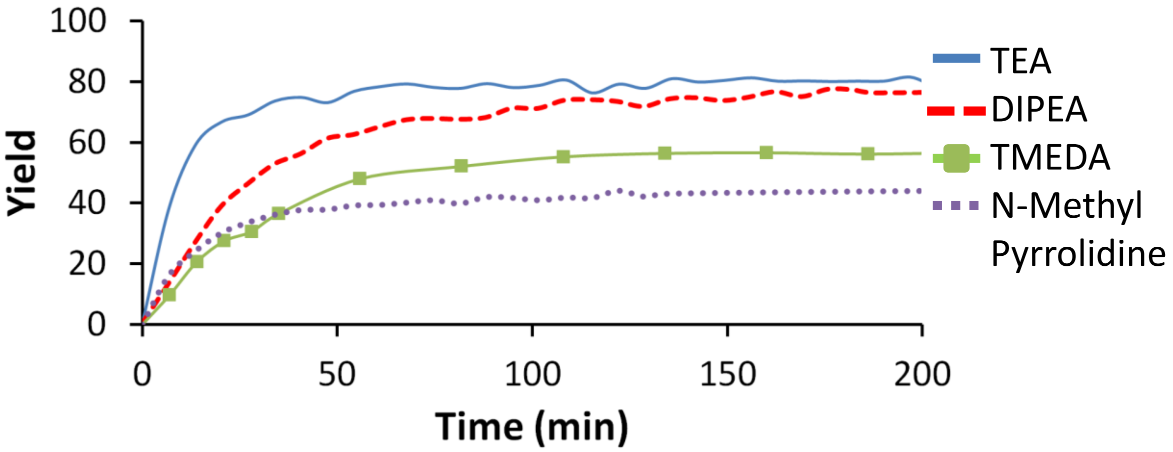
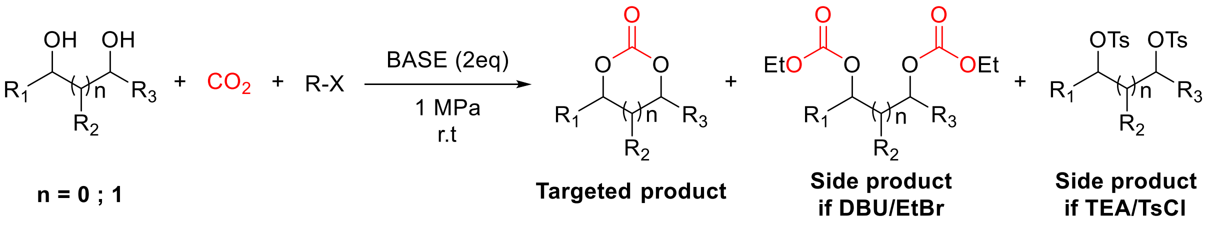


Figure 19: Yield of propylene carbonate (PC) with the reaction time for various organic bases. Reaction conditions are described in Table 4.

III-3) Substrate scope

Even if DBU/EtBr and TEA/TsCl promote the carbonation of diols under mild operative conditions, the benchmarking of their performances as well as their influence on the product selectivities has never been assessed. The coupling chemistry of different classes of alcohols (1,x-diols with x = 2, 3 or ≥ 4) with CO_2 to afford di-, tri- and tetrasubstituted ethylene carbonates, (substituted) trimethylene carbonates or acyclic biscarbonated compounds (Scheme 6) was then balanced regarding both activating systems. Insights into the products yield and selectivity (linear vs cyclic carbonates) are highlighted by benchmarking the performance metrics of both dual activation systems. This study will guide the reader to select the most efficient dual system and the optimal operating conditions to drive the selective formation of the envisioned (a)cyclic carbonate.

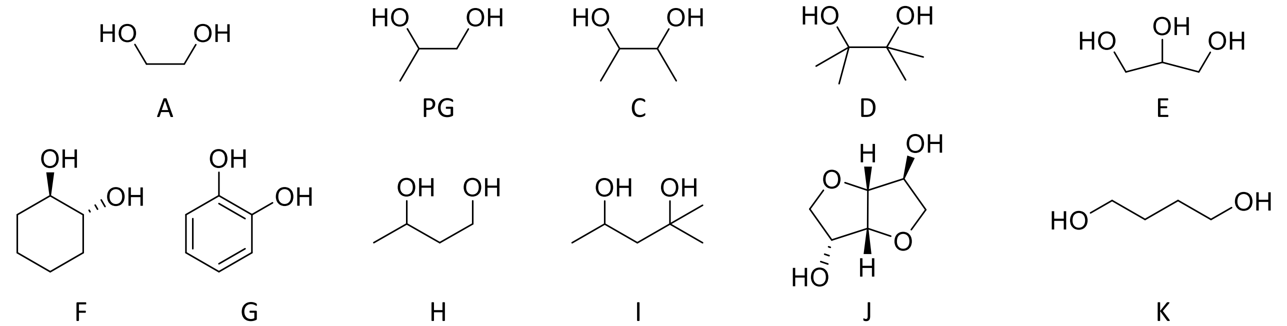


Scheme 6: Substrate scope comparison between the two dual agents DBU/EtBr and TEA/TsCl. Side products directly depend on the method used.

III-3-a) Selectivity for 1,2-diols substrates

Vicinal diols were expected to give ethylene carbonates analogues as the main product due to their known stability. However, depending on the structure of the 1,2-diol, a different selectivity toward the cyclic or biscarbonated linear product was observed (Table 5, entries 1-4) when DBU/EtBr was used. The carbonation of ethylene glycol (product A) afforded a mixture of biscarbonate and ethylene carbonate for DBU/EtBr as the activating system with a low selectivity in cyclic carbonate (39 %). When TEA/TsCl was used however, the yield in cyclic carbonate was improved from 19 % up to 44 % with a greater selectivity of 69 % (Table 5 entry 1). Side products (tosylated alcohols) were still observed at a 20 % yield. When the substrate was switched to propylene glycol (PG), great selectivity toward the cyclic carbonate was observed for both systems (Table 5 entry 2). Best results were obtained with TEA/TsCl as the dual system with a 79 % yield and 100 % selectivity of propylene carbonate. In a similar fashion as for product A, 2,3-butanediol (product C) displayed a poor yield and selectivity toward the cyclic carbonate when DBU/EtBr was used. Yet, the dual system TEA/TsCl provides a satisfying way to obtain mainly the corresponding cyclic carbonate with a moderate yield of 46 % with 100 % selectivity (Table 5 entry 3). We believe that double carbonation occurs in the case of products A and C when DBU/EtBr was used since both alcohol functions are equivalent due to the molecular symmetry. Moreover, small steric hindrance due to the presence of hydrogens or only one methyl must allow the double insertion of CO_2. Whereas no huge differences were observed between carbonation of the primary or secondary alcohol with DBU as a base when DFT calculations were performed, experimental results tend to demonstrate that non-equivalent alcohol functions favour the formation of 5 membered cyclic carbonates, as it is the case for PG. In the case of TEA, no double carbonation are expected as it was previously reported for 2,2-dimethylpropane-1,3-diol with a 100 % selectivity toward monocarbonated species, versus 41 % toward biscarbonated species when DBU was used as a base[45]. Tetrasubstituted Pinacol (product D) was poorly converted into the corresponding cyclic carbonate (diol conversion: 27 %) with however no double carbonation (Table 5, entry 4) with DBU/EtBr activating system, due to greater steric hindrance. However, the cyclic carbonate yield was greatly improved up to 67 % when TEA/TsCl was used, with 100 % selectivity toward the cyclic product. To the best of our knowledge, 4,4,5,5-tetramethyl-1,3-dioxolan-2-one was successfully synthesized from CO_2 for the first time, while other attempts using the CO_2/epoxide coupling failed to obtain this product [61]. Interestingly, glycerol (product E) was selectively converted into glycerol carbonate with a yield of 75 % using the dual system DBU/EtBr (Table 5, entry 5). This alkylating agent/organobase activating system surpasses the performance of TEA/TsCl that only afforded glycerol carbonate with a yield of 55 % with concomitant formation of 20 % of tosylated alcohols as side products, highlighting the substrate dependence for each method and the differences in selectivity.

Table 5: Substrate scope for the carbonation of diols for both dual activating systems DBU/EtBr and TEA/TsCl



Entry	Substrate	DBU/EtBr			TEA/TsCl		
		Yield cyclic carbonate[1] (%)	Yield biscarbonated[2] (%)	Selectivity cyclic carbonate	Yield cyclic carbonate[3] (%)	Yield tosylated alcohol[4] (%)	Selectivity cyclic carbonate (%)
1	A	19	29	39	44	20	69
2	PG	73	15	83	79 (55)[5]	0	100
3	C	20	27	42	46	0	100
4	D	27	0	100	67 (50)[5]	0	100
5	E	75 (60)[5]	0	100	55	20	73
6	F	0	54	0	90 (60)[5]	4	96
7	G	0	0	0	0	0	0
8	H	17	31	35	64 (39)[5]	12	84
9	I	15	54	22	84 (58)[5]	0	100
10	J	0	56	0	0	ND	/
11	K	0	51	0	0	ND	/

[1]: Yield of the corresponding carbonate after 20 h, estimated by quantitative ^{1}H NMR. Conditions: Diol (0.5 mmol); DBU (1 mmol); EtBr (1.2 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[2]: Yield of the corresponding biscarbonated compound after 20h, estimated by quantitative NMR. Conditions: Diol (0.5 mmol); DBU (1 mmol); EtBr (1.2 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[3]: Yield of the corresponding carbonate after 3h, estimated by quantitative NMR. Conditions: Diol (0.5 mmol); TEA (1 mmol); TsCl (0.5 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[4]: Yield of the corresponding tosylated alcohol after 3h, estimated by quantitative NMR. Conditions: Diol (0.5 mmol); TEA (1 mmol); TsCl (0.5 mmol); CH_2Cl_2 (200 µL); 1,3,5-trimethoxybenzene (0.166 mmol) as internal standard ; 1 MPa, r.t.

[5]: Isolated yields after purification for a couple of best results. Experiments were carried out again on a larger scale and products purified by column chromatography. See appendix for NMR spectra of pure products

These differences are even more highlighted when *trans*-1,2-cyclohexanediol (product F) was used as the substrate. In this case, cyclisation is disfavoured compared to other vicinal diols due to the trans configuration. Interestingly, the cyclic carbonate could still be synthetized in excellent yield (90 %, Table 5 entry 6) and selectivity close to 100 % with TEA/TsCl but not in the case of DBU/EtBr. For the latter, biscarbonation is favoured and biscarbonated compounds were selectively synthetized in good yield (54 %, Table 5 entry 6). Unfortunately, pyrocatechol (product G) could not be converted into any carbonates (Table 5 entry 7).

III-3-b) Selectivity for 1,3-diols substrates

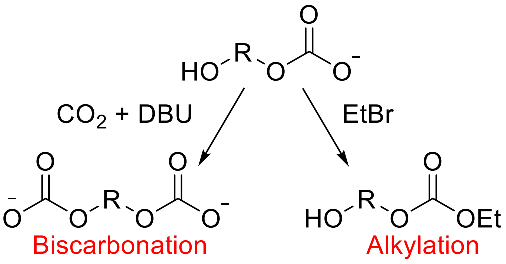
When the DBU/EtBr protocol was applied to the carbonation of 1,3 diols such as 1,3-butanediol (product H) and hexylene glycol (product I), linear biscarbonates were found as the major products (yield = 31 and 54 %, respectively) (Table 5, entries 8 and 9). The formation of the biscarbonated products was favoured due to a larger spacer between both alcohol moieties, in accordance to previous studies[45,46]. Experimentally, 6-membered cyclic carbonates were formed in good yields with great selectivities (Table 5, entries 8 and 9) using TEA/TsCl. Thus, one can tailor the selectivity toward the biscarbonated compounds or substituted trimethylene carbonate by opting for the adequate dual system. This study is particularly relevant as 6-membered cyclic carbonates are modular building blocks for polymer synthesis via ring-opening polymerization[19].

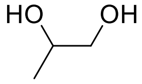
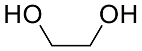
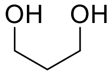
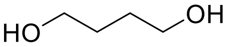
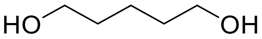
III-3-c) Selectivity for 1,x-diols substrates ($x \geq 4$)

Coupling CO_2 with diols with a larger spacer is expected to favour the carbonation of both alcohol moieties with the formation of acyclic biscarbonates. These compounds are indeed exclusively obtained from 1,4-butanediol or isosorbide in moderate yields (Table 5, entries 10 and 11) with no formation of the 7-membered cyclic carbonates. No cyclic products were detected in the case of the TEA/TsCl system. A small fraction of dimers and trimers were detected indicating the system is still reactive for this class of diols.

In order to deeply understand the selectivity between cyclisation or biscarbonation depending on the nature of the diol when DBU is used as the base, DFT calculations were performed at the *M062X/6-311g(d,p)* level. For each diol, the activation barriers of the alkylation and biscarbonation steps were compared. For both calculations, the starting point was the optimized geometry of monocarbonated species (product of step 1, see Scheme 4 and Fig. 9). Firstly, biscarbonation was not considered in the reaction pathway with PG as the diol, since its activation barrier is 3.3 kcal/mol higher than the activation barrier of alkylation (Table 6, entry 1), which explains the low percentage of biscarbonated products (≤ 15 %). Moreover, all other activation barriers for the conversion of PG into propylene carbonate are lower than 23.3 kcal/mol (Fig. 9). For ethylene glycol (Table 6, entry 2), both activation barriers are of similar magnitude, indicating that both pathways would compete, which is consistent with experimental results (Table 5, entry 1). As the length of the spacer between both alcohol functions is increased, the activation barrier for biscarbonation decreases whereas alkylation barrier remains around 20 kcal/mol (Table 6, entries 3, 4 and 5). These results support the experimental data collected in Table 5 where 1,3 diols yielded a mixture of (substituted) trimethylene carbonates and biscarbonated products, whereas 1,4-butanediol and Isosorbide only yielded the biscarbonated product.

Table 6: DFT calculation (M062X/6-311g(d,p)) for the comparison between monocarbonation followed by alkylation versus carbonation of both alcohol moieties (biscarbonation).



Entry	Substrate	$\Delta G_2^{\ddagger}$ (kcal/mol)[1] **Alkylation**	$\Delta G_2^{\ddagger}$ (kcal/mol)[1] **Biscarbonation**
1		20.0	23.3
2		20.0	19.7
3		22.2	13.3
4		23.0	16.1
5		22.6	11.9

[1]: Gibbs Free Energy activation were calculated by the difference of Gibbs Free Energy of the transition state and the corresponding optimized reaction intermediates.

IV) Conclusion

In this work, deep investigations of a model reaction for the coupling of propylene glycol and CO_2 under mild conditions (25 °C ; 1 MPa) promoted by two different metal-free dual activating systems led to a fine understanding of these carbonation reactions. The protocol was optimized thanks to mechanistic and kinetic studies of various parameters reported for the first time, such as influence of the pressure, temperature, solvent and nature of the alkyl halide. Most importantly, extension to other diols using both synthetic pathways provided a powerful guide for the reader to choose the best dual activating system regarding the desired product. If cyclic carbonates are highly desired, TEA/TsCl gives the most interesting results with fast kinetics to afford selectively 5- and 6- membered carbonates. However, DBU/EtBr must be used for the selective synthesis of glycerol carbonate from glycerol. The latter is also effective to tailor selectivity toward biscarbonated compounds when 1,x diols (x ≥ 3) are used as substrates, as for instance to obtain biscarbonated isosorbide. DFT calculations supported the experimental results obtained. This benchmarking highlights the versatility of these organic based dual activating systems and demonstrates the substrate dependency of such carbonation reactions. Perspectives to improve the efficiency of the process would be to recycle these activating systems which are currently used in stoichiometric amounts. To this aim, polymer-supported organic (super)bases could be an alternative way to improve the recyclability of the system.

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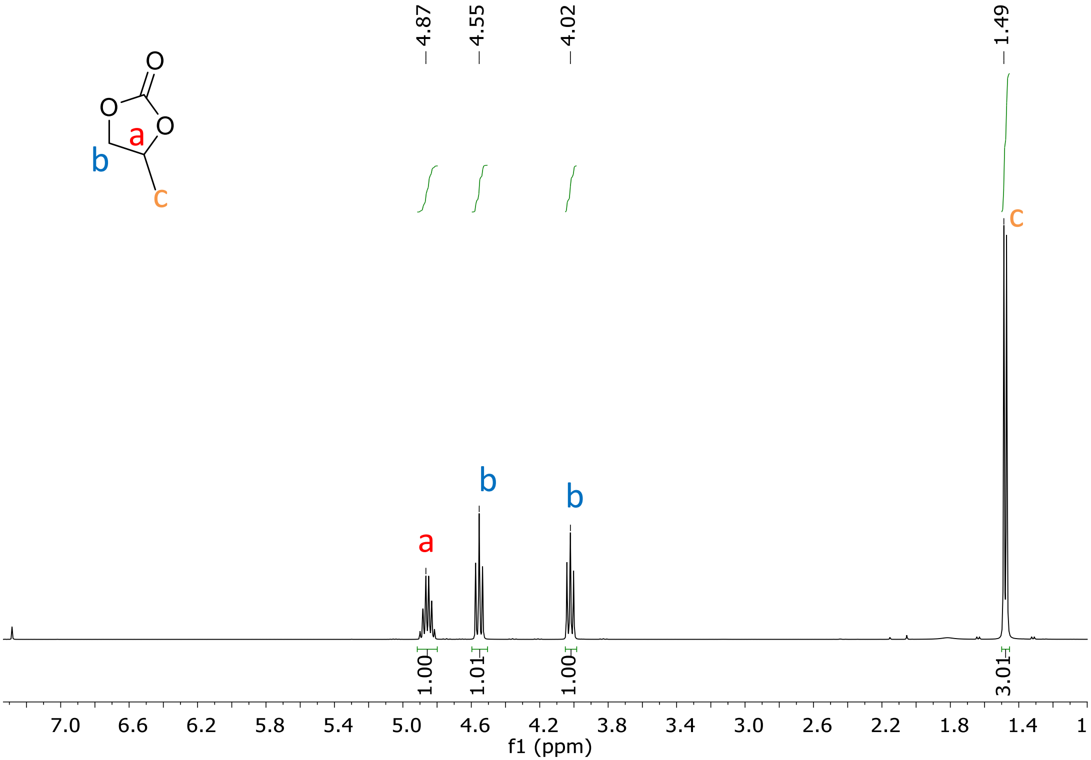
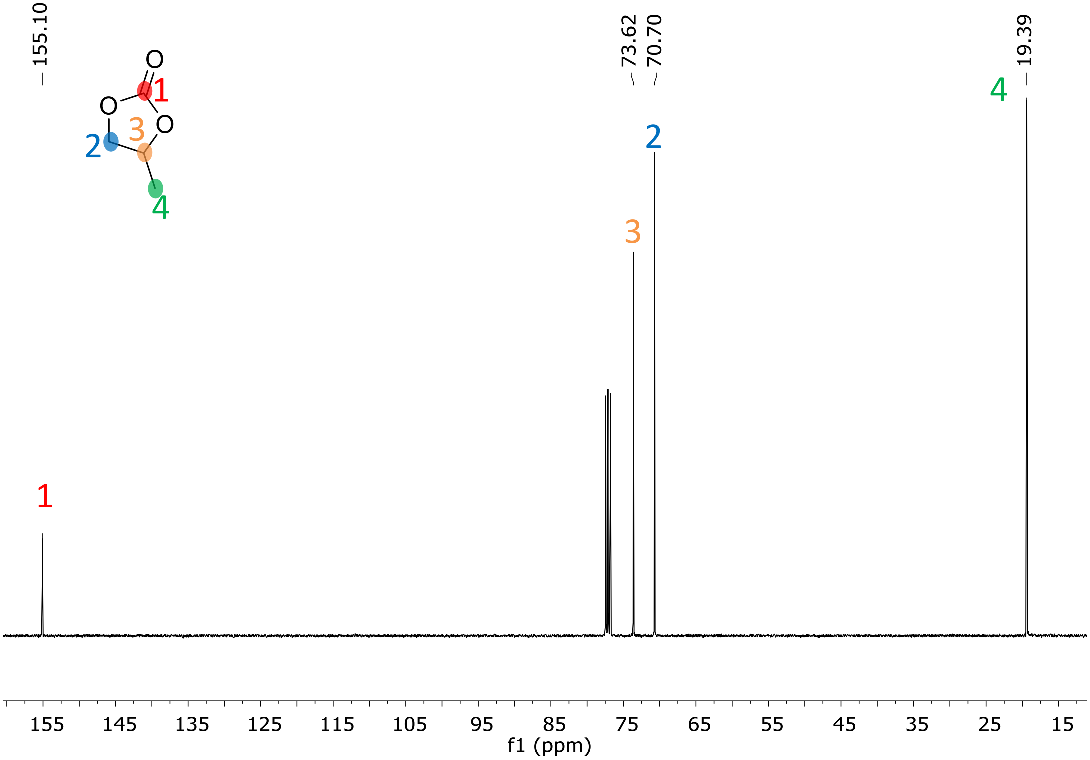
APPENDIX: Characterization of organic carbonates

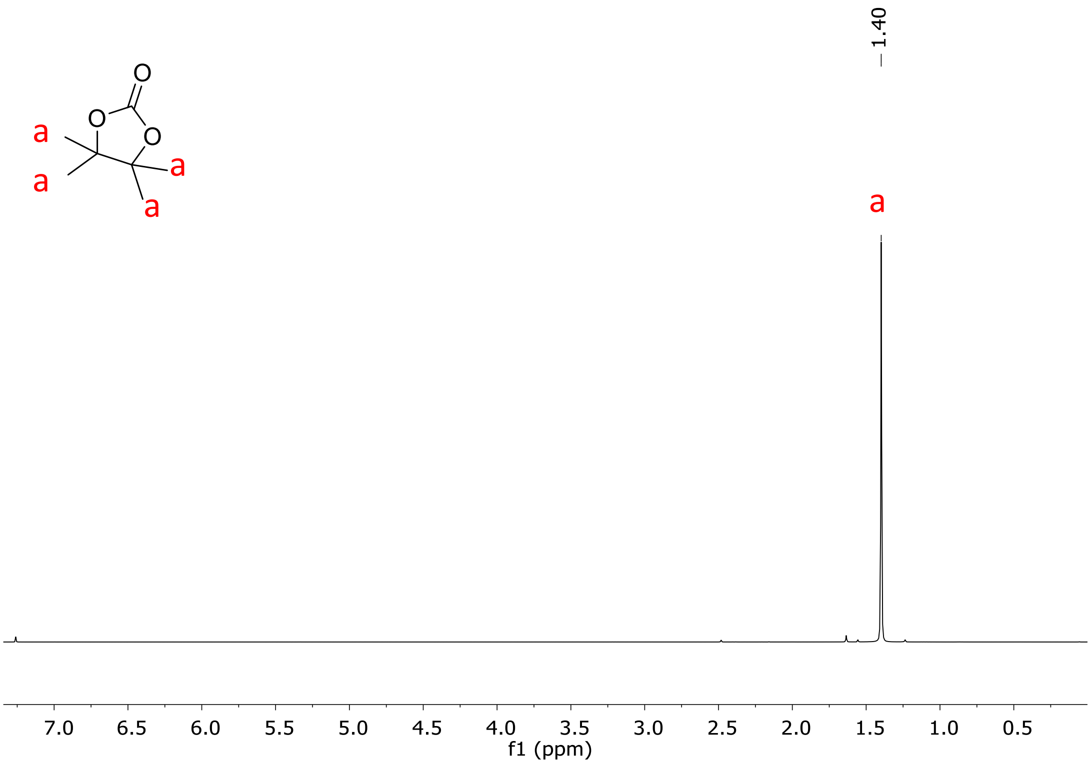
4-Methyl-1,3-dioxolan-2-one : The product was isolated as a colourless oil, 2.136 g (isolated yield 55 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.82-4.90 (m, 1 H), 4.55 (dd, *J* = 7.8 Hz, *J* = 8.3 Hz, 1 H), 4.02 (dd, *J* = 7.4 Hz, *J* = 8.3 Hz, 1 H), 1.49 (d, *J* = 6.2 Hz, 3 H).

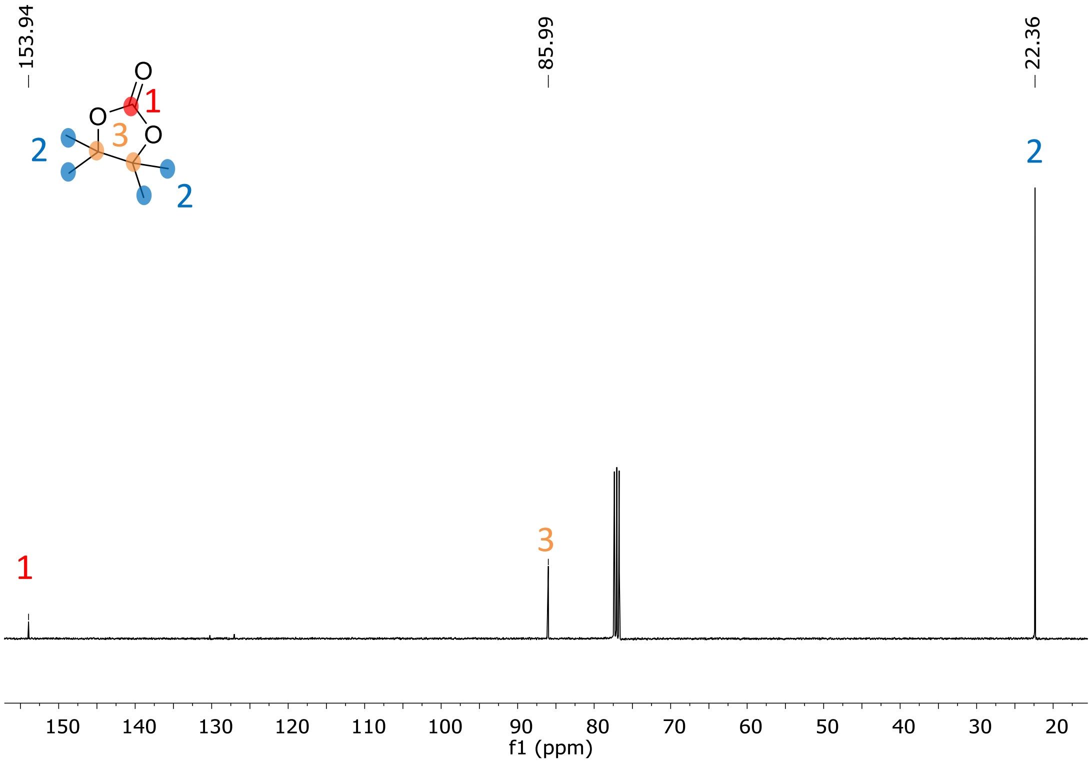
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 155.0, 73. 5, 70.6, 19.2





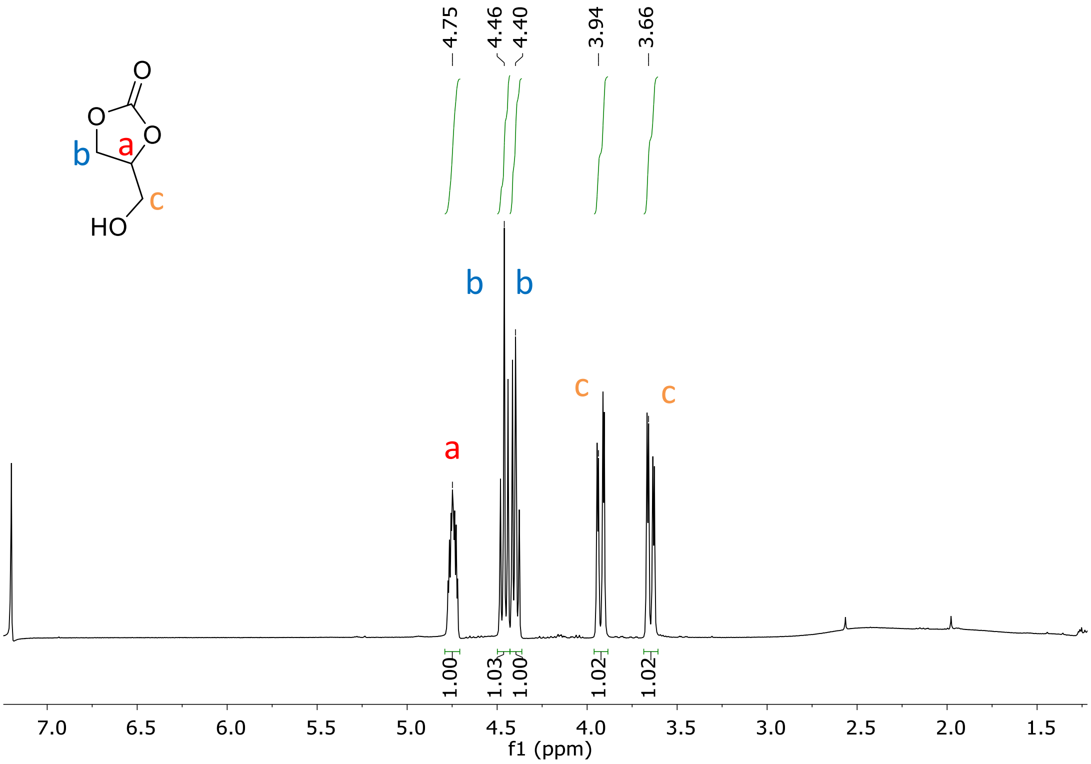
4,4,5,5-Tetramethyl-1,3-Dioxolan-2-one : The product was isolated as a white solid, 1.2976 g (isolated yield 50 %). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 1.40 (s, 12 H).
^{13}C NMR (400 MHz, CDCl3) δ (ppm): 153.9, 88.99, 22.36

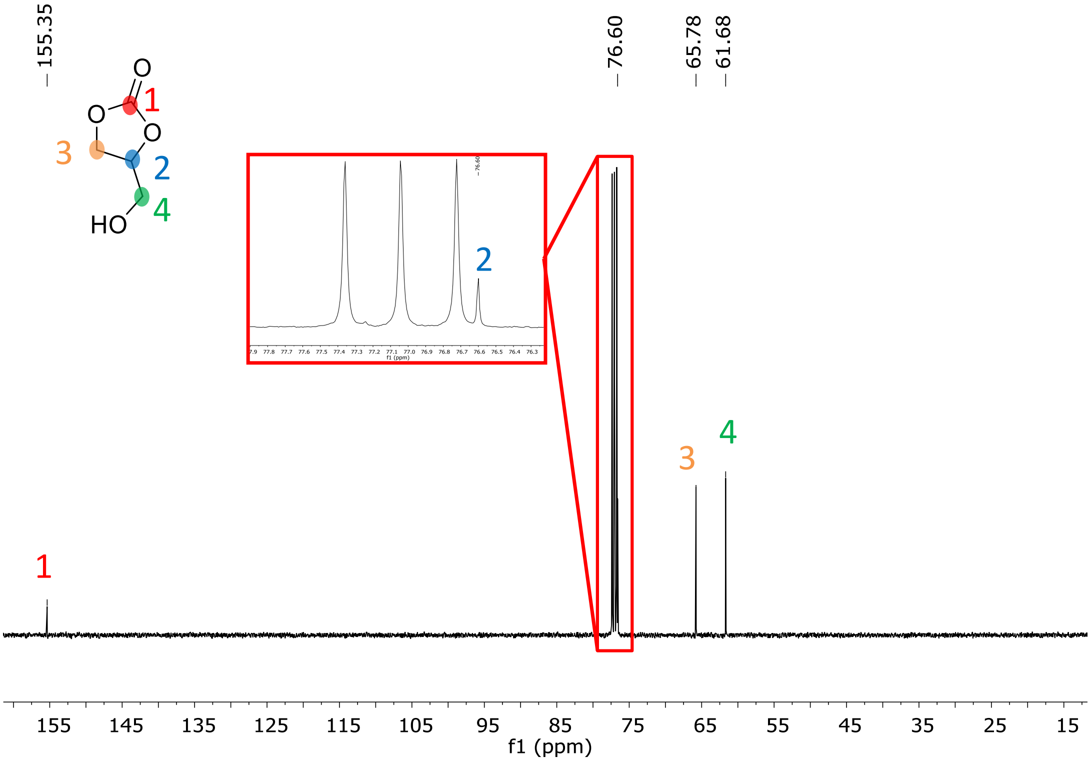




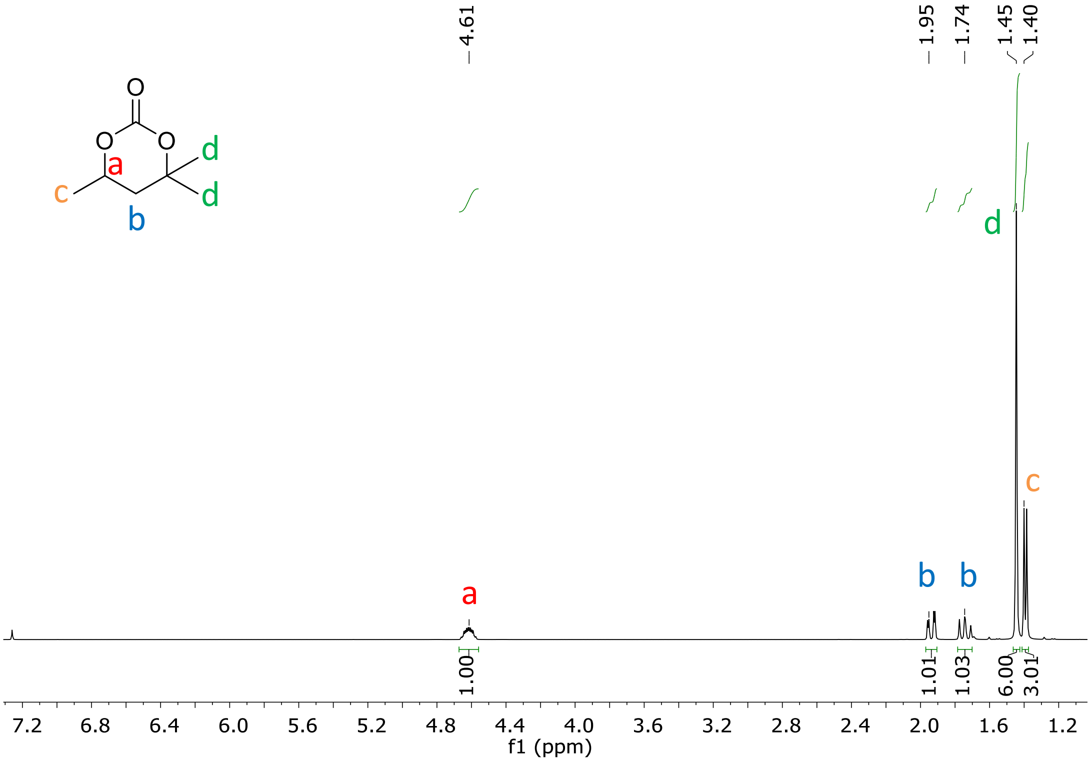
4-(Hydroxymethyl)-1,3-Dioxolan-2-one : The product was isolated as a colourless oil, 0.215 g (isolated yield 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.75 (m, 1 H), 4.46 (dd, *J* = 8.30 Hz, *J* = 8.46 Hz, 1 H); 4.40 (dd, *J* = 6.74 Hz, *J* = 8.23 Hz, 1 H); 3.94 (dd, *J* = 2.99 Hz, *J* = 9.91 Hz, 1 H); 3.66 (dd, *J* = 3.14 Hz, *J* = 9.38 Hz, 1 H).

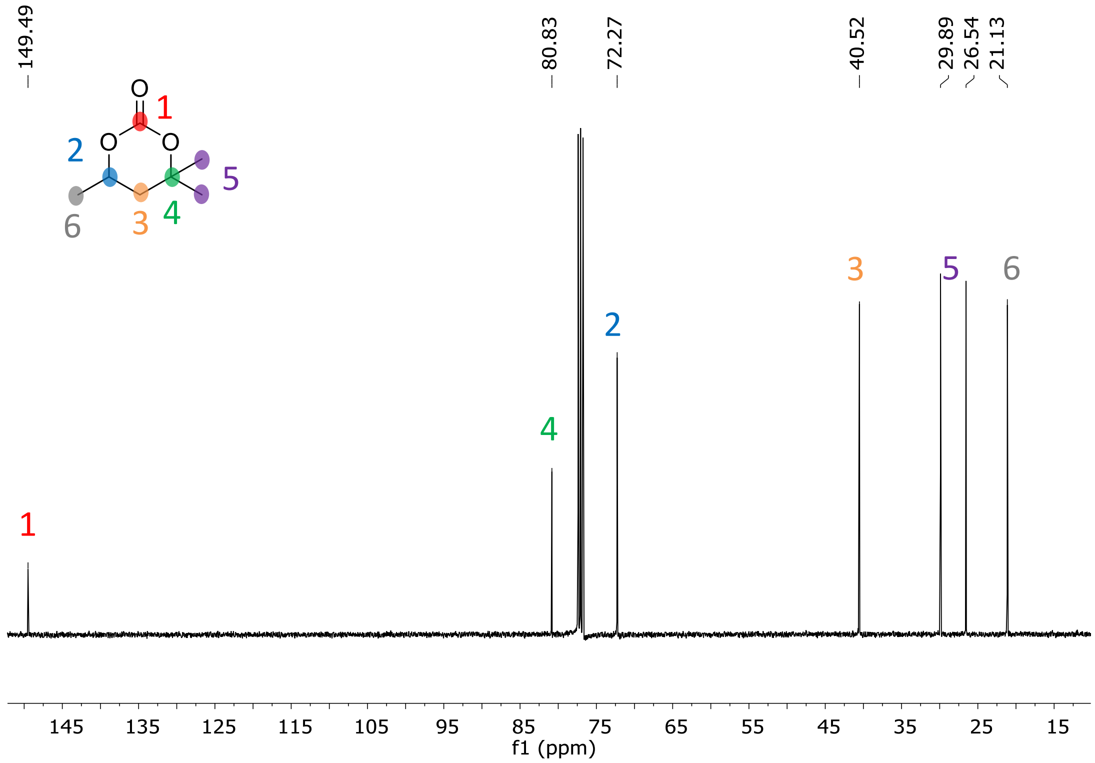
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 155.3, 76.6, 65.8, 61.7



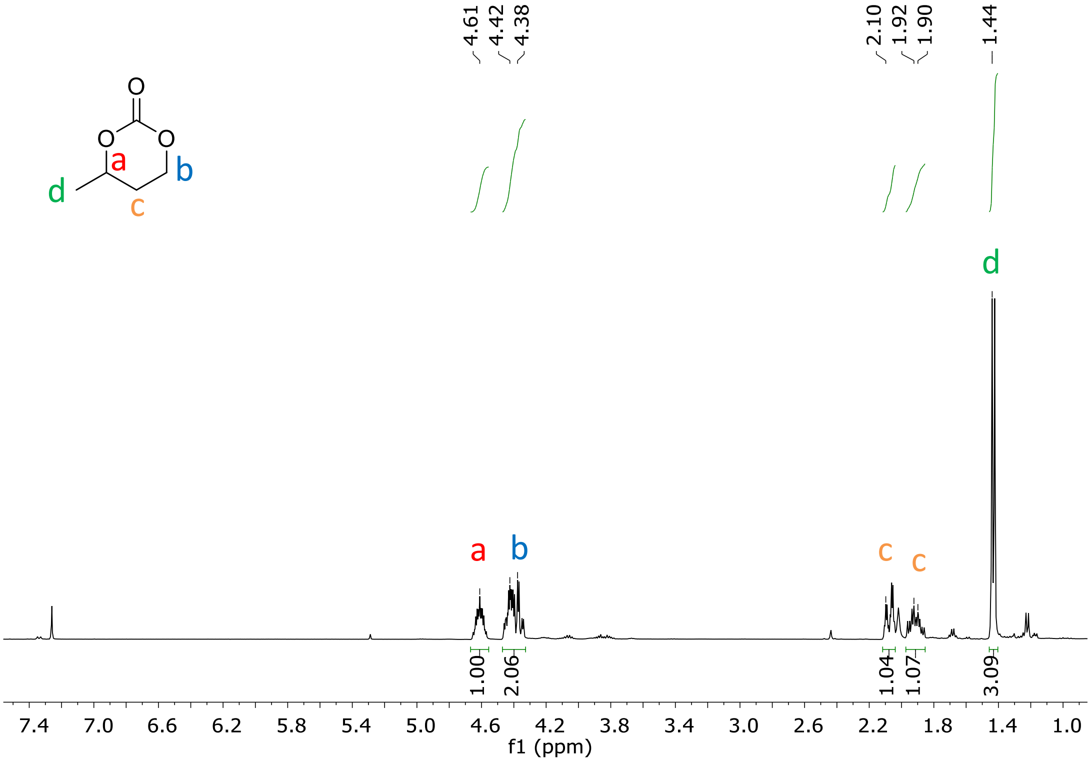


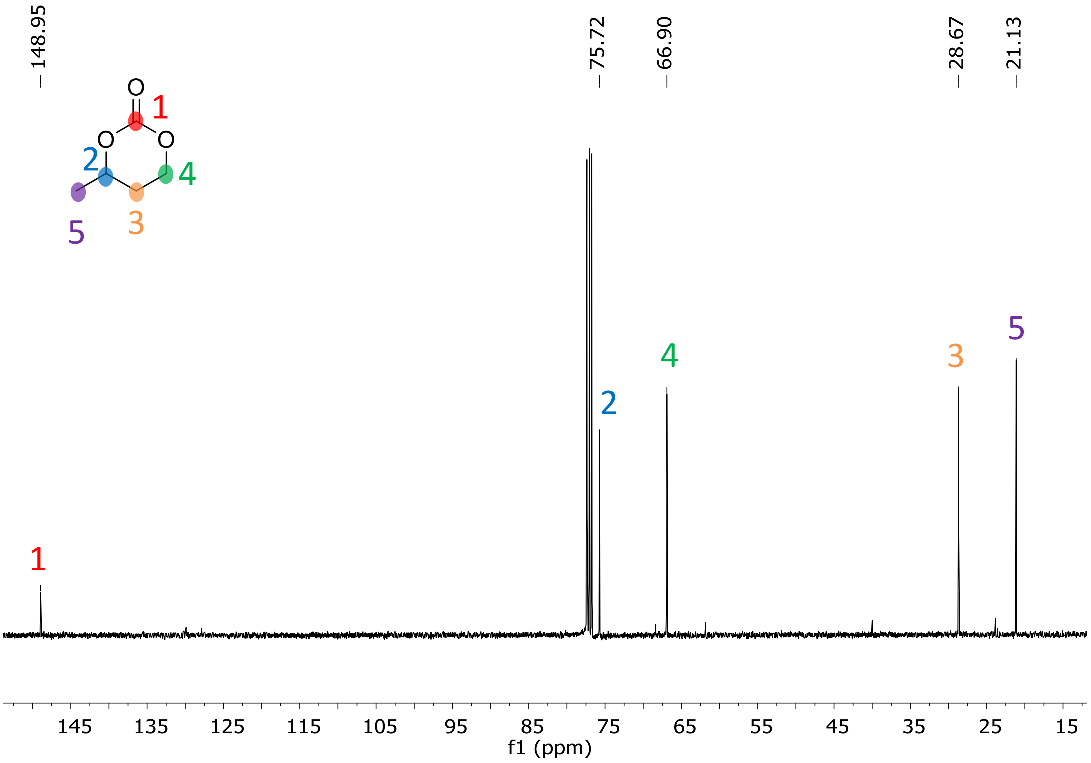
4,4,6-Trimethyl-1,3-Dioxan-2-one : The product was isolated as a white solid, 0.850 g (isolated yield 59 %). ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.63 (m, 1 H), 1.95 (dd, *J* =3.0 Hz, *J* = 11.1 Hz, 1 H); 1.74 (dd, *J* = 12.2 Hz, *J* = 13.8 Hz, 2 H); 1.45 (s, 6H); 1.40 (d, *J* = 6.2 Hz, 3 H).
^{13}C NMR (CDCl3, 100 MHz) δ (ppm): 149.5, 80.9, 72.3, 40.5, 29.9, 26.5, 21.1.





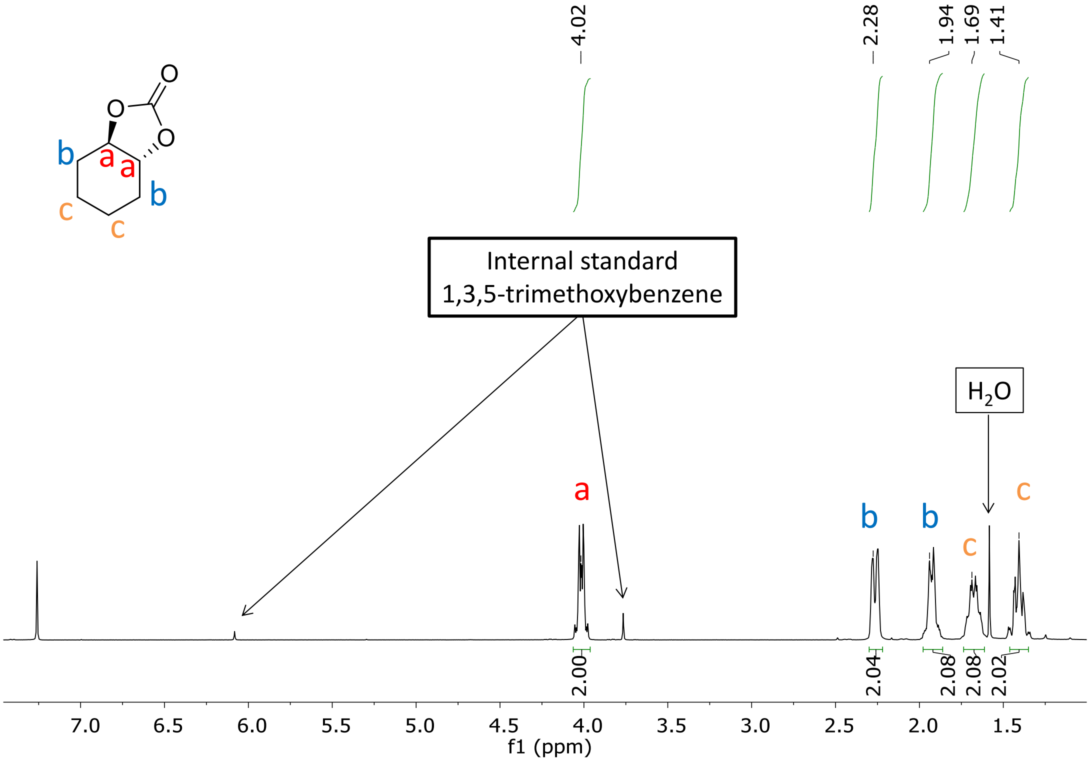
4-Methyl-[1,3]-dioxan-2-one : The product was isolated as a colourless oil, 0.452 g (isolated yield 39 %). ^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.57-4.65 (m, 1 H), 4.34-4.46 (m, 2 H), 2.04-2.11 (m, 1 H), 1.86-1.96 (m, 1 H), 1.44 (d, J = 6.3, 3 H.
^{13}C NMR (CDCl$_3$, 400 MHz) δ (ppm): 148.9, 75.7, 66.9, 28.7, 21.1

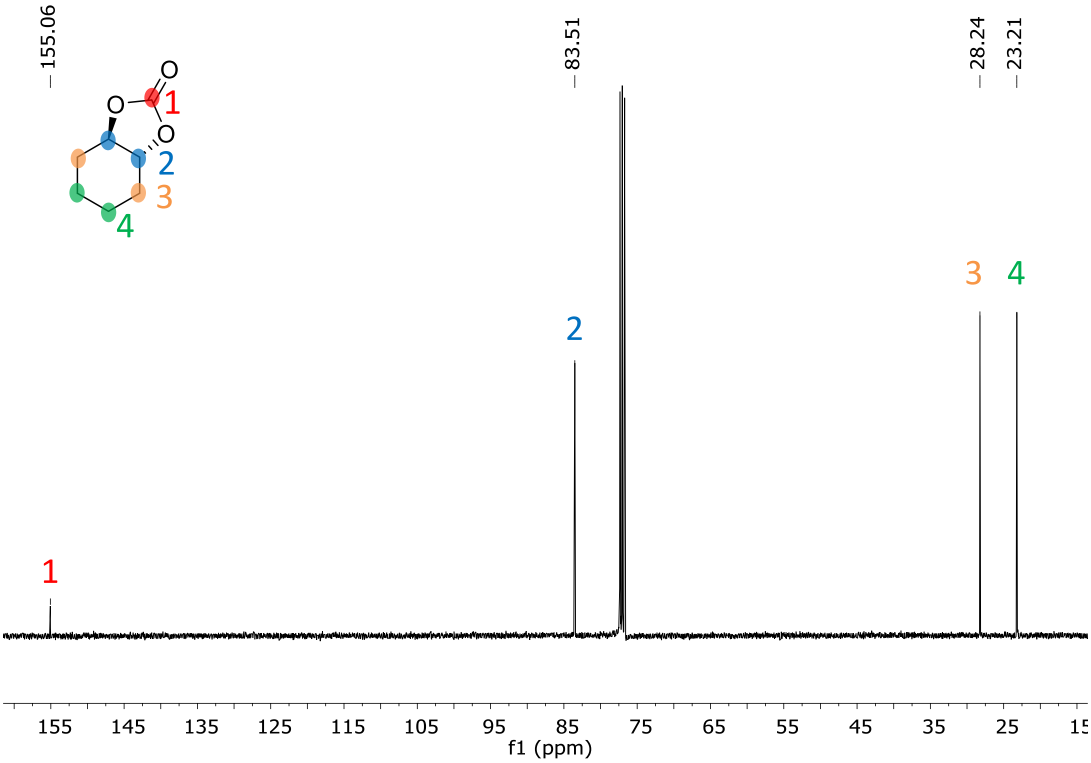




Hexahydro-,(3aR,7aR)-1,3-benzodioxol-2-one : The product was isolated as a white solid, 0.255 g (isolated yield 60 %). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 3.98-4.05 (m, 2 H), 2.23-2.30 (m, 2 H), 1.88-1.98 (m, 2 H), 1.63-1.73 (m, 2 H), 1.37-1.44 (m, 2 H).

13C NMR (400 MHz, CDCl3) δ (ppm): 155.0, 83.5, 28.2, 23.2





Chapter III:

Investigations on the direct copolymerization of Isosorbide and CO_2 using TEA/TsCl as dual organic system for the obtention of poly(isosorbide carbonate)

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I) Introduction

Isosorbide (ISB) is a bio-based diol derived from starch that exhibits a bicylic structure consisting in two *cis*-fused tetrahydrofuran rings (dianhydrohexitol)[1]. The specific chirality of this molecule renders both alcohols functions non-equivalent, as one alcohol moiety creates an intramolecular H-bonding ("endo" alcohol) whereas the other one does not ("exo" alcohol), as presented in Figure 1. Thanks to its bicyclic rigid structure, polycarbonates constructed with ISB as repeating unit are believed to display similar thermo-mechanical properties as aromatic polycarbonates and could potentially replace the use of toxic BPA for huge market applications[2]. As presented in chapter 1 (see section III-3-a-ii)), ISB has recently been used as a monomer in classical melt-polycondensation processes with the use of DMC or DPC as carbonylating agents. Extensive research on different catalytic systems, including metal salts[3], metal alkoxides [4,5], inorganic carbonates [6], ionic liquids [7-14], organic bases[15] and others[2,16-18] enabled the facile construction of defects-free PCs derived from isosorbide with M_n in the range of 14,000 to 55,000 g/mol. However, to the best of our knowledge, no direct coupling between ISB and CO_2 has been reported yet. Combining one step/one pot approach, i.e direct copolymerization of diols and CO_2, with the use of bio-based rigid substrate, e.g ISB, to afford non-aliphatic polycarbonates is of huge interest in terms of sustainability.

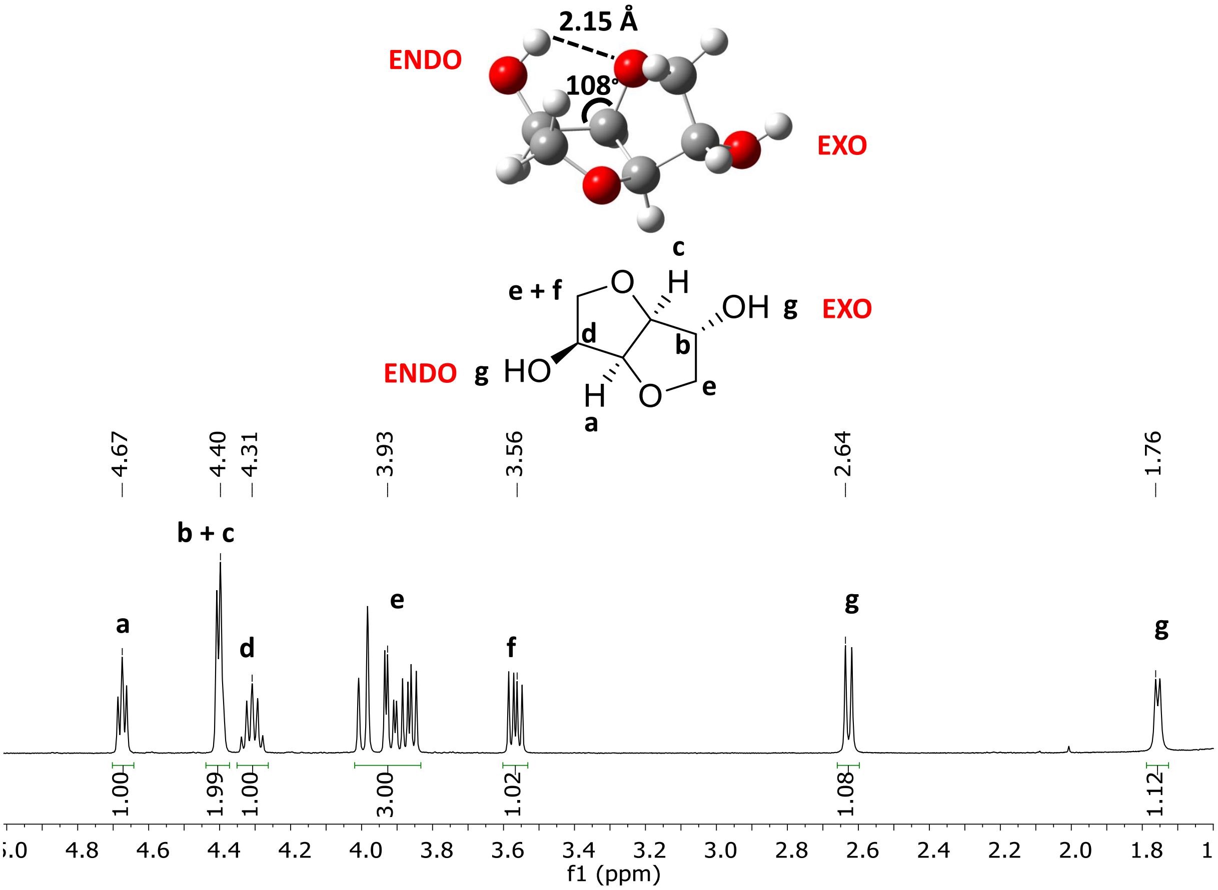
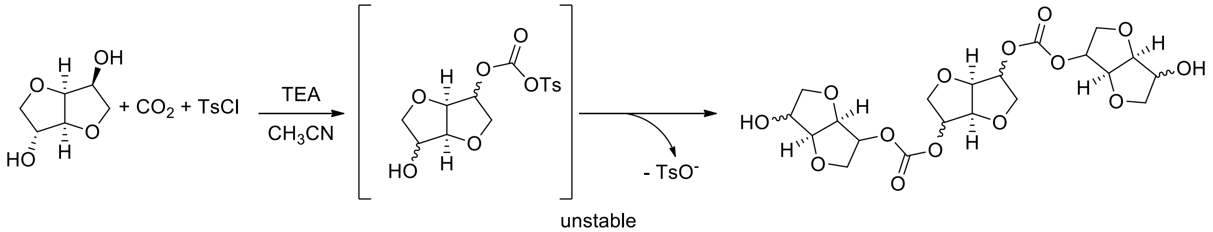


Figure 1: Molecular modelling and ^1H NMR spectrum of ISB which alcohol functions are non-equivalent due to intramolecular H-bonding.

As seen in chapter 2, diols with larger spacers than 3 carbon units are not prone to cyclisation when subjected to CO_2 pressure, but preferentially undergo double alkylation to afford bifunctional acyclic carbonates when specific DBU/Alkyl halide dual activating system is used. However, for the other dual activating system previously described, i.e TEA/TsCl, no stable double carbonated RCO_3Ts species could be isolated. Taking advantage of the high reactivity of this RCO_3Ts adduct, one can drive the formation of oligomers via transcarbonation with another diol if the chemical function ratio 1:1 is respected (one alcohol moiety for one RCO_3Ts moiety) by means of step-growth polymerization processes (see Scheme 1). The following results describe our attempts for the challenging direct copolymerization of ISB with CO_2 using one step/one pot approach with TEA/TsCl dual activating system.



Scheme 1: Synthetic strategy for the direct coupling of ISB and CO_2 using the TEA/TsCl dual activating system

II) Materials and methods

II-1) Material

Isosorbide (ISB, 95 %, Flurochem), Isomannide (ISM, 95 %, Fluorochem), Tosyl Chloride (TsCl, 99 %, Fluka), Triethylamine (TEA, 99 %, Alfa Aesar), N,N-Diisopropylethylamine (DIPEA, 99 %, Sigma Aldrich), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 99 %, TCI), Lithium Chloride (LiCl, 99 %, Sigma Aldrich), CO_2 (N27, Air Liquid), Acetonitrile (CH_3CN, Fisher) and Dimethyl formamide (DMF, Fisher) were all used as received and without further purification.

II-2) Methods

General procedure for kinetic studies:

The reactions were monitored *in-situ* by IR spectroscopy using a stainless steel reactor (80 mL) suitable for high pressure measurements (up to 400 bar) and high temperature (up to 100 °C) coupled with a FTMIR spectrometer from Bruker, equipped with an air-cooled globar source (12 V), a KBr beam splitter, a mechanical rocksolid interferometer, permanently aligned, a diamond ATR fiber probe IN350-T (Ø 6 mm), and a liquid nitrogen-cooled mercury cadmium telluride (MCT). Single beam spectra recorded in the spectral range (670−3500 cm−1) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 32 accumulated interferograms until the end of the reaction time. The reactor is equipped with a heating mantle, mechanical stirrer, manometer and gas inlets so that the reaction can be performed under controlled stirring, temperature and CO_2-pressure.

Diol (60 mmol) and TsCl (60 mmol) were loaded as solid powders in the clean dry stainless steel reactor equipped with the ATR probe. Acetonitrile (35 mL) was added to solubilize both solids at 70 °C. TEA (120 mmol) was then added to the mixture and the reactor was sealed so that it could be put under pressure. To best avoid side reations due to tosylation of alcohols moiety, it is worth noting that fast pressurization of the system once the base is added is preferable. First spectrum of ATR-IR kinetic monitoring was recorded before CO_2-pressurization, then every 25 sec.

General procedure for batch reactions:

Diol (6 mmol) and TsCl (6 mmol) were loaded in a clean dry stainless steel reactor equipped with a manometer and two gas inlet for CO_2 (de)pressurization. Acetonitrile (3.5 mL) was added to solubilize both solids. TEA (12 mmol) was then added to the mixture and the reactor was quickly sealed and placed in an oil bath to control the reaction temperature. Fast CO_2 pressurization was performed to best avoid side reactions (alcohol tosylation). At the end of reaction time, a mixture of solid salts and liquid solution was recovered and analysed by ATR-IR spectroscopy, ^{1}H NMR spectroscopy and SEC without further purification.

Nuclear magnetic resonance spectroscopy (NMR)

^{1}H and ^{13}C NMR spectra were recorded at 298 K with a Bruker advance 400 spectrometer operating at 400 MHz, on the Fourier transform mode. All NMR spectra were phased and baseline-corrected. The samples were prepared by dissolving 15-20 mg of product in 0.7 ml of a deuterated solvent ($CDCl_3$) and were calibrated with the 7.26ppm residual signal of $CDCl_3$.

Size-exclusion chromatography (SEC)

Number-average molecular weight (Mn) and molecular weight of peaks (Mp) of the different dimers, trimers and oligomers that could be separated were determined by size exclusion chromatography (SEC) in dimethylformamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate: 1 mL/min) with a Waters chromatograph equipped with two columns dedicated to the analysis of low molar mass polymers (PSS gram analytical 100 Å, separation range 300−60000 Da) and a precolumn (100 Å), a dual λ absorbance detector (Waters 2487), and a refractive index detector (Waters 2414). A previously established PS calibration curve was used.

Density Functional Theory (DFT) computational details

Preliminary calculations of equilibrium structures were performed using a semi-empirical model (AM1-D3H4) to determine the most stable conformations. These semi-empirical calculations were performed using the AMPAC software. The CHAIN algorithm was used for locating intermediates and transition states along the reaction path. The lowest energy structures obtained at the AM1-D3H4 level were further investigated using the Density Functional Theory method (DFT) implemented in the Gaussian 16 package. DFT calculations of geometries, energies, and vibrational frequencies reported in this article were carried out with the M06-2X functional using the 6-311G(d,p) basis set. All frequencies of each structure have also been calculated to verify the presence of a single imaginary frequency for transition states and the absence of imaginary frequency for ground states. The intrinsic reaction coordinate (IRC) method has been used to verify that the obtained transition states were effectively connected to the desired minima. For all activating systems, a wide range of possible configurations and interactions have been modelled and the more stable of them are reported in this work. To consider entropic effects, the energies mentioned in this study correspond to the Gibbs free energy (ΔG).

Alcohol conversion and selectivity toward carbonate linkages or tosylated alcohols

All integrations (int.) were calculated on the crude mixture.

- ISB : Peaks labelling are referred to Fig. 3
  - Int. for Carbonate linkages: A = $(\int Peak\ \boldsymbol{o})/2$
  - Int. for Tosylated alcohols: B = $(\int Peak\ \boldsymbol{n})/2 - A$
  - Int. for Non-reacted alcohols: C = $(\int Peak\ \boldsymbol{h} + \int Peak\ \boldsymbol{g})/2 - B$
  - Alcohol conversion: D = $1 - \frac{C}{A+B+C}$
  - Carbonate linkages selectivity: E = $\frac{A}{A+B}$
  - Tosylated alcohols selectivity: F = $\frac{B}{A+B}$
  - Endo/exo ratio: G = $\frac{\int Peak\ \boldsymbol{j}}{\int Peak\ \boldsymbol{l} - \int Peak\ \boldsymbol{j}}$

Equation 1: Conversion calculations for reactions involving ISB based on NMR peak attribution of Fig. 3.

- ISM : Peaks labelling are referred to Fig. 14
  - Int. for Carbonate linakges: A = $\int Peak\ \boldsymbol{j}$
  - Int. for Tosylated alcohols: B = $2 * \int Peak\ \boldsymbol{n}$
  - Int. for Non-reacted alcohols: C = $\int Peak\ \boldsymbol{i}$
  - Alcohol conversion: D = $1 - \frac{C}{A+B+C}$
  - Carbonate linkages selectivity: E = $\frac{A}{A+B}$
  - Tosylated alcohols selectivity: F = $\frac{B}{A+B}$

Equation 2: Conversion calculations for reactions involving ISM based on NMR peak attribution of Fig. 14.

III) Results and discussion

III-1) Preliminary investigations of ISB copolymerization with CO_2

The copolymerization between ISB (1 eq) and CO_2 using TEA as a base (2 eq) and TsCl (1 eq) as co-reagent was first achieved with *in-situ* ATR-IR kinetic monitoring (Figure 2) in acetonitrile at 70 °C under a CO_2 pressure of 1.5 MPa. Similarly to the results presented in chapter 2, absorption bands at 1230 cm^{-1} ; 1375 cm^{-1} and 1756 cm^{-1} attributed to stretching modes of TsO^- ; TsCl and the linear carbonate species respectively, were monitored over the reaction time. Concomitant decrease of TsCl species with increase of TsO^-, accompanied with slower increase of a linear carbonate were observed, indicating that a first coupling of ISB molecules via CO_2 carbonation occurs. The reaction quickly reaches equilibrium (1 h) with an absorption band value of TsCl going down to 42 % of the initial value, and rather low absorption of the linear carbonate band, so that low conversion is expected. The recovered reaction media is a mixture of undissolved salts and a liquid fraction. ^1H NMR characterization of the crude liquid product obtained after solvent evaporation is presented in Figure 3. In accordance with ATR-IR observations, carbonate linkages between ISB units could be detected with proton signal at 5.05 ppm (peak **o**) attributed to protons located on carbons in α-position of the carbonyl function. Both presences of TsCl (peaks **a** ; **b** ; **c**) and TsO^- (peaks **d** ; **e** ; **f**) species were evidenced. In addition, remaining non-reacted ISB alcohols species, either the diol itself or ISB moitey “chain-end” where only one alcohol function reacted to form a carbonate linkage (peaks **g** ; **h** ; **i** ; **j** ; **l**) were observed. Moreover, tosylated alcohols generated by side-reaction between ISB and TsCl (peaks **a** ; **b** ; **c** ; **h** ; **n** ; **p**) were identified. Analysis of the salts revealed the presence of protonated TEA in large quantities. Alcohol functions conversion into carbonate linkages or tosylated alcohols and their respective selectivity was calculated according to Equation 1 (see section II-2). In this case, 43 % conversion was achieved, with carbonate linkage selectivity of 77 % and 23 % for tosylated alcohols. GPC analysis, dedicated to low molar mass compounds, of the crude liquid fraction exhibited two distinct peaks attributed to monomer (ISB) and dimer, i.e two ISB units linked with carbonate function (Figure 4, red curve). The presence of trimers and tetramers is suggested by the rather large shape of the dimer peak. Attempts to precipitate the oligomers in methanol failed, in accordance with low molecular weights detected in GPC. The crude mixture was thus purified by dissolution in CH_2Cl_2 followed by liquid-liquid extraction using large volumes of water (3 times). The organic fraction was then dried and subjected to GPC analysis where monomers were efficiently removed (Figure 4, blue curve). Further 2D NMR characterization to confirm peak attributions in Figure 3 was performed (^1H NMR spectrum of the purified product is shown in Fig. 5). To better investigate the reactivity of ISB toward tosylation of the alcohol moieties, a control experiment in the same conditions but without the addition of CO_2 was carried out (see Fig. 6 for ^1H NMR spectrum). After 20 h of reaction, no carbonate linkages could be observed as expected, but a conversion of alcohols of 41 % into tosylated alcohols was observed in the crude mixture. As a reminder, a stoichiometric amount of TsCl and ISB was used, so that 50 % of alcohol conversion could be observed if the tosylation reaction goes to completion.

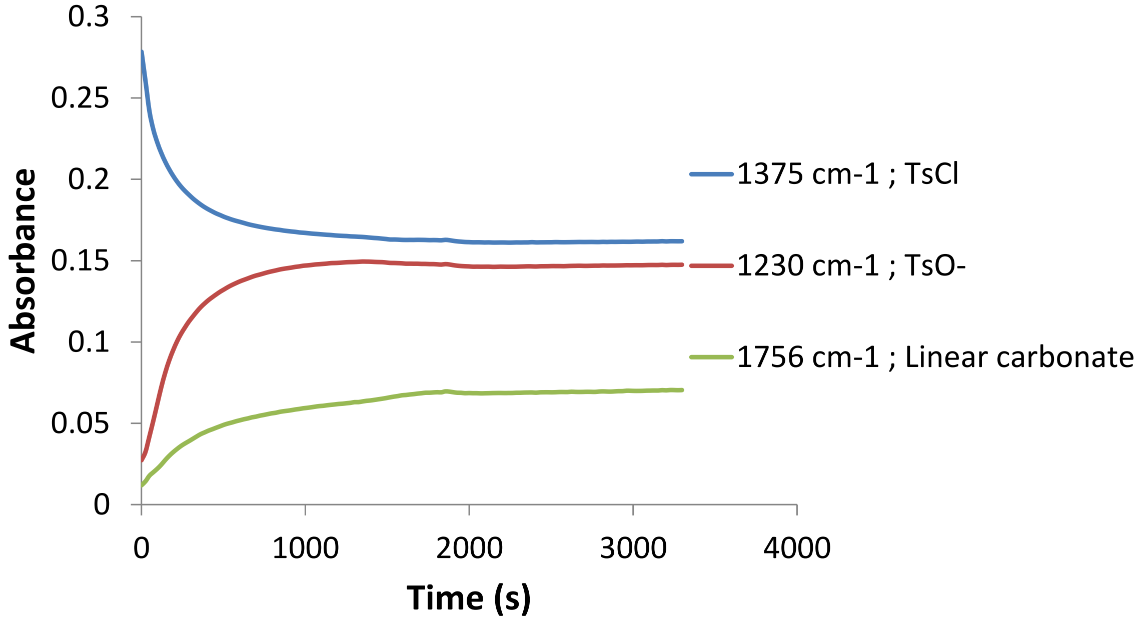


Figure 2: *In-situ* ATR-IR kinetic monitoring in standard conditions : ISB (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([ISB] = 1.2 mol/L).

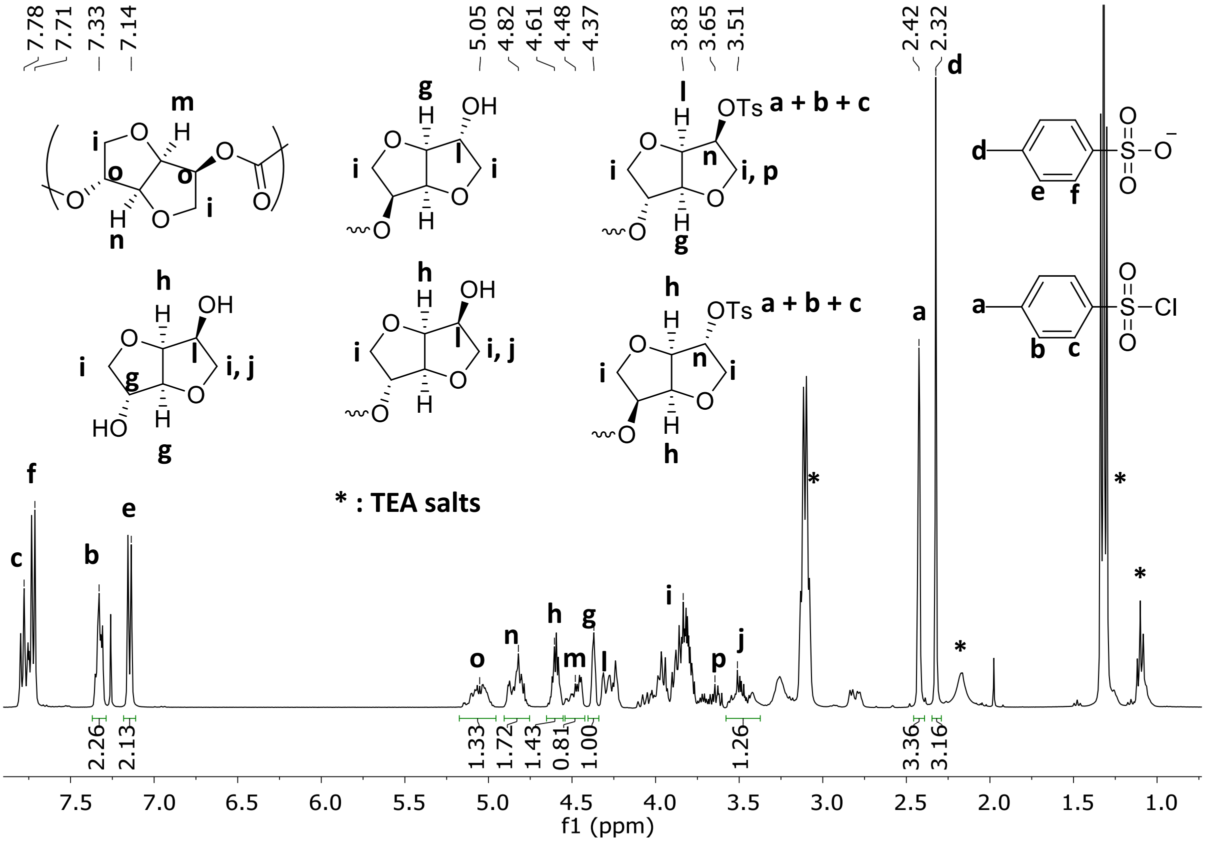


Figure 3: ^{1}H NMR spectrum of the crude liquid fraction recovered after reaction. Conditions : ISB (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([ISB] = 1.2 mol/L).

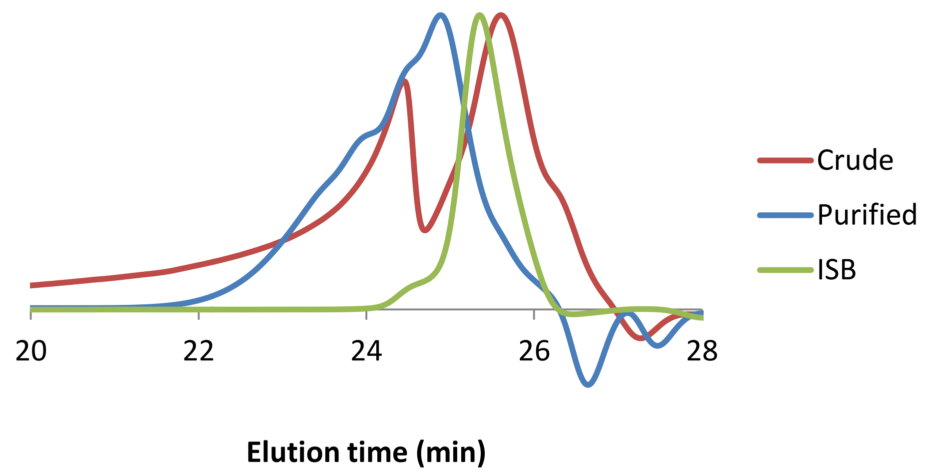


Figure 4: GPC chromatograms of crude liquid fraction, purified dimer and ISB.

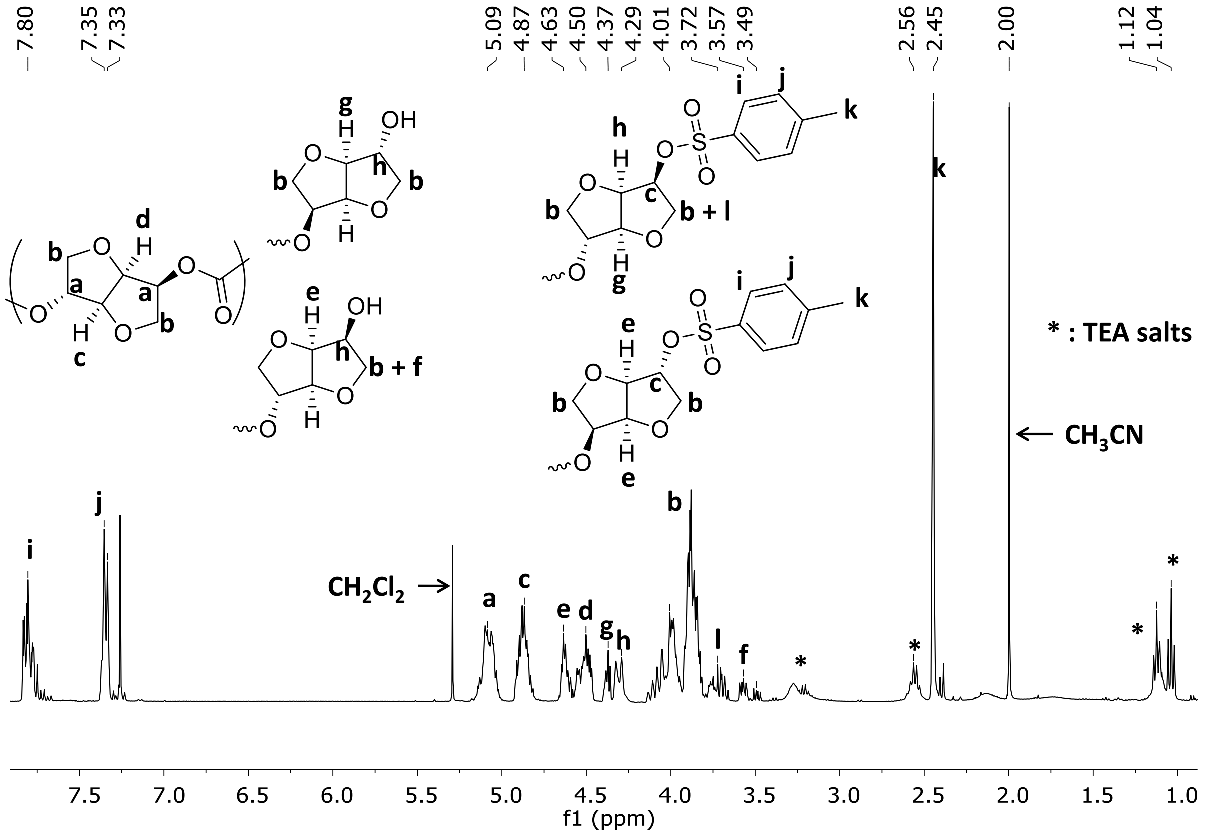


Figure 5: ^{1}H NMR spectrum of the purified product obtained after liquid-liquid extraction to remove organic salts. Conditions : ISB (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([ISB] = 1.2 mol/L).

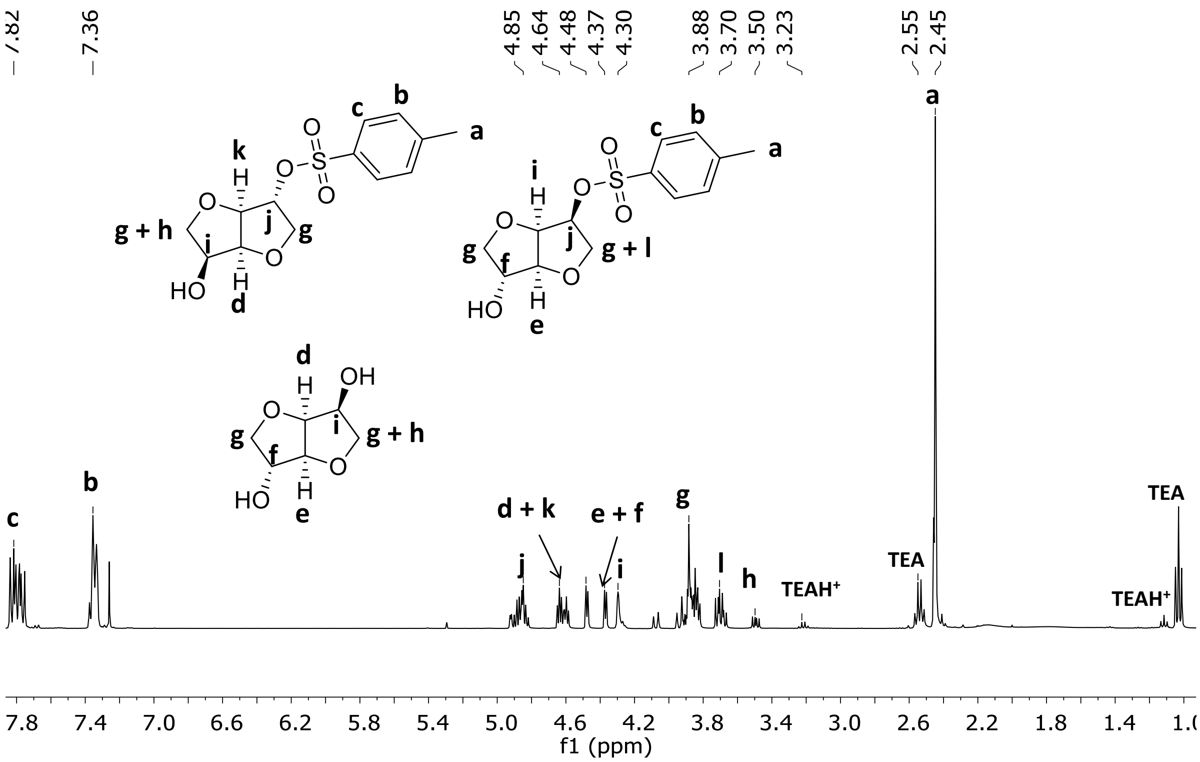


Figure 6: ^{1}H NMR spectrum of the purified control experiment without the presence of CO_2. No carbonate linkages were detected, but tosylation of the alcohol moieties occurred. ISB (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; no CO_2 ; acetonitrile ([ISB] = 1.2 mol/L).

III-2) Experimental conditions screening

In order to increase ISB conversion and to improve the molar mass of the oligomers, several experimental conditions were tested (Table 1). Temperature, pressure and concentration effects on the direct copolymerization of ISB and CO_2 were evaluated in comparison with the first experimental result obtained with standard conditions (Table 1, entry 1).

At a fixed pressure of 1.5 MPa, changes in ISB concentrations from 1.2 mol/L to 0.9 mol/L had little effect on the ISB conversion and selectivity (Table 1, entries 1-2). One would expect better conversion and selectivity toward carbonation and further transcarbonation when heating the system, as CO_2 solubility in the reaction media would be increased and disparities between “endo” and “exo” alcohols minimized. Increasing the temperature to 100 °C led to endo/exo ratio close to 1 but with lower ISB conversion (Table 1, entry 3). When T = 120 °C was applied, the selectivity toward formation of the carbonate linkages was significantly decreased to 45 % (Table 1, entry 4) which is detrimental for the desired chain extension. Surprisingly, the alcohol conversion remained low (up to 49 %) and preferentially reacted with TsCl at higher temperature. For all temperatures, no increase in the molar masses were observed, and only dimers were likely formed (see Fig. 7 for GPC chromatograms).

Table 1: Temperature, concentration, pressure, catalyst and solvent effect on the ISB and CO_2 direct copolymerization. Reaction conditions: ISB (1 eq) ; TEA (2 eq); TsCl (1 eq) ; 20 h.

Entry	P_{CO2} (MPa)	T (°C)	[ISB] mol/L	Alcohol conv (%)[a]	Carbonate linkage selectivity (%)[a]	Tosylated alcohols selectivity (%)[a]	endo /exo ratio[a]	M_n (g/mol)	Peaks in GPC (g/mol)[b]
1	1.5	70	1.2	43	77	23	0.59	830	500 ; 1100
2	1.5	70	0.9	45	76	24	0.43	/	450 ; 800
3	1.5	100	0.9	38	77	23	0.98	/	320 ; 492 ; 703
4	1.5	120	0.9	49	45	55	0.84	/	480 ; 696
5	0.1	70	1.2	32	26	74	1.21	529	365 ; 677 ; 963
6[c]	1.5	70	1.2	34	100	0	0.30	554	320 ; 687 ; 954
7[d]	1.5	70	1.2	26	90	10	0.35	619	351 ; 687 ; 954
8[e]	1.5	70	1.2	31	100	0	0.44	541	332 ; 692 ; 945
9[f]	1.5	70	1.2	34	100	0	0.21	658	354 ; 701 ; 964

Experimental conditions: ISB (1eq) ; TsCl (1eq) ; Base (2eq) ; Catalyst (0.1eq) in CH_3CN.

[a] Calculated from eq. 1

[b] Peak mass reported after GPC-LM analysis of the liquid fraction

[c] TBD was used as a catalyst (0.1 eq)

[d] TBA/PhO$^-$ was used as a catalyst (0.1 eq)

[e] LiCl was used as a catalyst (0.1 eq)

[f] DMF was used as the solvent

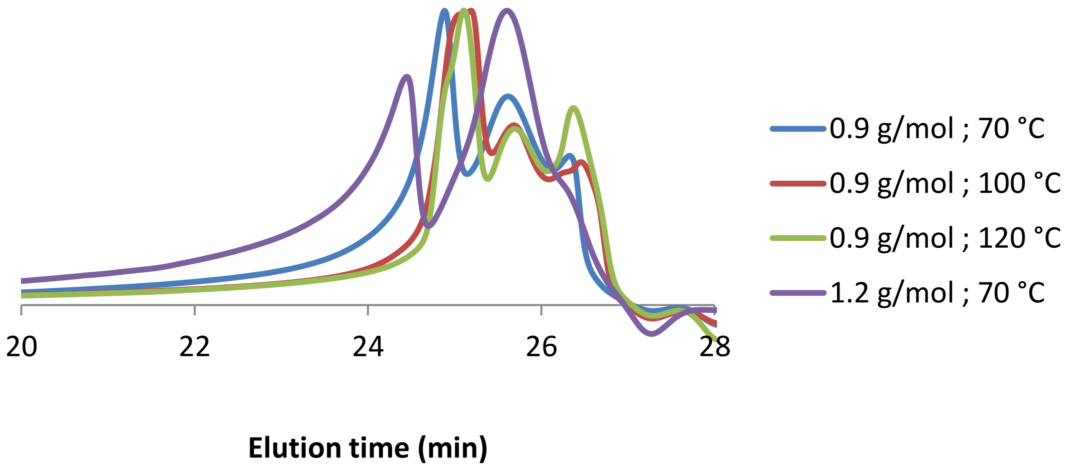


Figure 7: GPC chromatograms with different temperatures and concentrations (Table 1, entries 1-4).

As expected, decreasing the CO_2 pressure to 0.1 MPa led to a great increase of tosylated alcohols selectivity with rather low alcohol functions conversion (32 %, Table 1, entry 5). Still, dimers could be formed as displayed by the GPC chromatogram presented in Figure 8. Interestingly, a shoulder toward higher molar masses suggests the presence of trimers in small quantities.

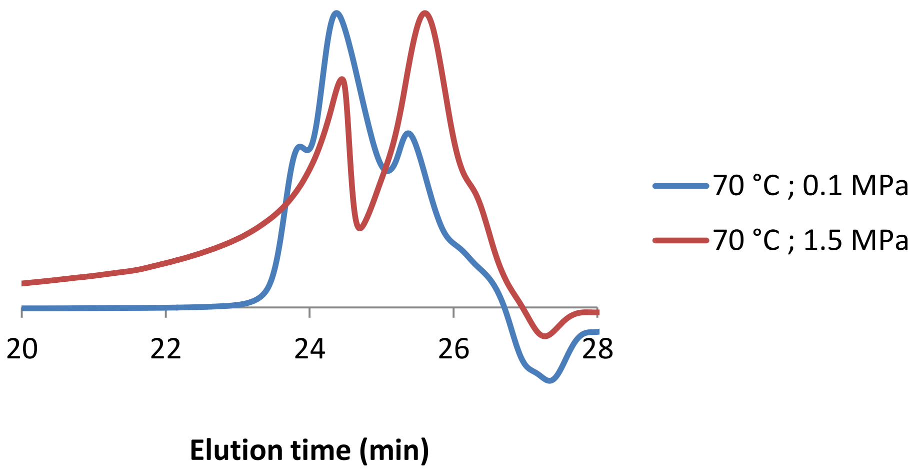


Figure 8: GPC chromatograms with different pressures (Table 1, entries 1 and 5)

To prevent the tosylation of alcohols as a side reaction that considerably limit the formation of oligocarbonates, catalysts, namely TBD, TBA/PhO$^-$ and LiCl, were added to the system to activate alcohol functions and favorize transcarbonation reactions once CO_2 has been fixed onto ISB with TEA as the base. Interestingly, carbonate linkages were exclusively formed using TBD and LiCl, and only 10 % selectivity toward alcohol tosylation was observed using TBA/PhO$^-$ (Table 1, entries 6-8). However, unexpected low conversion of alcohol functions was reported, correlated with low molar masses afforded (mainly dimers and trimers, see Fig. 9 for GPC chromatograms). These results highlight the activity of such catalysts to promote transcarbonation of ISB carbonates with ISB monomers, even though the main limitation remains in low ISB alcohols conversion.

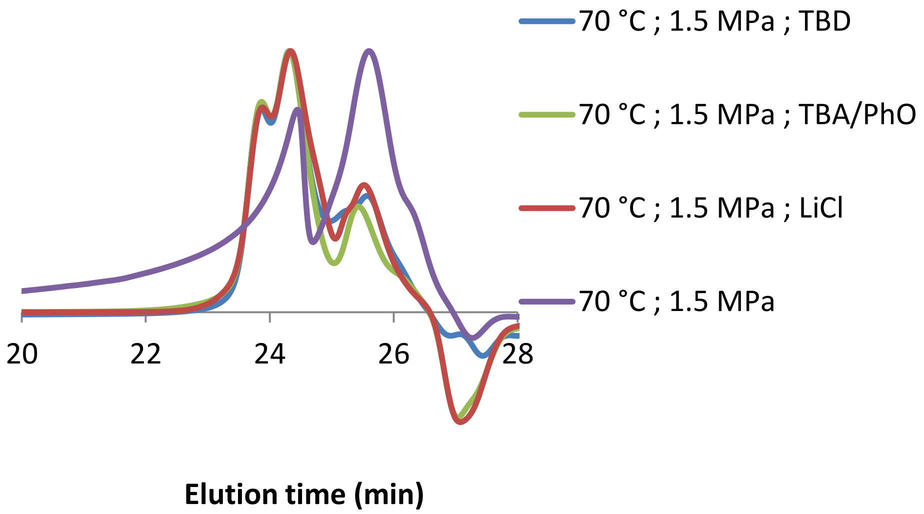


Figure 9: GPC chromatograms with different catalysts (Table 1, entries 1 & 6-8).

Changing the solvent to DMF (Table 1, entry 9) also proved its efficiency to eliminate the formation of tosylated alcohols without the need of additional catalysts. Still, low alcohol conversion of 34 % was obtained. GPC chromatogram (Fig. 10) indicates that trimers and dimers were formed in similar quantities, indicating the role of the solvent for such transcarbonation reactions.

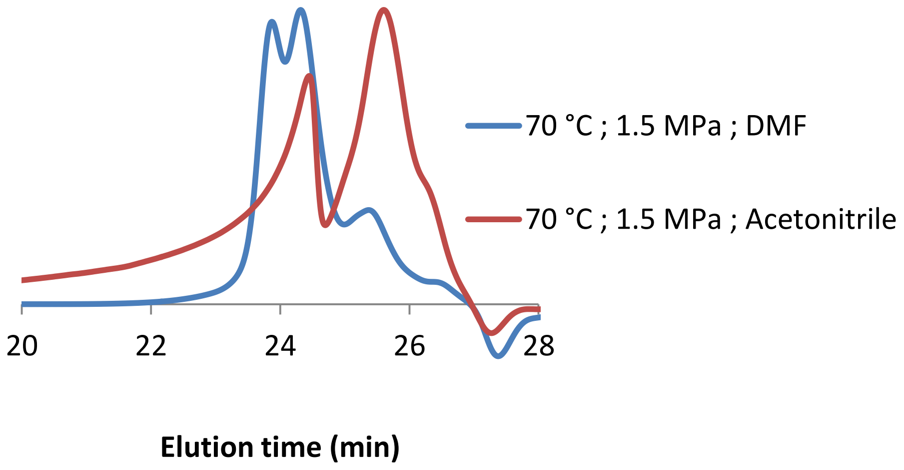
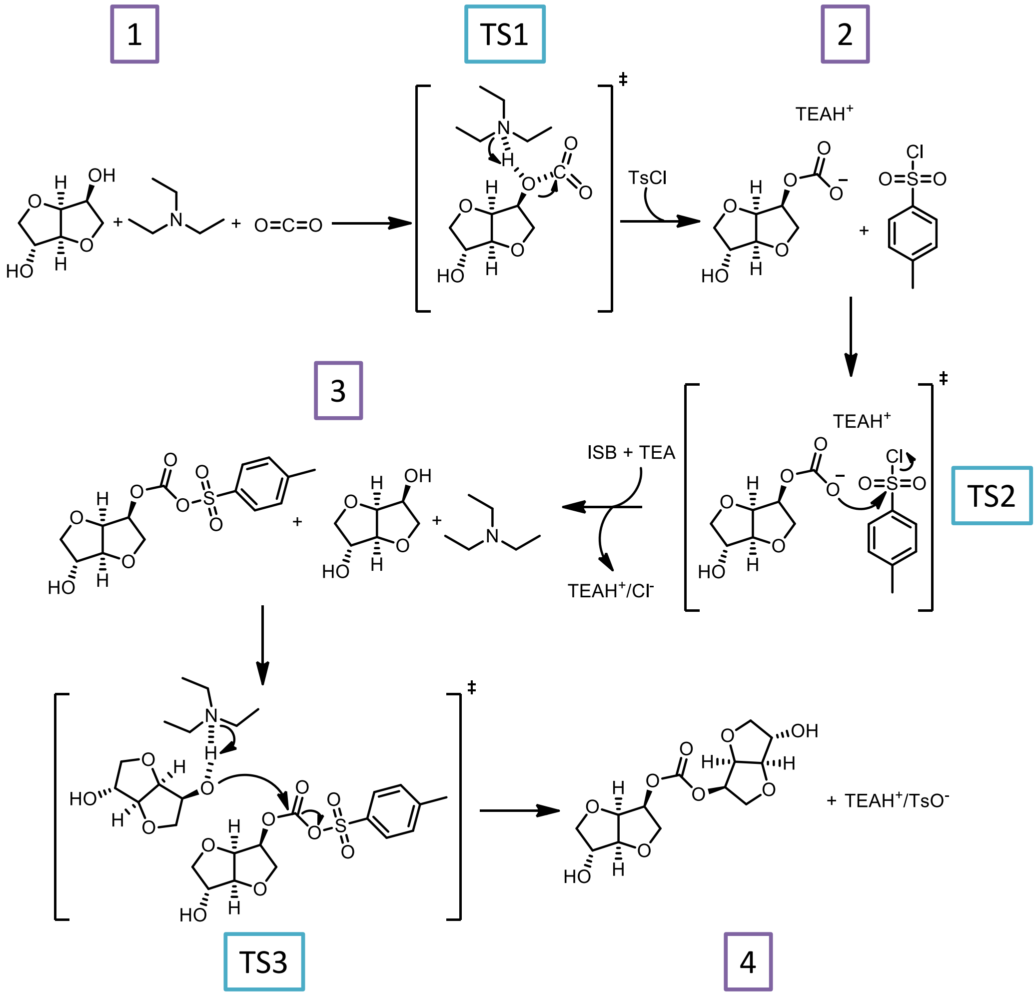


Figure 10: GPC chromatogram with different solvents (Table 1, entries 1 and 9).

For all reported cases where carbonate linkages were preferentially formed over tosylation of alcohols, endo/exo ratio values were lower than 1 (down to 0.21 when DMF was used as the solvent, Table 1 entry 9), indicating greater reactivity of the "endo" alcohol. To confirm these experimental observations, molecular modelling was performed via DFT calculations conducted at the M062X/6-311g(d,p) level. Comparison of reactivities between "endo" alcohol and "exo" alcohol were conducted as follow: a first carbonation using TEA/TsCl as the dual activating system was separatly modelled on "endo" and "exo" alcohol, followed by tosylation of the hemicarbonate anion formed, in a similar fashion as reported in chapter 2. Then, transcarbonations by an other ISB molecule were carried out in order to obtain each possible cases, e.g "endo-endo" ; "endo-exo" and "exo-exo" carbonate linkages. Scheme 2 presents all the different calculated steps with intermediates and isolated transition states (TS) in the case of an "endo-endo" carbonate linkage formation. Regarding the energetic diagram, presented in Figure 11, the "exo" alcohol displays higher activation barrier for the carbonation step (step 1 ; TS1) than the "endo" alcohol (11.6 kcal/mol vs 9.0 kcal/mol). In addition, for the transcarbonation step (step 3 ; TS3), introducing an "exo" linkage would increase the activation barrier. Indeed, formation of an "endo-endo" linkage shows a $\Delta G_{TS3}^{\ddagger}$ = 13.4 kcal/mol ; "endo-exo" a $\Delta G_{TS3}^{\ddagger}$ = 15.7 kcal/mol ; and "exo-exo" a $\Delta G_{TS3}^{\ddagger}$ =17.1 kcal/mol. Thus, one can conclude that the "endo" alcohol would preferentially react for both the carbonation and the transcarbonation step of the reaction, which is consistent with the experimental observations (endo/exo ratio below 1).



Scheme 2: Mechanism proposal for the formation of “endo-endo” carbonate linkage from ISB, CO_2 and TEA/TsCl. Energetic diagram is presented in Fig. 11.

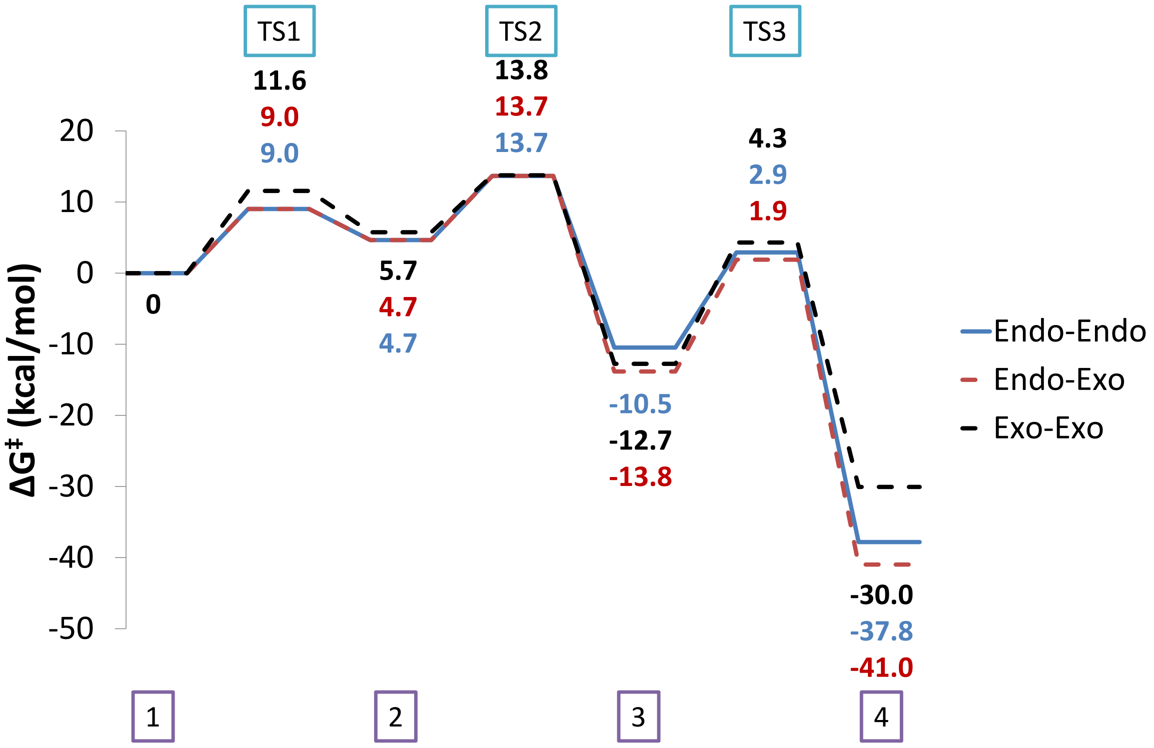


Figure 11: DFT computed pathway (M062X/6-311g(d,p)) comparison of “endo-endo” ; “endo-exo” and “exo-exo” carbonate linkages formation. Purple numbers correspond to optimized reaction intermediates shown in Scheme 2 (Van Der Waals interaction were accounted). Transision states (TS) were optimized usisng the same molecular species as in the intermediates.

III-3) Isomannide-based copolymerization with CO_2

Isomannide (ISM) is a stereoisomer of isosorbide, also obtained from starch, which presents two equivalent “endo” alcohol moieties (see Fig. 12). As previous results indicates better reactivity for the “endo” alcohol, ISM was tested as a monomer for the direct copolymerization with CO_2 using TEA/TsCl as the dual activating system with similar experimental conditions as for ISB. Effect of the addition of a catalyst was evaluated. Results are presented in Table 2 and conversions and selectivities were calculated according to Equation 2 (see section II-2). Similarly, *in-situ* ATR-IR kinetic monitoring was performed for the standard conditions of 70 °C, 1.5 MPa CO_2 pressure in acetonitrile (Table 2, entry 1). Results are presented in Figure 13, and same conclusions could be drawn: the concomittant formation of TsO^- species with consumption of TsCl, accompanied with the formation of linear carbonate species. ^{1}H NMR spectra of the crude product is presented in Figure 14, where peaks of ISM, oligomers, and tosylated ISM were identified. Compared to ISB, better alcohol conversion was obtained (66 %) but with preferential selectivity toward tosylation of the alcohols (68 % selectivity). This result highlights the higher reactivity of “endo” alcohols activated by the TEA/TsCl system but with poor control of the selectivity toward formation of carbonate linkages. Comparison of kinetic monitoring of the linear carbonate absorption band (1750 cm^{-1}), presented in Figure 15, confirms the presence of more carbonate moieties in the case of ISB with higher absorbance value when the same experimental conditions were applied.

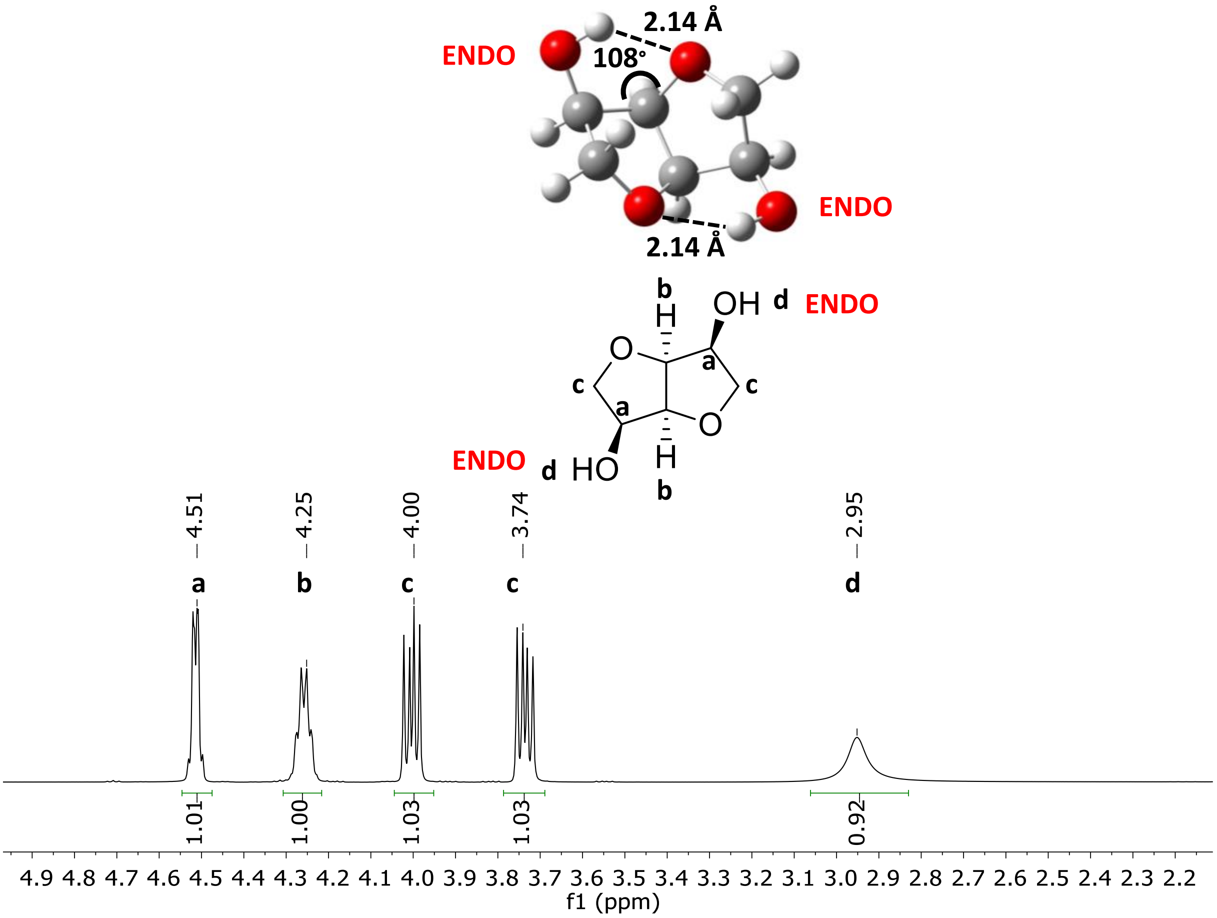


Figure 12: Molecular modelling and ^{1}H NMR spectrum of ISM which alcohol functions are equivalent, both involving intramolecular H-bonding.

Table 2: Catalyst effect on the ISM and CO_2 direct copolymerization. Reaction conditions: ISM (1 eq) ; TEA (2 eq); TsCl (1 eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([ISM] = 1.2 mol/L) ; 20 h.

Entry	Alcohol conv (%)[a]	Carbonate linkage selectivity (%)[a]	Tosylated alcohols selectivity (%)[a]	M_n (g/mol)	Peaks in GPC (g/mol)[b]
1	66	32	68	590	296 ; 683 ; 954
2[c]	65	56	44	533	315 ; 698 ; 945
3[d]	40	76	24	520	327 ; 693 ; 945
4[e]	40	45	55	524	335 ; 695 ; 948

Experimental conditions: ISB (1eq) ; TsCl (1eq) ; Base (2eq) ; Catalyst (0.1eq) in CH_3CN.

[a] Calculated from eq. 2

[b] Peak mass reported after GPC-LM analysis of the liquid fraction

[c] TBD was used as a catalyst (0.1 eq)

[d] TBA/PhO^- was used as a catalyst (0.1 eq)

[e] LiCl was used as a catalyst (0.1 eq)

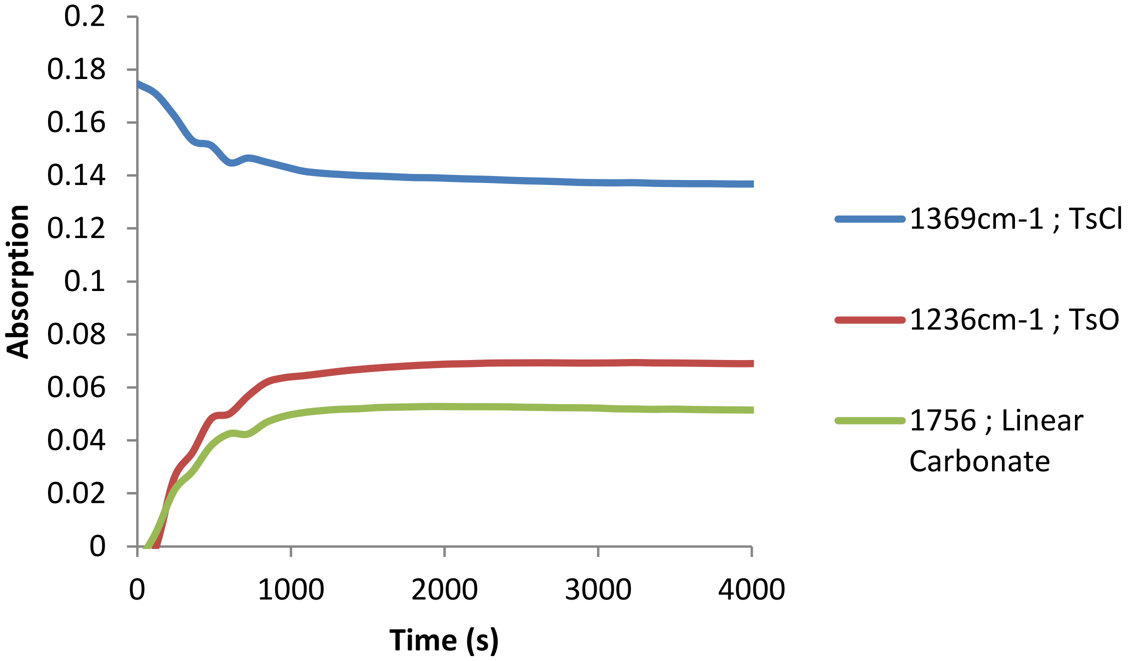


Figure 13: *In-situ* ATR-IR kinetic monitoring in standard conditions : ISM (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([ISM] = 1.2 mol/L).

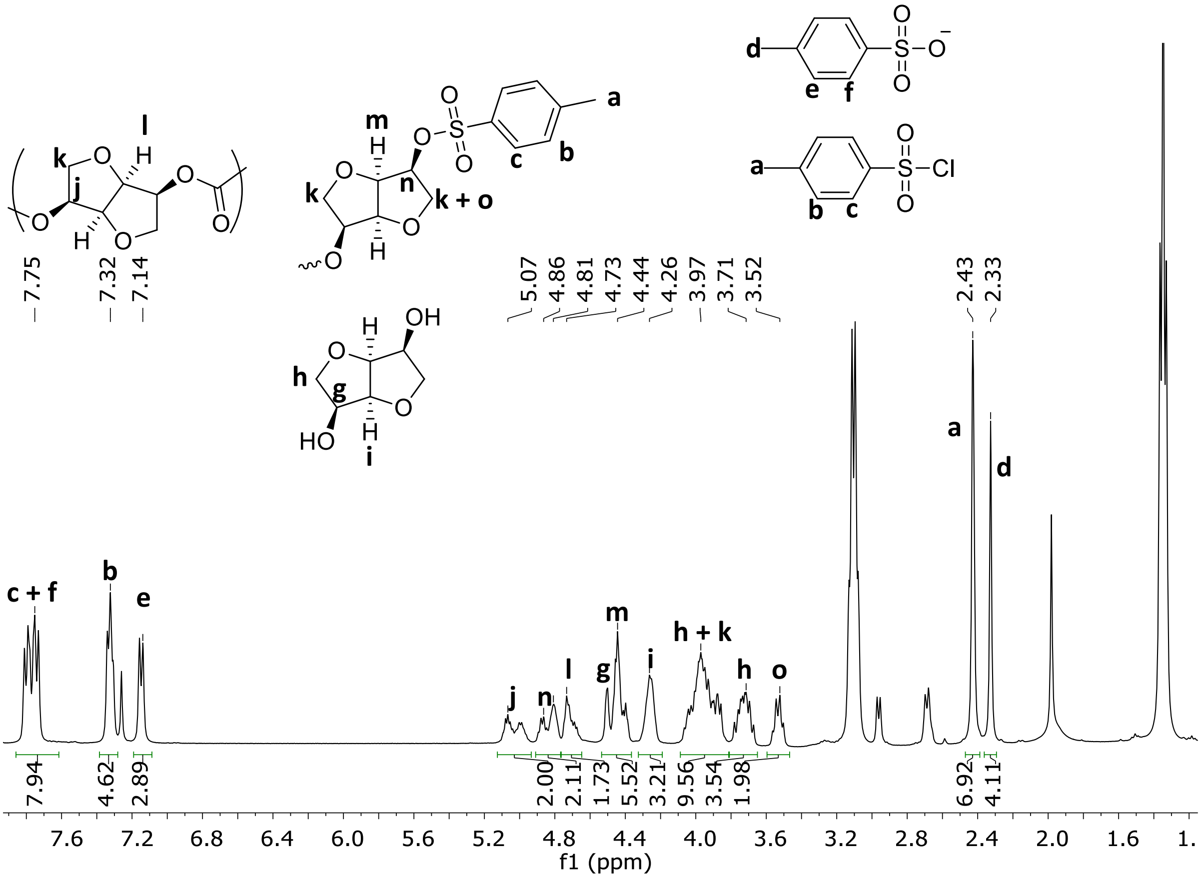


Figure 14: ^{1}H NMR spectrum of the crude liquid fraction recovered after reaction. Conditions : ISM (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([ISM] = 1.2 mol/L).

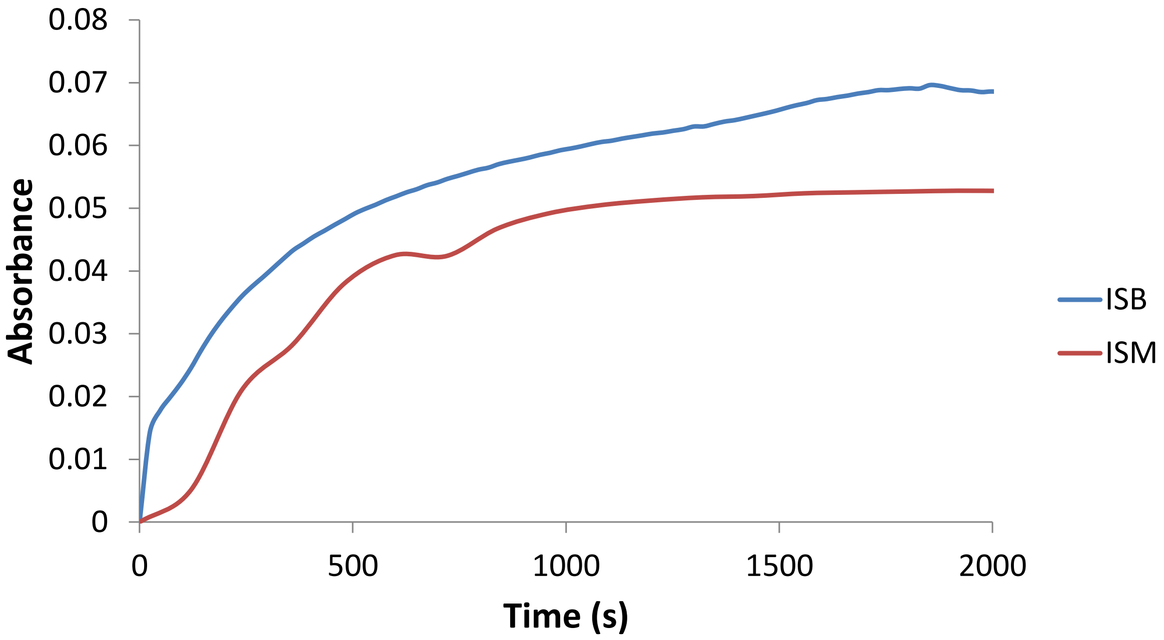


Figure 15: Comparison of *in-situ* ATR-IR kinetic monitoring of linear carbonate absorbtion band (1750 cm^{-1}) in standard conditions : diol (1eq) ; TEA (2eq) ; TsCl (1eq) ; 70 °C ; 1.5 MPa ; acetonitrile ([diol] = 1.2 mol/L).

To overcome this limitation, catalysts were added to drive the selectivity toward carbonate linkages and transcarbonation. TBD could increase this selectivity up to 56 % without detrimental effect on the alcohol conversion (Table 2 entry 2). TBA/PhO^{-} afforded even better selectivity of 76 % but with lower alcohol conversion of 40 % (Table 2, entry 3). Regarding LiCl, mitigated result was obtained with moderate alcohol conversion and selectivity toward carbonate linkages (Table 2, entry 4). GPC chromatograms presented in Figure 16 confirm the presence of dimers in large quantities for all reactions, with appearance of trimers in higher amounts for TBD and TBA/PhO^{-}, in accordance with selectivities and conversions observed with such catalysts. Still, no great increase of the molar masses was obtained as it was expected by switching from ISB to ISM.

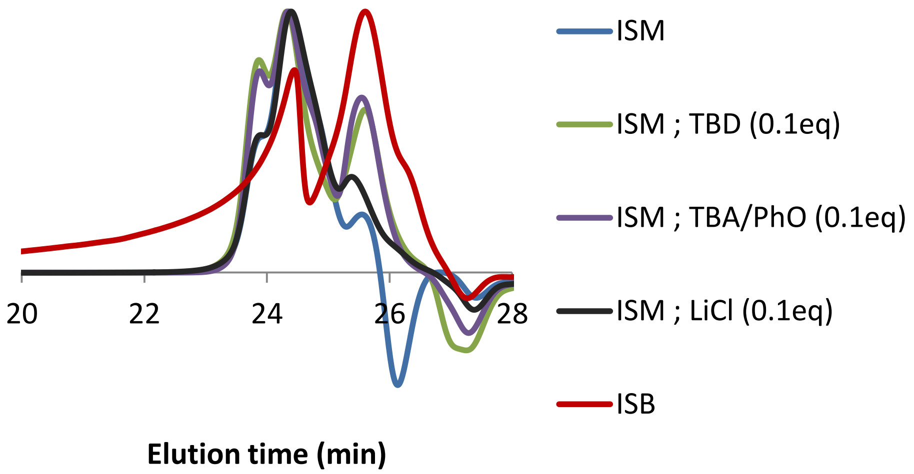


Figure 16: GPC chromatograms of direct copolymerization between ISM and CO_2 with TEA/TsCl dual activating system and different catalysts in standard conditions (70 °C ; 1.5 MPa CO_2 ; acetonitrile ; 20 h, see Table 2)

IV) Conclusion

To conclude, organic dual activating system TEA/TsCl doesn't seem to be suitable for the direct copolymerization of CO_2 with dianhydrohexitols (i.e ISB and ISM) as efforts to obtain polycarbonates resulted mostly in the formation of dimers and trimers for the different experimental conditions screened. A careful investigation on the reactivity disparities for the "endo" and "exo" alcohol moities and their selectivity toward formation of carbonate linkages or tosylation of the alcohols was carried out to better understand the system limitations. The addition of catalysts could drive the carbonation and transcarbonation of alcohols, but estimated conversions remained unsatisfying for such copolymerization processes. Moreover, presence of side reactions due to the use of TsCl in large amounts would perturbate the stoichiometry between alcohol and carbonate functions which have a detrimental effect on the chain extension. In addition, the use of excess of base (2 equivalents) and stoichiometric amounts of TsCl that are not recovered at the end of the reaction generates sustainability concerns that are not compensated with promising results for the challenging direct copolymerization of diols and CO_2. Even though formation of polycarbonates via this copolymerization strategy reported in the litterature relies on the use of heavy systems (excess of bases, co-reagents, dehydrative agents…) as described in chapter 2 (Section III-1)), no further experiments were conducted in this regard. A different and innovative approach for the formation of CO_2- and bio-based polycarbonates is proposed in chapter 4.

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Chapter IV:

Introducing new CO_2 and bio-based carbonate monomers for the melt polycondensation with diols to produce polycarbonates

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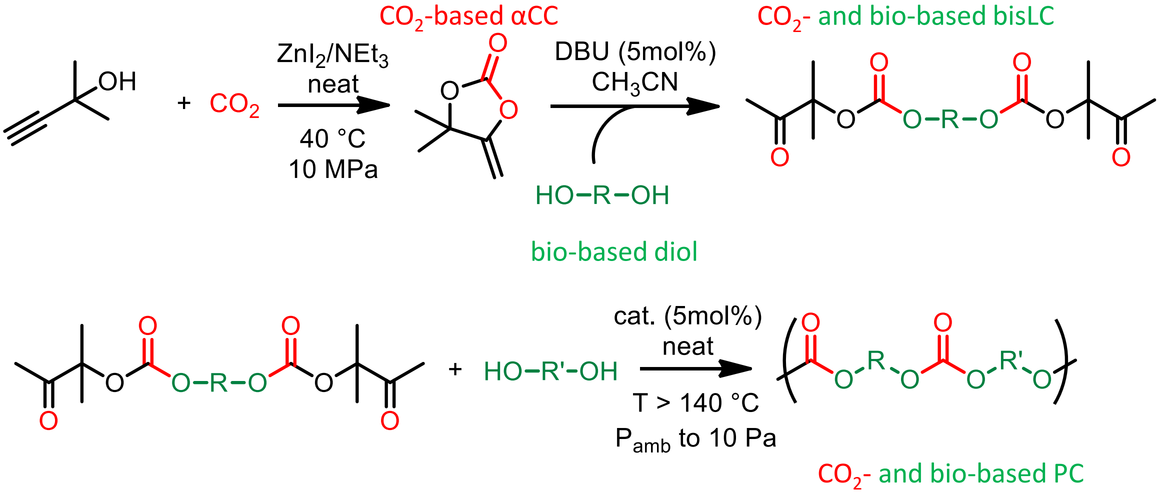
APPENDIX : CHARACTERIZATION OF BISLC MONOMERS.. 186

I) Introduction

Polycarbonates (PC) are useful trademarked polymers finding many applications, from everyday/commodity use (organic glasses, helmet, packaging…) to added-value biomaterials (scaffolds for tissue engineering, hydrogels or drug delivery systems, ink for 3D printing). By tuning their molecular structure, one can dictate the final properties of the PC. For instance, high impact resistance, thermal stability and appealing optic properties are usually obtained with PC presenting aromatic structures, whereas biocompatibility, biodegradability and lower T_g are achieved with aliphatic repeating units[1,2]. To date, aromatic PC are usually produced by melt polycondensation[3], while ring-opening (co)polymerization (RO(CO)P) is generally preferred for aliphatic PC synthesis[4] (see Chapter 1 – section III)). However, both methods require the use of toxic reagents (phosgene, bisphenol-A, epoxides precursors ...) or organic solvents. In line with the sustainable vision of our modern society, synthesizing greener synthons for the production of more eco-friendly polycarbonates is an absolute priority. In this optic, the combination of CO_2-based and bio-based synthons looks highly attractive. Among them, biorenewable alcohols with diversified chemical structures are candidates of choice as they are easily accessible from multiple natural sources[5]. Beside, CO_2 represents a promising substitute to phosgene and imposes itself as a valuable carbonylating agent in the (industrial) synthesis of two monomers entering in the fabrication of PCs by melt polycondensation, i.e. dimethyl- and diphenyl-carbonates (DMC and DPC), by the fixation of CO_2 onto methanol or phenol. So far, isosorbide-based PCs have been recently introduced as new materials in polymer sciences as they display thermo-mechanical properties and a transparency analogous to traditional aromatic PCs derived from bisphenol A[6]. Initially made by reactions with phosgene, new synthetic protocols employing DMC and DPC are now emerging for the fabrication of this next generation of sustainable PC via melt polycondensation. By smart choice of the catalyst, selective activation of the endo or exo alcohol moiety of isosorbide can be controlled to drive the formation of high molar masses polymers[7]. Nevertheless, these melt polycondensation approaches suffer from limitations. For instance, decarboxylative side alkylation reactions of the OH moieties (either from the monomer or the polymer chain ends) occur with DMC via attack onto the methyl site of DMC[8]. This terminates the chain by an unreactive function preventing the further chain-extension, limiting the PC molar masses. Additionally, despite methanol is highly volatile, the methanolate fragment in DMC is a poor leaving group which weakens the driving force thus making the equilibrium hard to displace in favour of the PC formation. One should also underline as a weakness, the volatility of DMC under vacuum, making challenging the adjustment of the stoichiometry of the reaction while any deviation of the stoichiometry stops the chains growth. Beside, DPC has also been considered as carbonylating agents, as phenolate is a much better leaving group than methanolate. However, its high boiling point induces harsh experimental conditions such as high temperature and vacuum to obtain high molar mass PCs[9].

Herein, we aim at introducing a new approach to fabricate PCs by step-growth polymerization using CO_2- and bio-based building blocks with tunable structure. CO_2-based α-alkylidene cyclic carbonates (αCC) are candidates of choice to replace DPC and DMC as their facile regioselective ring-opening by alcohols is a way to deliver acyclic oxo-carbonate species. Interestingly, these newly created molecules display a specific structure which, upon condensation with a second alcohol moiety would release a hydroxyketone such as 3-hydroxy-3-methyl-2-butanone that is expected to be a good leaving group (better than MeOH of DMC) as it is a tertiary alcohol with a rather low boiling point at 140 °C (lower than phenol of DPC). Reported examples for the synthesis of 5-membered cyclic carbonates from the coupling of αCC with vicinal diols demonstrated the reactivity and regioselective ring-opening of these αCC with hydroxyketone release[10-12]. Thus, by carefully choosing 1,x-diols with x > 3, one would expect to carbonate both alcohol functions rather than unfavored cycle formation, providing bifunctional linear oxo-carbonate suitable for chain extension by transcarbonation. Preliminary results on the direct coupling of diols (here 1,4-butanediol) with αCC, namely 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (DMACC) in a one pot / two steps manner showed the difficulty to obtain oligomers/PCs. Mainly, finding the right catalytic system to promote both DMACC regioselective opening for carbonation of alcohols and later transcarbonation reactions for chain-extension without significant amount of side reactions appeared to be very challenging in neat conditions. Moreover, the low boiling point of DMACC was not suitable for melt-polycondensation experimental conditions, causing stoichiometric deviations for the chain-extension step. Thus, to alleviate the problem, we first synthesized new acyclic bis-oxo-carbonate monomers (bisLC) from biobased diols and DMACC in a controlled manner, which were isolated and purified. In a second step, their melt polycondensation with diols was studied to design CO_2- and bio-based PCs (see Scheme 1).



Scheme 1: Synthetic strategy for the fabrication of CO_2- and bio-based PCs

II) Material and methods

II-1) Material

Isosorbide (ISB, 98 %, Sigma Aldrich), 1,4-Butanediol (99 %, Sigma Aldrich), 2-methyl-3-butyn-2-ol (98 %, Sigma Aldrich), Zinc Chloride ($ZnCl_2$, 98 %, Sigma Aldrich), Zinc Iodide (ZnI_2, 98 %, Sigma Aldrich), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, 98 %, Sigma Aldrich), Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95 %, Sigma Aldrich), 4-Dimethylaminopyridine (DMAP, 99 %, Sigma Aldrich), tetrabutylammonium bromide (TBA/Br, 99 %, Sigma Aldrich), Isomannide (ISM, 95 %, Fluorochem), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 99 %, Fluorochem), 1,4-benzenedimethanol (99 %, TCI), Triethylamine (TEA, 99 %, Alfa Aesar), Aluminium Chloride ($AlCl_3$, 99 %, Fluka), Lithium Chloride (LiCl, 99 %, Janssen) were all used as received and without further purification.

II-2) Methods

II-2-a) Characterization techniques

Nuclear magnetic resonance spectroscopy (NMR)

^1H and ^{13}C NMR spectra were recorded at 298 K with a Bruker advance 400 spectrometer operating at 400 MHz, on the Fourier transform mode. All NMR spectra were phased and baseline-corrected. The samples were prepared by dissolving 15-20 mg of product in 0.7 mL of a deuterated solvent ($CDCl_3$) and were calibrated with the 7.26 ppm residual signal of $CDCl_3$.

Size-exclusion chromatography (SEC)

Number-average molecular weight (M_n) and dispersity (Đ) of the oligomers and polymers were determined by size exclusion chromatography (SEC) in dimethylformamide (DMF) containing LiBr (0.025 M) at 55 °C (flow rate, 1 mL/min) with a Agilent 1260 Infinity 2 chromatograph equipped with three columns (PSS gram 1000 Å (x2), 30 Å) and Agilent 1260 Infinity 2 RI, UV and ELS detectors.

Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR)

ATR-IR spectra on liquid and solid samples were recorded using a iD5 diamond-ATR accessory coupled with a Nicolet iS5 (ThermoScientific) equipped with a mid-infrared EverGlo source, a KBr beamsplitter and a DTGS (Deuterated TriGlycine Sulphate) KBr detector. Single beam spectra recorded in the spectral range (500-4000 cm^{-1}) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 32 accumulated interferograms

Thermogravimetric Analysis (TGA)

TGA analysis was performed on a TGA2 instrument from Mettler Toledo. Around 5 mg of sample was flushed with nitrogen (50 mL/min) for 10 min at 30 °C. The sample was then heated at 20 °C/min until 600 °C under a nitrogen atmosphere (50 mL/min). Degradation temperature was estimated after a degradation of the sample of 5 % of its original mass.

Differential Scanning Calorimetry (DSC)

DSC analysis was performed on a DSC 250 from TA instruments using hermetic aluminium pans, indium standard for calibration and N_2 as the purge gas. Around 5 mg of sampled were cooled at -60 °C at 10 °C/min, followed by an isotherm at -60 °C for 2 min, then heated to 200 °C at 10 °C/min, followed by an isotherm at 200 °C for 2 min. These cycles were repeated twice. The last ramp of temperature (-60 °C to 200 °C) was used to determine the T_g.

General procedure for the kinetic study of bisLC monomers synthesis

The reactions were monitored *in-situ* by IR spectroscopy using a stainless-steel reactor (80 mL) coupled with a FT-MIR spectrometer from Bruker, equipped with an air-cooled globar source (12 V), a KBr beam splitter, a mechanical rocksolid interferometer, permanently aligned, a diamond ATR fiber probe IN350-T (Ø 6 mm), and a liquid nitrogen-cooled mercury cadmium telluride (MCT). Single beam spectra recorded in the spectral range (670–3500 cm−1) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 32 accumulated interferograms until the end of the reaction time. The reactor is equipped with a heating mantle and a mechanical stirrer so that the reaction can be performed under controlled stirring and temperature.

Density Functional Theory (DFT) computational details

Preliminary calculations of equilibrium structures were performed using a semi-empirical model (AM1-D3H4) to determine the most stable conformations. These semi-empirical calculations were performed using the AMPAC software. The CHAIN algorithm was used for locating intermediates and transition states along the reaction path. The lowest energy structures obtained at the AM1-D3H4 level were further investigated using the Density Functional Theory method (DFT) implemented in the Gaussian 16 package. DFT calculations of geometries, energies, and vibrational frequencies reported in this article were carried out with the M06-2X functional using the 6-311G(d,p) basis set. All frequencies of each structure have also been calculated to verify the presence of a single imaginary frequency for transition states and the absence of imaginary frequency for ground states. The intrinsic reaction coordinate (IRC) method has been used to verify that the obtained transition states were effectively connected to the desired minima. For all activating systems, a wide range of possible configurations and interactions have been modelled and the more stable of them are reported in this work. To consider entropic effects, the energies mentioned in this study correspond to the Gibbs free energy (ΔG).

II-2-b) Experimental protocols

Synthesis of tetrabutylammonium phenolate

In a 100ml round bottom flask equipped with a magnetic bar were introduced 1.2422 g (13.2 mmol) of phenol and 10 ml of methanol. The flask was placed into an ice bath, while stirring, 13.2 ml (13.2 mmol) of a solution of tetrabutylammonium hydroxide solution (1mol/L in methanol) ($N(Bu)_4OH$) was added dropwise using a syringe. The mixture was led under stirring at room temperature for 48 h. Afterwards, MeOH was removed in vacuum before drying of the salt under vacuum at 50 °C for 24 h.

Synthesis of 4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (DMACC)

In a stainless-steel autoclave of 250 mL were loaded 20g of ZnI_2, 72 mL of TEA and 50 mL of 2-methyl-3-butyn-2-ol. The autoclave was sealed and heated to 40 °C. CO_2 pressure of 10 MPa was applied for 24 h with mechanical stirring. At the end of reaction time, the crude mixture was transferred to rotavapor to remove the excess of TEA. The recovered fraction was purified by flash chromatography onto silica using CH2Cl2 as eluent, followed by later distillation to remove zinc salts and obtain pure DMACC.

General synthetic procedure for the batch synthesis of bisLC monomers

In a 250 mL round bottom flask equipped with a magnetic stirrer, diol (1 eq, 58.55 mmol) and DMACC (2 eq, 117.1 mmol, 15 g) were solubilised in 60 mL of acetonitrile (or DMSO in the case of 1,4-benzenedimethanol) at 25 °C. After complete solubilisation, DBU (0.05 eq, 2.93 mmol, 437 µL) was added to the solution. The reaction was left 2 h at 25 °C. At the end of reaction time, acetic acid (437 µL) was added to the mixture to quench the catalytic activity of DBU. 60 mL of CH_2Cl_2 was added to the solution, and bisLC monomers were purified by liquid-liquid extraction (3 times) using large volume of H_2O. Pure bisLC monomers were recovered after evaporation of the organic phase.

General synthetic procedure for the oligomerization step study

In a 10 mL round bottom flask equipped with a magnetic stirrer, diol (1 eq, 2.49 mmol), corresponding bisLC monomer (1 eq, 2.49 mmol) and catalyst (0.05 eq, 0.124 mmol) were loaded. The reactor was flushed with N_2 for 10 min to avoid potential water contamination, and then sealed. The round bottom flask was immersed in an oiled bath at the desired temperature for the desired reaction time.

General synthetic procedure for the obtention of polycarbonates

In a 10 mL round bottom flask equipped with a magnetic stirrer, diol (1 eq, 2.49 mmol), corresponding bisLC monomer (1 eq, 2.49 mmol) and catalyst (0.05 eq, 0.124 mmol) were loaded. The reactor was connected to a cold trap, itself connected to a vacuum pump thanks to a pipe. It was flushed with N_2 for 10 min to avoid potential water contamination, and then sealed. The round bottom flask was immersed in an oiled bath at the desired temperature for a specific oligomerization time. Then, for the chain extension step, vacuum was gradually applied by progressively opening the valve connected to the cold trap to remove the polycondensation by-product. After 3h of chain extension step, a vacuum of 10 Pa was measured. When specified, temperature could be increased right after application of vacuum. At the end of the reaction time, polymers were recovered in the solid state and dissolved in CH_2Cl_2, followed by reprecipitation in MeOH. The evaporated fraction recovered in the cold trap was analysed by ^1H NMR and ATR-IR.

Synthetic procedure for the obtention of poly(carbonate-co-urethane)

In a 10 mL round bottom flask equipped with a magnetic stirrer under inert atmosphere, purified poly(isosorbide carbonate) previously synthetized (200 mg) was solubilized in dry DMF (2 mL) at 80 °C. Number of alcohol functions chain ends of the hydroxyl telechelic polymer was calculated by ^1H NMR as followed: it was assumed that all polymer chains were capped by endo or exo OH functions. Signals of exo and endo alcohols (at 4.38 ppm and 3.57 ppm respectively) were integrated so that their sum was equalled to 2 (two remaining alcohols functions per chain). Integration of signal at 4.88 ppm, accounting for 1 H in the polymer backbone, would then lead to estimation of the DP. The purified polymer DP used for these step-growth polymerization was of 6, which corresponds to a *Mn* = 1,030 g/mol, versus 1,970 g/mol displayed by SEC analysis. Number of moles of alcohols functions could then be estimated to 0.388 mmol. 4,4'-methylene diphenyl diisocyanate (0.194 mmol, 48.5 mg) was added under inert atmosphere so that equimolar amount of isocyanate and alcohol functions was respected. Dibutyltin dilaurate (0.01mass%, 2.5 mg) was added under inert atmosphere. The reaction was left at 80 °C for 4 h.

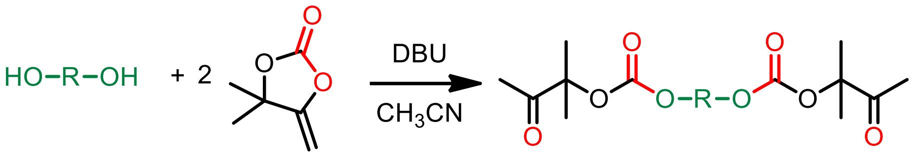
III) Results and Discussion

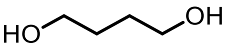
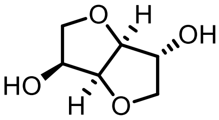
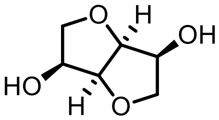
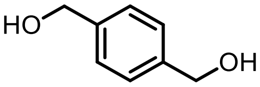
III-1) Monomer synthesis

αCCs are highly reactive synthons which result from the CO_2 fixation onto propargylic alcohols. Their synthesis is well referred in the literature so that αCCs were prepared according to previous studies using a state-of-the-art Zinc catalyst[13]. Thanks to the presence of an exocyclic double bond, they are considered as "activated" cyclic carbonates as they undergo facile and highly regioselective alcoholysis in the presence of an organic base under non-demanding operative conditions. Thus, αCCs can be seen as an activated form of CO_2, way more reactive than CO_2 itself. Taking advantage of its reactivity, four new bis-oxo-carbonates were synthesized by simple carbonation of biobased diols (1,4-butanediol, Isosorbide, Isomannide and 1,4-benzene dimethanol) with two equivalents of αCCs at 25°C with DBU (5 mol% compared to alcohol) as the base and MeCN or DMSO as a solvent. Results are presented in Table 1. The four bifunctional linear carbonates (bisLC) were obtained in excellent isolated yields, above 70 %.

Deeper mechanistic and kinetic insights were performed on the model reaction between 1,4-butanediol as substrate and DMACC, thanks to DFT calculations coupled with *in-situ* ATR-IR monitoring. Typical spectra recorded at different reaction times as well as absorbance of characteristic bands over time are presented in Fig. 1. The well-defined bands of αCC ($\nu_{C=O}^{carbonate} = 1820$ cm^{-1} ; $\nu_{C=C}^{double\ bond} = 1680$ cm^{-1}) decrease over time with concomitant appearance of characteristic bands of linear carbonates and ketones ($\nu_{C=O}^{carbonate} = 1750$ cm^{-1} ; $\nu_{C=O}^{ketone} = 1720$ cm^{-1}). The reaction reaches completion after only 2 h at 25 °C. Careful comparison of the kinetic curves led to observation of a faster decrease for the cyclic carbonate absorption band (blue curve, Fig. 1b) than for the double bond absorption band (purple curve, Fig. 1b), suggesting a multi-step mechanism for this reaction. As already reported in the literature[14], the expected mechanism consists in the nucleophilic attack of an alcohol moiety onto the electrophilic carbonyl center, followed by the regioselective ring-opening toward the enol, later stabilized on the ketone form. Presence of DBU as the base would increase the alcohol nucleophilicity through hydrogen bonding. Two equivalents of αCC are needed to carbonate both alcohol functions.

Table 1: Synthesis of bisLC from different bio-based diols and DMACC. Reaction conditions: diol (1 eq) ; DMACC (2 eq) ; DBU (0.05 eq) ; 25 °C ; 2 h



Diol	Conversion (αCC)	Isolated Yield (%)	T_m (°C)	$T_d^{5\%}$ (°C)	bisLC name
	> 99	85	54	226	bisLC1
	> 99	80	89	213	bisLC2
	>99	70	107.5	199	bisLC3
	> 99	75	132	233	bisLC4

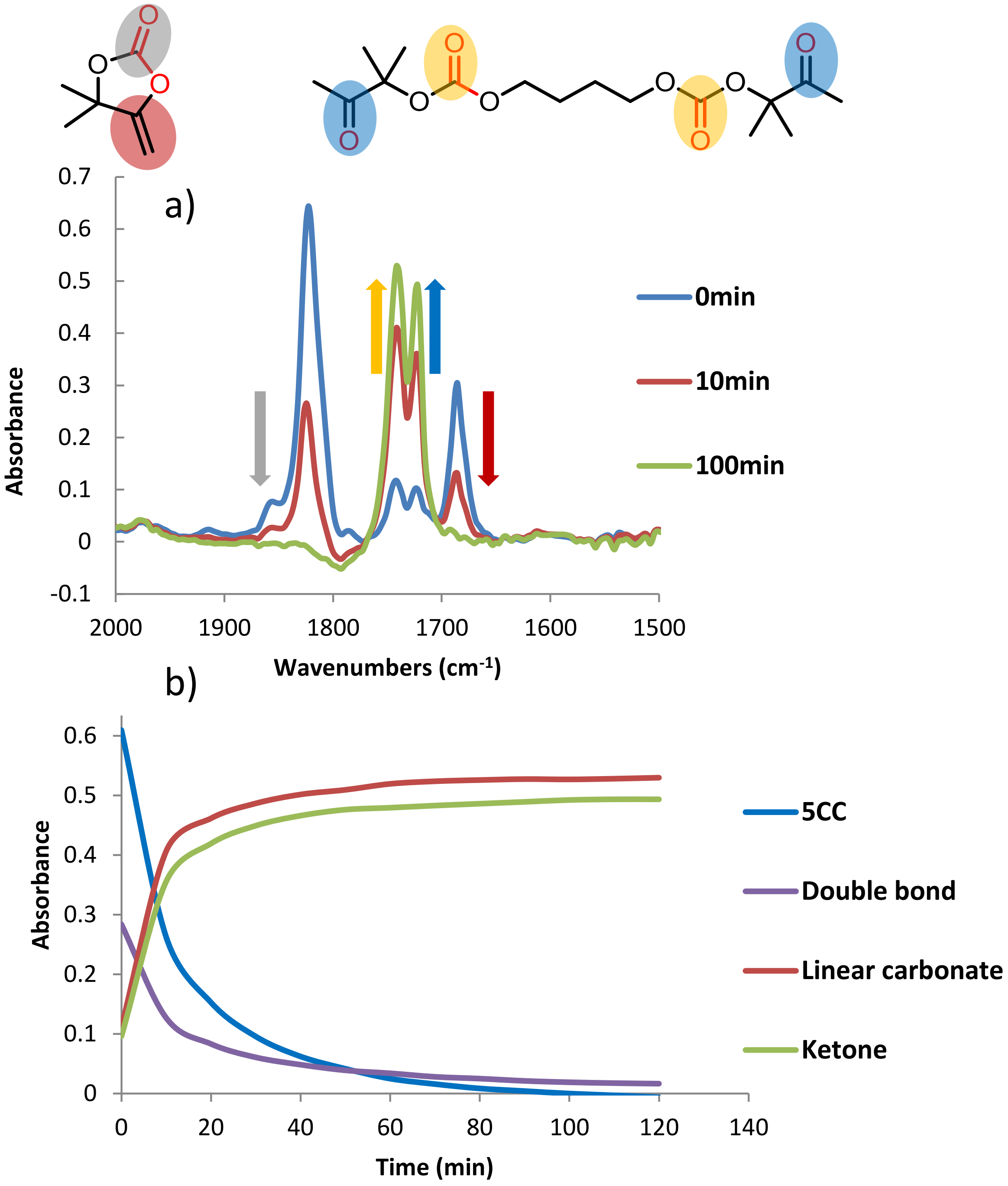


Figure 1: (a) ATR-IR spectra overlay at different reaction times for the synthesis of bisLC1. (b) Kinetic monitoring of characteristic absorption bands over reaction time (5CC = 1820 cm^{-1} ; Double bond = 1680 cm^{-1} ; Linear carbonate = 1740 cm^{-1} ; Ketone = 1720 cm^{-1}) for the synthesis of bisLC1.

To confirm the mechanistic proposal derived from the experimental observations, DFT calculations were conducted at the M062X/6-311g(d,p) level. The different intermediates and transition states (TS) obtained are represented in Fig. 2, and the energetic profile calculated from intermediates and TS is presented in Fig. 3. As expected, first H-bond interaction between DBU and one alcohol moiety renders the O atom more nucleophilic, which is able to attack onto the electrophilic carbonyl center, leading to intermediate 2 (Fig.

2). The latter would undergo regioselective ring-opening facilitated by proton transfer carried by DBU to form of a linear carbonate with an enol function (intermediate 3, Fig. 2). Once again, the keto-enol tautomerism in basic conditions will drive the regioselective opening, to finally furnish the ketone form as the highly favoured product of this αCC alcoholysis. This tautomerism occurs via proton transfer from the oxygen to the CH_2 of the olefinic bond aided by DBU (TS3, Fig. 2). The charge distribution shows that the double bond is slightly more nucleophilic than the oxygen (Mulliken charges of -0.574 vs -0.539) which explains why DBU preferentially creates H-bonding with the OH rather than the CH_2. By repetition of the reaction pathway of the newly created intermediate with a second αCC unit, one delivers the bis-oxo-carbonate monomer (Intermediate 4 ; Fig. 2).

Regarding the energetic profile (Fig. 3), the highest activation barrier is observed for TS1 and TS4 as they both represent the same step of the reaction, i.e. the nucleophilic attack of the alcohol moiety onto the carbonyl function, with $\Delta G_{TS1}^{\ddagger}$ = 24.9 kcal/mol and $\Delta G_{TS4}^{\ddagger}$ = 25.7 kcal/mol. The fast and facile synthesis of these new bisLC can be justified by the overall low activation barriers in the presence of DBU, and with a product formation which Gibbs Free Energy is 20 kcal/mol lower than the reactants. Surprisingly, the keto-enol tautomerism displays a high activation barrier of $\Delta G_{TS3}^{\ddagger}$ = 22.7 kcal/mol and $\Delta G_{TS6}^{\ddagger}$ = 24 kcal/mol, but are not the highest barriers of the profile. In both cases (TS3 and TS6), the ketone intermediate is more stable than the enol, in accordance with experimental results.

Finally, the thermal characterization of the new bisLC monomers was realized to determine i) their melting temperature, and consequently, the minimum temperature required to drive their melt condensation (see next section) and ii) their thermal degradation, providing an indication of the maximal processing temperature to avoid the monomer decomposition during the polymerization. Due to their different structural features, bisLC display melting points ranging from 54 °C for aliphatic 1,4-butanediol based bisLC up to 132 °C for aromatic 1,4-benzene dimethanol based bisLC as well as thermal stabilities ranging from 199 °C to 233 °C. See appendix for full characterizations by ^{1}H NMR, ^{13}C NMR and HRMS.

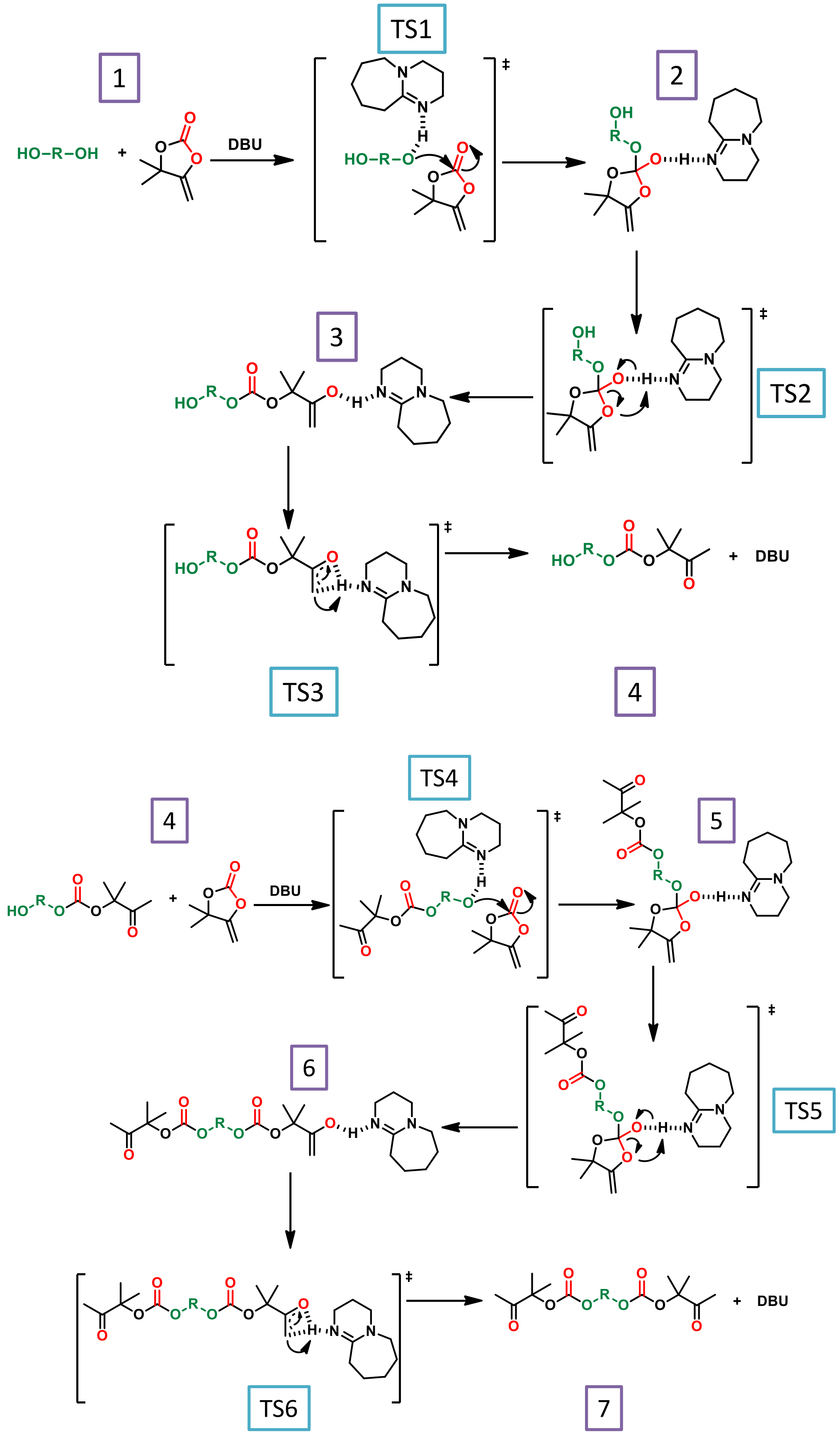


Figure 2: Mechanism proposal for the formation of bisLC1 from 1,4-butanediol and DMACC catalysed by DBU.

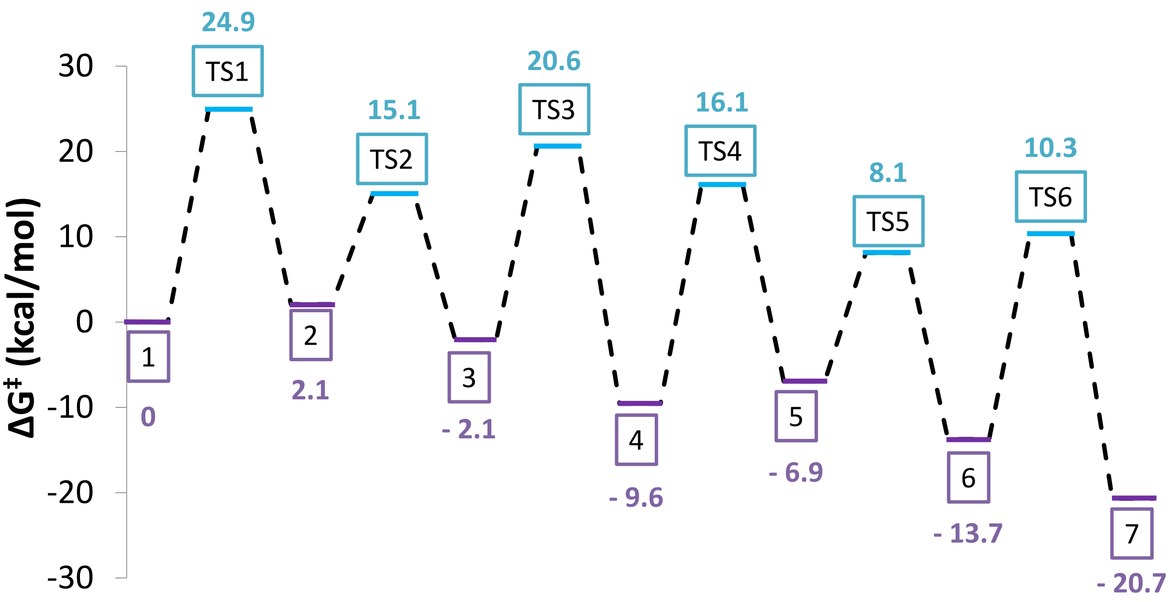


Figure 3: DFT computed pathway (*M062X/6-311g(d,p)*) of model reaction as depicted in Figure 2. Purple numbers correspond to optimized reaction intermediates shown in Figure 2 (Van Der Waals interactions were accounted). Transition states (TS) were optimized using the same molecular species as in the intermediates.

III-2) Polymer synthesis

PCs were then fabricated via melt-polycondensation of bisLC either by using diols comonomers with identical (R = R’, Fig. 4, homopolycarbonate) or different (R ≠ R’, Fig. 4, heteropolycarbonate) structural radicals to the one that served to synthesize the bis-oxo-carbonates. As overall strategy, the melt-polycondensation processes are carried out in a one-pot/two-steps fashion. In the first “oligomerization step”, both monomers are mixed in the melt state under nitrogen atmosphere to design oligocarbonates via transcarbonation. Then, vacuum is applied to remove hydroxyketone and shift the polymerization equilibrium towards the formation of polycarbonates in the so-called “chain extension step”. The aim of this work was to obtain CO_2-based PCs containing isosorbide repeating units. However, due to the complexity of such systems brought by the presence of two non-equivalent “endo” and “exo” alcohols functions with different reactivities and chiral centers, the synthesis of PC from bisLC and diols of simpler structural features was firstly investigated. Thus, the synthesis of poly(butylene carbonate) from 1,4-butanediol and its bisLC analogue was first considered (R = R’ = $(CH_2)_4$, Fig. 4).

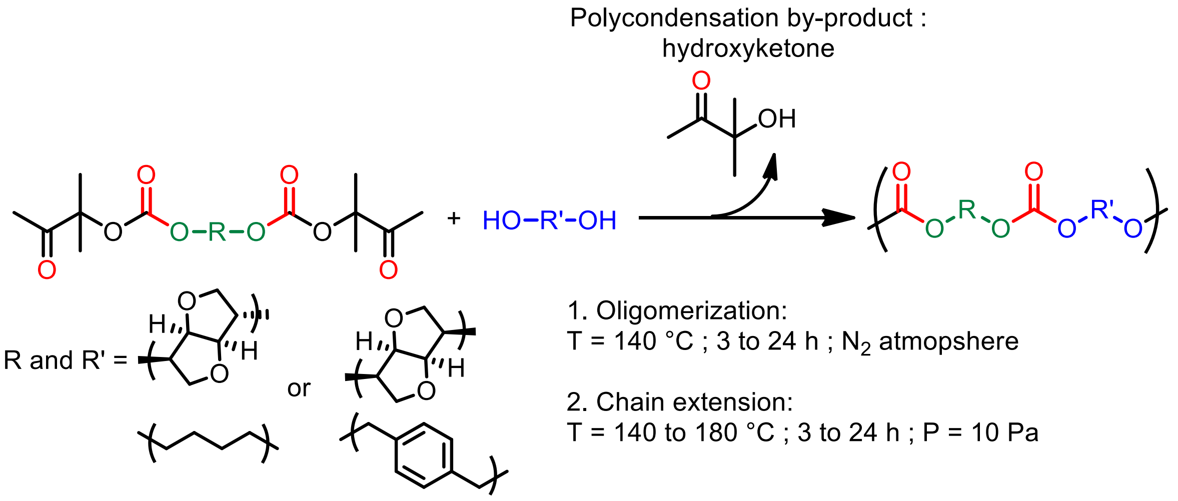


Figure 4: Melt-polycondensation strategy to afford (co)polycarbonates from previously synthetized bisLC and diols.

III-2-a) Poly(butylene carbonate) synthesis

III-2-a-i) Oligomerization step

The oligomerization of butane-1,4-diyl bis(2-methyl-3-oxobutan-2-yl) dicarbonate (bisLC1) with 1,4-butanediol was first realized for 16 h at temperatures ranging from 100 to 140 °C. Under catalyst-free conditions, no oligomerization was observed in these experimental conditions (Table 2, entries 1 and 2). By addition of LiCl as a catalyst (5mol%), even though no oligomer was detected, a side-reaction promoted the formation of 5-membered cyclic carbonates (5CC) as evidenced in the ATR-IR spectra by the presence of a characteristic absorption band $\nu_{C=O}^{5CC}$ at 1805 cm^{-1}, see Fig. 5. The formation of this 5CC is favoured by increasing the temperature (higher absorbance at 120 °C than at 100 °C) and is accompanied with progressive decreasing of the ketone function absorption signal at 1680 cm^{-1}. Inspired from a recent report [14], the suggested pathway for the 5CC formation from 1,4-butanediol and bisLC1 involves a first attack of the oxo- moiety by the OH to form a ketal intermediate that is further involved in a cascade cyclisation to deliver the cyclic carbonate (Scheme 2). Interestingly, oligomers with *Mn* of 1,470 g/mol were obtained at 140 °C after 16 h (Table 2, entry 5), alongside with 5CC formation. GPC chromatograms presented in Figure 6 shows the relevance of long reaction times to increase the molar masses of the so-produced oligocarbonates.

Table 2: Oligomerization tests with different temperature. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; catalyst (0.05 eq)

Entry	T (°C)	Time	Catalyst	M_n (g/mol)	Observations
1	100	16h	/	/	No oligomers. No side reactions
2	140	16h	/	/	No oligomers. No side reactions
3	100	16h	LiCl	/	No oligomers. Presence of 5CC
4	120	16h	LiCl	/	No oligomers. Presence of 5CC
5	140	16h	LiCl	1,470	Oligomers. Presence of 5CC

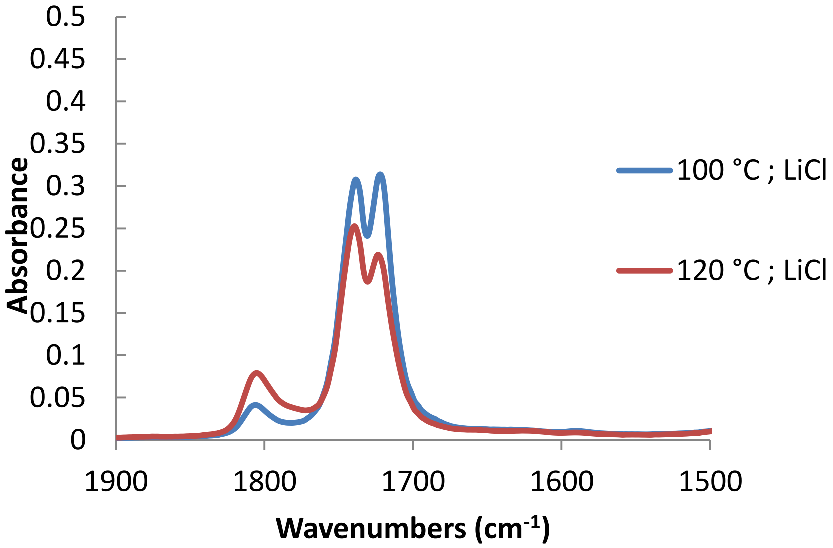
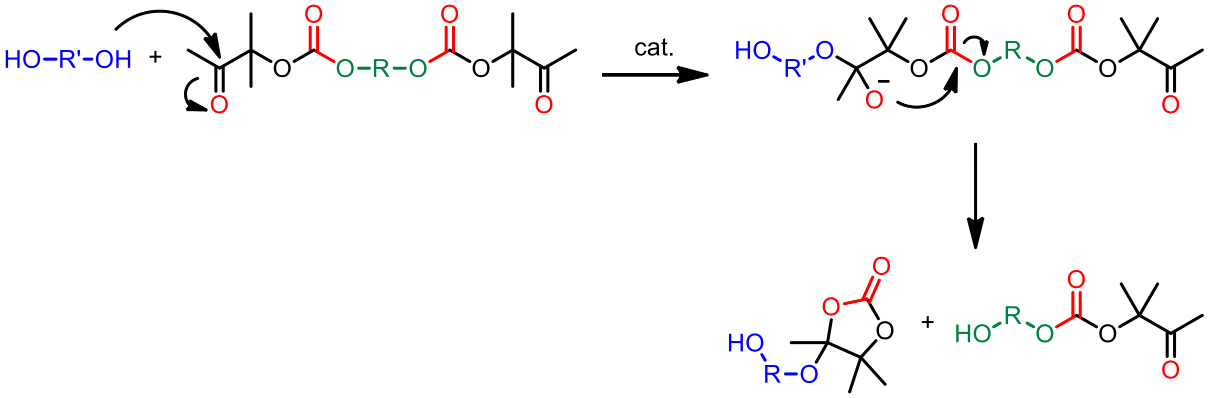


Figure 5: ATR-IR spectra of crude mixture obtained after oligomerization step. Presence of undesired 5CC compound is evidenced with absorption band at 1800 cm^{-1}.



Scheme 2: Proposed mechanism for the formation of 5CC compound as side-reaction in the oligomerization step. Adapted from [14].

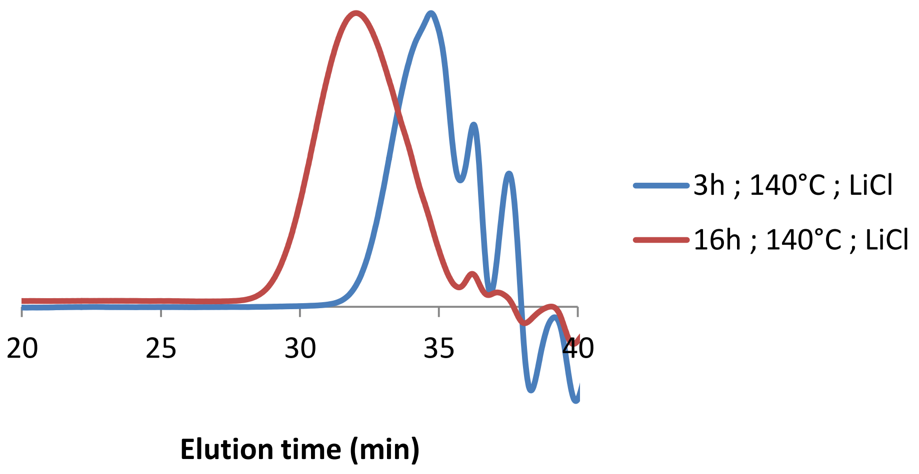


Figure 6: GPC chromatograms obtained after 3 h and 16 h for the same experimental conditions (0.05 eq of LiCl ; 140 °C),

^{1}H NMR characterization of the very complex crude product is presented in Figure 7 and highlights the presence of bisLC1, oligocarbonates, hydroxyketone and 1,4-butanediol. The additional peak at 3.50 ppm could possibly be attributed to the CH_2 of an exocyclic ether group which is in accordance with the 5CC proposed structure. This assumption is further supported by methyl signals at 1.40, 1.43 and 1.51 ppm (peaks **k** and **j**) fixed to the 5CC ring. Supplementary peaks are also observed at 1.19, 1.27 and 1.36 ppm (peaks **m** and **n**) and could derive from a degradation product of the 5CC which formation is probably favoured by the presence of the catalyst and the high temperature. Scheme 3 proposes two competitive hypothetical pathways for the thermal 5CC ring-opening by alcohols, i.e via the “carbonyl”, the “quaternary carbon” or the “hemiacetal carbonate”. These suggested side reactions lead to formation of multiple by-products hardly distinguishable in ^{1}H NMR. As seen in chapter I (section III-2-a), the carbonyl attack by an alcohol is very challenging, even for the most simple ethylene carbonate substrate in the presence of appropriate catalyst at high temperature, so it was not considered as a favourable pathway for the transformation of the tetrasubtituted 5CC. The “quaternary carbon” attack by an alcohol (Scheme 3b, red pathway) seems compromised as this type of carbon is most likely unreactive. However, the 5CC displays structural features similar to hemiacetal esters. Inspired by the known chemistry of these chemicals [15,16], the generated 5CC could be seen as an hemiacetal carbonate trapped under a cyclic form which reactivity and ring-opening could be similar to hemiacetal esters. The 5CC could undergo a nucleophilic attack by the alcohol via the “hemiacetal-type” carbon (Scheme 3b, blue pathway) provoking the ring-opening of the cyclic molecule. This results in the formation of a carbonic acid that spontaneously decomposes into a new tertiary alcohol. The driving force of the reaction probably arises from the release of CO_2. This latest hypothesis may explain the presence of additional peaks at 1.19, 1.27 and 1.36 ppm that could be attributed to the 3 newly created methyl group and that are delivered in a 2/1 ratio via ^{1}H NMR quantification.

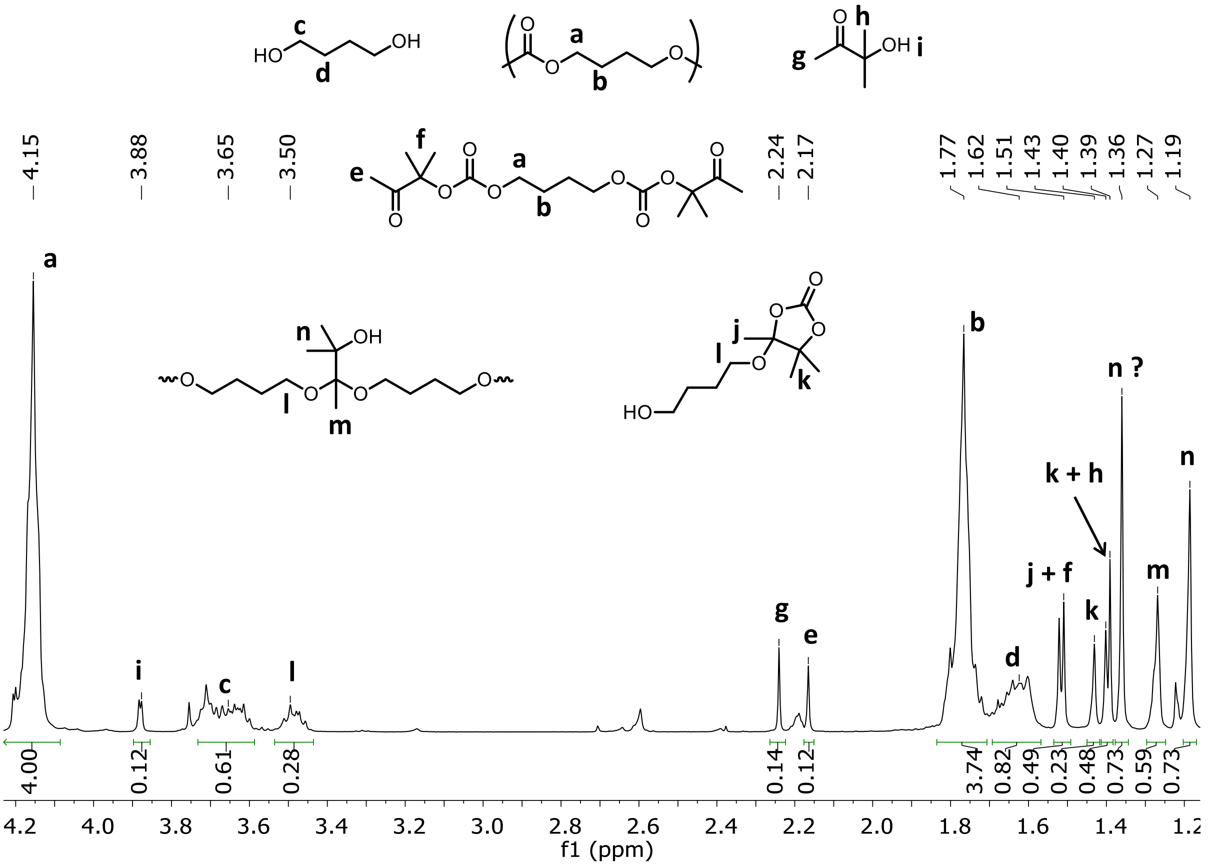
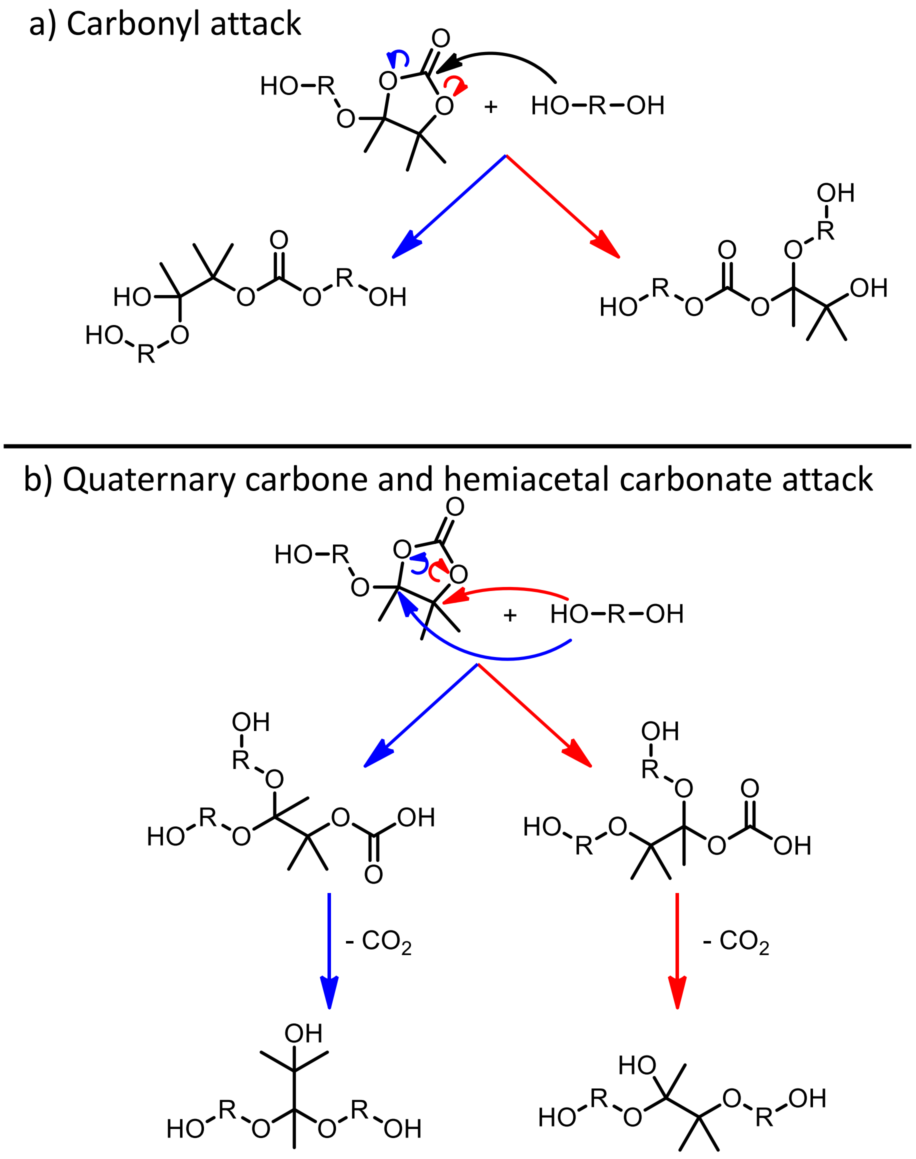


Figure 7: ^{1}H NMR spectrum of the crude product recovered after the oligomerization step. Conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C ; 16 h.

However, one would like to underline our attempts to isolate the various products (chromatography, precipitation, dialysis) for structural confirmation. Unfortunately, this task remained unsuccessful so that the NMR spectra remained highly complex. One also postulates that the so-produced tertiary alcohol is poorly reactive but at high temperature, additional side-reactions promoted by this moiety can not be excluded. It should be noted that the hydroxyketone boiling point is of 140 °C, which explains the threshold at 140 °C to activate this reaction.



Scheme 3: Mechanism proposal for the degradation of the 5CC side product formed during the oligomerization step.

To prevent the formation of undesired 5CC side-products that could limit the molar masses of the oligomers and/or PCs, various catalysts were tested at the selected temperature of 140 °C for 20 h. Results are summarized in Table 3. Two different types of catalysts were used. On the one hand, Lewis acids ($AlCl_3$; $ZnCl_2$; $Sn(Oct)_2$) are expected to activate carbonyl functions by increasing their electrophilicity and thus their reactivities with regards to alcohols. On the other hand, organic bases (TBD ; DBU ; DMAP ; TBA/PhO^-) would activate the alcohol functions to promote transcarbonation reactions by increasing their nucleophilicity. The Lewis acid were found ineffective in catalysing the oligomers formation as only traces of 5CC by-products were observed (Table 3, entries 1-3). The presence of 5CC was also detected for all organobases, but TBD, DBU, DMAP and tetrabutyl ammonium phenolate (TBA/PhO^-) could afford oligocarbonates with relatively low molecular weights (Table 3, entries 4-7). These results indicate that the C=O of the ketone function of bisLC1 displays competitive reactivity/electrophilic character with the carbonyl of the carbonate in such operating conditions towards diols as the nucleophile. Formation of 5CC is thermodynamically favourable and is assumed to be the driving force of the side-reactions observed.

Table 3: Oligomerization tests with different catalysts. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; catalyst (0.05 eq)

Entry	T (°C)	Time	Catalyst	M_n (g/mol)	Observations
1	140	20h	$AlCl_3$	/	No oligomers. Presence of 5CC
2	140	20h	$ZnCl_2$	/	No oligomers. Presence of 5CC
3	140	20h	$Sn(Oct)_2$	/	No oligomers. Presence of 5CC
4	140	20h	TBD	< 400	Few oligomers. Presence of 5CC
5	140	20h	DBU	< 400	Few oligomers. Presence 5CC
6	140	20h	DMAP	600	Oligomers. Presence of 5CC
7	140	20h	TBA/PhO	500	Few oligomers. Presence of 5CC during reaction. No 5CC at the end of reaction

Interestingly, in the case of TBA/PhO$^-$, 5CC was detected during oligomerization time after sampling at 1 h and 3 h (Fig. 8, orange and green curve) but could not be observed at the end of reaction time (Fig. 8, purple curve). ^{1}H NMR analysis of crude products in the specific region of 1 ppm to 2.3 ppm after 1 h, 3 h and 20 h using TBA/PhO$^-$ as catalyst is presented in Figure 9. In accordance with ATR-IR observations, progressive decreasing of the methyl peaks **d** (1.52 ppm) and **e** (1.43 and 1.40 ppm) to total disappearance after 20 h is correlated to the concomitant increase of peaks **g** (1.19 ppm) and **h** (1.27 ppm) indicating the consumption of the 5CC by ring-opening as already discussed previously with LiCl catalyst. It should be noted that decrease of the intensity of peaks **i** (2.24 ppm) and **j** (1.39 ppm) assigned to hydroxyketone is due to its evaporation during sampling, as the reaction temperature of 140 °C is also the boiling point of hydroxyketone. At the end of reaction time (Fig. 9, green curve), the bisLC1 monomer was totally consumed since peaks **a** (2.17 ppm) and **b** (1.51 ppm) totally disappeared, once again highlighting the occurrence of both transcarbonation with hydroxyketone release and 5CC formation with later ring-opening. However, it is hardly possible to calculate selectivities toward transcarbonation (desired product) or 5CC formation (side product) since 5CC formation is always accompanied with its ring-opening which signals are not correctly attributed, especially for the peak at 1.36 ppm. Additionally, both bisLC1 monomers and oligomers present similar chemical shifts due to their analogue structures, inducing peak overlapping that would alter their relative peak integration.

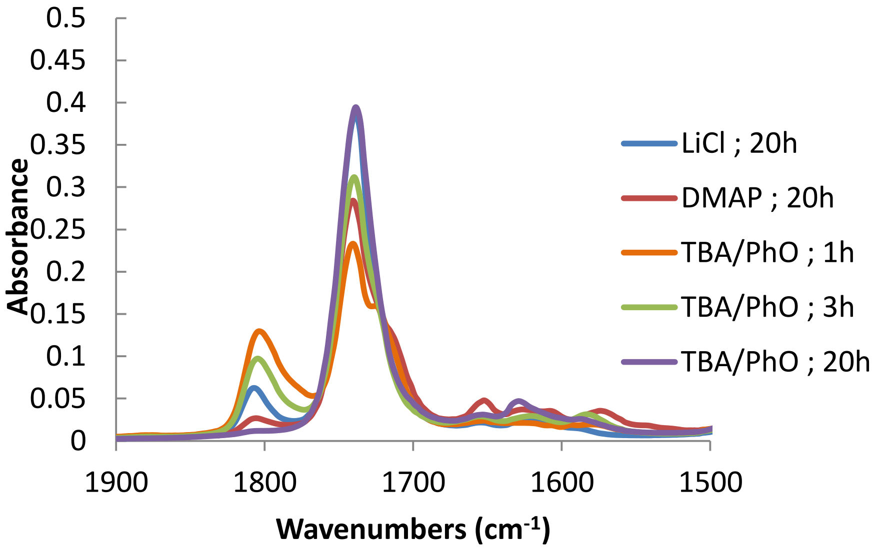


Figure 8: ATR-IR spectra of crude mixture obtained after oligomerization step. Presence of undesired 5CC compound is evidenced with absorption band at 1800 cm^{-1}, but could not be seen at the end of reaction time using TBA/PhO as catalyst.

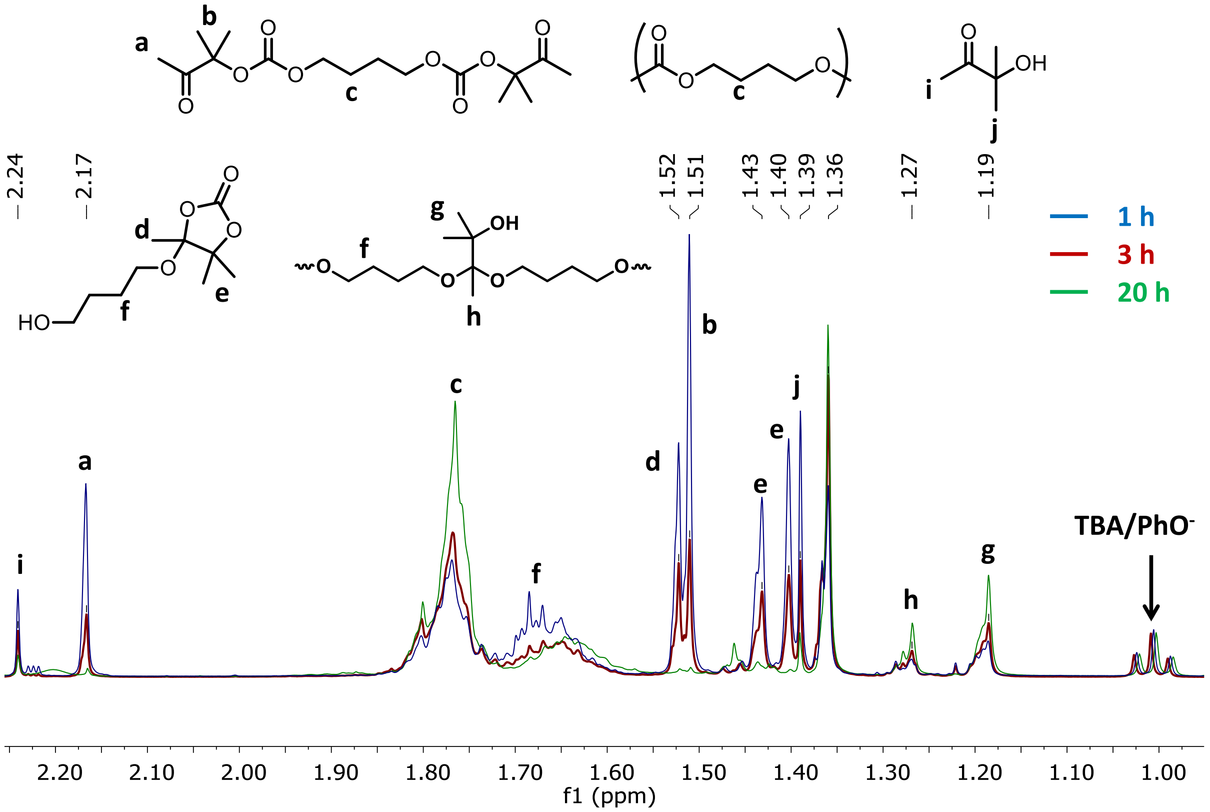


Figure 9: ^{1}H NMR spectra overlay of crude mixture obtained after 1 h ; 3 h ; and 20 h using TBA/PhO as the catalyst for the oligomerization step.

GPC chromatograms comparison of oligocarbonates synthesized with DMAP and TBA/PhO$^-$ catalyst that afforded oligomers with a molar mass of 500-600 g/mol, with previous results obtained with LiCl is presented in Fig. 10. So far, the best result in terms of affordable molar masses and 1,4-butanediol conversion is still obtained with LiCl as the catalyst, despite the 5CC generation alongside with oligocarbonates.

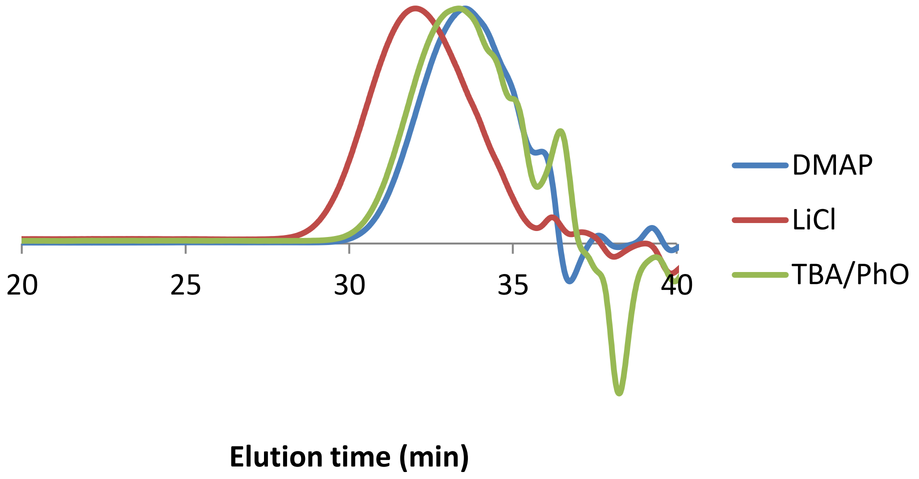


Figure 10: GPC chromatograms of crude mixture obtained after oligomerization step for different catalysts. Conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; catalyst (0.05 eq) ; 140 °C ; 20 h.

III-2-a-ii) Chain-extension step

The synthesis of poly(butylene carbonate) (R = R' = $(CH_2)_4$) was then carried out taking into account previous observations derived from the oligomerization step. Results are presented in Table 4. The chain-extension only consisted on applying a high vacuum to the reaction media to quantitatively remove the hydroxyketone ($T_{boiling}$ = 140 °C). Vacuum was increased progressively to reach the final pressure of 10 Pa. It should be noted that the oligomerization and chain-extension steps are carried out in the same batch (one pot/ two steps). Due to the aliphatic structures of monomers, low T_g and melting points (T_m) are expected for the final polymer (T_g = -32 °C ; T_m = 56 °C for poly(butylene carbonate) of M_n = 40,000 g/mol[17]), so that this step was realized at a temperature identical to the one of the oligomerization step. No apparent chain mobility limitation caused by a viscosity increase of the reaction media was observed, and satisfying stirring could be maintained. As TBA/PhO^- proved its efficiency for the oligomerization leading to low molar mass oligocarbonates with no traces of remaining 5CC observed (as shown previously by ^1H NMR and ATR-IR after 20 h), it was first tested for the overall polycondensation process, with oligomerization time and chain-extension time of 24 h. Surprisingly, only low molar mass oligocarbonates were afforded with M_n = 520 g/mol (Table 4, entry 1) after 48 h. Compared to the oligomerization step, no molar mass increase occurred but lower 1,4-butanediol conversion was observed, probably due to thermal degradation of short oligocarbonates exposed to high temperature for a long time (48 h at 140 °C) in basic conditions, such as unzipping, β-H transfers or decarboxylation that have already been reported for oligomers with much higher molar masses (M_n > 5,000 g/mol)[18].

Table 4: Chain-extension tests with different catalysts, oligomerization and chan-extension times. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; catalyst (0.05 eq) ; 140 °C

Entry	Catalyst	Oligomerization time	Chain-extension time	M_n (crude) g/mol ; [D]	M_n (precipitated) g/mol ; [D]	T_g (°C)	T_d (°C)	Tm (°C)
1	TBA/PhO	24h	24h	520 [1.82]	ND[a]	ND	ND	ND
2	LiCl	3h	3h	1,500 [1.63]	ND[a]	ND	ND	ND
3	LiCl	3h	24h	2,150 [2.04]	8,000 [1.30]	-35	278	35
4	LiCl	24h	24h	2,900 [2.06]	11,000 [1.30]	-39	252	35

[a] : Precipitation failed due to the low molar masses of the chains

When LiCl was used as the catalyst, poly(butylene carbonate) could be obtained, with M_n in the range of 1,500 to 2,900 g/mol (Table 4, entries 2-4). Increasing both oligomerization and chain-extension time was beneficial for higher molar masses and a typical polycondensation dispersity of 2 on the crude product was obtained for longer chain-extension time (Table 4, entries 3-4). The SEC chromatograms of the crude polymers synthesized with the most effective catalysts are presented in Figure 11 and underline the growth of the PC chains. Typical ^{1}H NMR spectra of crude mixture with LiCl as catalyst is presented in Figure 12a. Alike oligomers, the microstructural characterization of the chains reveals peaks correlated to poly(butylene carbonate), 1,4-butanediol and ketal linkages. However, the multiple peaks observed initially in the 1.10 – 1.60 ppm for the oligomers are now reduced to three singlets at respectively 1.36 ; 1.27 and 1.19 ppm, similarly to what was obtained with TBA/PhO$^-$ after 20 h of oligomerization step (see Fig. 9) . Once again, it is suggested that these signals come from ring opening of the 5CC side product, leading to incorporation of ketal defects in the polymer chain. Further 2D NMR, presented in Figure 13a and 13b, confirmed their nature of terminal CH_3, likely originating from methyl substituents found on 5CC side-products. Interestingly, HMBC analysis indicated that these CH_3 are close to carbon with chemical shifts of 76 ppm, likely a quaternary carbon bearing two methyls and an alcohol function, and of 100 ppm, likely a ketal carbon. Regarding the peak at 3.50 ppm (see Fig. 12), the 2D NMR spectra (Figure 13b) could confirm the formation of a methylene attached to the hemiketal carbonate linkages CH_2 in alpha position of a ketal linkage (protons correlated with carbon shifted at 62 ppm), but HMBC did not reveal any correlation with carbon shifted to 100 ppm.

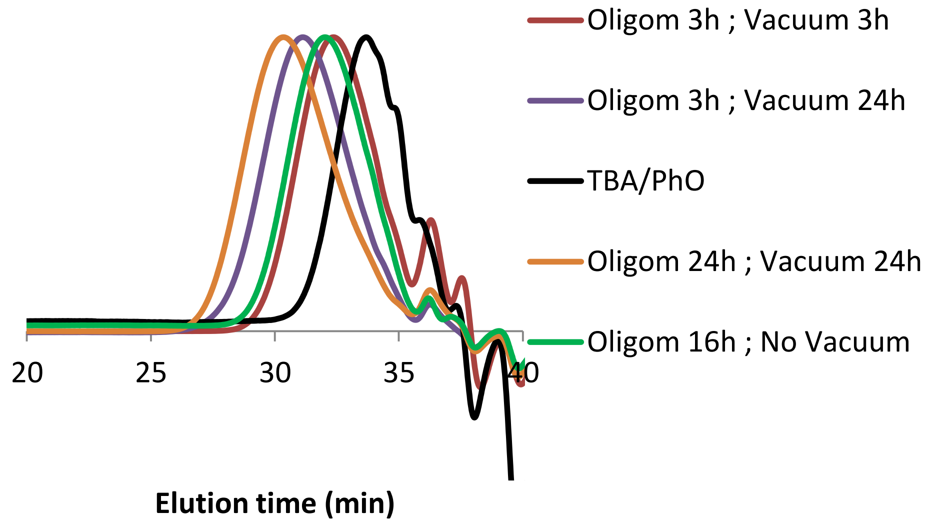


Figure 11: GPC chromatograms of crude mixture obtained after chain-extension step. When not specified, catalyst used was LiCl (see Table 4 for more details). Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; catalyst (0.05 eq)

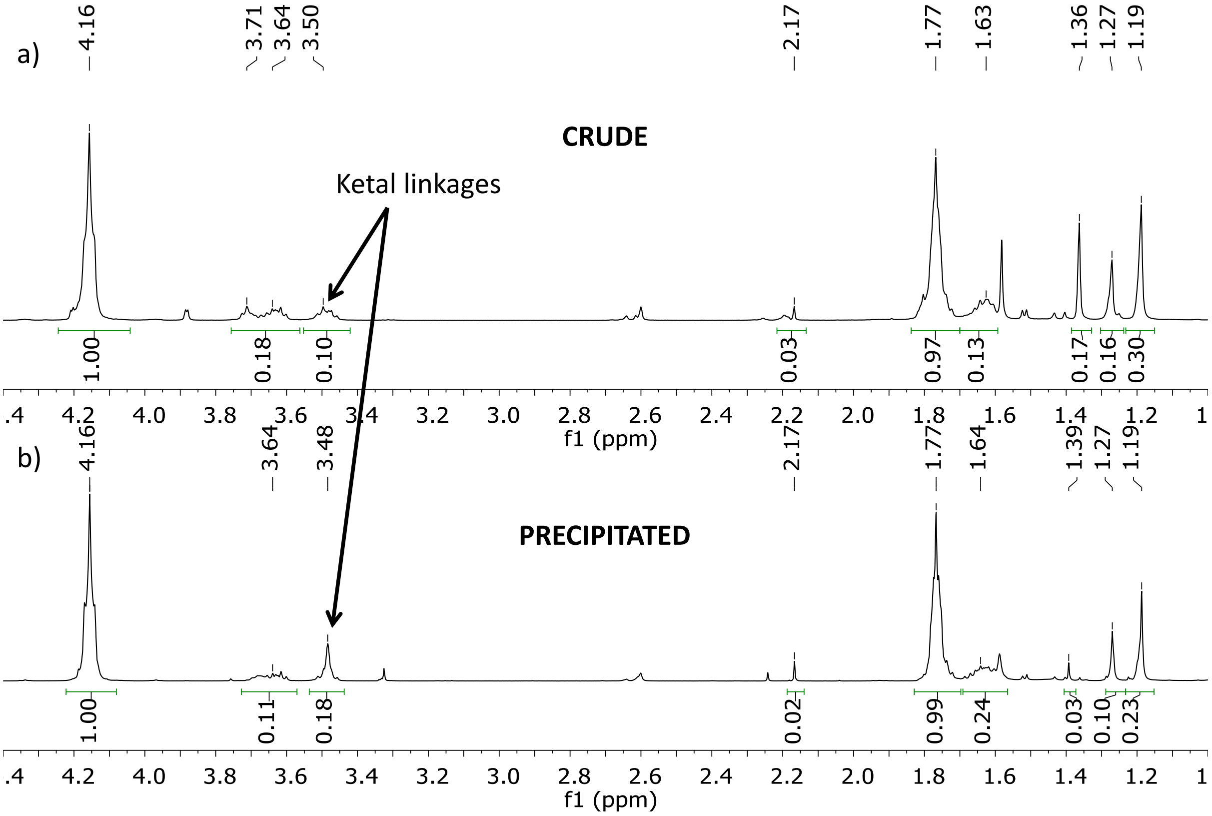


Figure 12: ^{1}H NMR spectra of crude (a) and precipitated (b) products obtained after chain-extension step. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C ; 48 h.

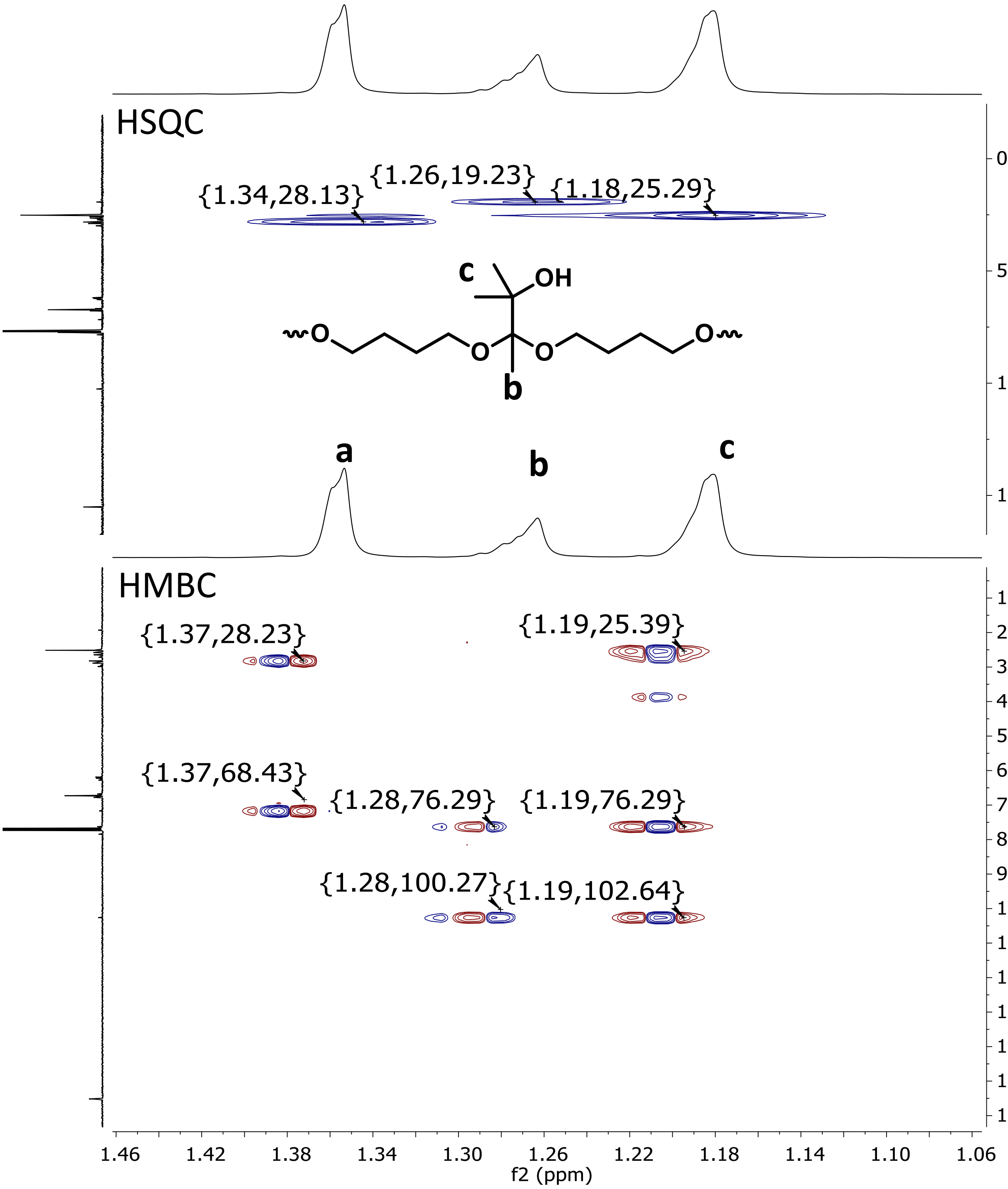


Figure 13a: HSQC and HMBC NMR analysis in the region of 1 – 1.5 ppm of the crude mixture obtained after chain-extension step. Peak **a** could not be properly identified and assigned to a specific chemical structure. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C ; 48 h.

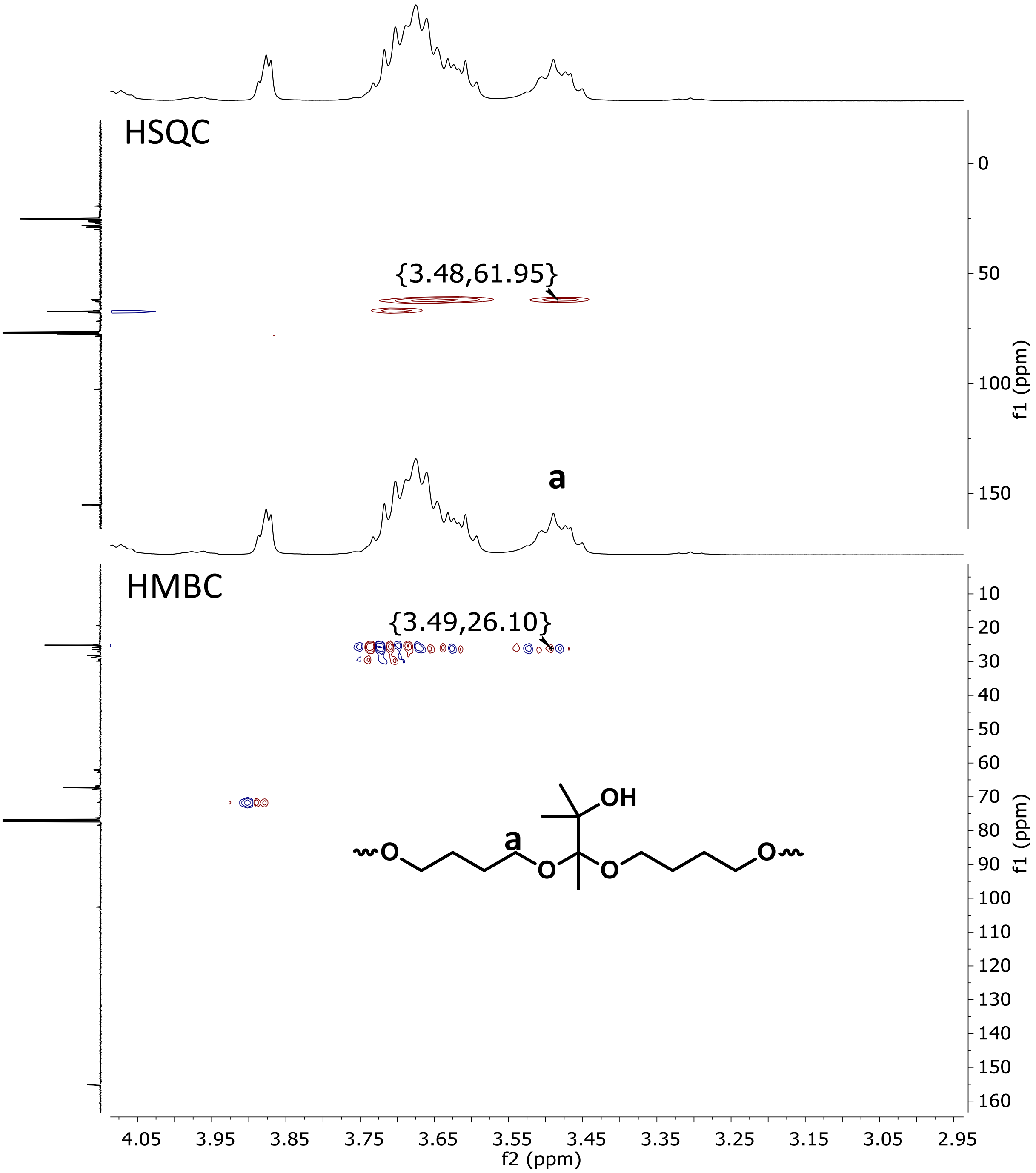


Figure 13b: HSQC and HMBC NMR analysis in the region of 1 – 1.5 ppm of the crude mixture obtained after chain-extension step. Peak **a** could not be properly identified and assigned to a specific chemical structure. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C ; 48 h.

ATR-IR characterization of the crude sample further confirms the absence of 5CC moieties within the polymer microstructure. The evaporated fraction was also recovered in a cold trap and analysed by ^{1}H NMR to identify the structure of the released product (Figure 14). One would expect to obtain pure hydroxyketone, but several additional signals attributed to 1,4-butanediol, bisLC1 and 5CC derivatives could be detected. Indeed, due to their relative volatility at 140 °C under reduce pressure of 10 Pa, and due to the incomplete conversion of 1,4-butanediol after 20 h of oligomerization, they are likely to evaporate in such experimental conditions, which provokes a deviation of the perfect stoichiometry with detrimental effect on the final molar masses (see below).

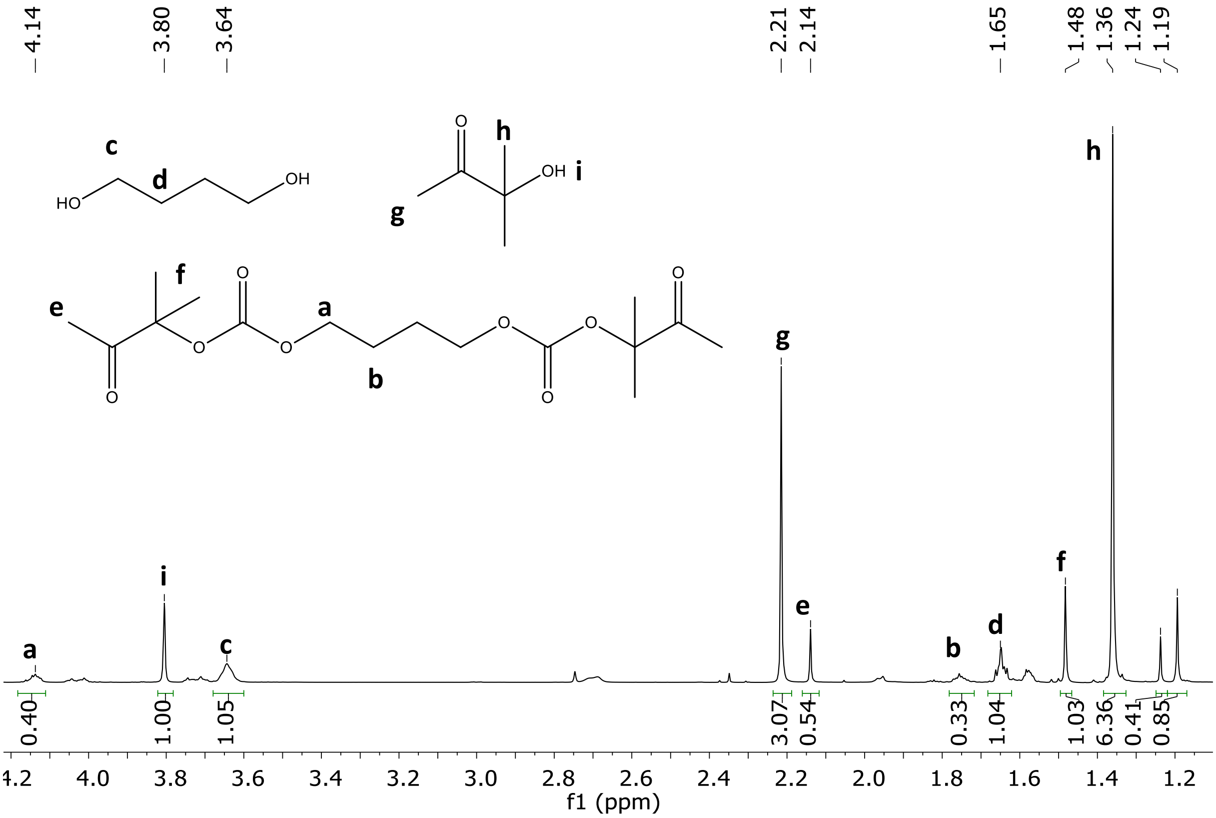


Figure 14: ^{1}H NMR spectrum of the fraction recovered in the cold trap after chain-extension step under vacuum. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C ; 48 h.

When molecular weights were high enough, solubilisation of the crude mixture in dichloromethane followed by reprecipitation in methanol led to the isolation of polycarbonates with M_n up to 11,000 g/mol (Table 4, entry 4), with eliminations of short chains (see Fig. 15 for GPC chromatograms). However, the overall recovered mass of polymer is rather low compared to monomers loading (around 20 % recovered), likely due to the solubility of shorter chains in methanol. ^{1}H NMR spectrum of precipitated polymer obtained with LiCl as catalyst is presented in Figure 12b. Even though the peak at 1.37 ppm tends to disappear after reprecipitation, meaning that it belongs to low molar masses species, singlets at 1.27 and 1.19 ppm could still be attributed to the polymer backbone. The ^{13}C NMR spectrum of the precipitated polymer is presented in Figure 16. Interestingly, the chains are end-capped by OH (methylene signal at 3.64 ppm) and oxo-carbonate (methyl signal at 2.17 ppm) moieties as evidenced in Figure 12b. However, the comparison of the relative integrations of both signals indicates that the hydroxyl chain ends were largely dominant (> 98%). In this regard, stoichiometry of alcohols and carbonate functions of chain ends is not respected which is in accordance with side-reactions observed, and explains the limitations in terms of molar masses.

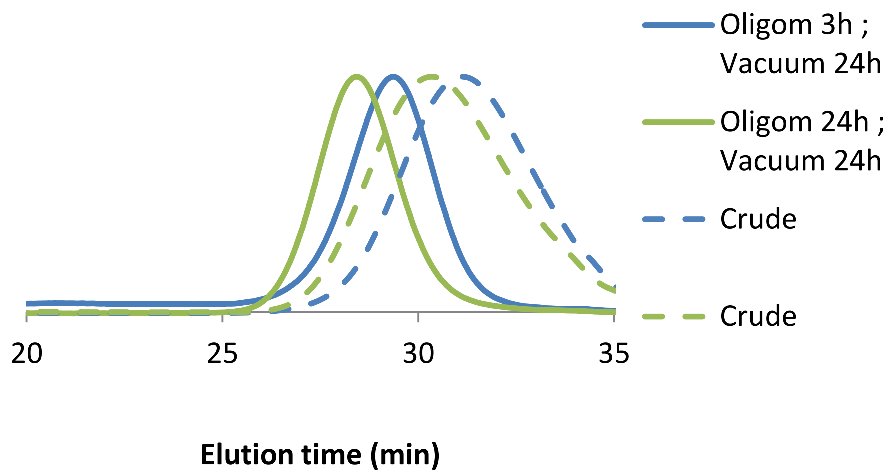


Figure 15: GPC chromatograms comparison between crude mixtures and precipitated products. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C

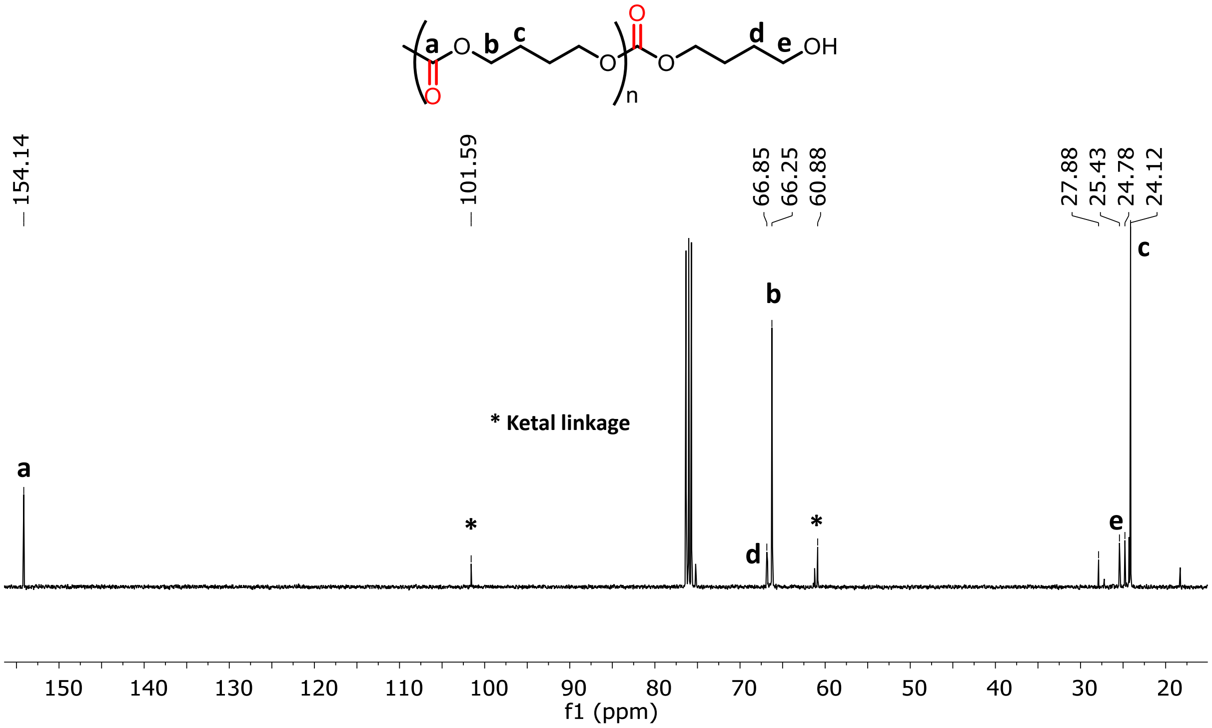


Figure 16: ^{13}C NMR spectrum of the precipitated product obtained after chain-extension step. Experimental conditions: 1,4-butanediol (1 eq) ; bisLC1 (1 eq) ; LiCl (0.05 eq) ; 140 °C ; 48 h.

Thermal properties of precipitated polymers were evaluated via TGA and DSC analysis. As expected due to their aliphatic structures, they display a low T_g (- 35 °C and – 39 °C respectively) and are semi-crystalline with melting points at 35 °C.

III-2-b) Poly(isosorbide carbonate) synthesis

Synthesis of poly(isosorbide carbonate) is of high interest as it could potentially compete with the traditional phosgene and BPA-based aromatic polycarbonates in terms of mechanical and thermal properties. Thus, the previous study on the melt polycondensation of bisLC1 with 1,4-butanediol as the building block was extended to isosorbide and its bisLC2 analogue (R = R' = isosorbide in Fig. 4). Similarly to section II-1), the same protocol was applied, i.e. an oligomerization step followed by the chain-extension.

III-2-b-i) Oligomerization step

Unlike 1,4-butanediol, isosorbide displays two non-equivalent alcohol moieties with different reactivities, namely “endo” alcohol and “exo” alcohol (see Chapter 3). By choosing an appropriate catalyst, both alcohol moieties can be selectively activated, balancing the difference of reactivities. Thus, it is crucial for polycondensation processes to keep the endo/exo ratio of isosorbide end-capped polymer chains close to 1 to obtain high molar masses and prevent potential unactivation of one of the alcohol moiety by the catalytic system, which would prevent chain-extension. Capitalizing on our previous investigations, various catalysts, including Lewis acids, organobases and organic complexes were tested at 140 °C for 24 h to build oligomers. Results are presented in Table 5. As a general remark, similarly to what was observed with 1,4-butanediol, no oligomers could be formed without the presence of 5CC as side-products. Selected examples of ATR-IR spectra of oligomers are presented in Fig. 17 to illustrate this observation. Lewis acids ($ZnCl_2$, $AlCl_3$, $Sn(Oct)_2$) were ineffective catalysts and no oligomer was produced even if some of them ($ZnCl_2$ and $Sn(Oct)_2$) provided 5CCs in traces (Table 5, entries 3-5). The utilization of organobases (DBU, TBD) or basic ionic liquid (TBA/PhO) delivered oligomers with M_n = 450-600 g/mol - as attested by ATR-IR spectroscopy highlighting the characteristic signal of the ketone at 1720 cm^{-1} of the bisLC2 monomer that tended to disappear - as well as a 5-membered cyclic carbonate – carbonyl stretching at 1805 cm^{-1} (Table 5, entries 6-9). These results indicate that both transcarbonation and side cyclization occurred simultaneously. DMAP didn't afford oligomer (Table 5, entry 8) but the characteristic carbonyl bands at 1805 cm^{-1} (Fig. 17, black curve) detected within the ATR-IR spectrum reveals the formation of the 5CC. Finally, organic complexes made of a superbase (DBU or TBD) with methane sulfonic acid (MSA) or benzoic acid (BA) and known for their high thermal stabilities in transesterification reaction[19], were tested as potential transcarbonation catalysts (Table 5, entries 10-13). Surprisingly, only the DBU:BA complex furnished oligomers (M_n = 460 g/mol) with concomitant formation of the 5CC. Alike previous study with bisLC1, LiCl was the most active catalyst providing oligomers with the highest M_n of 800 g/mol even if the formation of 5CC could not be avoided. Interestingly, with DBU and DBU:BA catalytic systems, the endo/exo OH ratio was estimated to 0.67 and 0.51, respectively, suggesting a preferential activation of the endo OH of isosorbide. Other bases such as TBD or TBA/PhO^- as well as LiCl furnished endo/exo OH ratios of 0.9 to 1.04, indicating that both alcohols moieties of isosorbide are activated and do react in a similar fashion. Alike 1,4-butanediol, LiCl seems to be the most suitable catalyst for the melt-polycondensation of isosorbide with its bisLC2 analogue.

Table 5: Oligomerization tests with different catalysts. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; catalyst (0.05 eq)

Entry	T (°C)	Time	Catalyst	M_n (g/mol)	endo/exo	Observations
1	140	3h	LiCl	380	0.84	Oligomers. Presence of 5CC
2	140	24h	LiCl	800	1.04	Oligomers. Presence of 5CC
3	140	24h	$ZnCl_2$	/	/	No oligomers. Presence of 5CC
4	140	24h	$AlCl_3$	/	/	No oligomers. No side-products
5	140	24h	$Sn(Oct)_2$	/	/	No oligomers. Presence of 5CC
6	140	24h	TBA/PhO	450	0.92	Few oligomers. Presence of 5CC
7	140	24h	DBU	650	0.67	Oligomers. Presence of 5CC
8	140	24h	DMAP	/	/	No oligomers. Presence of 5CC
9	140	24h	TBD	600	0.90	Oligomers. Presence of 5CC
10	140	24h	DBU:MSA[a]	/	/	No oligomers. No side-products
11	140	24h	DBU:BA[a]	460	0.51	Few oligomers. Presence of 5CC
12	140	24h	DMPA:MSA[a]	/	/	No oligomers. No side-products
13	140	24h	TBD:MSA[a]	/	/	No oligomers. No side-products

[a]: Organic salts known to be stable at high temperature were prepared according to previous study where their chemical structures are described[19]

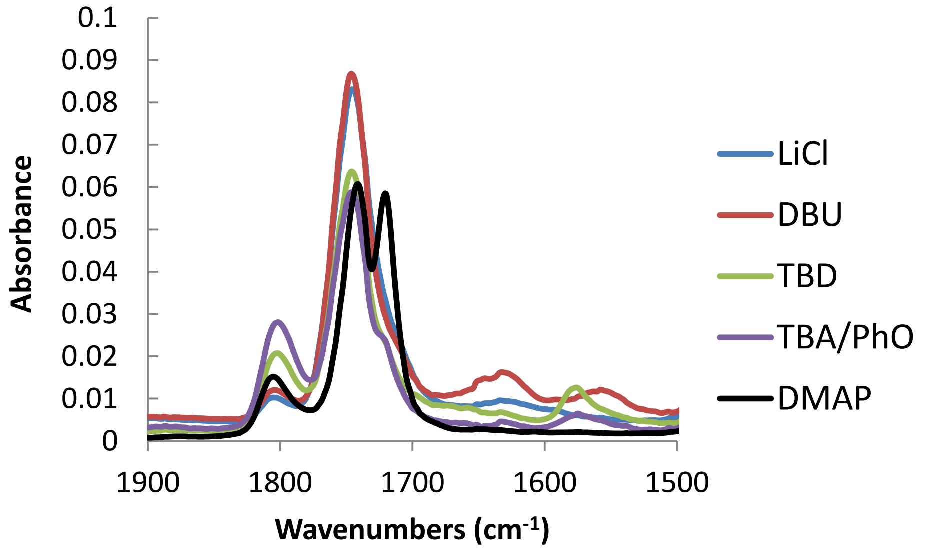


Figure 17: ATR-IR spectra of the crude mixtures obtained after the oligomerization step. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; catalyst (0.05 eq) ; 140°C ; 24 h

^{1}H NMR characterization of the crude mixture obtained after 24 h with LiCl is depicted in Figure 18. As described before, presence of 5CC could generate multiple side-products that could explain non-assigned peak in the region of 1.10 – 1.70 ppm. In accordance with previous studies[9,20,21], the “endo” alcohol moiety was assigned to peak at 3.57 ppm (peak **f**, methine) and 4.64 ppm (peak **e**, 1 H), whereas the "exo" one was assigned to the methine signal at 4.38 ppm (peak **g**, 1 H).

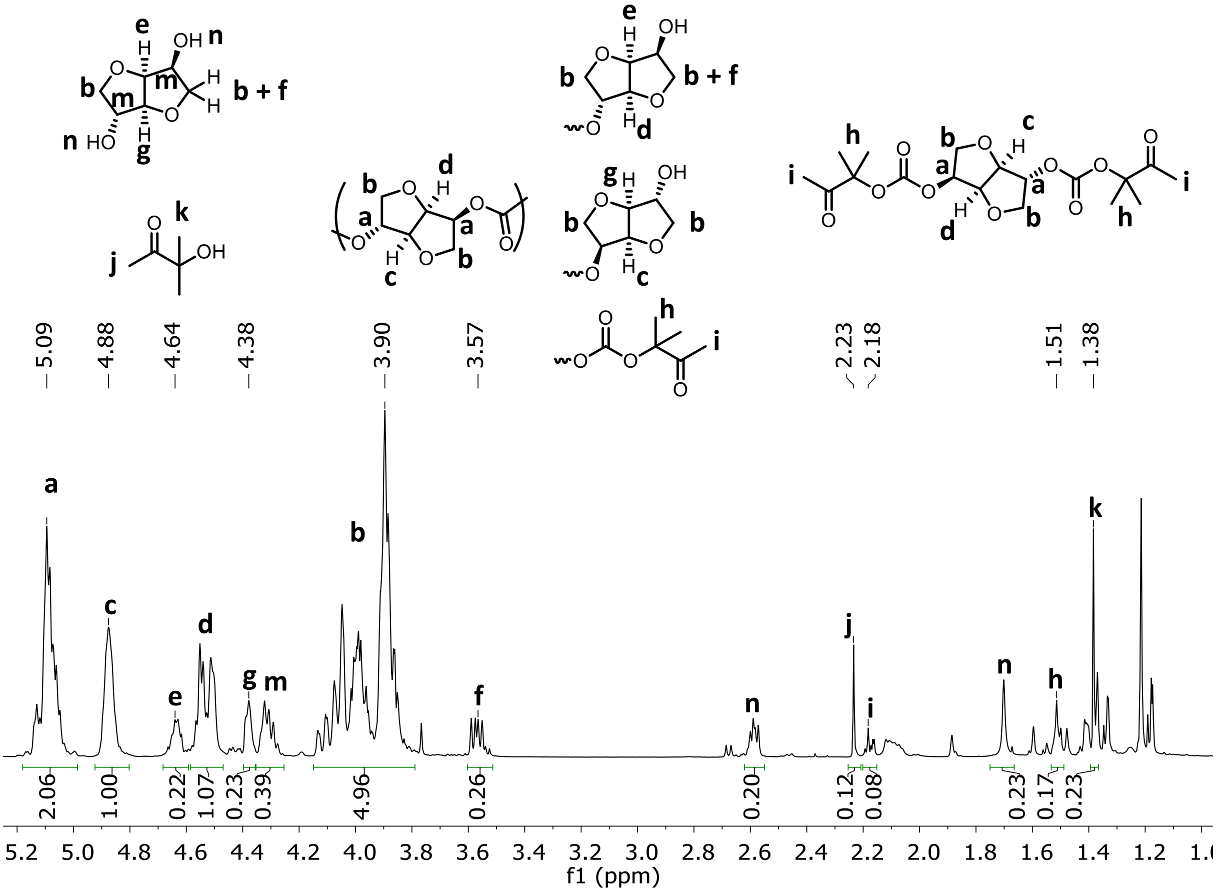


Figure 18: ^{1}H NMR of the crude mixture obtained after oligomerization step using LiCl as the catalyst. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq) ; 140°C ; 24 h

Figure 19 illustrates the SEC chromatograms of the crude polymer synthesized with most efficient catalysts. The presence of oligomers (dimers, trimers, tetramers and longer oligomers) is evidenced with multiple shoulders on the SEC profile when DBU, TBD and TBA/PhO$^-$ were used as catalysts, whereas LiCl delivered oligomers with higher molar masses. Still, unlike 1,4-butanediol, the molar masses of the oligomers are low, even though the repeating units (isosorbide carbonate) are of higher mass, indicating lower diol conversion and thus lower DP.

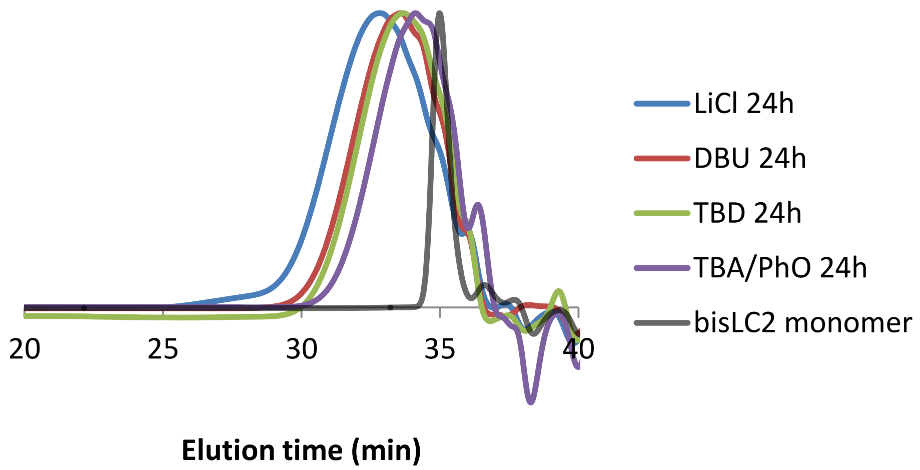


Figure 19: GPC chromatograms of the crude mixtures obtained after oligomerization step. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; catalyst (0.05 eq) ; 140°C ; 24 h

III-2-b-ii) Chain-extension step

Based on the oligomerization step observations, the synthesis of poly(isosorbide carbonate) was carried out using LiCl as the catalyst. Various oligomerization and chain extension times and temperatures were tested to evaluate their influence on polymer molar mass and its thermal properties. Results are presented in Table 6. But, prior results discussion, one would like to underline a general observation. The so-produced polymers were most of the time hardly soluble in common organic solvents (acetonitrile, tetrahydrofuran, dichloromethane, chloroform, dimethylformamide, dimethylsulfoxide…) rendering their purification and structural characterization hard to perform accurately. These solubility concerns are not reported in the literature for homopoly(isosorbide carbonate), and, in our case, are most likely due to defects in the polymer backbone or partial crosslinking/branching caused by side-reactions. This is illustrated by the SEC profiles (see Fig. 20) of the polymers recorded in DMF as the eluent that present a bimodal-like shape with a sharp peak at long elution times and a broad shoulder at short elution times. This second broad peak was attributed to the presence of aggregates in DMF which formation was confirmed by DLS measurements that exhibited two particles sizes (13.9 nm, st. dev = 3.6 and 133.9 nm, st. dev = 44.1 in number distribution). Thus, dispersity and number average molar mass M_n could be biased. By overlaying the chromatograms, one can still compare different polymer populations and assess which one has the higher molecular weights.

According to our previous investigations, the chain extension of the oligomers was conducted for 6 h at 140 °C under high vacuum (Table 6, entry 1). Surprisingly, the resulting crude mixture only afforded oligocarbonates of M_n = 700 g/mol, which is rather similar to the value obtained after the oligomerization step. Still, reprecipitation in methanol allowed the recovery of higher molar masses chains (M_n = 2,500 g/mol), which represented 25 % in mass of the crude mixture. Contrary to what was obtained at the end of the oligomerization step, the endo/exo ratio is of 1.7 which indicates a lower reactivity for the "endo" alcohol. When the chain extension temperature was increased to 180 °C, a polymer with a slightly higher molar mass of 3,000 g/mol (after precipitation) could be afforded (Table 6, entry 2), supposedly due to a lowering of the reaction media viscosity. Indeed, chain mobility limitations were observed when the reaction was left at 140 °C as soon as the chain extension step started and satisfying stirring of the reaction media could not be maintained. Thus, it is believed that, for the same reaction time, increasing the temperature would allow more transcarbonation reactions as alcohol and carbonate functions on different oligomers are more likely to collide. Similarly, increasing the reaction time of the chain extension step from 6 h to 20 h led to significant increase of molar masses of the crude sample up to 2,200 g/mol (Table 6, entries 3-4, Figure 20).

Table 6: Chain-extension tests with different oligomerization and chain-extension times and temperature. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq)

Entry	Oligomerization		Chain extension[a]		Mn ; (Crude ; g/mol) ; [D]	Mn ; (Precipitated ; g/mol) ; [D]	endo/exo[b]	Tg (°C)	Td (°C)
	Time	T°C	Time	T°C					
1	24h	140°C	6h	140°C	700 ; [1.86]	2500 ; [3.2]	1.7	119	273
2	24h	140°C	6h	180°C	800 ; [79]*	3000 ; [32]*	1.6	118	275
3	3h	140°C	20h	140°C	1400 ; [12]*	2780 ; [12]*	2	124	288
4	3h	140°C	20h	180°C	2200 ; [15]*	2100 ; [8.56]*	1.75	132	305
5[c]	3h	140°C	20h	180°C	782 ; [1.63]	1880 ; [1.21]	2.11	116	300
6[d]	3h	140°C	20h	180°C	860 ; [1.67]	2000 ; [1.21]	1.75	121	310
7[e]	3h	140°C	20h	180°C	880 ; [1.64]	2000 ; [1.40]	1.88	122	292
8[f]	3h	140°C	3h	140°C	1500 ; [1.96]	2700 ; [1.48]	1.58	124	306
9[f]	3h	140°C	3h	240°C[g]	3100 ; [3.6]	2200 ; [3.0]	0.91	124	327

[a]: Light vacuum was first applied, and then increased after 3h to reach 10 Pa. When specified, T°C was increased to 180°C after 3h at light vacuum.

[b]: endo/exo ratio was calculated by ^{1}H NMR on the precipitated polymers.

[c]: 1.1eq of ISB was used instead of 1.

[d]: 1.05eq of ISB was used instead of 1.

[e]: 1.05eq of bisLC was used instead of 1.

[f]: Specific polycondensation reactor was used to overcome mass transfer limitations.

[g]: T °C was increased by 20°C every 30min. Final T °C of 240°C was applied for 30min.

*: Unrealistic values of dispersities biased by the presence of significant amounts of aggregates

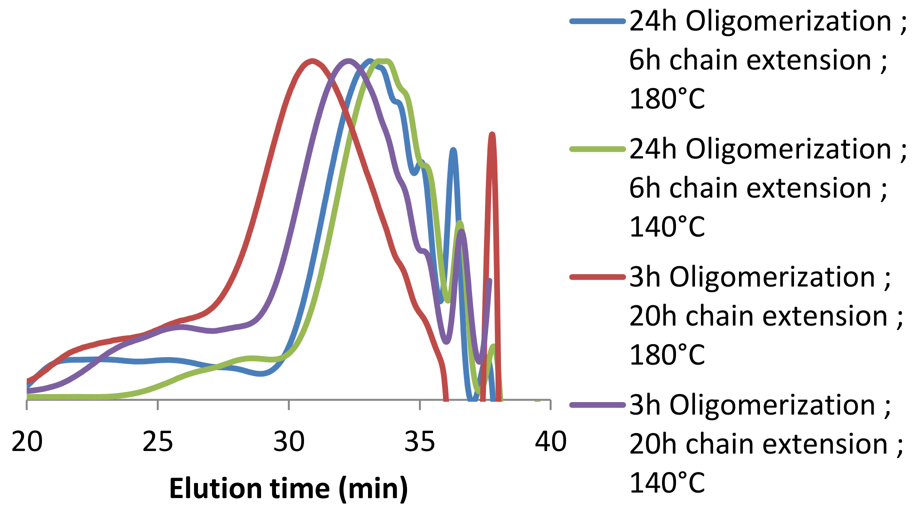


Figure 20: GPC chromatograms of crude mixtures after chain-extension step for different oligomerization and chain-extension times and temperatures. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq)

Typical ^{1}H NMR spectra of the crude and precipitated polymers are presented in Figure 21. As no cyclic carbonate traces were detected in ATR-IR (see Fig. 22), the two peaks at 1.17 and 1.21 ppm were assigned to defects within the polymer microstructure resulting from 5CC ring opening or side products. After reprecipitation, the ratio between the integration values of these peaks and signals specific to the isosorbide chain ends decreased, in accordance with short chains removal evidenced by GPC analysis (Fig. 20). As it was mentioned in the case of 1,4-butanediol, the final polymer synthesized seems to only have isosorbide alcohol moieties as chain ends, as no bisLC2 signals could be found via NMR characterization. Stoichiometric deviations caused by 5CC formation and its ring-opening as side reaction thus justify the limitations in terms of affordable molar masses. However, the evaporated fraction recovered in the cold trap did not justify the absence of side products in the crude mixture, as pure hydroxyketone was collected at the end of the chain-extension step (see Figure 23 for ^{1}H NMR and ATR-IR spectra). ^{13}C NMR spectrum of the precipitated polymer, presented in Figure 24, showed characteristic isosorbide carbonate linkages with peak resonance at 154 ppm, 153.5 ppm and 153.2 ppm (peak **a**) indicating a random distribution of endo-endo, endo-exo and exo-exo carbonate linkages in the polymer backbone. The non-assigned peak in the region of 70 – 90 ppm can be correlated to isosorbide chain ends entities, confirmed by 2D NMR. The unidentified peak at 27 ppm was correlated to peaks at 1.17 and 1.21 ppm in ^{1}H NMR, supposedly due to defects in the polymer backbone brought by 5CC ring opening side reactions. Alike the supposition we did for poly(butylene carbonate), these signals could correspond to a ketal linkage but the complexities of the NMR spectra as well as the chemistry behind the polymerization system prevent us to draw any undoubtable conclusions.

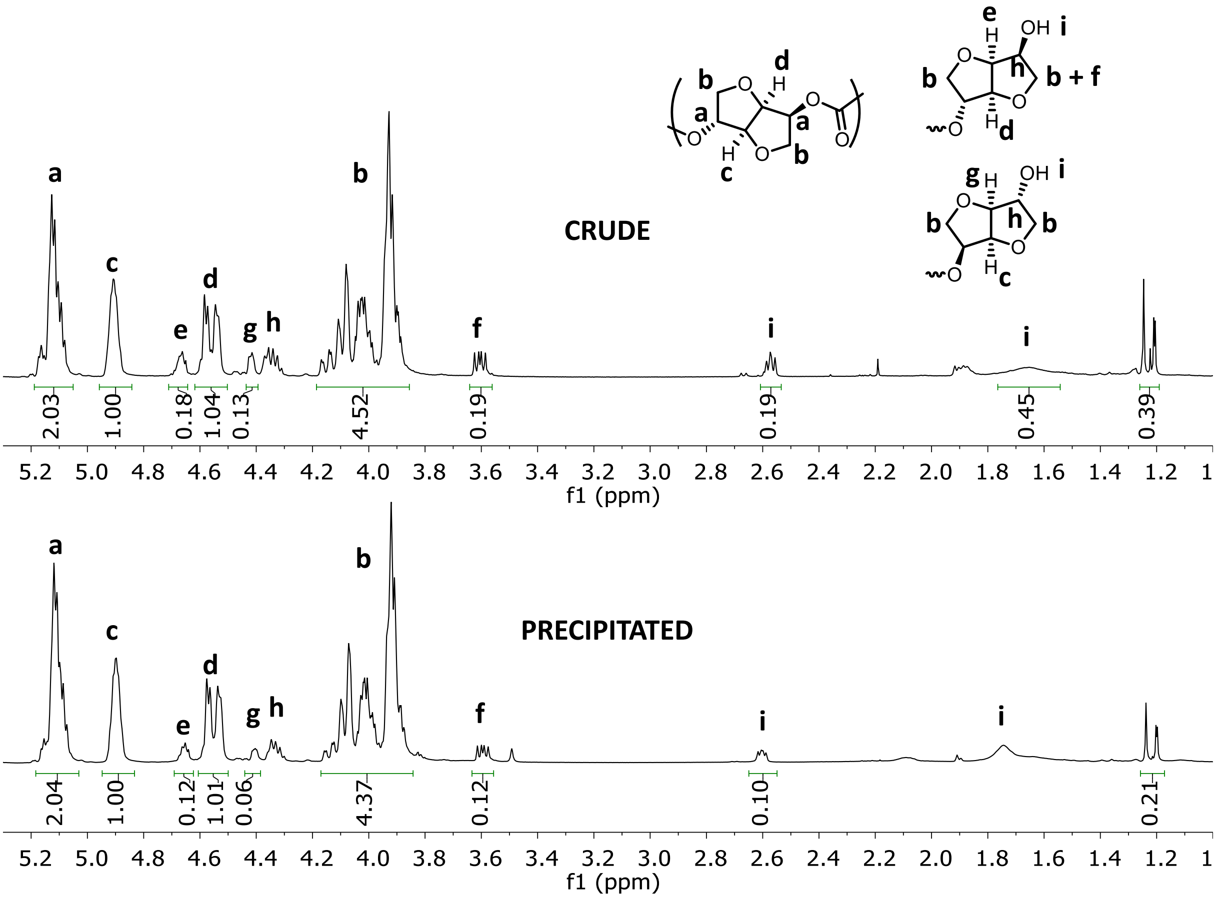


Figure 21: ^{1}H NMR spectra of crude (a) and precipitated (b) products obtained after chain-extension step. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq) ; 140 °C for both steps ; 23 h (Table 6 entry 3)

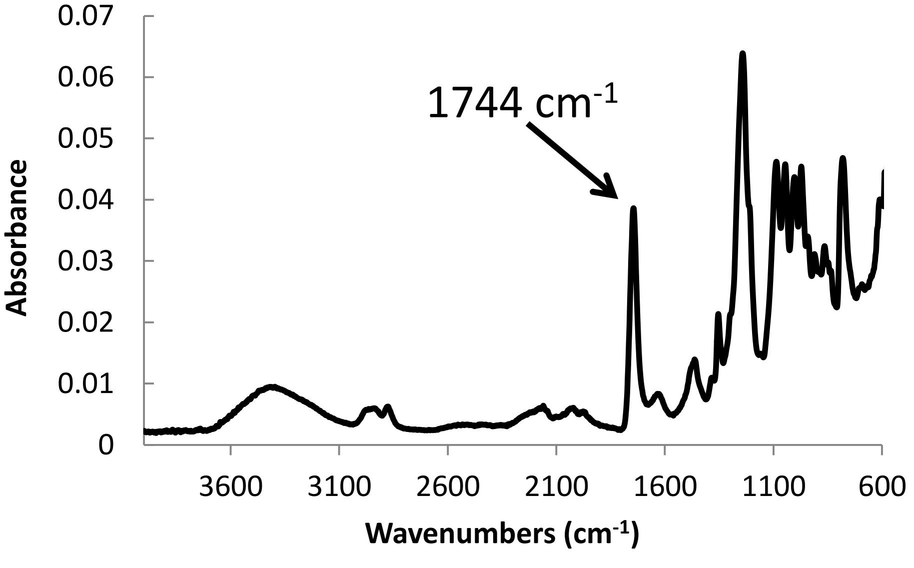


Figure 22: ATR-IR spectrum of the crude mixture obtained after chain-extension step. No 5CC could be detected. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq) ; 140 °C for both steps ; 23 h (Table 6 entry 3)

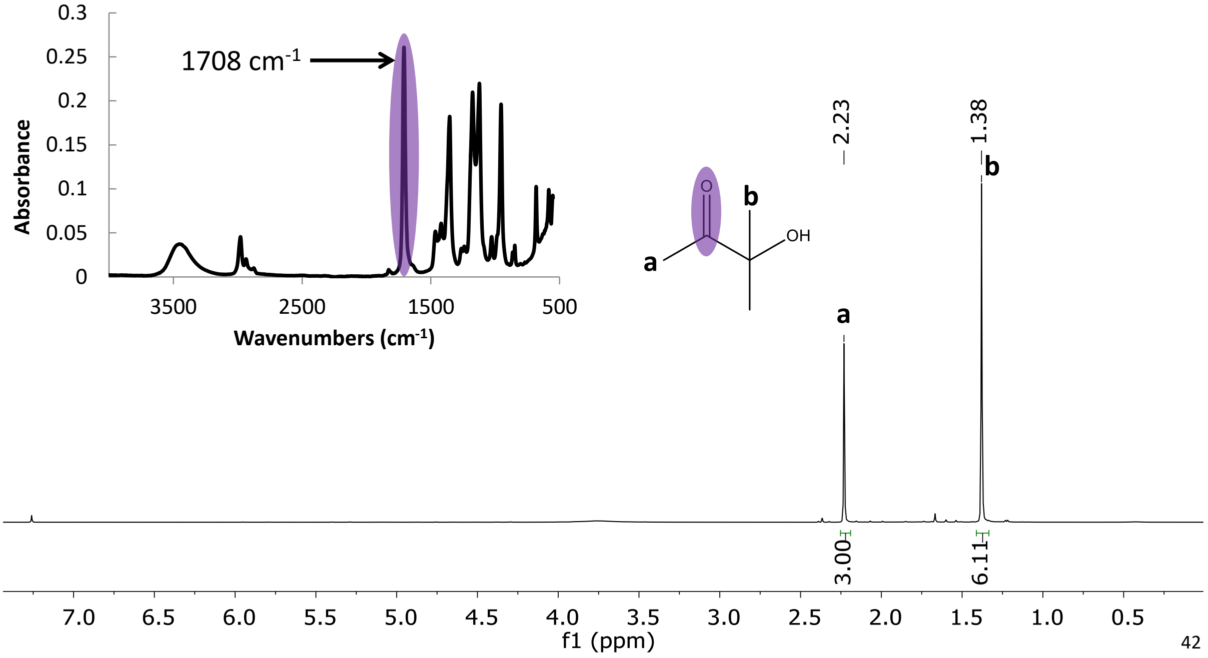


Figure 23: ATR-IR and ^{1}H NMR spectra of the recovered fraction in the cold trap after chain-extension step. Pure hydroxyketone is collected. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq) ; 140 °C for both steps ; 23 h (Table 6 entry 3)

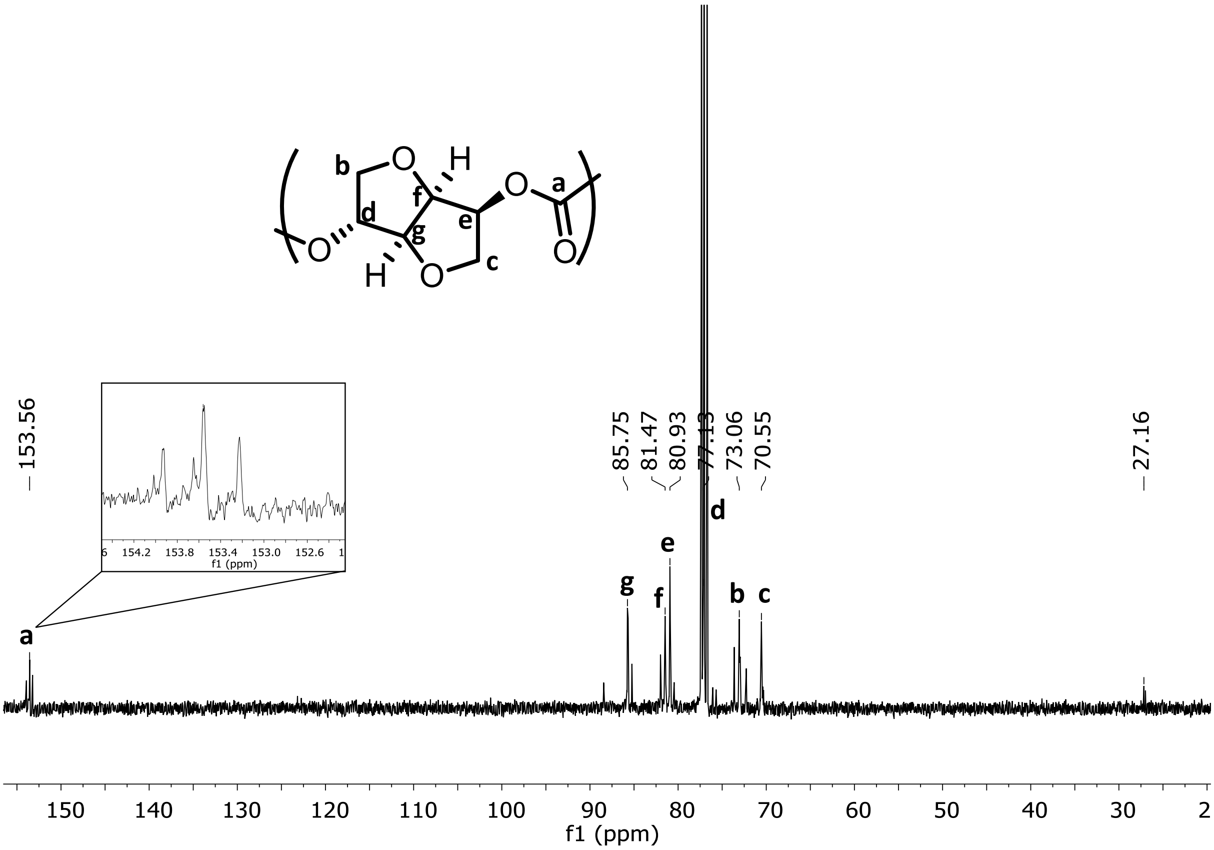


Figure 24: ^{13}C NMR spectrum of the precipitated polymer obtained after chain-extension step. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq) ; 140 °C for both steps ; 23 h (Table 6 entry 3)

Changing the number of equivalents of monomers to better avoid stoichiometric concerns was tried, but did not prove its efficiency on the overall molar masses afforded for both the crude and precipitated polycarbonates (Table 6, entries 5-7). As chain mobility limitations due to high viscosity increase seem to prevent from satisfying chain-extension of the oligocarbonates, experiments were carried out in a proper high-temperature polycondensation reactor equipped with mechanical stirrer. Due to limited access to the equipment (provided by UMons partner – CIRMAP Laboratory), shorter reaction times were applied. Still, great increase of the molar masses was observed at 140 °C after only 3 h of oligomerization and 3 h of chain-extension step compared to results obtained in glass flasks (Table 6, entry 8). Applying a temperature ramp of 40 °C/h up to 240 °C led to the best result in terms of molar masses with M_n up to 3,100 g/mol of the crude sample (see Fig. 25 for GPC chromatograms) and endo/exo ratio close to 1 (0.91; Table 6, entry 9).

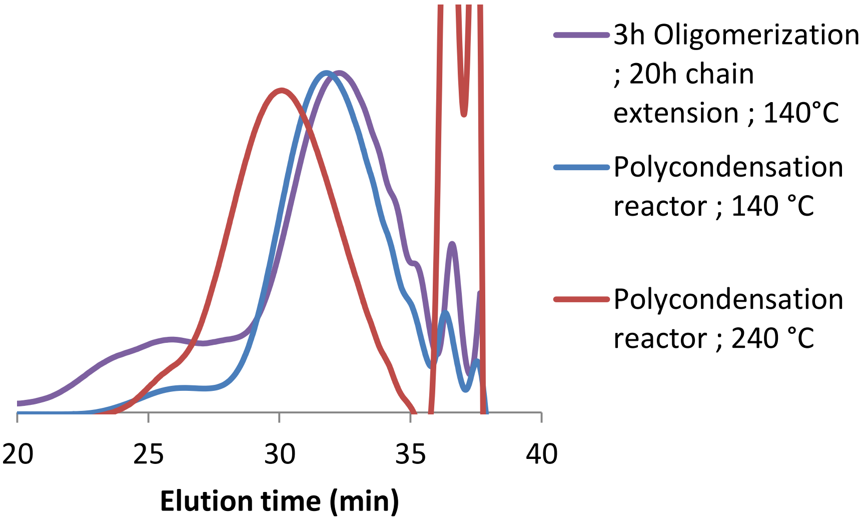


Figure 25: GPC chromatograms comparison of polycondensation reactor performances over glass reactors. Experimental conditions: Isosorbide (1 eq) ; bisLC2 (1 eq) ; LiCl (0.05 eq).

To compare our approach with more traditional polycondensation methods for the synthesis of poly(isosorbide carbonate), the standard conditions of 3 h for the oligomerization step and 20 h for the chain extension step at 140 °C were applied using DPC as the carbonylating agent instead of bisLC2, with LiCl as the catalyst. Higher M_n was obtained using DPC (M_n = 5,500 ; Đ = 2.14, endo/exo = 2.15) as highlighted by the SEC chromatograms, presented in Fig. 26, that compares molecular weights obtained using DPC or our approach. In addition, the polymer was well soluble in DMF in accordance with previous reports in the literature, indicating that solubility concerns for poly(isosorbide carbonate) using bisLC2 as monomer should be brought by side-reactions, generating defaults or partial crosslinking/branching of the polymer backbone. In fact, ^{1}H NMR spectra (see Fig. 27) of the crude product obtained with DPC showed no defect with absence of peaks at 1.17 ppm and 1.21 ppm. Interestingly, both alcohol and carbonate chain ends (peak **h** and **i**) could be identified, presumably in equimolar quantities. Even if our approach is not yet competitive with DPC, the molar mass of the DPC polymer is also limited supposedly due to challenging removal of phenol as the polycondensation by-product at 140 °C, as well as chain mobility limitations.

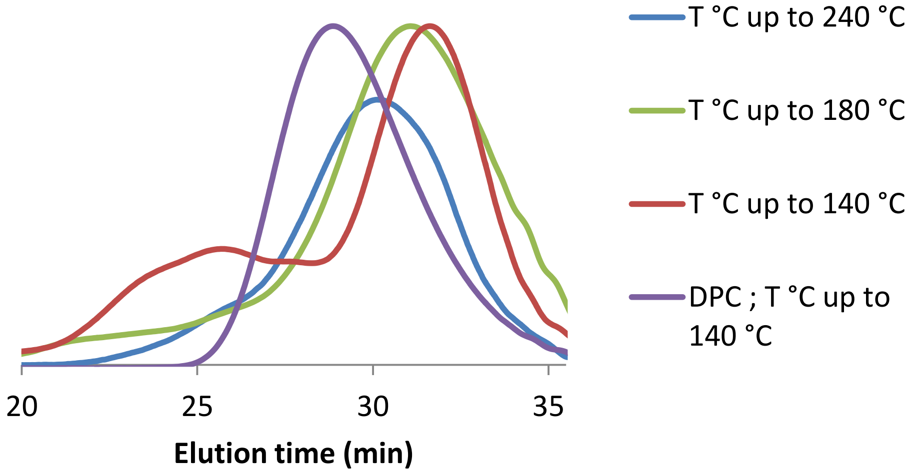


Figure 26: GPC chromatograms comparison between using bisLC2 or DPC as carbonalyting agent. If not specified, the monomer used with Isosorbide was bisLC2.

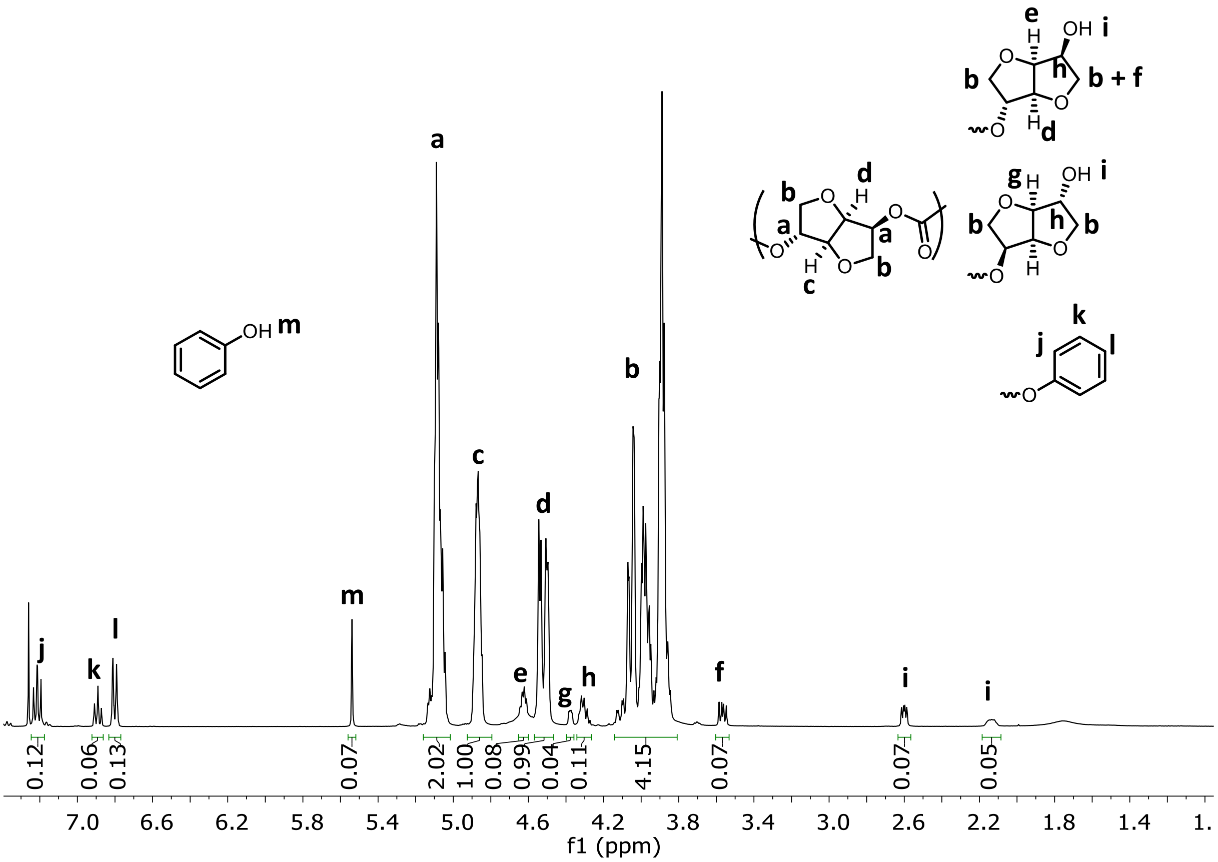
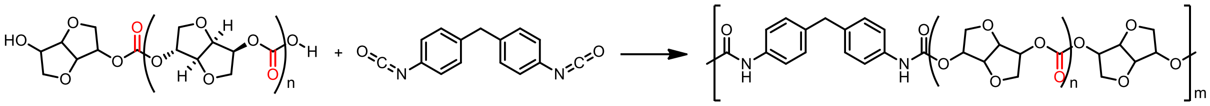


Figure 27: ^{1}H NMR spectrum of the crude mixture obtained after chain-extension step using conventional DPC as carbonylating agent. No defects were observed. Experimental conditions: Isosorbide (1 eq) ; DPC (1 eq) ; LiCl (0.05 eq).

Regarding thermal properties, no significant differences of T_g and T_d were observed for all poly(isosorbide carbonates) synthesized, apart from the known fact that T_g and T_d increase when M_n increase. Still, T_g in the range of 119 – 132 °C are consistent with the rather low M_n obtained when compared to the literature [21-23].

III-2-b-iii) CO_2-based polyurethane synthesis with poly(isosorbide carbonate)

Capitalizing on previous polymer characterizations and hypotheses we did, one can assume that poly(isosorbide carbonate) chains are mostly end-capped by OH functions, so that they can be considered as hydroxyl telechelic polycarbonates that could serve as polyol to build polyurethane. To confirm our predictions, the step-growth copolymerization of a representative poly(isosorbide carbonate) (recalculated M_n = 1,030 g/mol from NMR on the base of the chain ends, see experimental section for details) with 4,4'-methylene diphenyl diisocyanate (MDI) was carried out in dry DMF to obtain CO_2- and partially bio-based poly(carbonate-*co*-urethane) using dibutyltin dilaurate as a catalyst under N_2 atmosphere (see Scheme 4).



Scheme 4: Synthesis of poly(carbonate-*co*-urethane) using hydroxyl telechelic poly(isosorbide carbonate) and MDI

After only 2 h of reaction, significant increase of the viscosity was observed, preventing satisfying stirring of the solution. The obtained crude mixture was composed of polymer swollen by DMF (gel-like material), so it was dried under vacuum at 140 °C for 2 h. The recovered solid was hardly soluble in common organic solvents, but could be partly dissolved in a large volume of DMF. The soluble fraction was subjected to SEC analysis and ^{1} H NMR characterizations. In accordance with viscosity increase during the reaction, increase of molar mass could be observed in GPC (see Fig. 28, M_n = 3,000 g/mol ; Đ = 2.41.). The ^{1} H NMR spectrum (see Fig. 29) confirmed the consumption of OH functions with significant decreasing of chain-ends signals at 3.57 ppm ; 4.38 ppm and 4.64 ppm, and appearance of aromatic protons indicating incorporation of MDI structure in the polymer backbone. Due to the partial solubility of the obtained gel-like material, the NMR spectrum might not be representative of the final copolymer, and more investigation should be carried out to better understand the molecular structure. However, improvement of thermal properties with a new T_g of 152 °C for the poly(carbonate-*co*-urethane) synthetized is consistent with an increase of the molar mass, indicating successful chain extension of hydroxyl telechelic poly(isosorbide carbonate) with MDI.

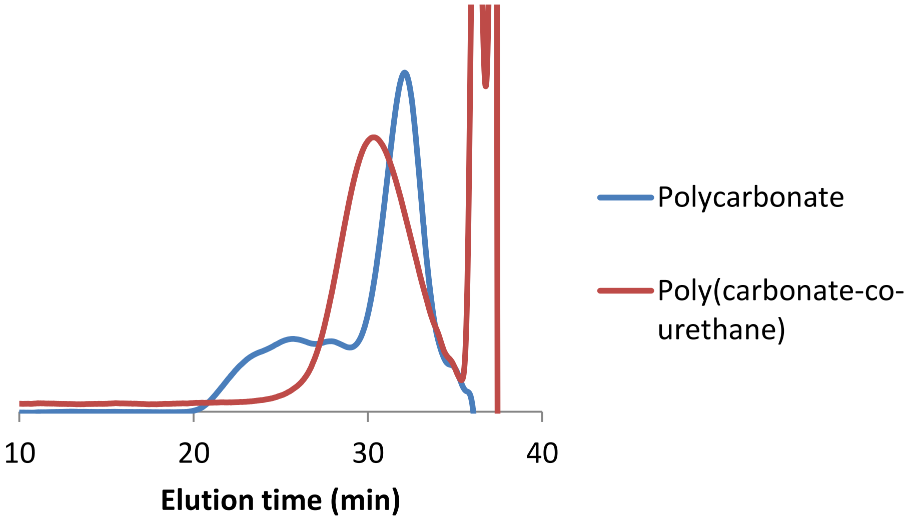


Figure 28: GPC chromatograms of the crude mixture of poly(carbonate-*co*-urethane) synthetized (red curve) and the precursor poly(isosorbide carbonate) used as hydroxyl telechelic polymer (blue curve)

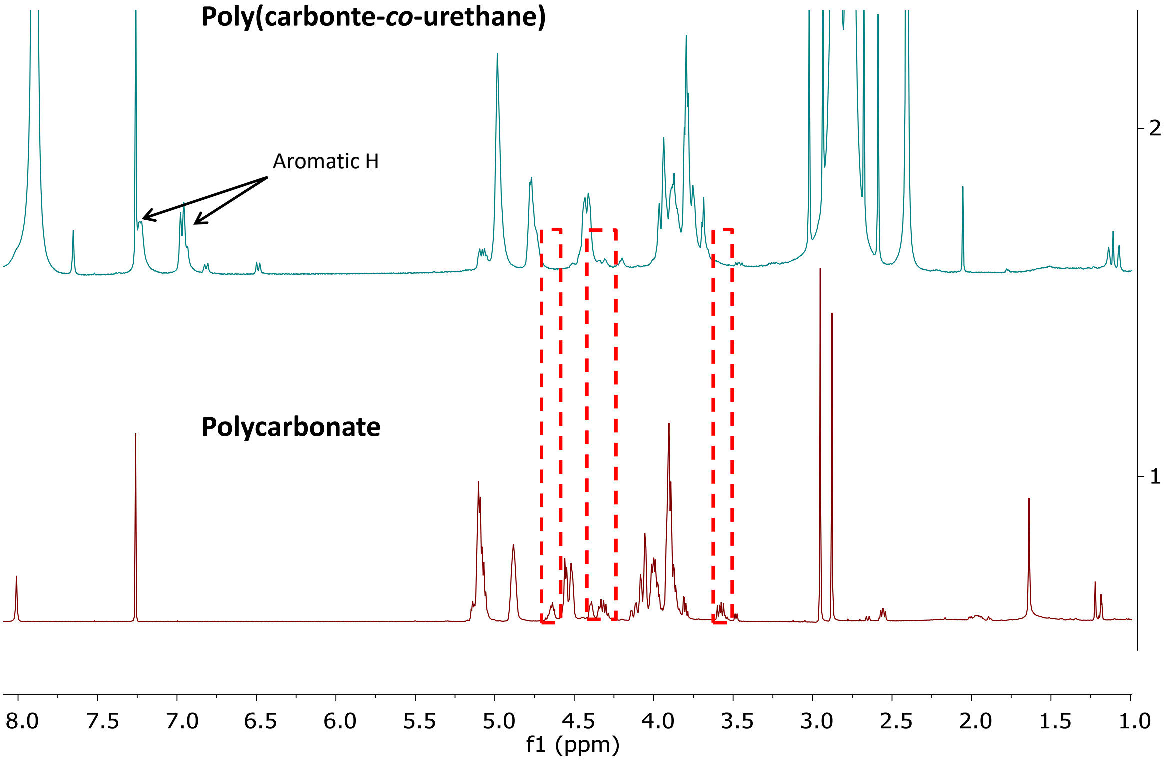


Figure 29: ^{1}H NMR spectra comparison of the poly(carbonate-*co*-urethane) synthetized and the precursor poly(isosorbide carbonate) used as hydroxyl telechelic polymer

III-2-c) Co-polycarbonate synthesis with isosorbide and bisLC monomers

To extend the scope of isosorbide-based polycarbonates as new carbonylating agents, “hetero”polycondensations of isosorbide with bisLC of different structures (where R ≠ R’, see Fig. 4) were carried out. This would provide copolycarbonates alternating isosorbide carbonate and other carbonate units within the same polymer skeleton. The experimental approach was similar to our previous studies. Oligomerization time and temperature were set to 3 h and 140 °C, whereas chain-extension was performed during 20 h at 140 °C or 180 °C. Incorporating aliphatic butylene motif within the polymer microstructure would lower the T_g while it is expected to increase with the aromatic phenylenebis(methylene) motif compared to a pure homopoly(isosorbide carbonate). Regarding isomannide, similar properties to poly(isosorbide carbonate) are expected. Results are presented in Table 7.

Poly(isosorbide-*co*-isomannide carbonate) could be obtained with relatively low M_n = 540 g/mol compared to homopoly(isosorbide carbonate) in similar conditions (see Table 7 entry 1). This result suggests that “endo” carbonate linkages of isomannide-based bisLC3 display poor reactivity toward transcarbonation reactions with isosorbide as the diol. Still, reprecipitation in methanol afforded polycarbonates of M_n = 1,970 g/mol (60 % of crude mixture mass recovered). The estimated final endo/exo ratio calculated by ^{1}H NMR on the precipitated polymer (see Fig. 30 for NMR spectrum) is of 1.45. The isosorbide/isomannide composition (peak **c** ; 1 H versus peak **e** ; 2 H) of the polymer backbone is of 1.33 meaning that the polymer chains are more likely terminated by isosorbide structures, which is in accordance with previous observations (OH terminated polymers). No bisLC3 signals could be found via NMR characterization. Alike homopoly(isosorbide carbonate), signals at 1.22 ppm and 1.18 ppm were observed, suggesting the presence of defects in the polymer backbone that result from side reactions, probably the ketal linkage formation. The SEC chromatogram of the precipitated polymer (Fig. 31, red curve) displayed the same solubilisation concerns as encountered with homopoly(isosorbide carbonate).

Poly(isosorbide-*co*-butylene carbonate) were obtained with moderate M_n of 1,400 g/mol (crude sample, Table 7, entry 2) using LiCl as the catalyst. Reprecipitation in methanol led to isolation of polymer chains of M_n = 3,000 g/mol, but in very low amount (around 15 % of mass recovered from the crude mixture). Characterization by ^{1}H NMR indicated an endo/exo ratio of 1.8, but a strange isosorbide/butylene composition within the polymer backbone of 0.59 was calculated. However, when the catalyst was changed to TBA/PhO$^-$, an increase of the molar mass of the precipitated polymers was measured with a M_n of 4,500 g/mol (Table 7, entry 3). The ^{1}H NMR characterization of the purified polymer (see Fig. 32) highlighted an endo/exo ratio of 2 but an isosorbide/butanediol ratio of 0.83 (peak **f** ; 1 H versus peak **b** ; 4 H). Additionally, signals attributed to bisLC1 chain ends were detected (peak **i** ; 3 H and peak **j** ; 6 H), meaning that the reaction might have not come to completion. Once more, difficulties to fully solubilize the polymer surely indicate the occurrence of side-reactions during the oligomerization and chain-extension step, as the SEC chromatogram also displays a bimodal-like shape (Fig 29, purple curve).

Poly(isosorbide-*co*-phenylenebis(methylene) carbonate) was synthesized according previous procedure, even though the high melting point of bisLC4 (132 °C) should quickly increase the viscosity of reaction media and consequently induce chain mobility limitations. Still, the crude polymer displayed a M_n of 1,000 g/mol (Table 7, entry 4) but was not totally soluble in common organic solvents, and hardly soluble in DMF as shown by the unrealistic dispersity value of 82 obtained in SEC, which is attributed to formation of aggregates. Thus, no NMR characterization could be performed, and thermal analysis by DSC and TGA were performed on the solid crude product since no precipitation of the polymer could be achieved. ATR-IR spectrum of the crude product, presented in Figure 33, indicates that the obtained polymer is a polycarbonate with characteristic band at 1742 cm^{-1}. A shoulder around 1700 cm^{-1} could be observed with relatively low intensity, suggesting that remaining ketone function of the unreacted bisLC4 monomer is present. This signal could also correspond to carbonate chain ends with ketone function, indicating that the reaction has not come to completion.

Regarding the thermal properties of the “hetero”copolycarbonates, all DSC analyses, presented in Figure 34, displayed a single T_g, which is in accordance with the expected alternating nature of the copolymers. A low T_g of 115 °C was obtained for poly(isosorbide-co-isomannide carbonate) due to low molecular weight of 1,970 g/mol. Interestingly, poly(isosorbide-co-butylene carbonate) displayed a T_g of 30 °C which is in between of what was obtained for both homopolycarbonates separately (around 120 °C for homopoly(isosorbide carbonate) and around – 40 °C for homopoly(butylene carbonate)), indicating that thermal properties of the copolycarbonate can be tuned by incorporating different repeating units. Poly(isosorbide-co-phenylenebis(methylene) carbonate) displayed an unexpectedly low T_g of 60 °C, supposedly due to the low molar masses afforded and the absence of purification of the sample.

Table 7: Chain extension tests using different bisLC structures for the obtention of copolycarbonates. Experimental conditions: Isosorbide (1 eq) ; bisLC (1 eq) ; catalyst (0.05 eq) ; 140 °C for oligomerization step (3 h) ; 140 °C or 180 °C for chain extension step (20 h)

Entry	bisLC structure	CATA	Chain extension T°C	Mn ; (Crude ; g/mol) ; [D]	Mn ; (Precipitated g/mol) ; [D]	T_g (°C)	T_d (°C)
1	Isomannide (bisLC3)	LiCl	180 °C	540 ; [1.73]	1,970 ; [1.25]	115	290
2	Butanediol (bisLC1)	LiCl	140 °C	1,400 ; [2.11]	3,000 ; [1.68]	ND	260
3	Butanediol (bisLC1)	TBA/PhO	140 °C	ND	4,500 ; [1.84]	30	277
4	Benzene dimethanol (bisLC4)	LiCl	180 °C	1,000 ; [82]*	ND	60	237

*: Unrealistic values of dispersity biased by the presence of significant amounts of aggregates

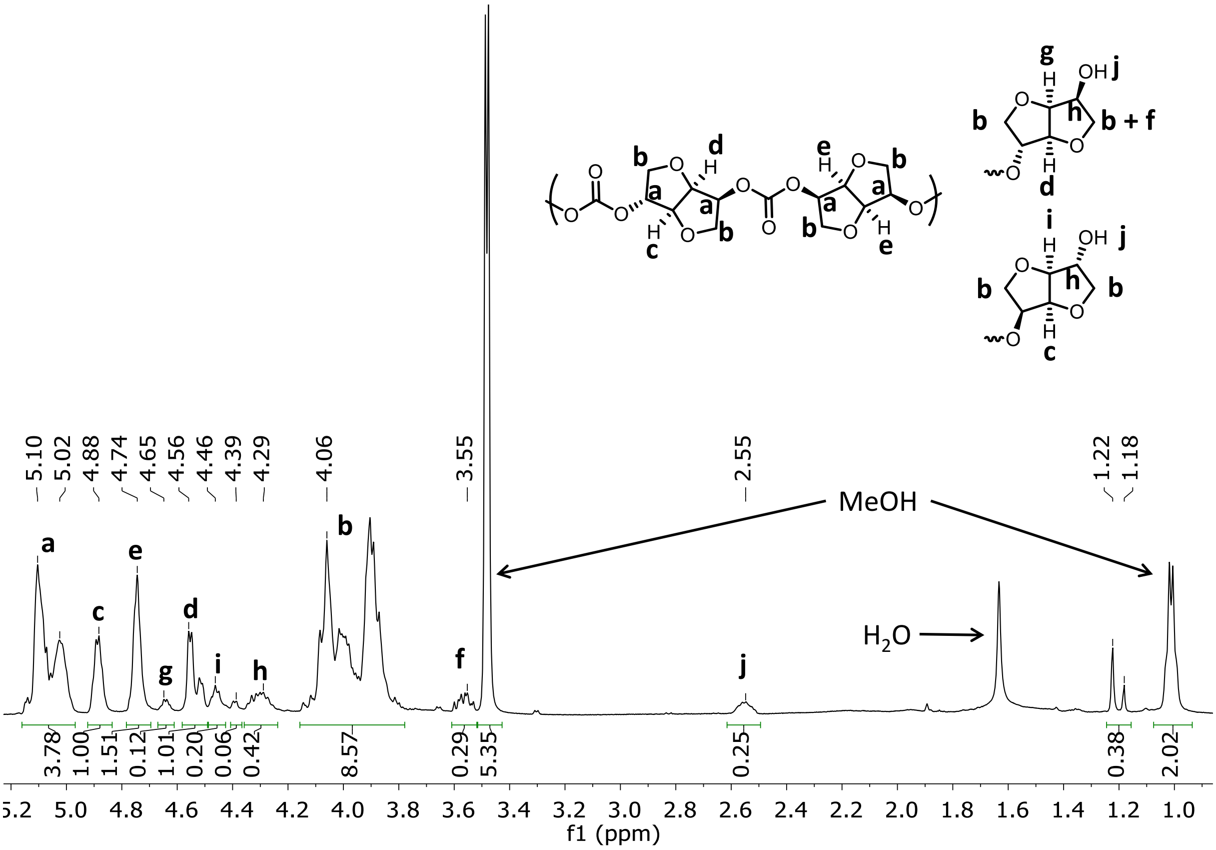


Figure 30: ^{1}H NMR spectrum of the precipitated poly(isosorbide-*co*-isomannide carbonate) obtained after chain extension. Experimental conditions: Isosorbide (1 eq) ; bisLC3 (1 eq) ; LiCl (0.05 eq) ; 23 h (Table 7, entry 1)

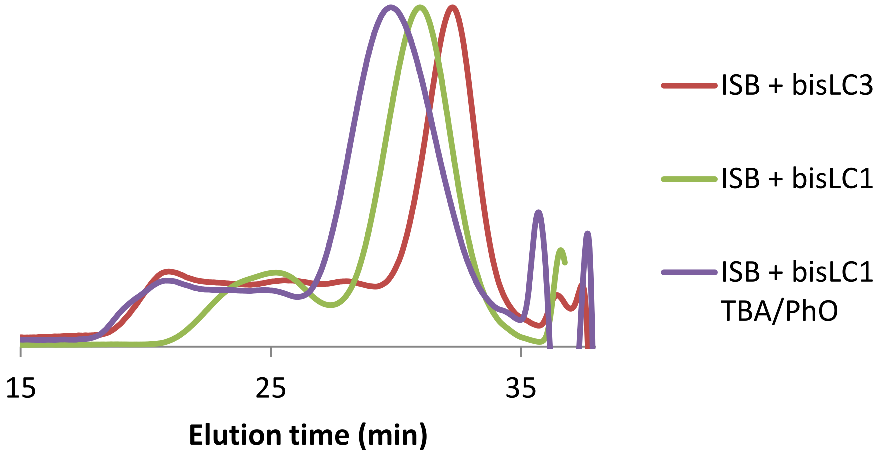


Figure 31: GPC chromatograms of the precipitated copolycarbonates obtained after chain extension. Experimental conditions: Isosorbide (1 eq) ; bisLC3 (1 eq) ; catalyst (0.05 eq) ; 23 h. If not specified, the catalyst used was LiCl

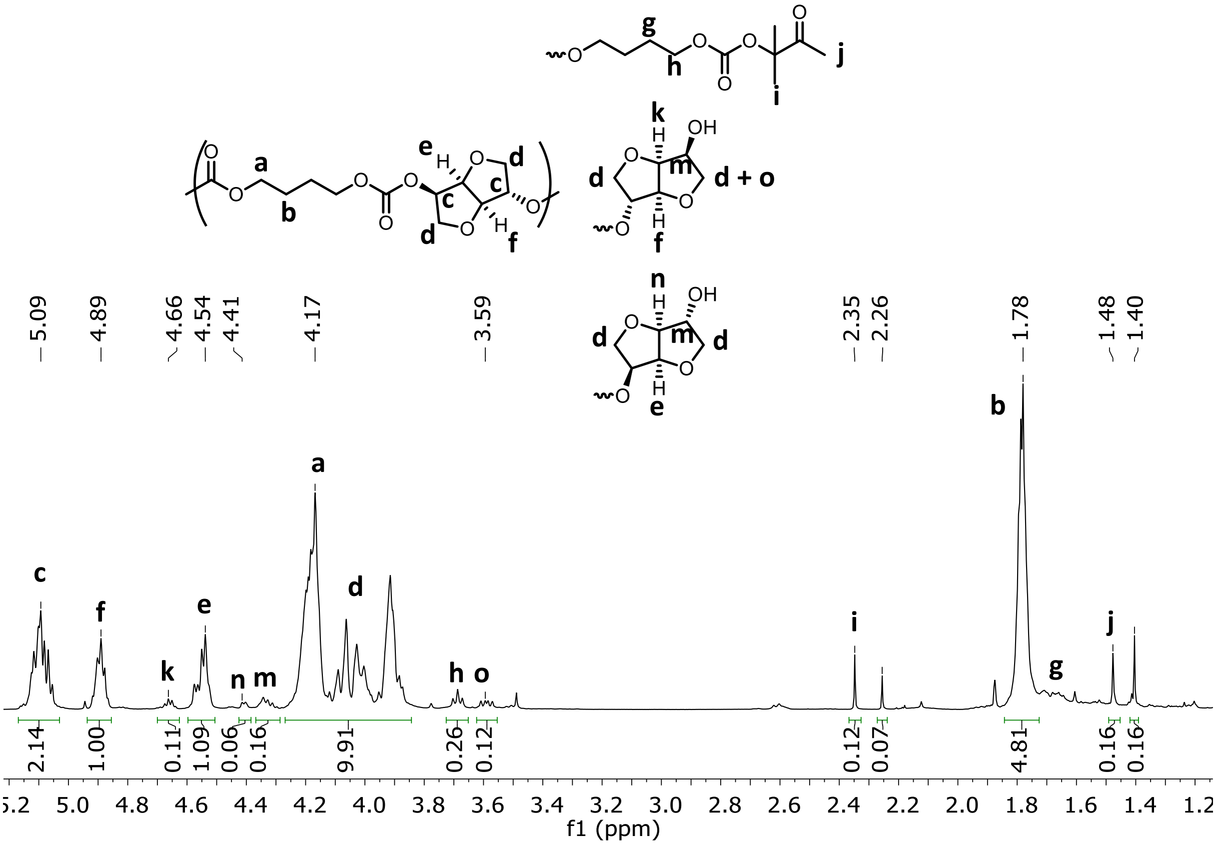


Figure 32: ^{1}H NMR spectrum of the precipitated poly(isosorbide-*co*-butylene carbonate) obtained after chain extension. Experimental conditions: Isosorbide (1 eq) ; bisLC1 (1 eq) ; TBA/PhO$^-$ (0.05 eq) ; 23 h (Table 7, entry 3)

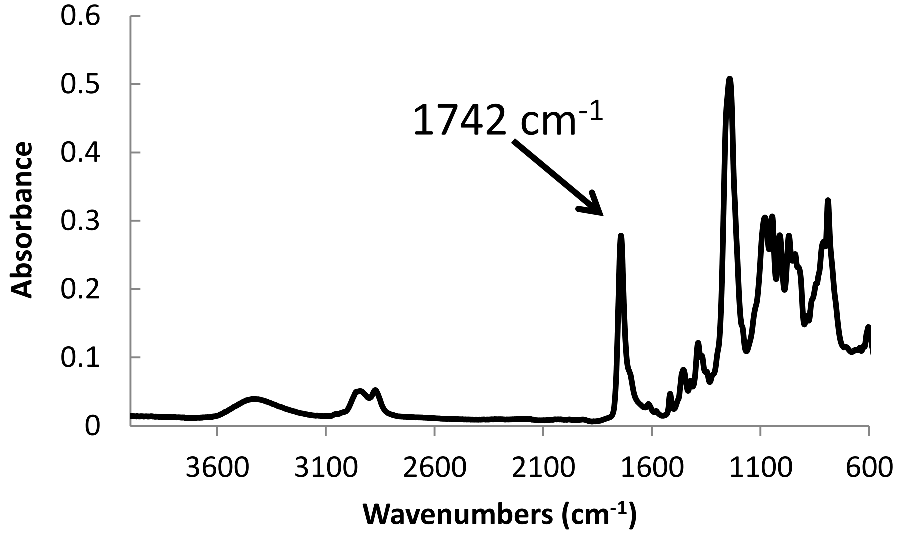


Figure 33: ATR-IR spectrum of the crude poly(isosorbide-*co*-phenylenebis(methylene) carbonate) obtained after chain extension. Experimental conditions: Isosorbide (1 eq) ; bisLC4 (1 eq) ; LiCl (0.05 eq) ; 23 h (Table 7, entry 4)

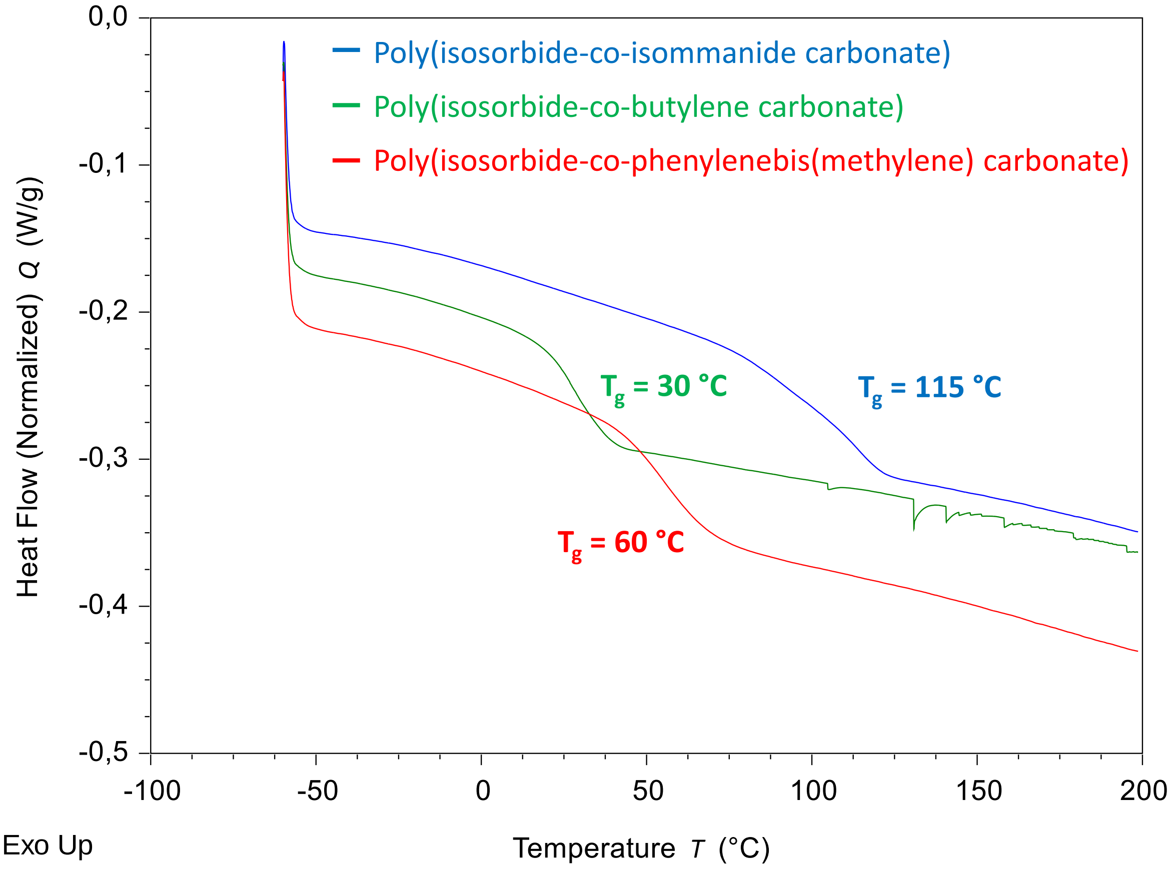


Figure 34: DSC curves of the copolycarbonates obtained after chain extension

IV) CONCLUSION :

A set of new bio- and CO_2-based bis-oxo-carbonate synthons were successfully synthesized from 1,x-diols (with x > 3) and αCC in a simple and efficient manner to broaden the scope of accessible monomers entering in the production of polycarbonates. Deep understanding of the mechanism was proposed by kinetic monitoring and molecular modelling techniques, opening the way for future greener synthesis of chemicals and polymer materials. By modulating the diol structure, new building blocks with tunable properties (melting temperature, thermal degradation) can be envisaged, e.g. by incorporation of aliphatic, cyclic, aromatic motifs with different pendant groups on the monomers. Notably, this synthetic strategy involving CO_2-based αCC could be extended to secondary diamines instead of diols for the synthesis of bis-oxo-carbamate monomers. Polycarbonates were then synthesized via melt-polycondensation processes including a first oligomerisation step followed by the chain extension under vacuum. A careful investigation of the reactivities of the newly created bis-oxo-carbonate monomers and structural elucidation of the oligomer/polymer microstructure highlighted unexpected side reactions due to the presence of a ketone moiety, i.e. the formation of thermodynamically favoured 5CC which induced stoichiometric deviations that would perturb chain-extension of the oligomers and their decomposition, probably to deliver a ketal linkage. One would like to underline our attempts to elucidate the exact polymer microstructure by complementing our analyses with MALDI-

TOF characterization. However the highly complex spectra prevented us to draw any conclusion in view of the multiple population of chains with different chains ends and possible repeating units. Still, poly(butylene carbonate) and poly(isosorbide carbonate), as well as copolycarbonates with two different repeating units were isolated and purified with moderate molecular weights. So far, detailed identification of side reactions leading to incorporation of defects in the polymer backbone was not fully achieved, but hypothetical pathways were proposed for the formation of ketal linkages by ring-opening of 5CC side-product that could explain unassigned peaks observed in ^{1}H NMR. Unfortunately, model reactions on mono-functional organic molecules that would help to better understand the different reactivities and side-reactions were not possible in this case as experimental conditions (melt-state, high temperature) are not suitable for such chemicals. To improve the range of affordable molar masses of polycarbonates for the obtention of valuable materials in terms of thermo-mechanical properties, efforts on the catalytic system to selectively activate the transcarbonation reaction without the occurrence of side reactions on the ketone group are needed. Another way to achieve this aim would be to protect the ketone group under the form of acetals prior the melt-polycondensation step. However, such protecting strategy would require an additional step and optimization of the monomer post-modification.

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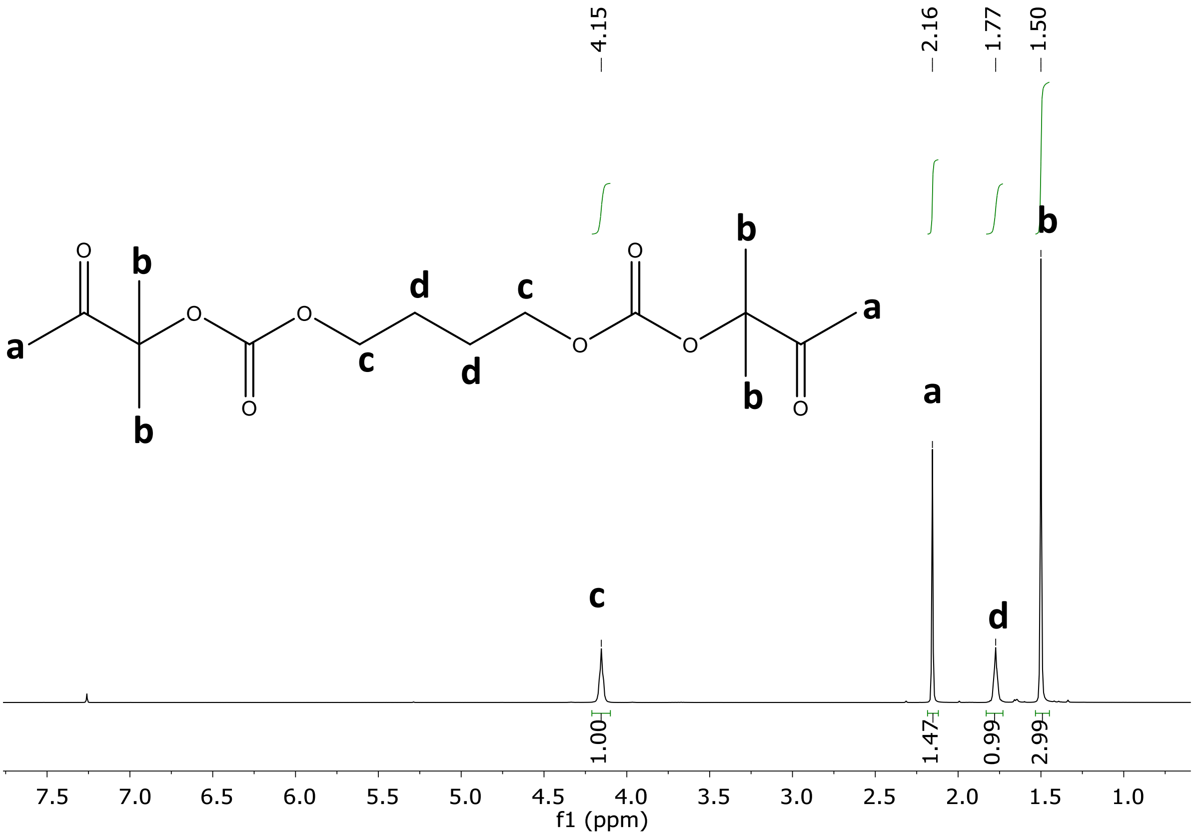
APPENDIX : CHARACTERIZATION OF BISLC MONOMERS

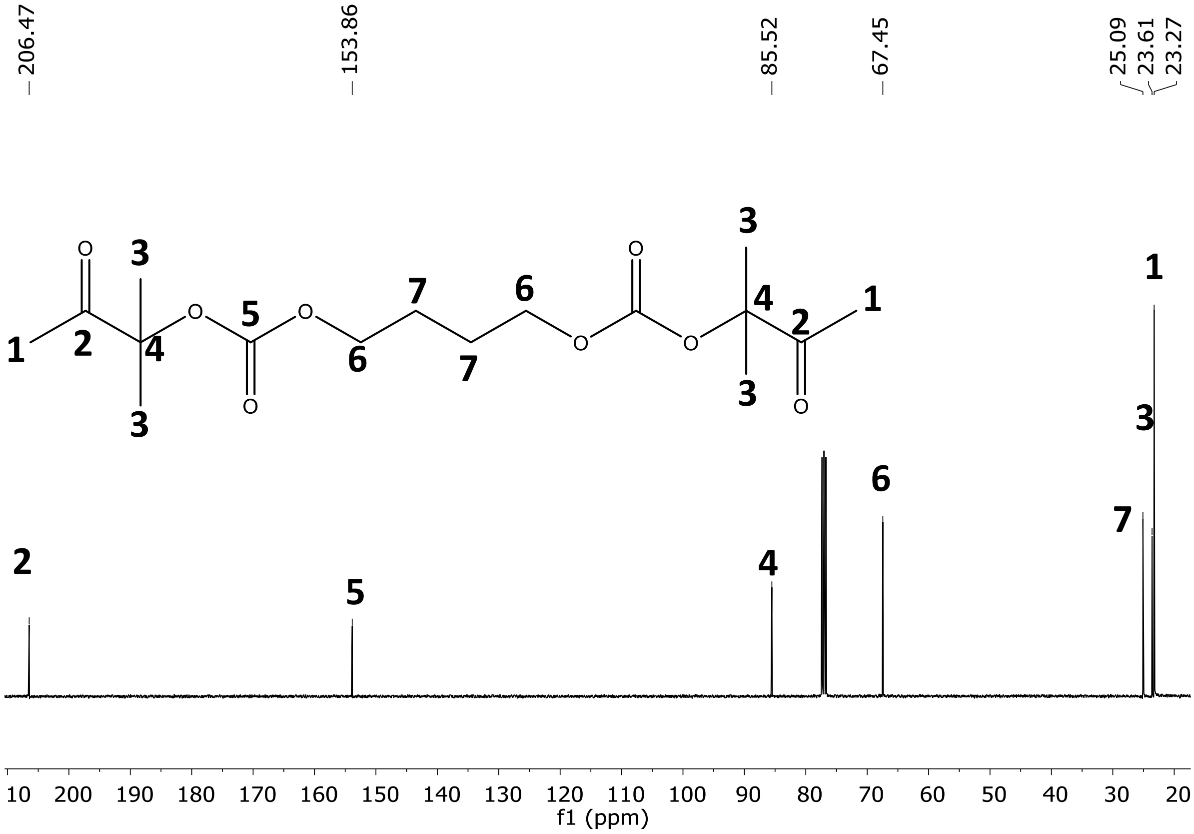
^1H and ^{13}C NMR spectra were phase and baseline corrected, recorded in $CDCl_3$ and calibrated with the 7.26 ppm residual signal of $CDCl_3$.

HRMS (High Resolution Mass Spectrometry) data were recorded on a Q-Exactive spectrometer from ThermoFisher in ESI technique (electrospray ionization) or on positive mode (3500 V). All samples were diluted in a 10/90 CH_2Cl_2/MeOH mixture and added with 40 µL of lock mass. Analyses were performed at the UCL (Université Catholique de Louvain) in the ASM Mass Lab.

Molecules were named thanks to ChemDraw Ultra Software (version 12.0.2.1076)

- **butane-1,4-diyl bis(2-methyl-3-oxobutan-2-yl) dicarbonate (bisLC1)**





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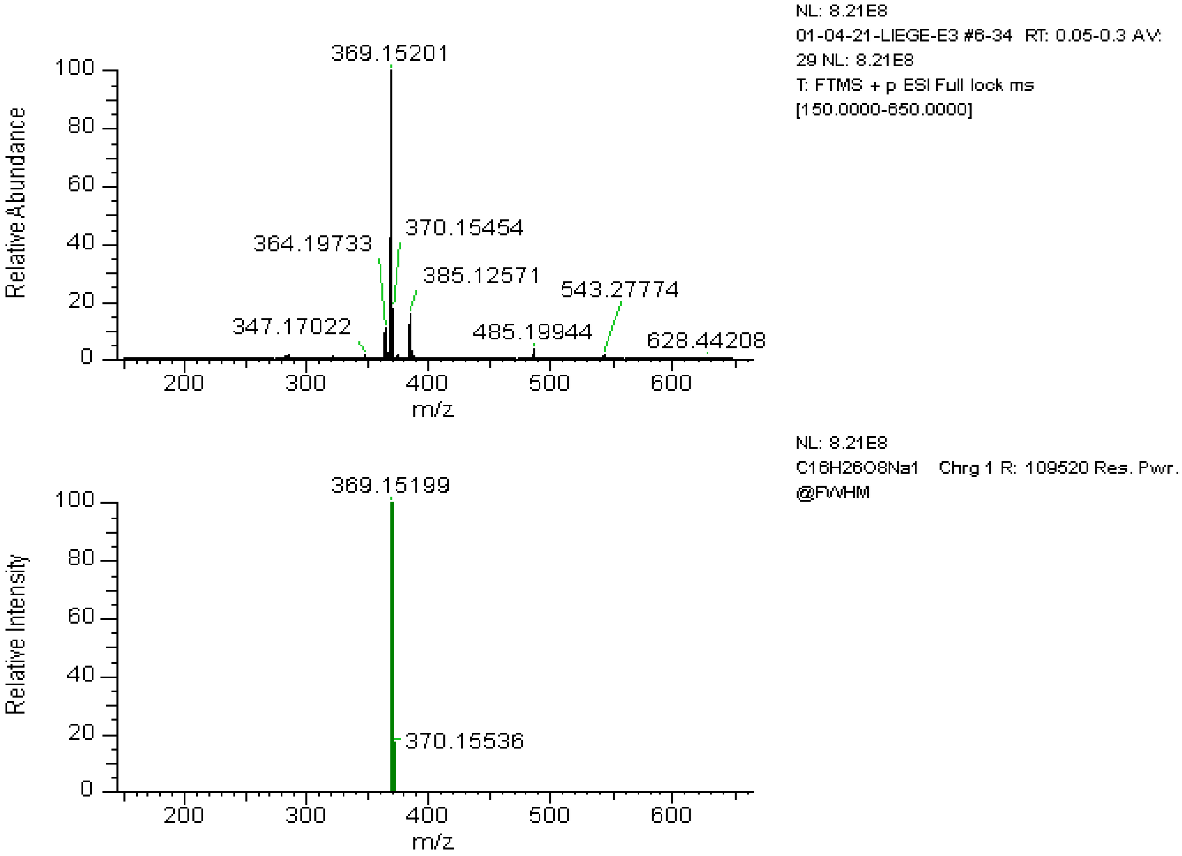

Elemental Composition Results

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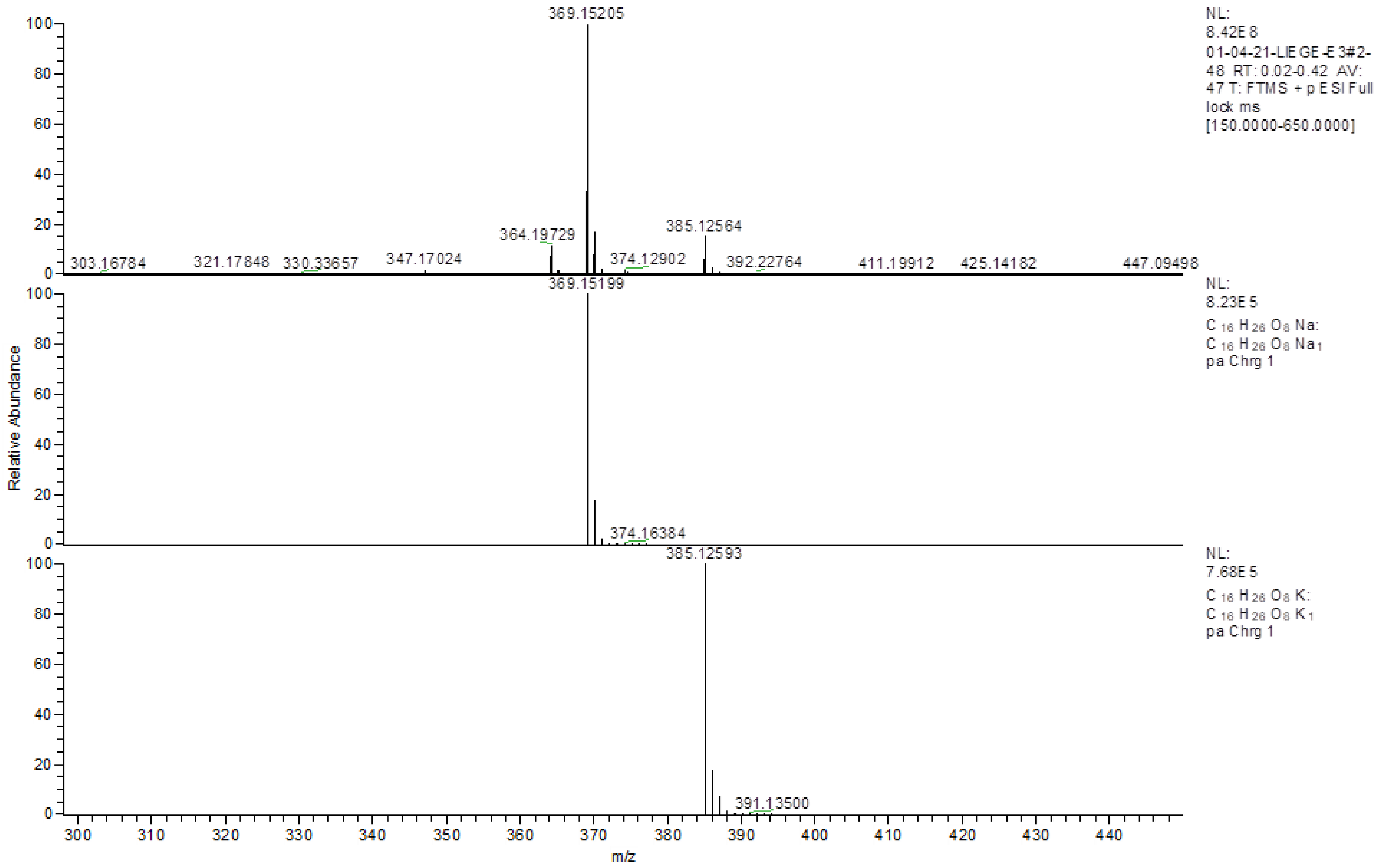
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C 16 H 26 O 8 K:
C 16 H 26 O 8 K 1
pa Chrg 1
Relative Abundance
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60
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20
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300
310
320
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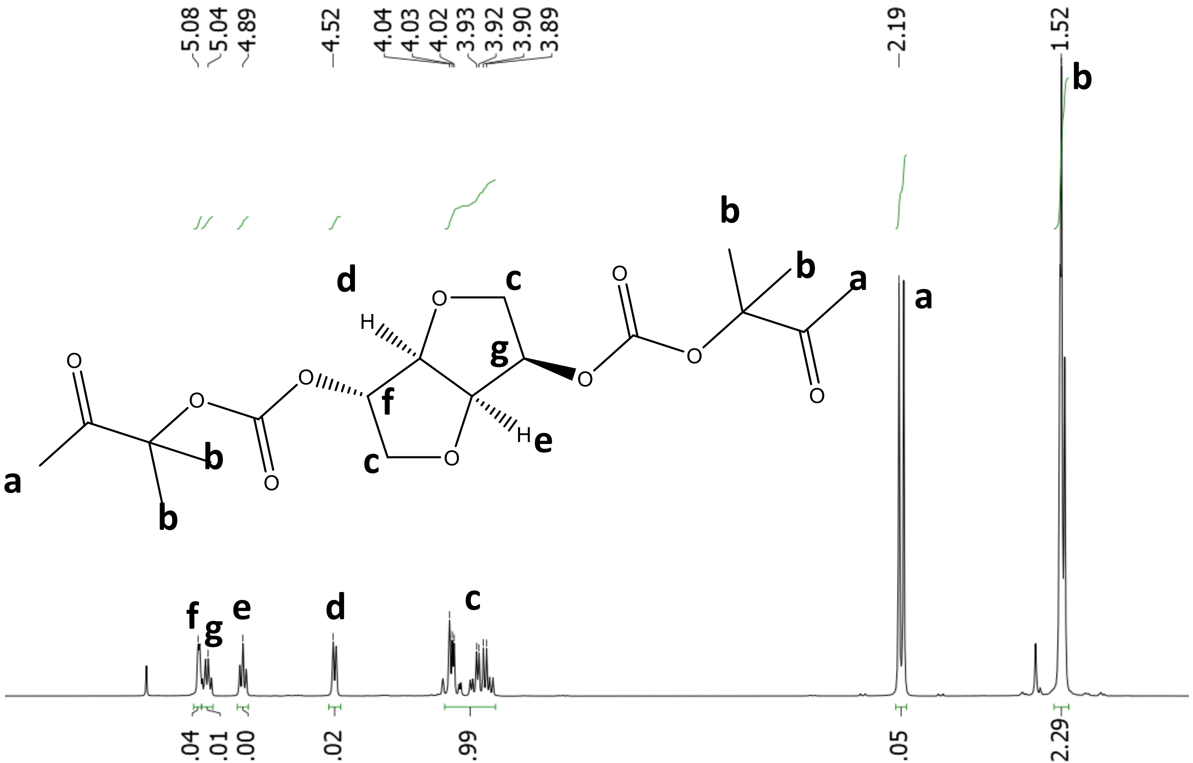
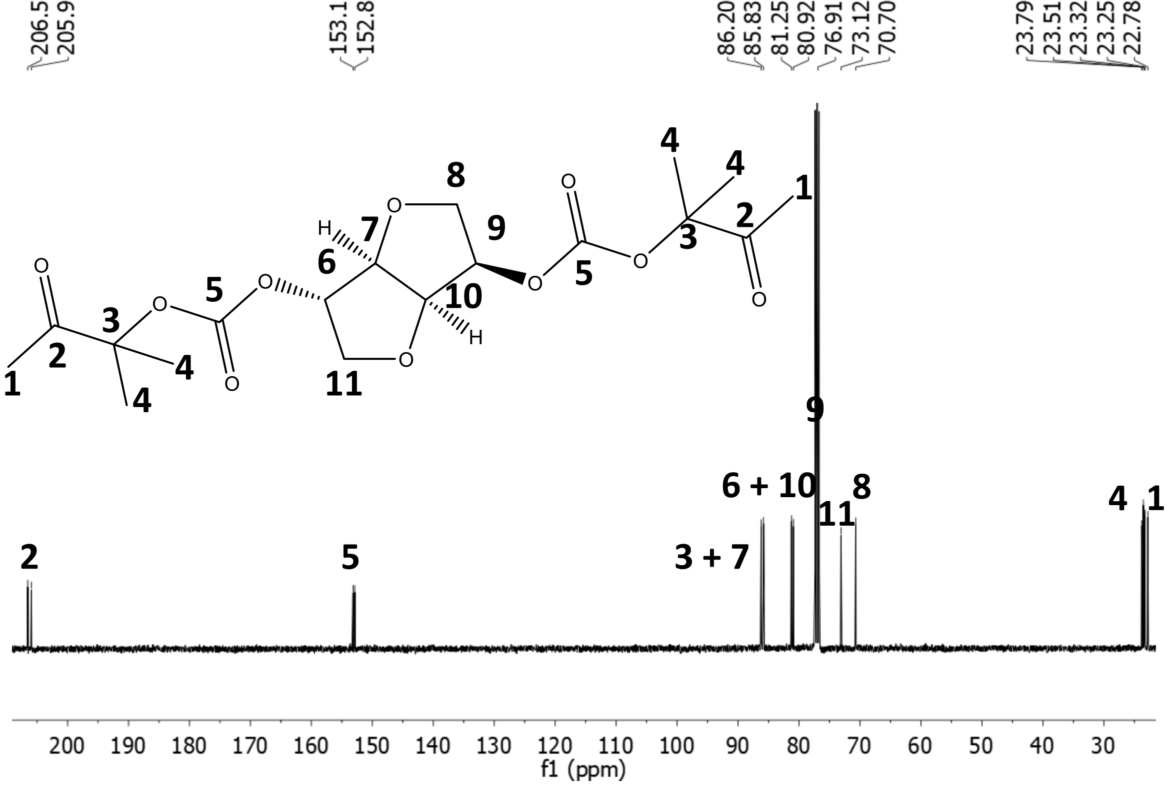
350
360
370
380
390
400
410
420
430
440
m/z

- **(3R,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-diyl bis(2-methyl-3-oxobutan-2-yl) dicarbonate (bisLC2)**





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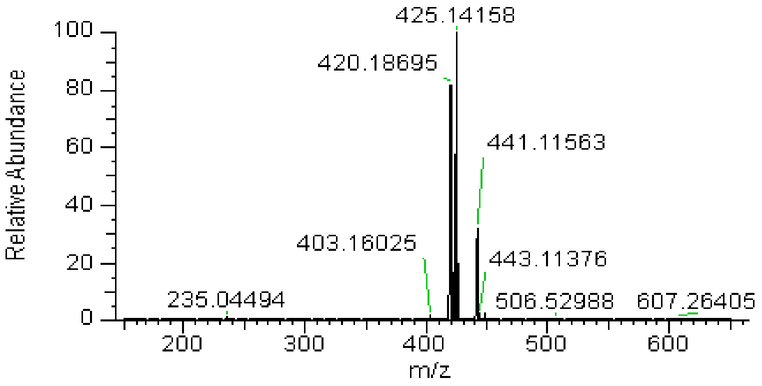

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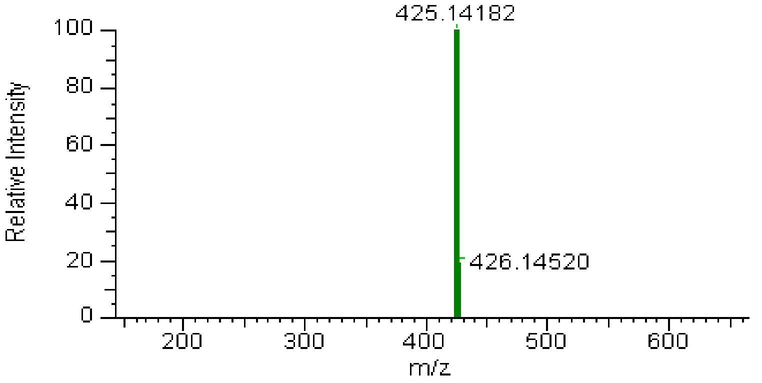

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Pwr. @FWHM

Elemental Composition Results

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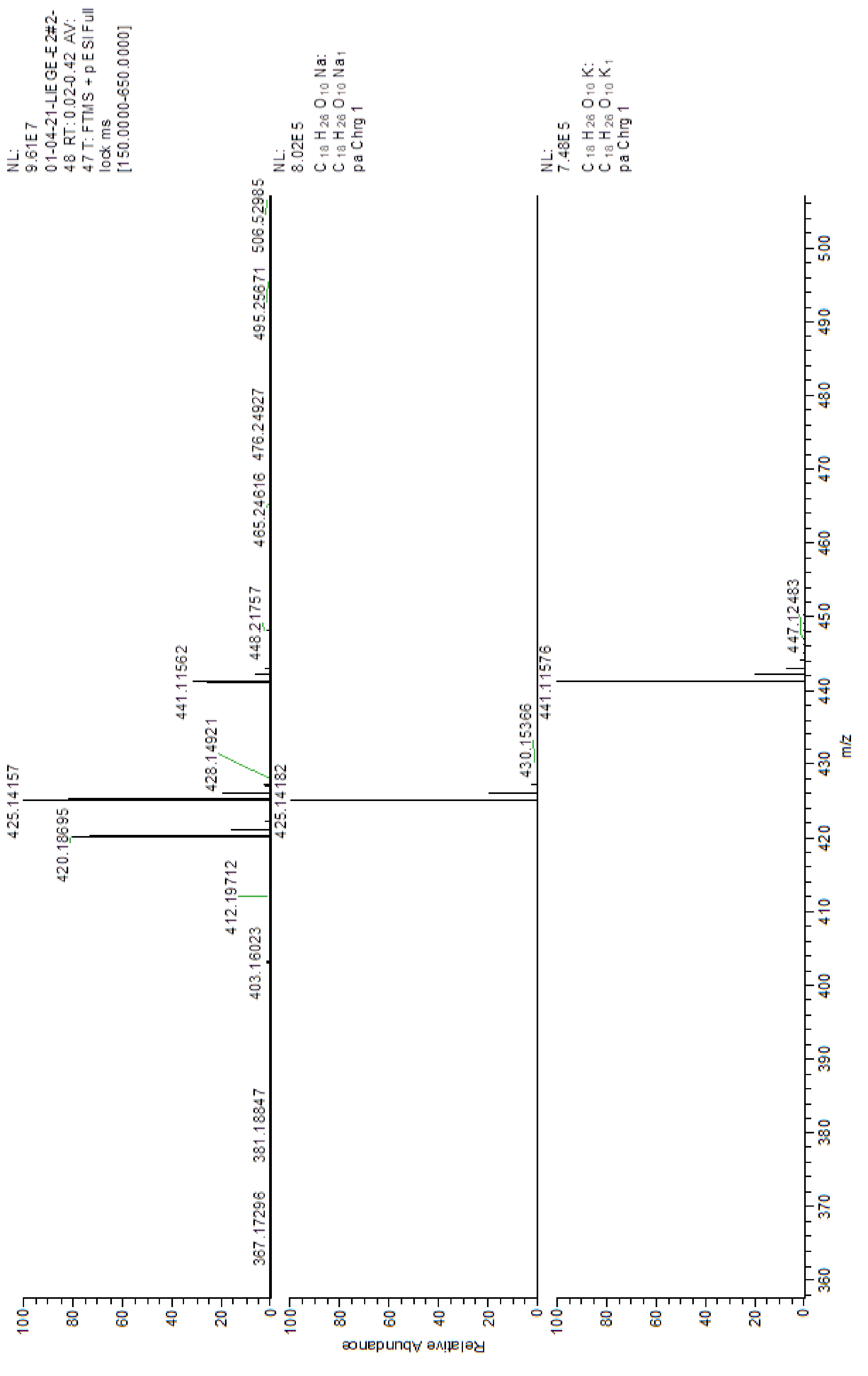
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$C_{18}H_{26}O_{10}K_1$
pa Chrg 1
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441.11576
447.12483
Relative Abundance
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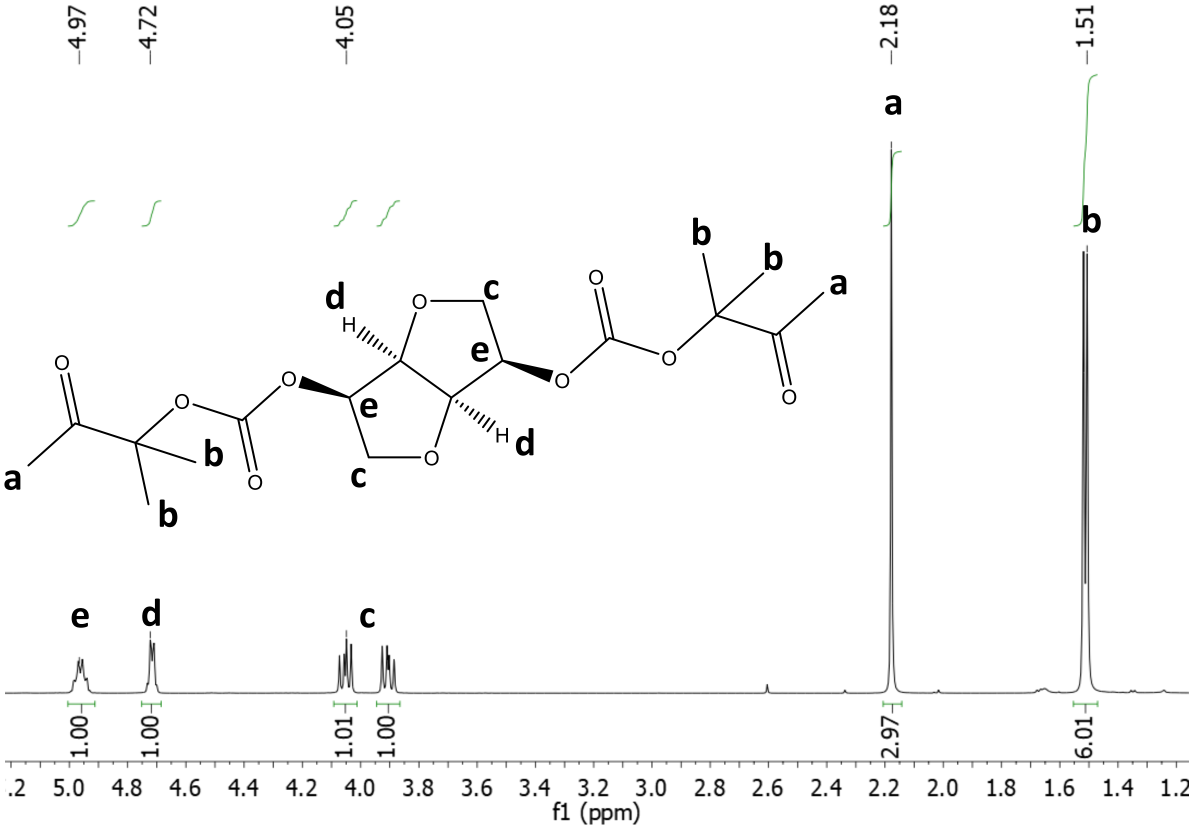
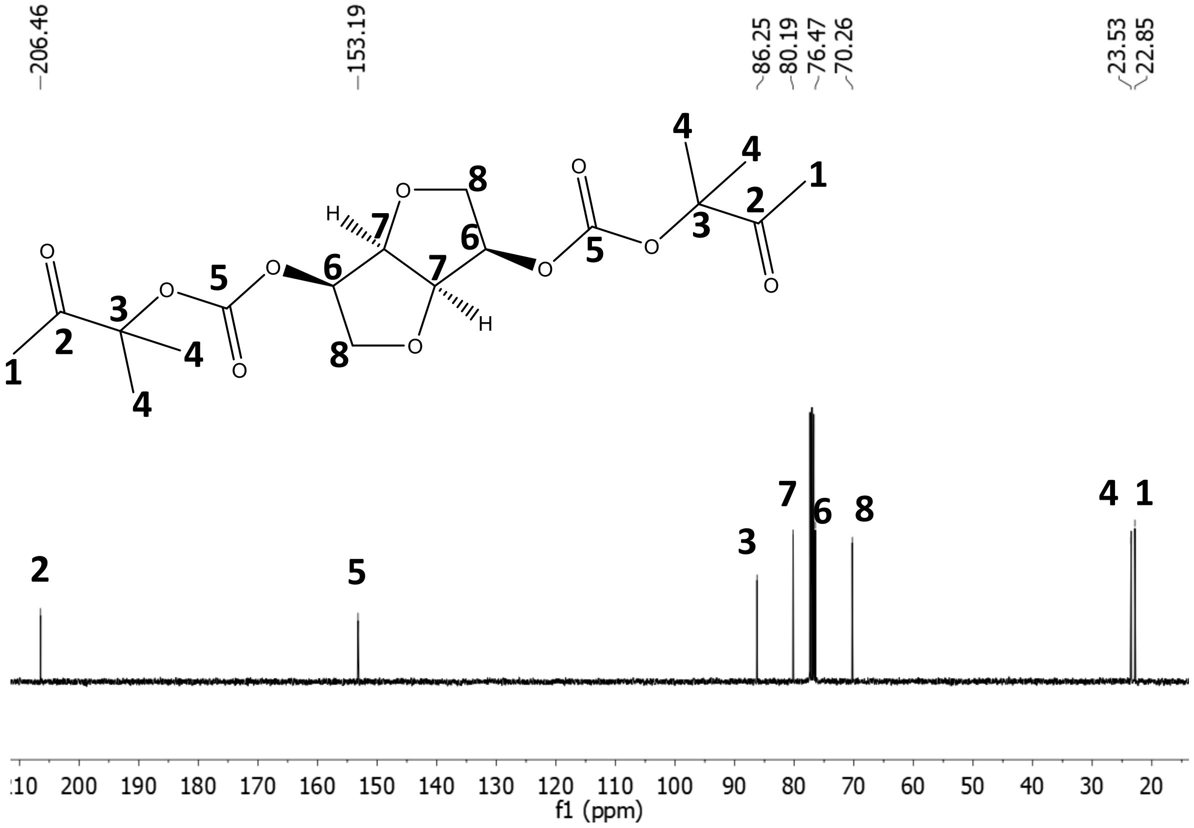
80
60
40
20
0
360
370
380
390
400
410
420
430
440
450
460
470
480
490
500

- **(3S,3aS,6S,6aS)-hexahydrofuro[3,2-b]furan-3,6-diyl bis(2-methyl-3-oxobutan-2-yl) dicarbonate (bisLC3)**





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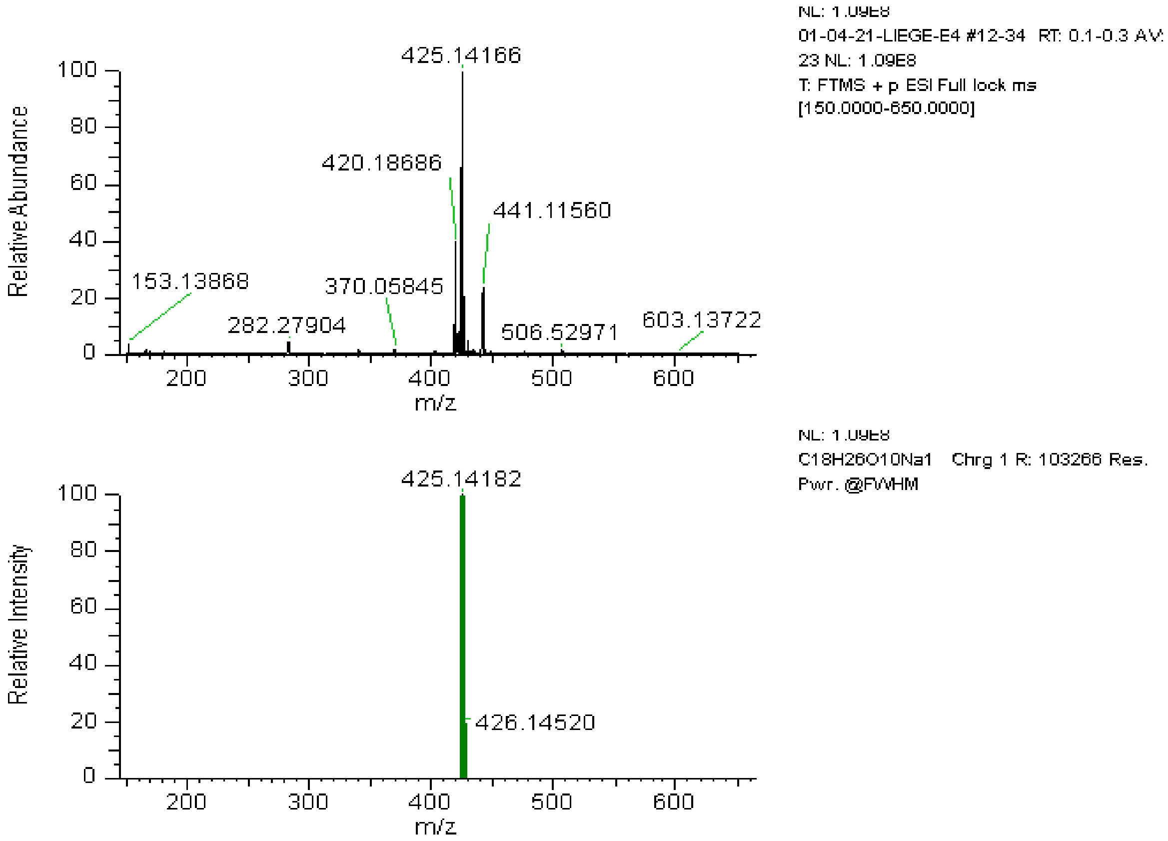

Elemental Composition Results

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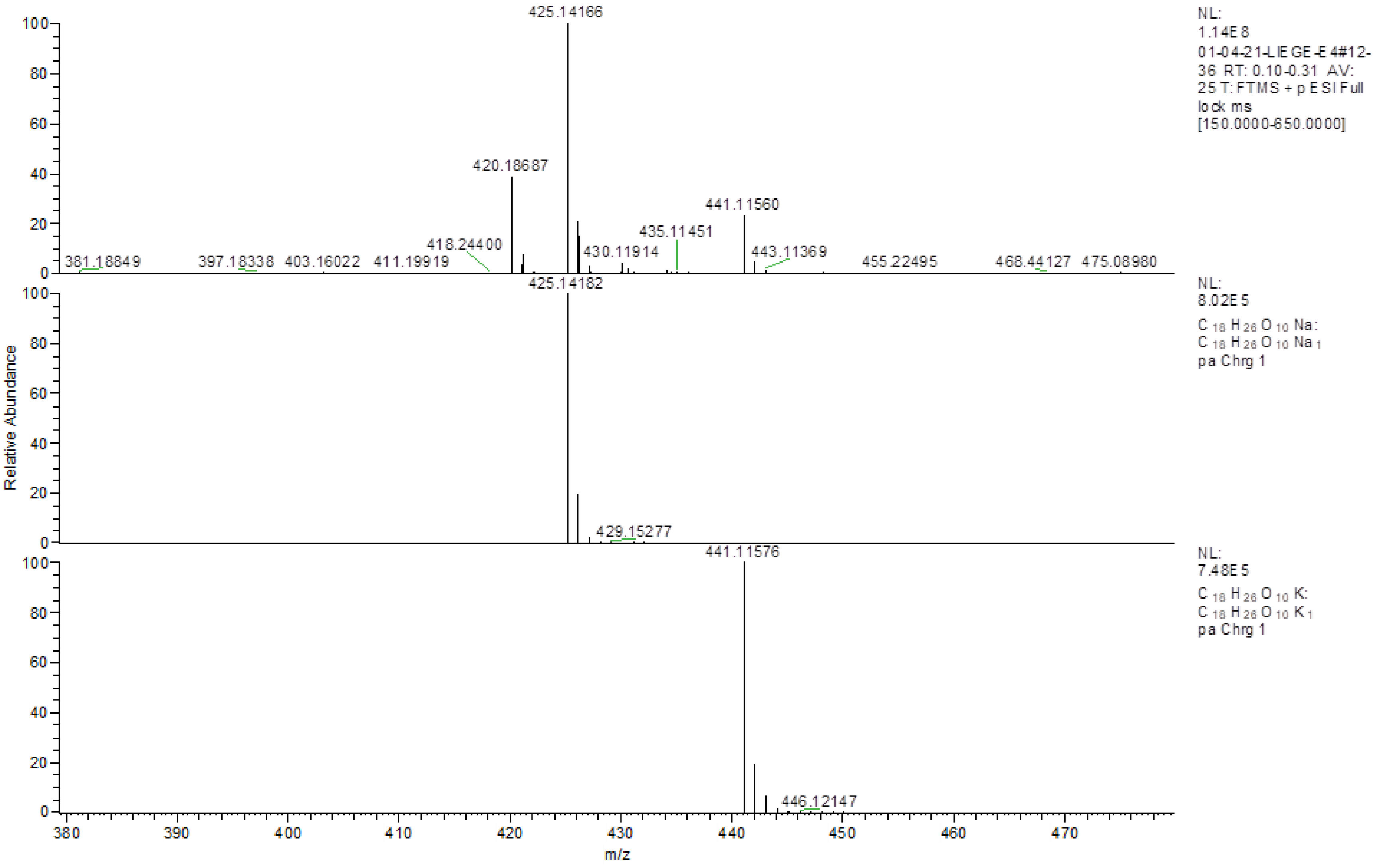
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C 18 H 26 O 10 Na:
C 18 H 26 O 10 Na 1
pa Chrg 1
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7.48E5
C 18 H 26 O 10 K:
C 18 H 26 O 10 K 1
pa Chrg 1
Relative Abundance
100
80
60
40
20
0
380
390
400
410
420
430
440
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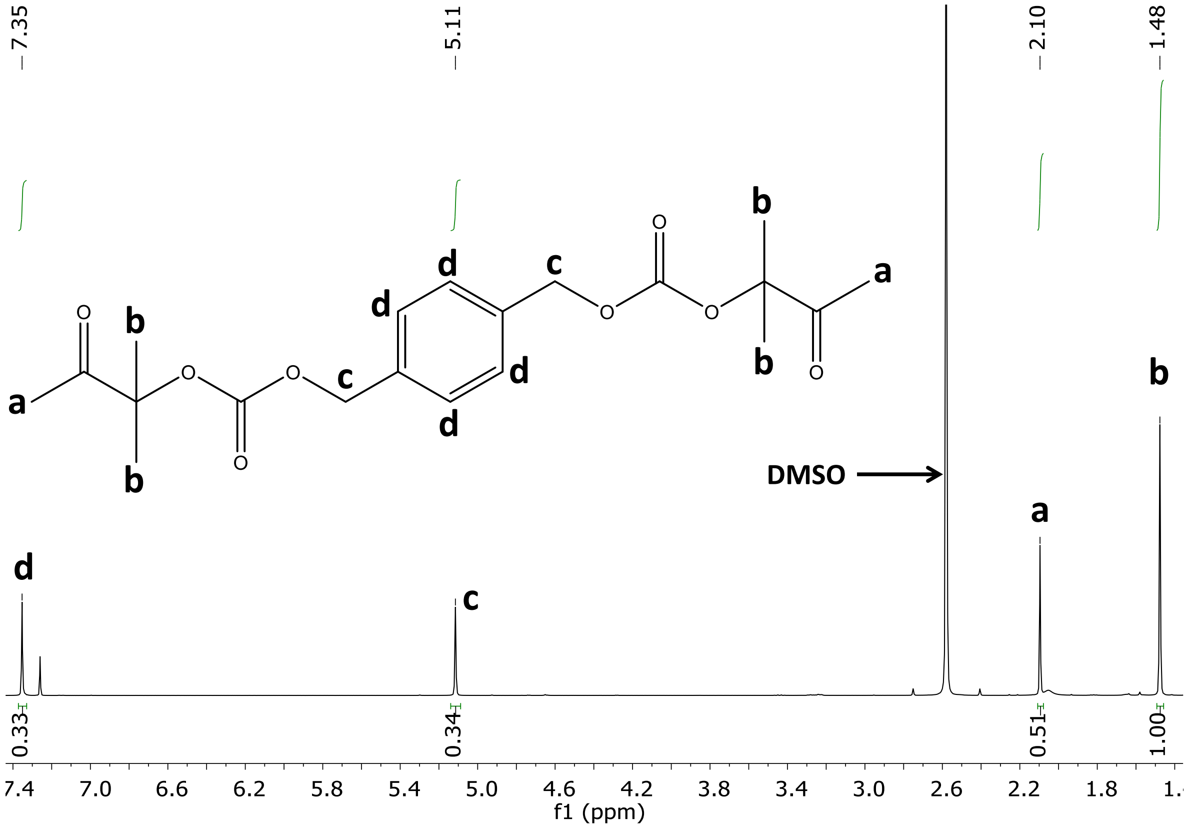
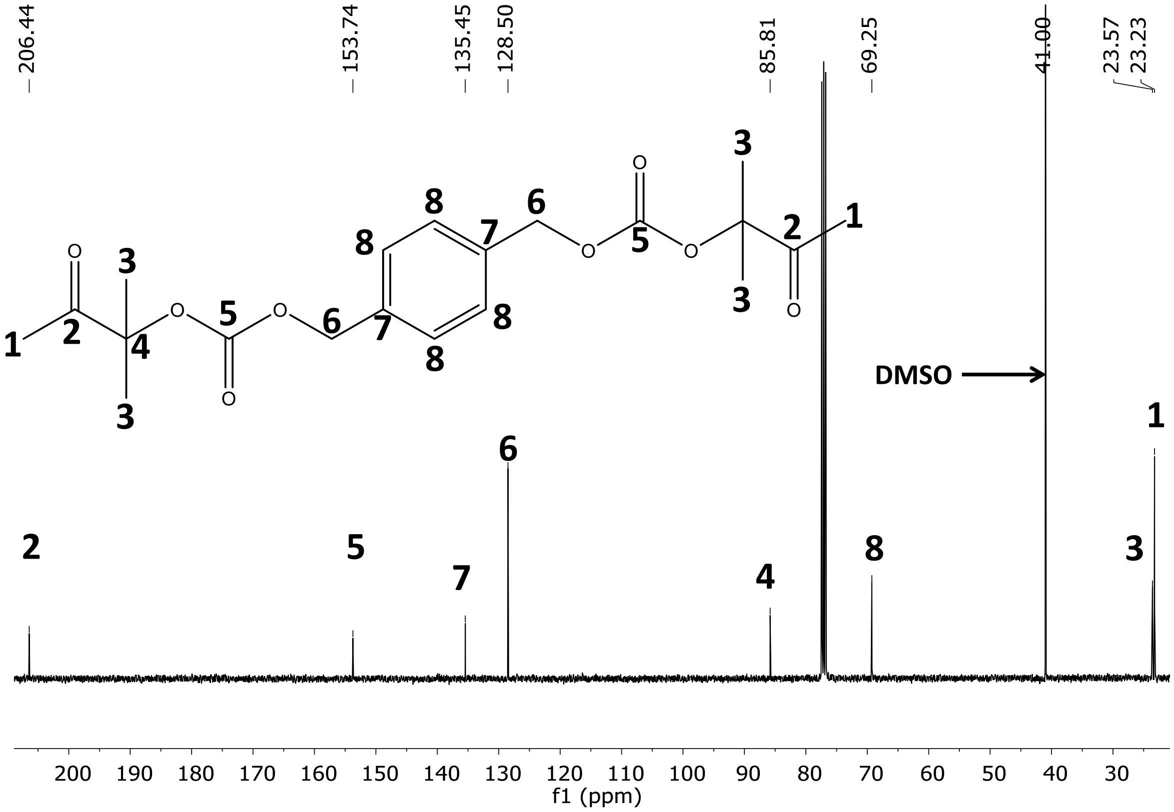
470
m/z

- **1,4-phenylenebis(methylene) bis(2-methyl-3-oxobutan-2-yl) dicarbonate (bisLC4)**





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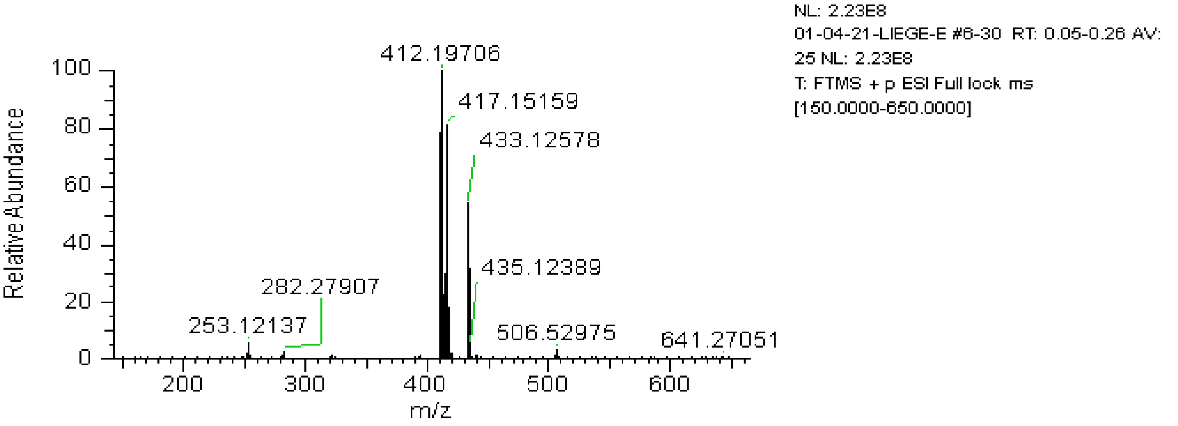

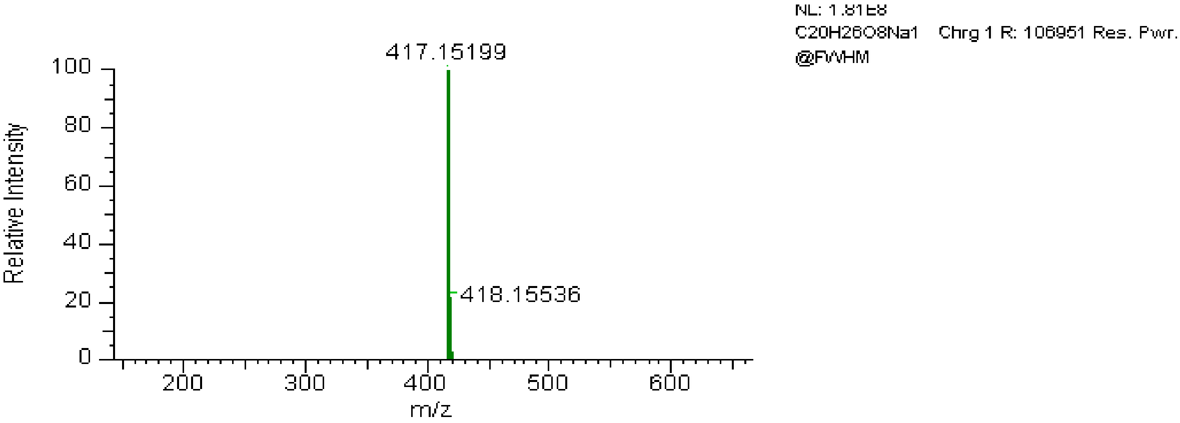

Elemental Composition Results

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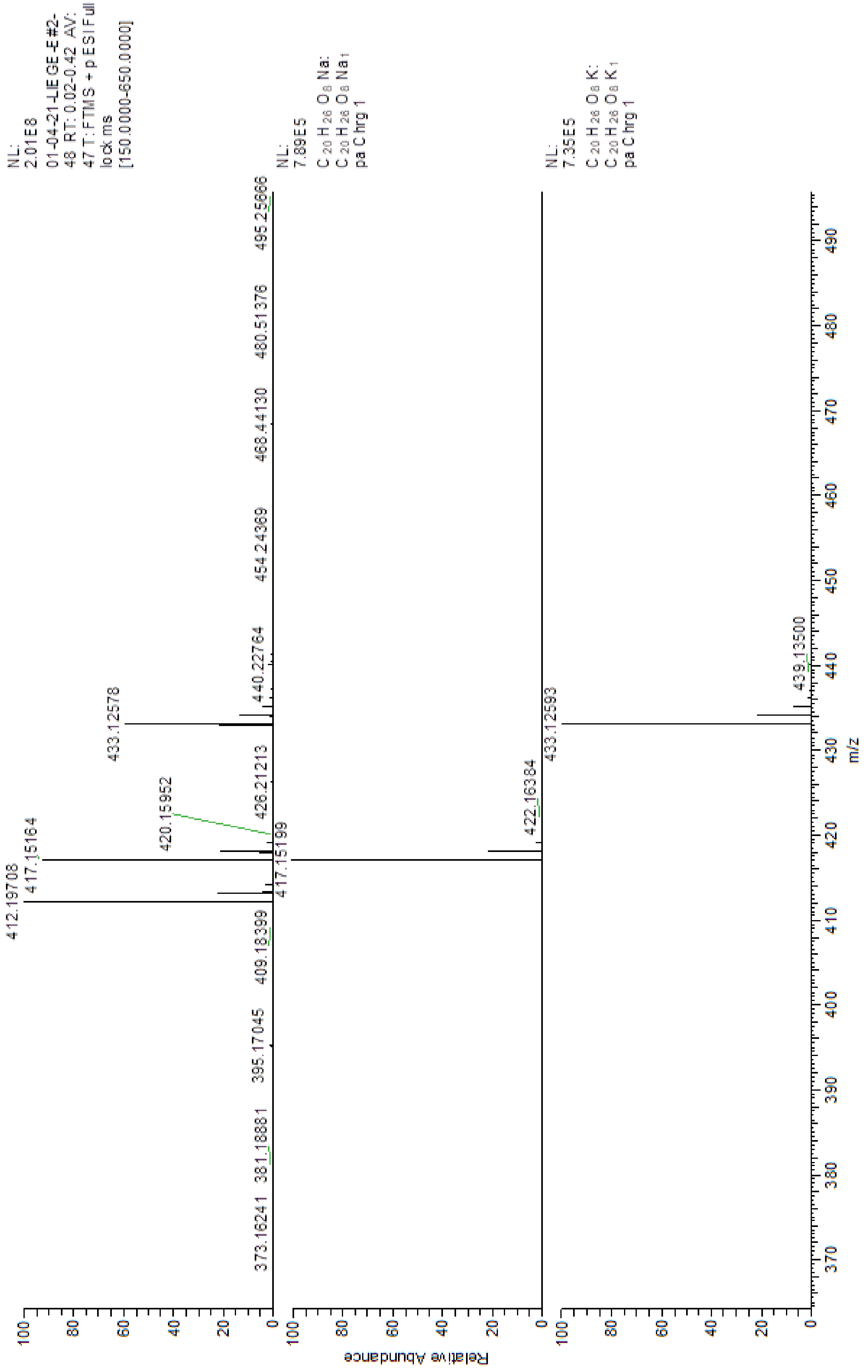
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7.89E5
C 20 H 28 O 8 Na:
C 20 H 28 O 8 Na 1
pa Chrg 1
417.15199
422.16384
NL:
7.35E5
C 20 H 28 O 8 K:
C 20 H 28 O 8 K 1
pa Chrg 1
433.12593
439.13500
Relative Abundance
100
80
60
40
20
0
370
380
390
400
410
420
430
440
450
460
470
480
490
m/z

General conclusions and outlooks

In an effort to develop new synthetic ways to valorize CO_2 into organic chemicals or materials, this research project aimed at investigating the coupling of alcohols with CO_2 in details for the formation of (a)cyclic carbonates and polycarbonates. The main limitation of these systems lies in the formation of water as a by-product, which considerably limits the yield of this reaction. Thus, quantitative removal of H_2O is mandatory to overcome thermodynamic limitations, and many different synthetic strategies were developed as reported in the first chapter of this thesis.

First, the study of the synthesis of (a)cyclic carbonates using the dual organic system DBU/EtBr to promote the coupling of CO_2 onto diols in a one pot/one step fashion was performed using ATR-IR *in-situ* monitoring to better understand the different steps involved in the reaction. The selected model reaction with propylene glycol to afford propylene carbonate was successfully conducted and a mechanism was proposed and supported by DFT calculations. Interestingly, it was concluded that the first step of the reaction involves a trimolecular interaction between the base (DBU), CO_2 and the diol, rather than spontaneous deprotonation of the alcohol by the base. The nature of the halide was also evaluated, evidencing EtBr as the most active for this coupling. Indeed, an SN_2 mechanism is involved during the reaction with nucleophilic attack of an hemicarbonate anion onto the alkyl halide, which is in accordance with EtCl being less reactive than EtBr and leading to lower yield. One should be careful using highly reactive alkyl halide such as methyl iodide as the presence of DBU as the base would generate side reactions, namely quaternization of the base, in competition with the desired carbonation. Thus, a synergistic effect was found between DBU and EtBr, if the system is rapidly put under CO_2 pressure. Competitive double carbonation followed by double alkylation could also occur, leading to the formation of bifunctional linear carbonates as valuable side-products. Effects of the temperature, pressure and nature of the solvent were also investigated. Another dual organic system, namely TEA/TsCl, was also tested and studied in details in a similar fashion for the coupling of propylene glycol with CO_2 to obtain propylene carbonate. As TEA is a milder base than DBU, no quaternization with the highly reactive TsCl could be observed as it was the case with DBU. Thus, reaction times could be considerably lowered using this new system, from 20 h using DBU/EtBr to 2 h using TEA/TsCl. Both dual activating systems were then subjected to a substrate scope to evaluate the influence of the nature of the diol, i.e 1,2- ; 1,3- ; 1,4-diols and isosorbide. As a general conclusion, 1,2 and 1,3 diols were successfully converted into their respective cyclic carbonates in good yields using TEA/TsCl, whereas double carbonation could be favoured in the case of DBU/EtBr, unless in the case of glycerol where glycerol carbonate was exclusively obtained with DBU/EtBr. However, 1,4-diols and isosorbide did not afford cyclic carbonates, as expected by their chemical structure that disfavour cyclization. Double carbonation was exclusively observed with DBU/EtBr, whereas traces of oligocarbonates where detected using TEA/TsCl.

Taking advantage of the previous observation, we pictured a new synthetic procedure for the direct copolymerization of CO_2 and isosorbide for the fabrication of poly(isosorbide carbonate) in a one pot/one step fashion. Indeed, as no cyclization was observed but carbonation could still be detected in ATR-IR, one could suggest that unstable RCO_3Ts adduct would be formed in the reaction medium under CO_2 pressure. This highly reactive adduct could later undergo transcarbonation reaction with another diol to obtain a carbonate dimer RCO_3R. As we are using bifunctional alcohols, oligomerization could then occur to afford oligocarbonates. Preliminary results comforted our prediction with isolation of dimers and trimers, but changing the experimental parameters (temperature, pressure, concentration, co-catalysts, solvent…) did not increase the molar masses. The main limitations lie in low isosorbide conversion as well as occurrence of alcohol tosylation as side reaction that would perturb the stoichiometry and thus prevent from satisfying chain extension. Besides, the use of TEA and TsCl in large excess which in addition are not regenerated at the end of the reaction, due to the need to remove quantitative amounts of wate, would lead to sustainability concerns. Therefore, no further experiments were conducted with such a heavy system. Nevertheless, we reported for the first time the challenging direct copolymerization of CO_2 with isosorbide in a one pot/ one step fashion under mild conditions (70 °C ; 1.5 CO_2 MPa pressure) to obtain oligocarbonates (mainly dimers and trimers).

As CO_2 is thermodynamically very stable, we figured out that direct copolymerization of CO_2 with complex substrate such as isosorbide was very challenging and not ideal. An innovative approach to obtain CO_2- and bio-based polycarbonates was thus adopted. As reported in the literature review, the synthesis of α-alkylidene cyclic carbonates (αCC) from CO_2 and propargylic alcohol is well controlled. These αCC can be seen as an activated form of CO_2 since their facile and highly regio-selective ring opening has already been reported. In this context, we synthesized a new set of CO_2- and bio-based monomers by ring opening of αCC with bio-based diols to obtain new acyclic bis-oxo-carbonate monomers (bisLC). Using DBU as a base, the synthesis of these new monomers was well controlled and a mechanism was proposed based on ATR-IR *in-situ* monitoring supported by DFT calculations. Then, the bisLC were subjected to melt polycondensation processes with the same set of diols to obtain homopolycarbonates. A first investigation on the synthesis of poly(butylene carbonate) was carried out to better understand the chemical reactivity of these new monomers, depending on different catalysts, reaction time and temperatures. After optimization of the experimental parameters, side reactions could still be observed due to the presence of a ketone functions on the bisLC. Because of the demanding reaction conditions of melt polycondensation (T > 140 °C), these side reactions could not be avoided, and formation of 5-membered cyclic carbonates by addition of an alcohol onto the ketone was identified, which would perturb the stoichiometry of the reaction. Still, poly(butylene carbonate) of M_n up to 11,000 g/mol was obtained after reprecipitation in methanol. This system was then extended to isosorbide and its bisLC analogue, and the occurrence of the same side reactions was observed. Solubility concerns were encountered, highlighting the presence of defects in the polymer backbone, or potential branching or crosslinking brought by a cascade of side reactions. Deep investigations using NMR, ATR-IR and GPC characterizations led us to propose a possible reaction pathway that could lead to the formation of ketal linkages in the polymer backbone. Poly(isosorbide carbonate) of M_n up to 3,000 g/mol was afforded using a proper polycondensation reactor to overcome chain mobility limitations. Interestingly, the synthesized polymers could be considered as hydroxyl telechelic polycarbonate as their chains were mostly capped by OH functions. Fabrication of poly(carbonate-*co*-urethane) using a preformed poly(isosorbide carbonate) and 4,4’-methylene diphenyl diisocyanate was successfully carried out, confirming our expectations. Finally, in order to demonstrate the versatility of our new monomers platform, synthesis of copolycarbonates mixing different diol and bisLC motifs was performed, and alternating copolycarbonate such as poly(isosorbide-co-isomannide carbonate), poly(isosorbide-co-butylene carbonate) and poly(isosorbide-co-phenylenebis(methylene) carbonate) were obtained with moderate molar masses. Thermal analysis by DSC revealed a single T_g tuned by the incorporation of aliphatic, cycloaliphatic or aromatic structures. Further investigations to prevent the formation of side products should be conducted, especially on catalytic systems that would preferentially activate the carbonate function rather than the ketone function of the bisLC, but we believe that these new monomers open the door for future alternative to conventionally used dimethyl and diphenyl carbonates.

Synthons CO_2 sourcés, de la synthèse à l'élaboration de polycarbonates à faible empreinte carbone

Résumé : Ce projet de recherche s'inscrit dans un cadre de valorisation du CO_2 pour l'élaboration de nouveaux monomères et polymères CO_2-sourcés (fixation chimique du CO_2). Plus précisément, ce projet cible l'étude du couplage d'alcools et de CO_2 dans le but d'obtenir des carbonates et polycarbonates à faible empreinte carbone. Le travail de thèse s'articule autour de deux étapes principales. Dans un premier temps, il s'agit de proposer une étude mécanistique sur la synthèse de carbonates (a)cycliques au départ d'alcools et de CO_2 dans des conditions douces (faible température et pression). À l'aide de suivis cinétiques par spectroscopie ATR-IR *in-situ* supportés par la modélisation moléculaire (calculs DFT), une comparaison de la performance de systèmes organiques duaux utilisés comme activateurs de ces réactions thermodynamiquement défavorables est décrite en détail. Notamment, les mécanismes réactionnels sont identifiés afin de comprendre les différentes réactivités et sélectivités observées. Dans un second temps, l'élaboration de polycarbonates CO_2- et bio-sourcés est étudiée, notamment pour la synthèse de polycarbonates d'isosorbide comme matériaux prometteurs aux propriétés analogues aux polycarbonates pétrosourcés conventionnels. Le couplage direct entre l'isosorbide et le CO_2 est tout d'abord étudié en faisant varier les conditions expérimentales. Cette copolymérisation directe étant très difficile due aux limitations thermodynamiques du couplage alcool/CO_2, une stratégie de synthèse de nouveaux monomères au départ d'alcools biosourcés et de CO_2 est alors proposée. Cette nouvelle plateforme de molécules permet ainsi la synthèse de polycarbonates aux structures moléculaires diversifiées par des procédés de polycondensation à l'état fondu. Une étude approfondie de la réactivité de ces monomères pour l'obtention de (co)polycarbonates est réalisée ainsi que la caractérisation physico-chimique des matériaux obtenus.

Mots clés : Valorisation du CO_2, (Poly)carbonates CO_2-sourcés, Polycarbonate bio-sourcés, ATR-IR *in-situ*, DFT, chimie durable

CO_2-based synthons, from the synthesis to the elaboration of low carbon footprint polycarbonates

ABSTRACT: This research project falls within the framework of CO_2 valorization for the development of new monomers and CO_2-based polymers (chemical fixation of CO_2). Specifically, this project targets the study of the coupling of alcohols and CO_2 for the fabrication of low carbon footprint carbonates and polycarbonates. This thesis work revolves around two main stages. The first step is to propose a mechanistic study on the synthesis of (a)cyclic carbonates from alcohols and CO_2 in mild conditions (low temperature and pressure). Using kinetic monitoring by *in-situ* ATR-IR spectroscopy supported by molecular modelling (DFT calculations), a careful comparison of dual organic systems, used as activators of these thermodynamically unfavorable reactions, and their performances on the synthesis of (a)cyclic carbonates is described in details . In particular, reaction mechanisms are identified to better understand the differences observed in reactivity and selectivity. In the second step, the development of CO_2- and bio-sourced polycarbonates is studied, especially for the synthesis of isosorbide polycarbonates as promising materials with properties similar to conventional petroleum-based polycarbonates. The direct coupling between isosorbide and CO_2 is first studied by varying the experimental conditions. Since this direct copolymerization is very difficult due to the thermodynamic limitations encountered during the alcohol / CO_2 coupling, a strategy for synthesizing new monomers from bio-based alcohols and CO_2 is then proposed. This new platform of molecules then allows for the synthesis of polycarbonates with tunable chemical structures by melt polycondensation. In this context, an in-depth study of the reactivity of these monomers for obtaining (co)polycarbonates is carried out as well as the physico-chemical characterisations of the synthesized materials.

KEYWORDS: CO_2 valorization, CO_2-based (poly)carbonates, biobased polycarbonates , ATR-IR *in-situ*, DFT, sustainable chemistry