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Activated Lipidic Cyclic Carbonates for Non-Isocyanate Polyurethane Synthesis

Océane Lamarzelle,^{a,b} Pierre-Luc Durand,^{a,b} Anne-Laure Wirotius,^{a,b} Guillaume Chollet,^c Etienne Grau^{a,b} and Henri Cramail^{a,b*}

Activated 5-membered cyclic carbonates were prepared from glycerol and fatty acid derivatives. Ester and ether moieties were introduced in β position to the cyclic carbonate, in order to enhance its reactivity towards amines. ^1H NMR kinetic investigation of the aminolysis of these cyclic carbonates demonstrated a higher reactivity compared to the one of alkyl substituted cyclic carbonates. In the case of ester-activated carbonates, a reactivity similar to the one of 6-membered ring cyclic carbonate was observed. Moreover, these carbonates exhibited amidation side-reactions with amines that could be however prevented by decreasing the temperature to room temperature. Poly(hydroxyurethane)s (PHUs) were then synthesized from these activated 5-membered ring cyclic carbonates at 70°C in DMF (1 mol.L⁻¹) and exhibited molar masses up to 13 700 g.mol⁻¹ with Tg in the ranges -26 to -10°C.

Introduction

Thermoplastic poly(hydroxyurethane)s (PHUs) raised industrial and academic research curiosity¹⁻⁷, since their synthesis is achieved *via* the ring opening of bis-cyclic carbonates with diamines, enabling the replacement of phosgene and isocyanates employed in the classical polyurethane (PU) manufacture. In view of the fossil fuel depletion, the use of building-blocks from renewable resources such as vegetable oils is on the rise.⁸ Combining PHUs synthesis and bio-based compounds, a large platform of fatty acid-based cyclic carbonates as poly(hydroxyurethane) precursors has already been synthesized by epoxidation/carbonation routes.^{3,9-11} However, such monomers exhibited a slow polymerization rate towards amines, due to the electron-releasing alkyl chains which deactivate the cyclic carbonates. To answer the problematic, academic research has developed larger sized-ring cyclic carbonates in order to increase their ring strain and so their reactivity towards aminolysis.¹²⁻¹⁷ Our research group has recently carried out the preparation of vegetable oil-based 6-membered cyclic carbonates from bio-sourced methyl undecenoate.¹⁸ An alternative route consists in inserting a heteroatom nearby the cyclic carbonate to improve/activate its reactivity.^{12, 13, 19-31} Herein, the synthesis of new activated lipidic cyclic carbonates from glycerol carbonate and epichlorohydrin has been achieved, leading respectively to an ester or an ether linkage in β position of the carbonate. After kinetic investigations of the cyclic carbonate aminolysis on model compounds, the corresponding activated bis-cyclic carbonates were polymerized with two diamines and exhibited enhanced reactivities. A specific focus on the side reactions that could occur in both model reaction and polymerization is also discussed.

Experimental

Materials and methods

Methyl 10-undecenoate (>96.0%), 10-undecen-1-ol (99%), decane-1,10-diamine (10DA, >98%), glycerol 1,2-carbonate (>90%), 1,3-dioxane-2-one (trimethylene carbonate, >98%), lithium aluminum hydride (LiAlH₄, 95%) and epichlorohydrin (>99%) were supplied by TCI, Europe. N,N-dimethylformamide (DMF, anhydrous grade), sodium hydrate (NaH) (60 % dispersion in mineral oil), sodium hydroxide (NaOH, pellet), tetrabutylammonium bromide (TBABr, 99%), ethyl chloroformate (97%), Grubbs 1st generation metathesis catalyst, Grubbs 3rd generation metathesis catalyst, hexylamine (99%), dimethyl carbonate (DMC, 99%), 1,2,4-trichlorobenzene (TCB, 99%), Oleoyl chloride (>80%), 1,2-epoxydodecane (90%) and

hydrochloric acid (33%) were obtained from Sigma-Aldrich. Triethylamine (TEA, 99%), sebacyl chloride (97%) and 1,2-epoxy-9-decene (96%) were purchased from Alfa Aesar. Oleyl alcohol (99%) and methyl oleate (99%) were purchased from Nu-Check-Prep. ITERG kindly provided 20g of **UndCC-ester**. All products and solvents (reagent grade) were used as received except otherwise mentioned. The solvents were of reagent grade quality and were purified wherever necessary according to the methods reported in the literature.

^1H and ^{13}C -NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ^1H and ^{13}C , respectively) by using CDCl₃ as a solvent at room temperature, except otherwise mentioned. ^{13}C DEPT (Distortionless Enhancement of Polarisation Transfer) and Two-dimensional analyses such as ^1H - ^1H COSY (COrrrelation Spectroscopy), ^1H - ^1H TOCSY (TOtal Correlation Spectroscopy), ^1H - ^{13}C HSQC (Heteronuclear Single Quantum Spectroscopy) and ^1H - ^{13}C HMBC (Heteronuclear Multiple Bond Correlation) were also performed. Infrared spectra (FTIR-ATR) were obtained on a Bruker-Tensor 27 spectrometer, equipped with a diamond crystal, using the attenuated total reflection mode. The spectra were acquired using 16 scans at a resolution of 4 wavenumbers. The gas chromatography analyses (GC) were performed by ITERG using a Shimadzu GC equipped with: Flame ionization detectors (FID, 380 °C) and Zebron ZB-5HT (5% phenyl - 95% dimethylpolysiloxane) 15 m x 0.25 mm ID, 0.1 μm thickness capillary column. The carrier gas was hydrogen. The column temperature was initially set at 60 °C (volume injected: 1 μl), then increased to 370 °C at a rate of 10 °C.min⁻¹ and held isothermally for 10 min. Size exclusion chromatography (SEC) analyses of PUs were performed in DMF (80°C) on a PL-GPC 50 plus Integrated GPC from Polymer Laboratories-Varian with a series of three columns from Polymer Laboratories (PLgel: PLgel 5 μm Guard (guard column 7.5 mm ID x 5.0 cm L); PLgel 5 μm MIXED-D (7.5 mm ID x 30.0 cm L) and PLgel 5 μm MIXED-D (7.5 mm ID x 30.0 cm L)). In both cases, the elution times of the filtered samples were monitored using RI detectors. Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -50 to 160 °C at 10 °C.min⁻¹ (additional isotherm of 15 min at 160°C at the end of the first cycle to remove the residual DMF) were performed and then the glass transition and melting temperatures were calculated from the second heating run. Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min⁻¹ under nitrogen atmosphere from room

temperature to 600°C, with an isotherm at 160°C for 15 min to remove the residual DMF. Mass spectra were performed by the Centre d'Etude Structurale et d'Analyse des Molécules Organiques (CESAMO) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in the negative/positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 20 µL sample loop into a 400 µL/min flow of methanol from the LC pump. Sample was dissolved in DCM at 1 mg/ml, and then 10 µl of this solution was diluted in 1 ml of methanol. DFT calculations were done using GAUSSIAN09³² with the B3PLYP hybrid functional and a high quality 6-311++G(d) basis set.

Standard procedure for kinetic experiments

The kinetic experiments were performed in NMR tube at 1 mol.L⁻¹ in DMSO-d₆, generally at 50°C and with a ratio 1:1 between cyclic carbonate and hexylamine. All reagents were dried on molecular sieves or distilled before the reaction. Hexylamine was dried under CaH₂ and distilled after drying. The cyclic carbonate was directly dried overnight in a NMR tube capped with a septum, under vacuum. 0.5 mL of dried DMSO-d₆ and 12.5 µL of TCB were added via the septum and the mixture was homogenized. The hexylamine (66 µL, 0.5 mmol, 1 eq.) was then added just before putting the tube in the NMR apparatus. The reaction mixture was then heated at the reaction temperature. The reaction was monitored with ¹H NMR spectroscopy with the disappearance of the cyclic carbonate protons for 2 days.

Standard procedure for polymerization

PHUs were prepared from the b5CC, Und-bCC-ether and Und-bCC-ester with 1,10-diaminodecane (**10DA**) and 1,3-cyclohexanebis(methylamine) (**6cDA**) as comonomers with a molar ratio 1 : 1. PHU syntheses were performed in DMF (1mol.L⁻¹) at 70°C into a schlenk tube under magnetic stirring and nitrogen atmosphere for 7 days. No catalysts were added for the polymerization reactions. Conversions were determined by ¹H NMR spectroscopy after 24h and 7 days of polymerization.

Mono-cyclic carbonate synthesis

UndCC-ether synthesis : (i) In a round-bottom flask, 10-undecen-1-ol (10 g, 58.7 mmol) was stirred with epichlorohydrin (54.35g, 587 mmol, 10 eq) and TBABr (1.89 g, 5.87 mmol, 0.1 eq) at room temperature for 30 min. NaOH was added via a 50% concentrated aqueous solution (70 mL, 0.88 mol, 15eq). After 24 hours of reaction at room temperature, the mixture reaction was diluted with 4 volumes of distilled water. The aqueous phase was extracted 3 times with 100 mL of ethyl acetate. The organic phase was then washed twice with 75 mL of water, dried over anhydrous magnesium sulfate, filtered and the remaining epichlorohydrin was removed on rotary evaporator. The ¹H NMR spectrum revealed a conversion of 72%. The compound **Und-epoxide** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 88:12) and obtained as a viscous transparent liquid. Yield=58%. ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.80 (m, 1H), 4.96 (m, 2H), 3.70 and 3.37 (dd, 2H), 3.49 (m, 2H), 3.14(m, 1H), 2.78 and 2.59 (t, 2H), 2.02 (m, 2H), 1.58-1.28 (m, 16H). ¹³C NMR (CDCl₃, 25°C, 100 MHz) δ (ppm):137.9 (CH=CH₂), 113.2 (CH=C₂H₂), 70.7 (OCH₂-CH₂), 70.4 (CH₂O-CH₂CH₂), 49.9 (CH₂-CH-CH₂O), 43.4 (CH₂-CH-CH₂O), 32.7 (CH₂-CH=CH₂), 28.7-25.1 (CH₂). (ii) The **Und-epoxide** (7.72g, 34.2 mmol) was first pre-mixed with the TBABr (0.24 g, 0.7 mmol, 3 wt%) in 5 mL of acetone. Then the mixture was placed in a reactor and heated up at 80°C. Once the temperature

got stabilized, CO₂ was slowly introduced into the reactor until 50 bars. After 3 days, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The mixture was reconcentrated on rotary evaporator. The ¹H NMR of the final mixture revealed a conversion of 98%. The **UndCC-ether** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 81:19), and obtained as a viscous transparent liquid. Yield=82%. ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.72 (m, 1H), 4.90 (m, 2H), 4.73 (m, 1H), 4.42-4.32 (t, 2H), 3.58 (m, 2H), 3.41 (t, 2H), 1.98 (dd, 2H), 1.48 (m, 2H), 1.21 (m, 14H). ¹³C NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 155.3 (OCOO), 138.8 (CH=CH₂); 114.2 (CH=C₂H₂), 74.7 (CH₂-CH-CH₂O), 71.8 (CH₂O-CH₂-CH₂), 68.8 (CH-CH₂O-CH₂), 66.1 (CH₂-CH-CH₂O), 33.6 (CH₂-CH=CH₂), 28.7-26.2 (CH₂). IR (cm⁻¹): 3075, 2979, 2928, 2850, 1760.

OleylCC-ether synthesis: (i) **Oleyl-epoxide** was synthesized using the same procedure than for **Und-epoxide**, but starting from oleyl alcohol. Viscous transparent oil was obtained and no purification was applied before carbonation. Conversion=78%. (ii) **OleylCC-ether** was synthesized using the same carbonation procedure as in **UndCC-ether** synthesis. Conversion = 99%. Viscous transparent oil was obtained after purification by flash chromatography with a mixture of cyclohexane and ethyl acetate as eluent (100:0 to 86:14). Yield = 46 %. ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.35 (m, 2H), 4.78 (m, 1H), 4.50 and 4.40 (t, 2H), 3.62 (m, 2H), 3.49 (t, 2H), 2.02 (m, 4H), 1.56-1.27 (m, 26H), 0.88 (t, 3H). ¹³C-NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 155.3 (OCOO), 130.1 (CH₂-CH=CH), 75.4 (CH-CH₂OCH₂), 72.10(CH₂O-CH₂-CH₂), 69.6 (CH-CH₂-OCH₂), 66.3 (CH₂-CH-CH₂O), 32.0-22.8 (CH₂), 27.3 (CH₂-CH=CH), 14.3(CH₃). IR (cm⁻¹): 3003, 2917, 2853, 1797, 1133.

UndCC-ester synthesis: (i) Into a round-bottom flask containing 1eq (250 g, 1.34 mol) of undecenoic acid, thionyl chloride (271.5 g, 2.28 mol) was added dropwise under inert atmosphere at 60°C and the formed SO₂ and HCl were trapped during the reaction (with gas traps containing aqueous sodium hydroxide solution). When the conversion (determined by GC) was quantitative (> 99%), the excess of thionyl chloride was distilled out and the product was stored at -18°C. Yield=99 % (ii) In a round-bottom flask, 1 eq (116.7 g, 0.99 mol) of glycerol carbonate and 1.3 eq (130.2 g, 1.29 mol) of triethylamine were diluted in 500 mL of dry THF. 1 eq (270 g, 0.99 mol) of undecenoyl chloride was added dropwise under inert atmosphere at 0°C. The mixture reaction was left 2h at room temperature and the conversion (determined by GC) reached 96%. **UndCC-ester** was then extracted with 250 mL of ethyl acetate and washed several times with 250 mL of water before solvent reconcentration. ITCG provided 20 g of the crude **UndCC-ester**, obtained as an oily white powder that could be purified by recrystallization in 100 mL of cold heptane. 73% yield was achieved after subsequent reconcentration of the recrystallization filtrate and recrystallization. ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.82 (m, 1H), 5.00 (m, 2H), 4.91 (m, 1H), 4.55 (t, 1H), 4.31 (m, 3H), 2.36 (t, 2H), 2.02 (m, 2H), 1.59-1.29 (m, 14H). ¹³C NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 173.6 (CH₂-OCO-CH₂), 154.2 (OCOO), 139.2 (CH=CH₂), 114.0 (CH=C₂H₂), 73.5 (CH-CH₂-OCO), 65.5 (CH₂-CH-CH₂-OCO), 62.7 (CH-CH₂-OCO), 34.4 (OCO-CH₂-CH₂), 33.9 (CH₂-CH=CH₂), 31.1-29.0 (CH₂), 24.9 (OCO-CH₂-CH₂). IR (cm⁻¹): 3081, 3000, 2920, 2853, 1781, 1733.

OleylCC-ester synthesis: **OleylCC-ester** was synthesized following the procedure (ii) used for **UndCC-ester** synthesis, but starting from oleyl chloride. The product was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 80:20)

and obtained as a viscous transparent liquid. Yield=47%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.32 (m, 2H), 4.91 (m, 1H), 4.57 (t, 1H), 4.34 (m, 3H), 2.36 (t, 2H), 1.99 (m, 4H), 1.62-1.29 (m, 22H), 0.85 (t, 3H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 173.4 ($\text{CH}_2\text{-OCO-CH}_2$), 154.6 (OCOO), 130.1 (CH=CH), 73.8 ($\text{CH-CH}_2\text{-OCO}$), 66.0 ($\text{CH}_2\text{-CH-CH}_2\text{-OCO}$), 62.9 ($\text{CH-CH}_2\text{-OCO}$), 34.0 ($\text{OCO-CH}_2\text{-CH}_2$), 31.9-29.2 (CH_2), 27.2 ($\text{CH}_2\text{-CH=CH}$), 24.9 ($\text{OCO-CH}_2\text{-CH}_2$), 22.7 (CH_2), 14.2 (CH_3). IR (cm^{-1}): 3000, 2920, 2858, 1792, 1738.

Und-6CC synthesis : (i) The methyl undecenoate (20 g, 100.9 mmol) was stirred with dimethyl carbonate (340 mL, 4.0 mol, 40 eq), NaH via a 60 wt% dispersion in mineral oil (6 g, 252.1 mmol, 2.5 eq) and DMF (7.8 mL, 109.9 mmol, 1 eq) at 60°C . After 24 hours of reaction, 435 mL of diluted hydrochloric acid was slowly added to the reaction mixture. The organic phase was then washed twice with 100 mL of water, dried over anhydrous sodium sulfate, filtered and then the remaining dimethyl carbonate was removed on rotary evaporator. The compound **Und-malonate** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 90:10) and obtained as a viscous liquid. Yield=58%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.79 (m, 1H), 4.95 (m, 2H), 3.73 (s, 6H), 3.35 (t, 1H), 2.04 (m, 2H), 1.88 (m, 2H), 1.29 (m, 10H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 170.1 (COOCH_3), 139.3 (CH=CH_2), 114.3 (CH=CH_2), 52.6 (C=OOCH_3), 51.9 ($\text{CH-(C=OOCH}_3)_2$), 33.9 ($\text{CH}_2\text{-CH=CH}_2$), 29.3-27.5 (CH_2). IR (cm^{-1}): 2924, 2854, 1734.

(ii) A solution of Und-malonate (10 g, 39.0 mmol) in THF (10 mL) was added to a solution of LiAlH_4 (6.1 g, 160.9 mmol, 4.1 eq.) in THF (80 mL) at 0°C . After the addition was completed, the reaction mixture was allowed to reach slowly room temperature and was refluxed at 80°C for 2 h. The reaction mixture was then cooled to 0°C , and 10 mL of hydrochloric acid solution (2N) was added dropwise. The product was then extracted three times with 50 mL of ethyl acetate. The organic layer was washed twice with 50 mL of NaCl saturated solution and water, dried over anhydrous sodium sulfate, filtered and then the solvent was removed on rotary evaporator. The **Und-1,3-diol** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 40:60). Yield=66%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.81 (m, 1H), 4.93 (m, 2H), 3.78-3.63 (m, 4H), 2.68 (s, 2.OH), 2.02 (m, 2H), 1.75 (m, 1H), 1.36-1.22 (m, 12H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 139.4 (CH=CH_2), 114.4 (CH=CH_2), 67.0 ($\text{CH-CH}_2\text{-OH}$), 42.2 ($\text{CH-CH}_2\text{-OH}$), 34.0 ($\text{CH}_2\text{-CH=CH}_2$), 30.1-27.4 (CH_2). IR (cm^{-1}): 3277, 2919, 2850.

(iii) To a solution of triethylamine (10.1 g, 100 mmol, 2 eq.) in THF (400 mL), **Und-1,3-diol** (10 g, 50 mmol) was added. Then ethyl chloroformate (10.8 g, 100 mmol) was added to the mixture at 0°C . The reaction mixture was stirred at room temperature for 7 hours. Precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated under vacuum. The **Und-6CC** was isolated from the reaction mixture by flash chromatography using a mixture of cyclohexane and ethyl acetate (100:0 to 60:40) and obtained as a viscous liquid with 99.5% purity determined by GC-FID. Yield=75%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.73 (m, 1H), 4.94 (m, 2H), 4.41 (m, 2H), 4.06 (m, 2H), 2.17 (m, 1H), 2.02 (m, 2H), 1.35-1.30 (m, 12H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 148.3 (OCOO), 139.1 (CH=CH_2), 114.7 (CH=CH_2), 72.5 ($\text{CH}_2\text{-OCOO}$), 34.0 ($\text{CH}_2\text{-CH=CH}_2$), 31.4 ($\text{CH-CH}_2\text{-OCOO}$), 29.5-26.7 (CH_2). IR (cm^{-1}): 3075, 2979, 2928, 2850, 1760.

Oleyl-6CC synthesis: **Oleyl-6CC** was synthesized following the procedure used for **Und-6CC** synthesis, but starting from methyl oleate. Viscous transparent oil was obtained after purification by flash chromatography with a mixture of cyclohexane and ethyl

acetate (100:0 to 60:40). Yield=43%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.33 (m, 2H), 4.41 (m, 2H), 4.13 (m, 2H), 2.22 (m, 1H), 2.02 (m, 4H), 1.28 (m, 22H), 0.91 (t, 3H). ^{13}C -NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 148.6 (OCOO), 130.6 and 129.2 (CH=CH), 72.4 ($\text{CH}_2\text{-OCOO}$), 32.0 (CH_2), 31.4 ($\text{CH-CH}_2\text{-OCOO}$), 29.9-22.7 (CH_2), 27.3 ($\text{CH}_2\text{-CH=CH}$), 14.1 (CH_3). IR (cm^{-1}): 3000, 2979, 2925, 2853, 1754.

Dec-5CC synthesis: The commercially available 1,2-epoxydodecane (3.02 g, 16.4 mmol) was first pre-mixed with TBABr (0.09 g, 0.28 mmol, 3 wt%) and 5 mL of acetone. Afterwards, the mixture was placed in a high-pressure autoclave and heated up at 80°C . Once the temperature got stabilized, CO_2 was slowly introduced into the reactor until 40 bars. After 3 days, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The ^1H NMR of the final mixture revealed a conversion of 98 %. The **Dec-5CC** was purified by flash chromatography using a mixture of cyclohexane: ethyl acetate (100:0 to 88:12). The product was isolated as transparent viscous oil with a yield of 90%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 4.70 (m, 1H), 4.49 (t, 1H), 4.06 (t, 1H), 1.80 (m, 1H), 1.65 (1H), 1.40-1.26 (16H), 0.89(t, 3H). ^{13}C -NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 155.3 (OCOO), 77.4 (CH-OCOO), 69.5 ($\text{CH}_2\text{-OCOO}$), 34.0 ($\text{CH}_2\text{-CH-OCOO}$), 31.9-22.7 (CH_2), 14.2 (CH_3). IR (cm^{-1}): 2925, 2848, 1789.

Bis-cyclic carbonate synthesis

Und-bCC-ether synthesis: Into a round-bottom flask, the **UndCC-ether** (5g, 18.5 mmol) and 1st generation Grubbs catalyst (76.2 mg, 0.093 mmol, 0.5% mol) were charged under nitrogen. The contents were vigorously stirred at 35°C for 24 hours. The equilibrium was driven thank to the removal under vacuum of the produced ethylene. The product was then purified with flash chromatography using a mixture of dichloromethane and methanol as eluent (100:0 to 95:5). **Und-bCC-ether** was obtained as a grey solid. Yield=53%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.38 (m, 2H), 4.80 (m, 2H), 4.49 and 4.39 (t, 4H), 3.64 (m, 4H), 3.50 (t, 4H), 1.97 (m, 4H), 1.56 (m, 6H), 1.27 (m, 26H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 154.5 (OCOO), 130.9 (CH=CH), 75.2 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 72.2 ($\text{CH-CH}_2\text{-OCH}_2$), 69.6 ($\text{CH}_2\text{-CH-CH}_2\text{O}$), 66.3 ($\text{CH}_2\text{CH-CH}_2\text{O}$), 32.7 ($\text{CH}_2\text{-CH=CH}$), 29.9-26.1 (CH_2). IR (cm^{-1}): 2923, 2850, 1792, 1141. $T_m=54^\circ\text{C}$.

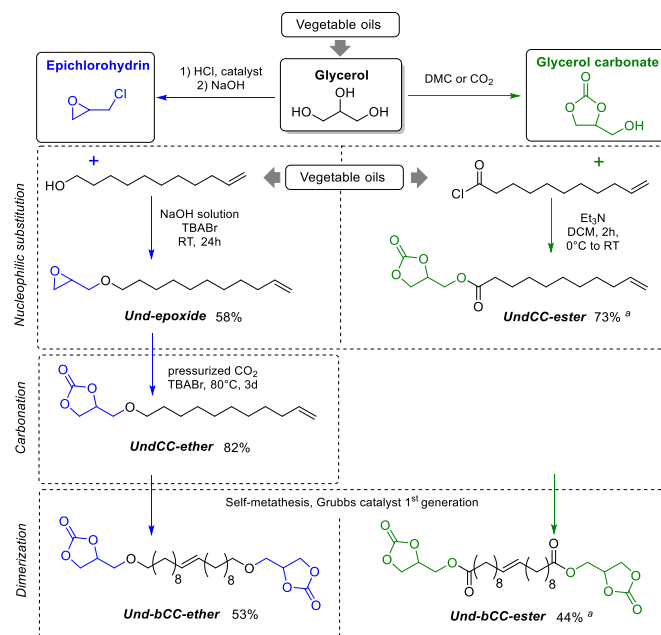
Und-bCC-ester synthesis: Into a round-bottom flask equipped with a mineral oil bubbler, the **UndCC-ester** (3g, 5.6 mmol) was mixed with 2 mL of dichloromethane. 1st generation Grubbs catalyst (42.6 mg, 0.028 mmol, 0.5% mol) was then charged under nitrogen. The contents were vigorously stirred at room temperature for 24 hours. The ^1H NMR revealed of conversion of 80%. The product was purified by recrystallization in 10 mL of cold dichloromethane (-80°) followed by a filtration and a washing with 30 mL of dichloromethane. **Und-bCC-ester** was obtained as a grey powder. Yield=44%. ^1H NMR (CDCl_3 , 25°C , 400 MHz) δ (ppm): 5.36 (m, 2H), 4.92 (m, 2H), 4.55 and 4.32 (t, 4H), 4.28 (t, 4H), 2.35 (t, 4H), 1.95 (m, 4H), 1.63-1.28 (24H). ^{13}C NMR (CDCl_3 , 25°C , 100 MHz) δ (ppm): 173.0 ($\text{CH}_2\text{-OCO-CH}_2$), 154.5 (OCOO), 130.5 (CH=CH), 73.7 ($\text{CH-CH}_2\text{-OCO}$), 65.7 ($\text{CH}_2\text{-CH-CH}_2\text{-OCO}$), 62.7 ($\text{CH-CH}_2\text{-OCO}$), 34.2 ($\text{OCO-CH}_2\text{-CH}_2$), 32.0 ($\text{CH}_2\text{-CH=CH}$), 29.4-28.5 (CH_2), 24.5 ($\text{OCO-CH}_2\text{-CH}_2$). IR (cm^{-1}): 2917, 2850, 1784, 1736. $T_m=111^\circ\text{C}$.

Seb-bCC-ester synthesis: In a round-bottom flask, 2.6 eq (5.14g, 43.4 mmol) of glycerol carbonate and 4 eq (9.02 mL, 66.8 mmol) of triethylamine were diluted in 10 mL of dry dichloromethane. 2.6 eq (4g, 16.7 mmol) of sebacyl chloride was slowly added under inert atmosphere at 0°C . The mixture reaction was left 2h at room temperature. Afterwards, the mixture was reconcentrated and 50

mL of petroleum ether was added to extract the **Seb-bCC-ester**. The triethylammonium salts formed during the reaction were filtered and the filtrate was washed three times with 25 mL of a 10% mol HCl solution, once with 25 mL of saturated NaHCO₃ solution and finally with 25 mL of brine. ¹H NMR indicated a quantitative conversion of 100%. After purification by flash chromatography using a mixture of dichloromethane and methanol (100:0 to 97:3), **Seb-bCC-ester** was obtained in 47% yield as a white powder. ¹H NMR (DMSO, 25°C, 400 MHz) δ (ppm): 5.01 (m, 2H), 4.56 and 4.25 (t, 4H), 4.29 (t, 4H), 2.31 (t, 4H), 1.53 (m, 4H), 1.25 (8H). ¹³C NMR (DMSO, 25°C, 100 MHz) δ (ppm): 173.8 (CH₂-OCO-CH₂), 154.1 (OCOO), 74.3 (CH-CH₂-OCO), 66.4 (CH₂-CH-CH₂-OCO), 62.8 (CH-CH₂-OCO), 33.3 (OCO-CH₂-CH₂), 28.5-28.2 (CH₂), 24.2 (OCO-CH₂-CH₂). IR (cm⁻¹): 2936, 2845, 1778, 1730. T_m = 84 °C.

b5CC synthesis : (i) The commercially available 1,2-epoxy-9-decene (7g, 45.4 mmol) was first pre-mixed with the TBABr (0.21 g, 0.64 mmol, 3 wt%). Then the mixture was placed in a reactor and heated up at 80°C. Once the temperature got stabilized, CO₂ was slowly introduced into the reactor until 50 bars. After 24 hours, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The ¹H NMR of the final mixture revealed a conversion of 94.5%. The product was purified by flash chromatography using a mixture of cyclohexane: ethyl acetate (100:0 to 70:30). Y=50%. ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.77 (m, 1H), 4.96 (m, 2H), 4.71 (m, 1H), 4.51 (t, 1H), 4.03 (t, 1H), 2.04 (m, 2H), 1.77 (m, 1H), 1.68 (m, 1H), 1.45-1.33 (m, 8H). ¹³C-NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 155.2 (OCOO), 139.0 (CH=CH₂), 114.5 (CH=CH₂), 77.4 (CH-OCOO), 69.5 (CH₂-OCOO), 34.0 (CH₂-CH-OCOO), 33.8 (CH₂-CH=CH₂), 29.1-28.8 (CH₂), 24.5 (CH₂-CH₂-CH-OCOO). IR (cm⁻¹): 2924, 2856, 1786. (ii) Into a round-bottom flask equipped with a mineral oil bubbler, 5g (1eq, 25mmol) of the carbonated 1,2-epoxy-9-decene was mixed with 50mL of distilled dichloromethane. 3rd generation Grubbs catalyst (76 mg, 0.13mmol, 0.5%) was then charged under nitrogen. The contents were vigorously stirred at room temperature. ¹H NMR revealed 93% of conversion in 3 days. Viscous transparent oil was obtained after purification by flash chromatography using 100% of cyclohexane as eluent. Yield = 65%. **b5CC** ¹H NMR (CDCl₃, 25°C, 400 MHz) δ (ppm): 5.37 (m, 2H), 4.69 (m, 2H), 4.49 and 4.03 (t, 4H), 1.96 (m, 4H), 1.78 and 1.66 (m, 4H), 1.46-1.34 (m, 16H). ¹³C-NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 155.2 (OCOO), 130.4 (CH=CH), 77.1 (CH-OCOO), 69.4 (CH₂-OCOO), 34.0 (CH₂-CH-OCOO), 33.8 (CH₂-CH=CH), 32.5-23.7 (CH₂). IR (cm⁻¹): 2923, 2850, 1786. T_m = -54 °C.

Monomer synthesis



Scheme 1 - Synthesis routes to activated lipidic bis-cyclic carbonates *UndCC-ether* (left) and *UndCC-ester* (right) with isolated yields.

^a The yield can be dramatically increased by subsequent reconcentration of the recrystallization filtrate and further recrystallizations.

Table 1 - Length of cyclic carbonate bonds and urethane formation enthalpies for different cyclic carbonate substituents -X calculated by DFT.

-X	Bond length (Å)	Bond length (Å)	ΔH _f (kJ.mol ⁻¹)	ΔH _f (kJ.mol ⁻¹)
-CH ₃	1.358	1.361	-14.91	-36.33
-OMe	1.358	1.363	-27.36	-55.90
-OC(O)Me	1.361	1.363	-57.96	-62.83

Two strategies, both using glycerol derivatives, were adopted for the synthesis of activated cyclic carbonates.

Firstly, lipidic cyclic carbonates with an ether moiety in β position of the carbonate ring could be easily obtained using epichlorohydrin as reagent, which is produced by chlorination of glycerol.³³ This “epichlorohydrin strategy” has already been adopted by several research groups for the synthesis of cyclic carbonates.^{26, 27, 29, 34, 35} As illustrated in Scheme 1, the synthesis of **Und-bCC-ether** from epichlorohydrin involved three steps (i) the nucleophilic substitution of the epichlorohydrin with undecen-1-ol (ii) the carbonation of the

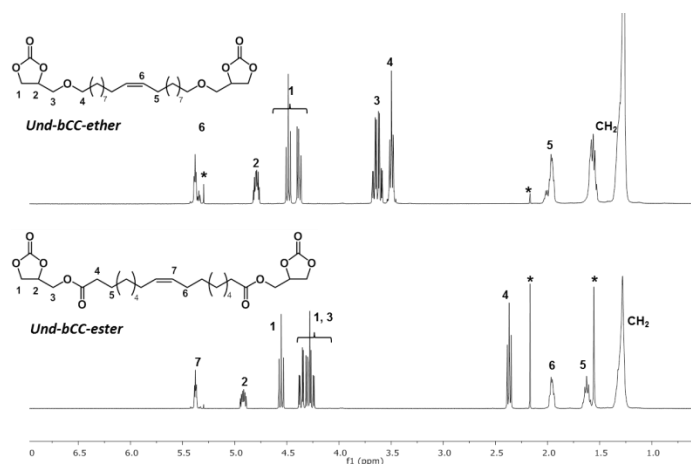


Figure 1 - Stacked ^1H NMR spectra of *Und-bCC-ether* and *Und-bCC-ester* in CDCl_3 .

resulting epoxide and finally (iii) the dimerization by metathesis reaction. The chemical structure of the resulting bis-cyclic carbonate as well as the different intermediates, were assessed by NMR spectroscopy and FTIR-ATR (see Figure 1 and ESI[†]). The **Und-epoxide** was synthesized for 24h at room temperature from 1eq of undecen-1-ol, using 10eq of epichlorohydrin, 15eq of NaOH via a 50%w solution and 0.1eq of TBABr as transfer agent. The conversion reached 72% and no side reactions were observed in these conditions. After extraction with ethyl acetate, the product was purified by flash chromatography (58% yield). The carbonation of the **Und-epoxide** was performed in an autoclave during 3 days at 80°C, at 40 bars of pressurized CO_2 using 3%wt TBABr as catalyst to reach full conversion. **UndCC-ether** was obtained as viscous transparent oil after flash chromatography (82% yield). The mono functional **UndCC-ether** was then “dimerized” via metathesis reaction of the terminal double bond. The reaction was processed at room temperature in dichloromethane under inert atmosphere using 0.5% mol of 1st generation Grubbs metathesis catalyst for the coupling. A conversion of 99% was achieved after 3 days as estimated by NMR spectroscopy. The **Und-bCC-ether** was obtained with a yield of 53% after flash chromatography (eluent: cyclohexane/ethyl acetate).

A second route to activated cyclic carbonates is based on the glycerol carbonate as building block that has been frequently employed to introduce the cyclic carbonate functionality onto different structures.^{17, 36-39}

In this case, bis-cyclic carbonates activated by an ester moiety in β position of the cycle were obtained by esterification between fatty acid chloride from undecenoic acid and glycerol carbonate (see Figure 1 and ESI[†]). **UndCC-ester** was purified by recrystallization in heptane and obtained in 73% yield. The dimerization was successfully achieved with the same reaction conditions than for **Und-bCC-ether** synthesis. Pure **Und-bCC-ester** was recrystallized in cold DCM (-20°C) with a yield of 44%. It should be mentioned that this molecule was recently synthesized by Bigot et al.⁴⁰ who used glycidol and undecenoic acid as starting materials.

Kinetic Measurements

In order to quantify the difference in reactivity between classical 5-membered cyclic carbonates and the synthesized activated cyclic

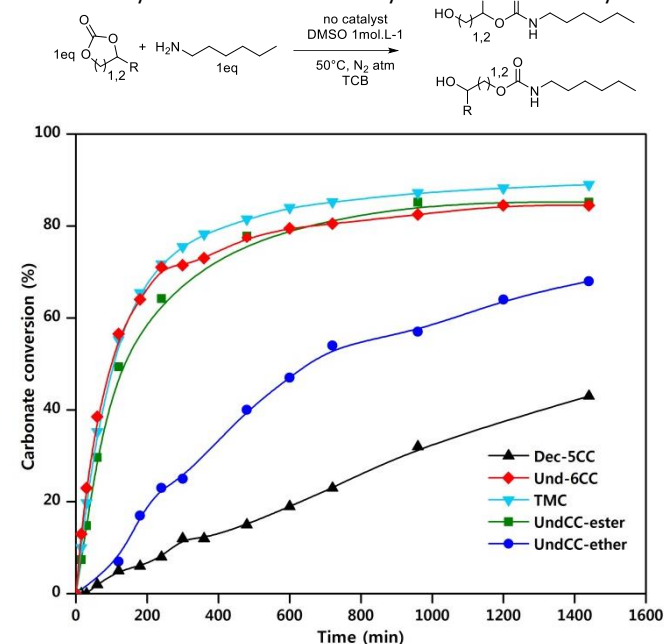


Figure 2 - Effect of various cyclic carbonate activations on the kinetic of the reactions with hexylamine followed by ^1H NMR. (50°C, 1 mol.L⁻¹ in DMSO-d₆, ratio 1:1)

Table 2 - Reaction rate constants obtained for the different model reactions between cyclic carbonates and hexylamine (ratio 1:1) in DMSO-d₆ (1 mol.L⁻¹).

Cyclic carbonate (CC)	Temperature (°C)	k_{app} (L.mol ⁻¹ .h ⁻¹) ^[a]
TMC	50	0.58
Und-6CC	50	0.44
UndCC-ester	25	0.15
	50	0.44
	70	0.80
UndCC-ether	50	0.09
Dec-5CC	50	0.03
Oleyl-6CC	50	0.58
OleylCC-ester	50	0.65 [0-1]h
		0.15 [1-6]h
OleylCC-ether	50	0.04

[a] Calculated upon the 6 first hours of the kinetics performed in NMR, using a second order kinetic law. (see ESI[†]).

carbonates, kinetic experiments were monitored *in situ* by ^1H NMR spectroscopy. Several monocyclic carbonates such as **TMC** (trimethylene carbonate), **UndCC-ester**, **UndCC-ether**, **Und-6CC** (5-(non-8-en-1-yl)-1,3-dioxan-2-one) and **Dec-5CC** (1-decene carbonate) were reacted with hexylamine at 25, 50 or 70°C, at 1 mol.L⁻¹ in DMSO-d₆, with trichlorobenzene (TCB) as internal reference. The cyclic carbonate conversion was followed by ^1H NMR for 24h. In a general trend, conversions of cyclic carbonates followed a second order kinetic law (allowing to extract k_{app}) until 50-60% of conversion. Then, the kinetics of the reaction slowed down and the conversion ultimately reached a plateau. This feature can be attributed to several parameters such as the limited diffusion occurring in the NMR tube, the solubility or the high amount of hydrogen-bonding due to the produced hydroxyl groups, hindering the reaction.

The **UndCC-ester** and **UndCC-ether** were compared to the reactive 6-membered ring cyclic carbonates **TMC** and **Und-6CC** from methyl undecenoate. A purely aliphatic 5-membered ring cyclic carbonate

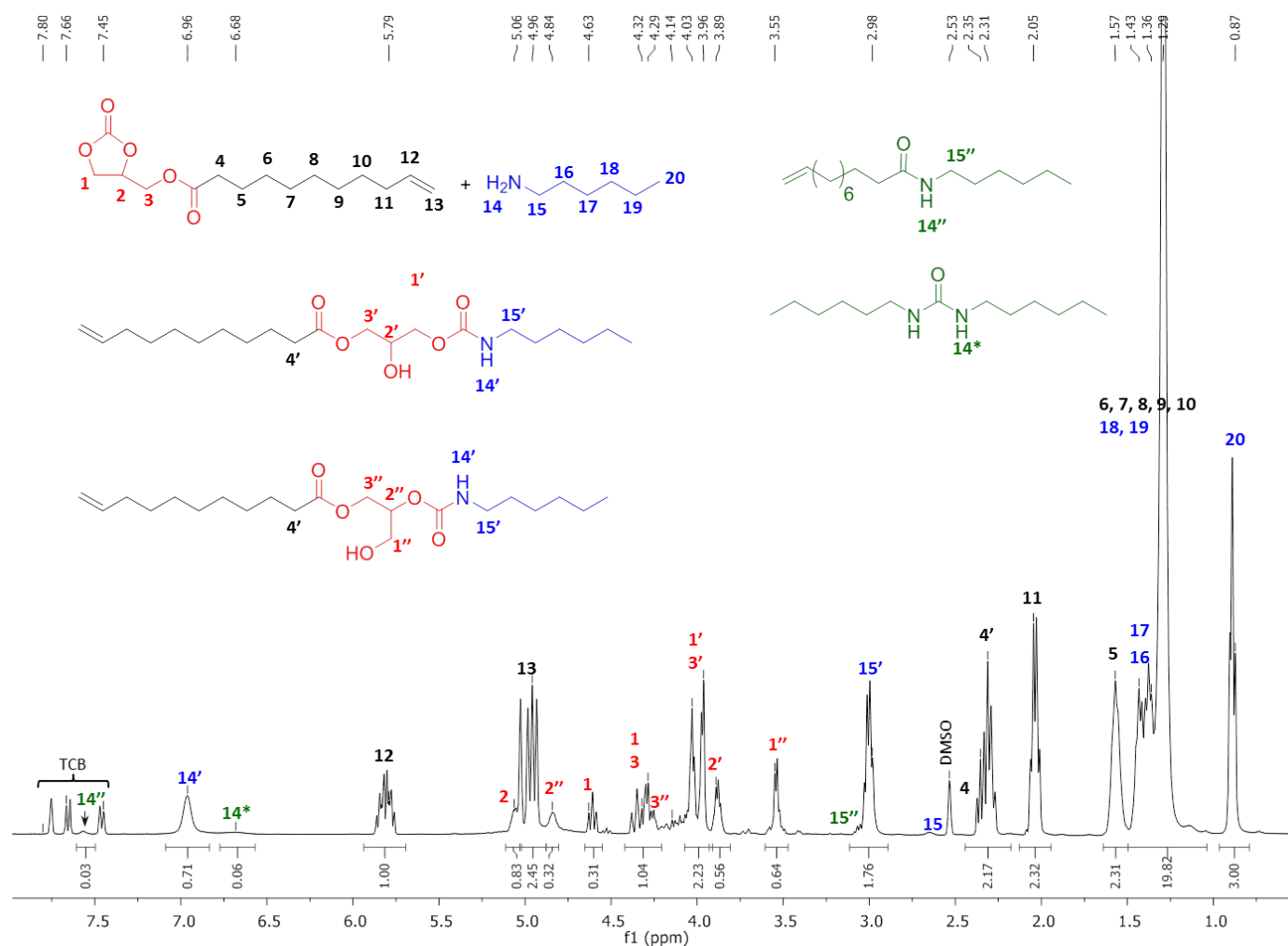
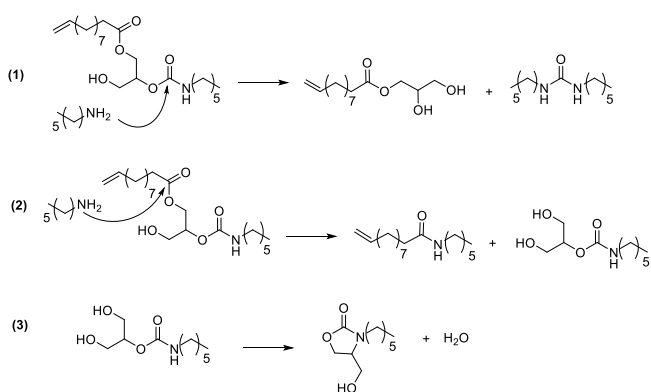


Figure 3 - ^1H NMR of the model reaction between *UndCC-ester* and n-hexylamine in DMSO- d_6 at $1\text{ mol}\cdot\text{L}^{-1}$ at 50°C after 2 days.



Scheme 2 - Possible side reactions between *UndCC-ester* and hexylamine: (1) urea formation, (2) amidification and (3) dehydration.

The enhancement of 5CC reactivity has already been described in the literature^{12, 13, 19-30} and was attributed to the negative inductive effect of the ester and ether groups in β position of the cycle moiety, explaining the highest conversions obtained for *UndCC-ether* and *UndCC-ester*. The latest displayed a similar reactivity to the lipidic *Und-6CC* and followed the same kinetic tendency as *TMC*. On the other hand, *UndCC-ether* kinetic profile clearly

Table 3 - Proportions of product and by-products during the model reaction of *UndCC-ester* and *UndCC-ether* with hexylamine at 50% conversion in cyclic carbonates.

Proportions (%)	<i>UndCC-ester</i>			<i>UndCC-ether</i>	<i>Dec-5CC</i>
	25°C	50°C	70°C	50°C	50°C
Urea ^[a]	2,8	2,7	nd [*]	2,9	4
Amide ^[a]	0	2,1	nd [*]	0	0
Urethane ^[a]	97,2	95,2	nd [*]	97,1	96
Ratio OH _I :OH _{II}	18 : 82	23 : 77	23:77	28 : 72	60:40

*signal shift at higher temperature, calculation of proportions impossible

(*Dec-5CC*) was also synthesized from 1,2-epoxydodecane and CO_2 in order to obtain a low benchmark and to see the effect of an heteroatom insertion within the aliphatic chain, on the reactivity of a 5CC. *Dec-5CC* exhibited the lowest reactivity in terms of aminolysis with hexylamine, as it is depicted in Figure 2.

demonstrates a lower reactivity than *UndCC-ester*. This feature could be assigned to the lower negative inductive effect and the higher positive mesomeric effect of the oxygen atom, stabilizing the cycle and decreasing its subsequent reactivity. From a kinetic point of view, DFT calculations exposed in Table 1 highlight the longer bond length and the ensuing enhanced reactivity towards ring-opening, when an ester moiety is placed nearby the cycle. The

increase of the bond length correlates with the minimized mesomeric effect in the case of the ester activation.

Thermodynamically speaking, the ester moiety exhibits a lower enthalpy of urethane formation, confirming the better carbonate activation. Additionally, the chain length effect has been investigated in model reaction. For that purpose, **OleylCC-ester**, **OleylCC-ether** and **Oleyl-6CC** were synthesized from methyl oleate derivatives. No influence of the chain length was observed on **Und-6CC** and **Oleyl-6CC** when kinetic experiments were carried out. Nevertheless, activated 5-CC were impacted by the number of carbons of the aliphatic chain (see ESI[†]). As an example, **OleylCC-ether** exhibited 51% conversion after 24h instead of 68 % for the corresponding C₁₁-synthon.

Model reactions on **UndCC-ester** were then monitored at 25°C and 70°C with regard to see the impact of the temperature on the ring opening kinetic of the cyclic carbonate. In order to estimate the reaction rate constants (k_{app}), $x/(1-x)$ (in which x represents the cyclic carbonate conversion) was plotted as a function of time (see ESI[†]). The second order kinetic law was verified upon the 6 first hours and the reaction rate constants were 0.15, 0.44 and 0.80 L.mol⁻¹.h⁻¹ at 25, 50 and 70°C respectively (Table 2).

From the Arrhenius plot (see ESI[†]), the activation energy of this mono-cyclic carbonate could be estimated at 27 kJ.mol⁻¹. In the literature, Endo and coll.¹³ reported activation energies of 10.1 and 24.6 kJ.mol⁻¹ for 5CC and 6CC respectively. Additionally, Maisonneuve et al.¹⁸ calculated from the Arrhenius plot an activation energy of 21 kJ.mol⁻¹ for **Und-6CC**, which supports its similar reactivity with **UndCC-ester**.

In addition to the analysis of carbonate consumption, these kinetics experiments allow us to investigate the side reactions during the aminolysis of cyclic carbonate (Scheme 2). The ¹H NMR proton of the **UndCC-ester** reaction with hexylamine is presented in Figure 3. The urethane signals appearance at 2.98 ppm as well as the progressive disappearance of protons characterizing the cyclic carbonate (5.06, 4.63 and 4.32 ppm) confirmed the hydroxyurethane formation. The major products from the model reaction were fully characterized using 1D and 2D NMR spectroscopy (see Figure 3 and ESI[†]) and the ratio between primary and secondary alcohols could easily be calculated by integration of protons **2'** and **2''** respectively (Figure 3). Nevertheless, by-products were also obtained during the model reaction between hexylamine and **UndCC-ester**. As it has already been described in prior studies, primary amines can react with urethane function to give ureas.^{9, 41, 42} HSQC, HMBC and TOCSY NMR analysis proved the presence of urea functions in the mixture, thanks to the assignment of correlated CH-OH (4.9 ppm) and CH₂-OH (4.05-4.15 ppm), characterizing the diol obtained during the formation of urea (Scheme 2-(1)). Its existence was also confirmed by ESI analysis (see

ESI[†]), as Caillol and coll.⁴² have recently done in a complete study about side reactions occurring during PHUs synthesis. A slight amount of oxazolidinones (Scheme 2-(3)) resulting from the dehydration of hydroxyurethanes was also detected by ESI analysis. Besides, it is also known that an ester function is prone to side reactions with primary amines.⁹ In our case, a few percentage of amidification was highlighted using ¹H NMR analysis, thanks to the distinctive labile proton of the amide at 7.6 ppm. ¹³C NMR analysis (see ESI[†]) could confirm the presence of the typical O=C-O carbon at 171.7 ppm. Percentages of major side reactions were calculated using specific labile H of urea (6.7 ppm), urethane (6.9 ppm) and amide (7.6 ppm) functions (see ESI[†]). The results are shown in the Table 3 for **UndCC-ester** and **UndCC-ether** at 50% of conversion in cyclic carbonates. Urea and amides were formed in relatively low proportions, as by-product percentages were not above 5% when 50% conversion in cyclic carbonates were reached, for all tested conditions. In the case of **UndCC-ester**, amidification reaction could be avoided by decreasing the temperature to 25°C. Still at 65 % conversion after 24h at 25°C, amide functions were not produced. However, urea formation appeared to be independent of the temperature and exhibited the same proportions at 25°C and 50°C. For the two activated mono-cyclic carbonates, the ratio isomer OH-I/isomer OH-II was found to be in accordance with the DFT calculations (Table 1) and with the literature, which has reported a clear trend for the formation of secondary hydroxyl groups during the ring-opening of cyclic carbonates by amines.²¹ However, the pure aliphatic 5CC exhibited 60% of primary alcohols and this trend has already been observed by Maisonneuve et al.¹¹ in a prior study (50% : 50%). Additionally, lowering the temperature from 50°C to 25°C could lead to the slight increase of produced secondary hydroxyl groups.

Poly(hydroxyurethane) synthesis

After these kinetic experiments, ether- and ester- activated 5-membered cyclic carbonates were tested in polymerization. PHUs were synthesized from **Und-bCC-ether**, **Und-bCC-ester**, **Seb-bCC-ester** (bis((2-oxo-1,3-dioxolan-4-yl)methyl) decanedioate) and **b5CC** (4,4'-(tetradec-7-ene-1,14-diyl)bis(1,3-dioxolan-2-one)) with 1,10-diaminododecane (**10DA**) and 1,3- cyclohexanebis(methylamine) (**6cDA**) as comonomers. The polymerizations were performed in DMF at 1mol.L⁻¹ at 70°C under nitrogen atmosphere without any catalyst.

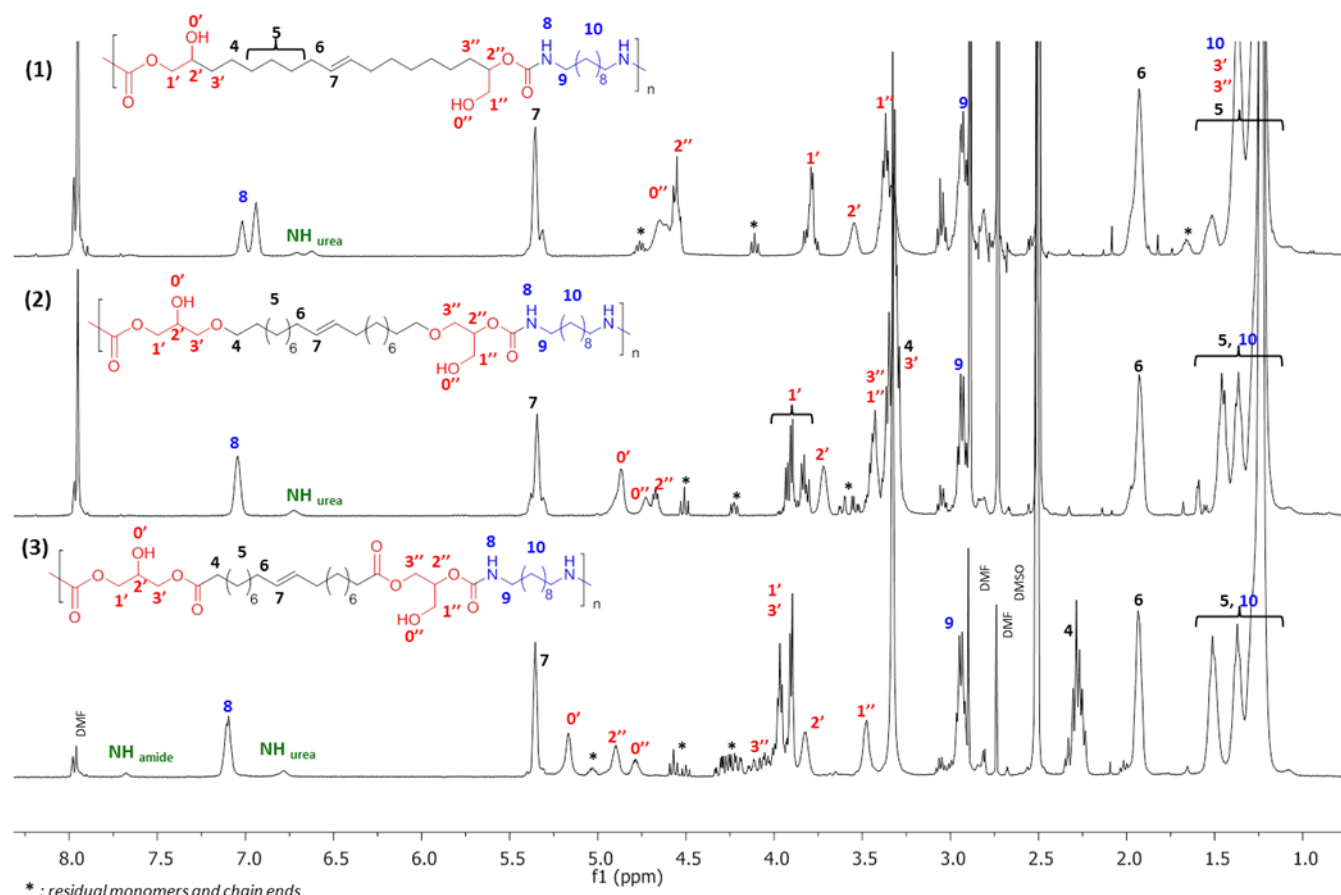
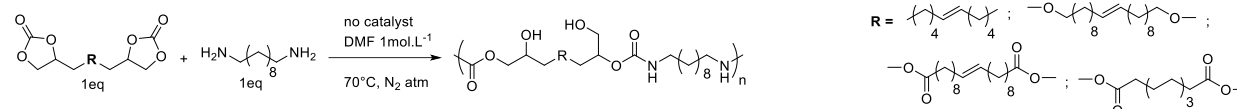


Figure 4 – Stacked ^1H NMR spectra of (1) PHU 1, (2) PHU 2 and (3) PHU 3 in DMSO- d_6 at the end of the polymerizations.

Table 4 - Characterization of PHUs obtained from bis-cyclic carbonates and diamines, in DMF (1mol.L^{-1}) at 70°C under nitrogen.



PHU	Bis-CC	Conversion 24h/7d (%)	Ratio $\text{OH}:\text{OH}_{\text{II}}^1$	Ratio Urea /Amide/Urethane ^{1,2}	M_n (g.mol^{-1}) [D] ¹	T_g ($^\circ\text{C}$) ^a	T_f ($^\circ\text{C}$) ^a	$T_{d5\%}$ ($^\circ\text{C}$) ^b
1	<i>b5CC</i>	84/89	59:41	11 / 0 / 89	6 000 [1.6]	-11	-	264
2	<i>Und-bCC-ether</i>	90/90	28:72	12 / 0 / 88	7 500 [1.7]	-26	54/77	270
3	<i>Und-bCC-ester</i>	88/91.5	41:59	9.6 / 2.6 / 87.8	12 000 [1.9]	-10	69/83	274
4	<i>Seb-bCC-ester</i>	nd /93.5	44:56	10.1 / 5.9 / 84	13 700 [3.7]	-17	-	251
5	<i>Und-bCC-ester</i> ³	nd /91.5	39:61	5.5 / 2.8 / 91.7	8 800 [1.8]	-10	-	253

¹: Determined at the end of the polymerization (7 days) ²: Determined using the relations (E), (E') and (E'') (see ESI⁺). ³: polymerized with 6cDA.

^a: Determined by DSC at $10^\circ\text{C.min}^{-1}$ from the second cycle. ; ^b: Determined by TGA at $10^\circ\text{C.min}^{-1}$ under nitrogen.;

Bulk polymerizations could not be achieved due to the high melting point of monomers. Besides, the temperature used was explained by solubility issues of the monomers in DMF at room temperature. Afterwards, the polymers were characterized without prior quenching and precipitation after 7 days. PHUs formation was followed by ^1H NMR with the disappearance of the signals in α -position nearby the cycle in the ranges 4.2-4.6 ppm, and with the presence of the characteristic protons $\text{CH}_2\text{-NHC(O)O}$ at 2.98 ppm. The PHU formation was confirmed by FTIR thanks to the appearance of bands at $1663\text{-}1684\text{ cm}^{-1}$ and $1505\text{-}1545\text{ cm}^{-1}$, which are attributed to the urethane function. The formation of -NH and-

OH groups was verified by the presence of a wide signal between 3600 and 3100 cm^{-1} . Besides, the chemical structures of **PHU 1**, **PHU 2** and **PHU 3** were elucidated thanks to ^1H , ^{13}C NMR and 2D NMR (COSY, HSQC) as illustrated in Figure 4. SEC data given in Table 4 presents molar masses in the range 6000 to 13700 g.mol^{-1} with dispersity comprised between 1.6 and 3.7 . In all cases, more secondary hydroxyl groups were formed during PHU synthesis as it

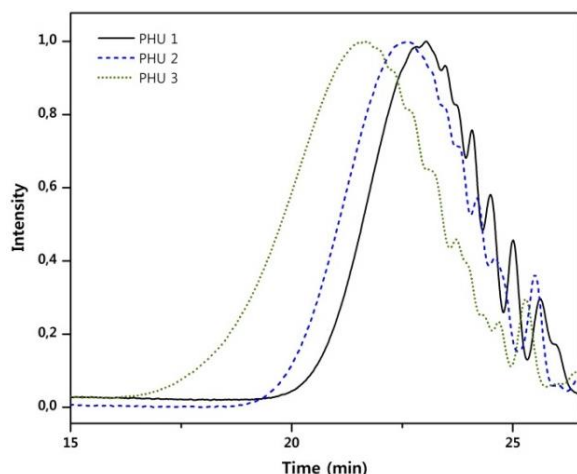


Figure 5 - Size exclusion chromatography of PHU1, PHU2 and PHU3 at the end of the polymerization (DMF, LiBr, PS standards).

has already been noticed in the prior art.^{25, 43, 44} As expected, the SEC chromatogram depicted in Figure 5 and the data given in Table 4 highlight the high molar masses obtained for **PHU 2** ($M_n = 7500 \text{ g}\cdot\text{mol}^{-1}$) and **PHU 3** ($M_n = 12000 \text{ g}\cdot\text{mol}^{-1}$), using respectively *UndCC-ether* and *UndCC-ester* as bis-cyclic carbonate; contrarily to **PHU 1** which exhibits a molar mass of $6000 \text{ g}\cdot\text{mol}^{-1}$. The latest results corroborate the prior kinetic measurements and the enhancement of the reactivity by adding ether or ester moieties nearby the cyclic carbonate.

In view of the equivalent structures and molar masses of *Und-bCC-ether* and *Und-bCC-ester*, the polymerization SEC profiles confirm the lower reactivity of the ether-activated dimer.

However, the formation of urea was observed in all cases (Table 4) and demonstrated the inevitable side reaction highlighted in the kinetic measurement part. MALDI-TOF analysis supports the formation of urea at the chain ends and inside the **PHU 3** backbone (see ESI[†]). Moreover, the amidification reaction, taking place during *Und-bCC-ester* polymerization, was detected with the characteristic labile proton of the amide (7.6 ppm) and by mean of MALDI-TOF analysis. *Und-bCC-ester* showed in polymerization a similar proportion of formed-amides than *UndCC-ester* in model reaction.

The effect of the cyclic-carbonate structure on properties was investigated through **PHU 3** and **PHU 4** formation using respectively a C_{20} and a C_{10} -ester activated dimer. **PHU 4** made with the shorter *Seb-CC-ester* displayed a molar mass of $13700 \text{ g}\cdot\text{mol}^{-1}$ with a dispersity of 3.7 that support its high reactivity. Nonetheless, the **PHU 4** demonstrated a proportion of 5.9% of amide functions, probably due to the higher density of ester linkages along the polymer backbone. The amidification reaction tended to decrease molar masses and to increase the dispersity by cleaving the polymer chains.

The thermal properties of the as-prepared PHUs were examined by DSC and TGA, using a prior isothermal procedure at 160°C for 15 min in order to remove DMF traces from the samples. The PHUs were semi-crystalline or amorphous depending on the monomer used. Relatively low T_g in the ranges -26 to -10°C conferred by the aliphatic monomer backbones were obtained. **PHU 2** and **PHU 3** showed two melting peaks (see ESI[†]) that could reveal two types of crystalline clusters or a segregation between soft and hard segments. Moreover, a cold recrystallization is observed at 33°C for the **PHU 3** due to the possible reorganization of polymer chains above the T_g . When the less reactive cyclic diamine **6cDA**⁴⁵ was used as comonomer with *Und-bCC-ester*, molar masses were significantly lowered from 12 000 to $8800 \text{ g}\cdot\text{mol}^{-1}$ and no

enhancement of thermal properties was detected. Besides, the ether-rotula structure of *Und-bCC-ether* conferred to **PHU 2** a T_g of -26°C , whereas **PHU 3** displayed a higher T_g imparted with a harder segmented monomer.

In addition, **PHU 4** was expected to reach higher T_g than -17°C , still this feature was assigned to the possible PHU plastification by shorter chains arising from amidification reaction.

Conclusions

In conclusion, activated 5-membered cyclic carbonates were synthesized from glycerol carbonate, epichlorohydrin and fatty acid derivatives. The two routes imply both 3 steps and the monomers result from green processes such as the carbonation of epoxides and glycerol with CO_2 , or the metathesis reaction which enable the use of mild conditions.⁴⁶

Focusing on the epichlorohydrin route, the inherent toxicity of this compound stands in contradiction with the production of isocyanate-free polyurethanes, which avoids the use of toxic phosgene. Nevertheless, the nucleophilic substitution between alcohols and epichlorohydrin has been extensively used for bringing an ether moiety nearby the cyclic carbonate in mild conditions.^{26, 27, 29, 34, 35} On the other hand, the glycerol route finds its limitation in the use of the reactive and dangerous thionyl chloride, especially in industrial processes.

The ester-activated monomers displayed a similar reactivity than 6-membered cyclic carbonates in model reaction with hexylamine. The lipidic activated 5-membered bis-cyclic carbonates were then successfully polymerized, with improved reactivity and molar masses, thanks to the insertion of a heteroatom in β position nearby the cyclic carbonate. Amidification side reaction occurring with ester-activated monomers could be controlled by decreasing the temperature or by minimizing the ester function content along the polymer backbone. Nevertheless, urea formation is unavoidable and remains the major side-reaction for both PHUs and PUs synthesis.

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Notes and references

† Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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SUPPLEMENTARY INFORMATION

Activated Lipidic Cyclic Carbonates for Non-Isocyanate Polyurethane Synthesis.

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Pessac, France, ^c ITERG, F-33600, Pessac, France

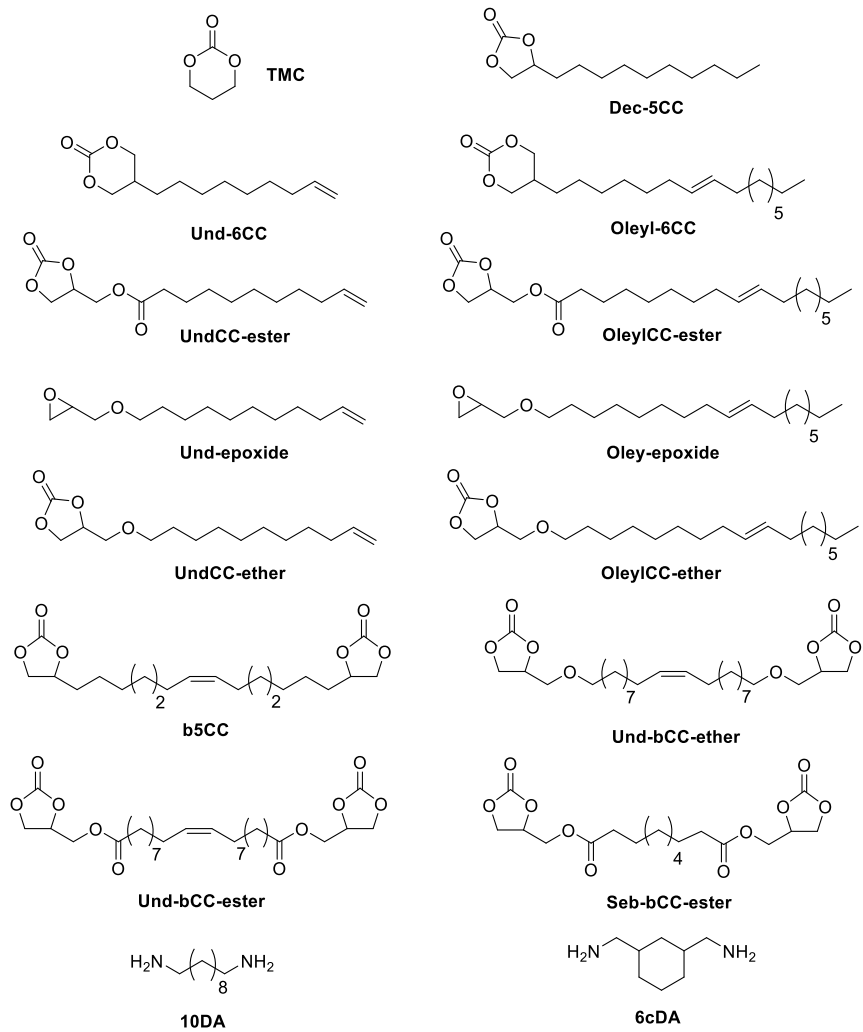
Supplementary Information Contents

1. Graphical data of mono-cyclic carbonates and bis-cyclic carbonates

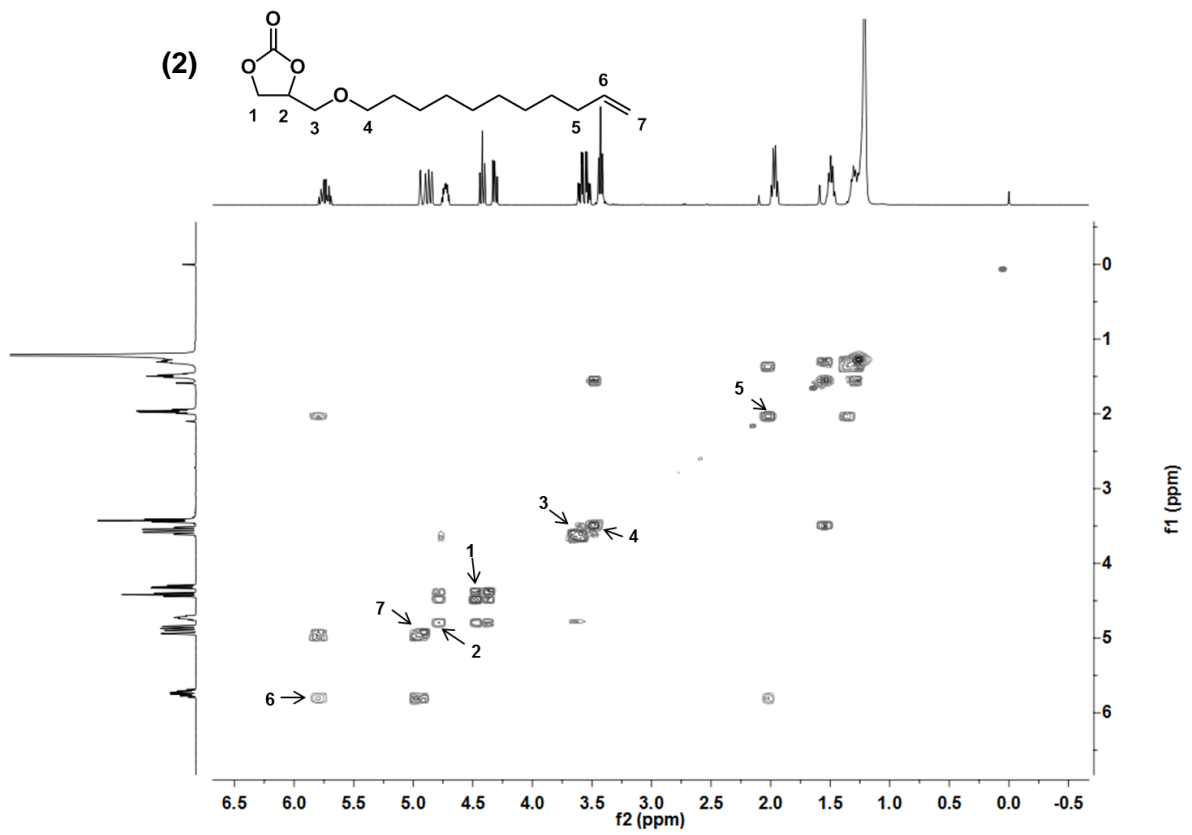
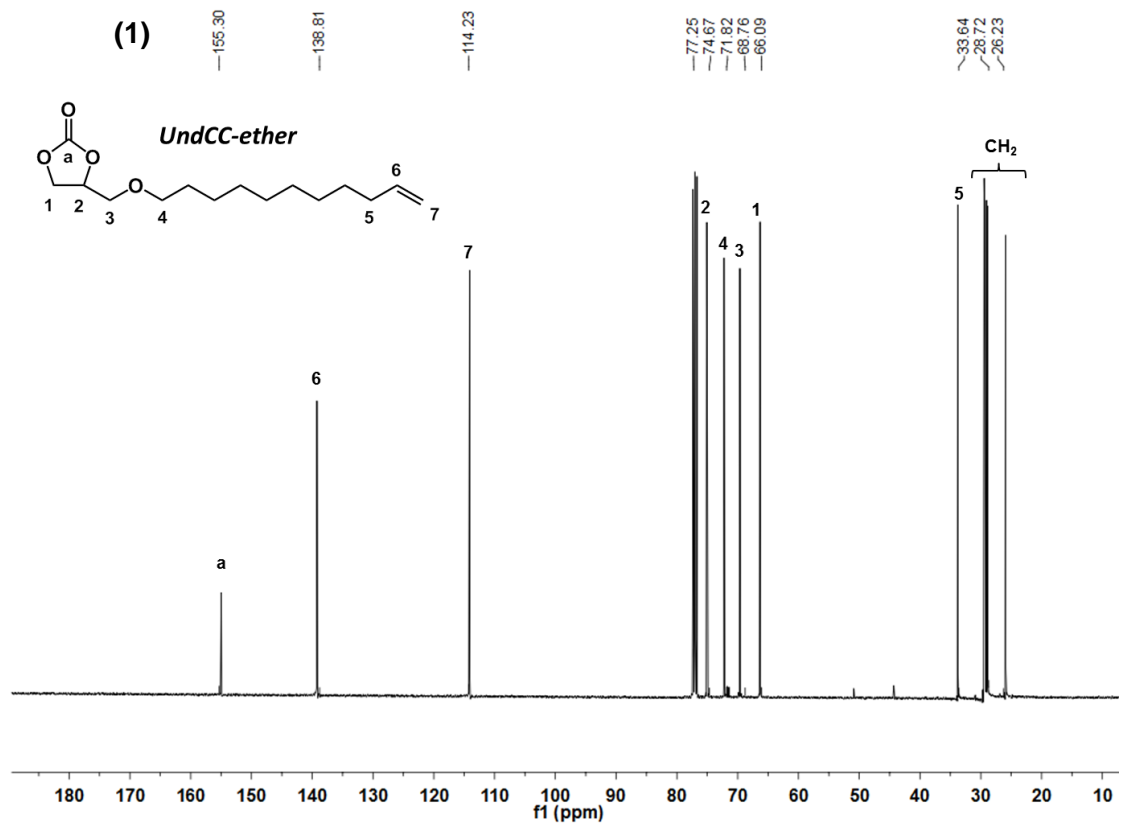
- 1.1. *Und-bCC-ether synthesis*
- 1.2. *Und-bCC-ester synthesis*
- 1.3. *Seb-bCC-ester synthesis*
- 1.4. *OleylCC-ether synthesis*
- 1.5. *OleylCC-ester synthesis*
- 1.6. *OleylCC-ester synthesis*
- 1.7. *b5CC synthesis*
- 1.8. *Und-6CC synthesis*
- 1.9. *Oleyl-6CC synthesis*

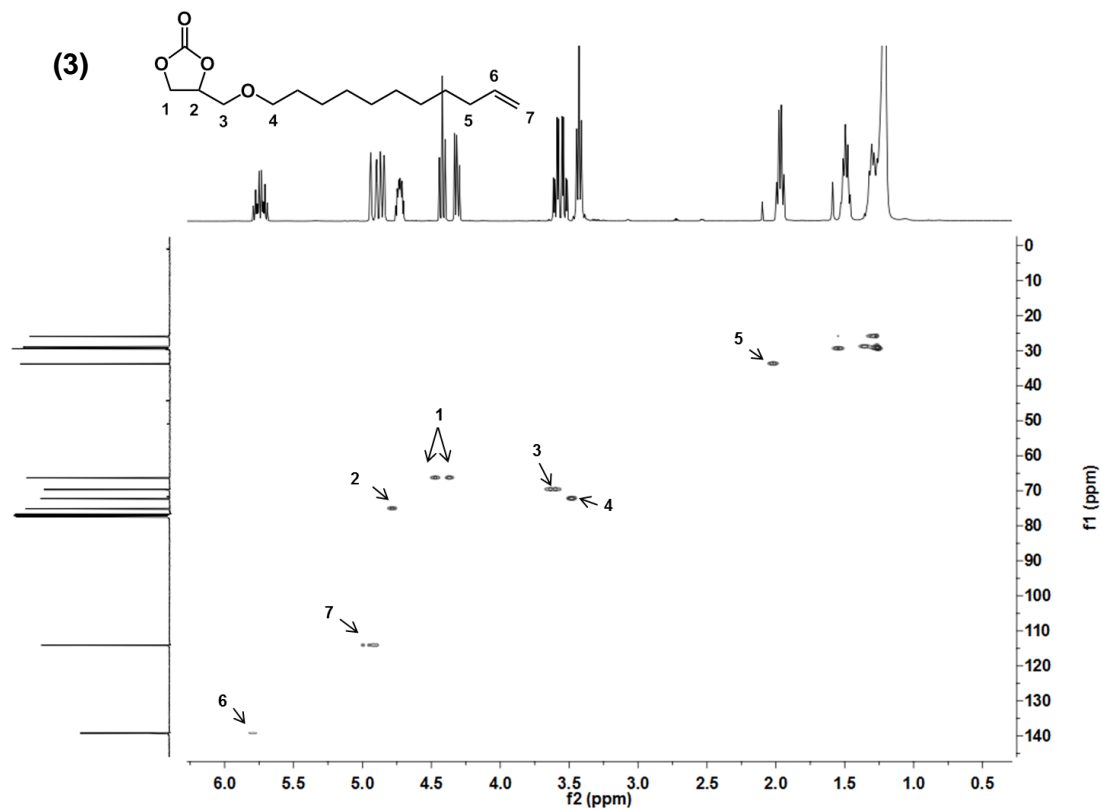
2. Graphical data of kinetic measurements

3. Graphical data of Poly(hydroxyurethane)s

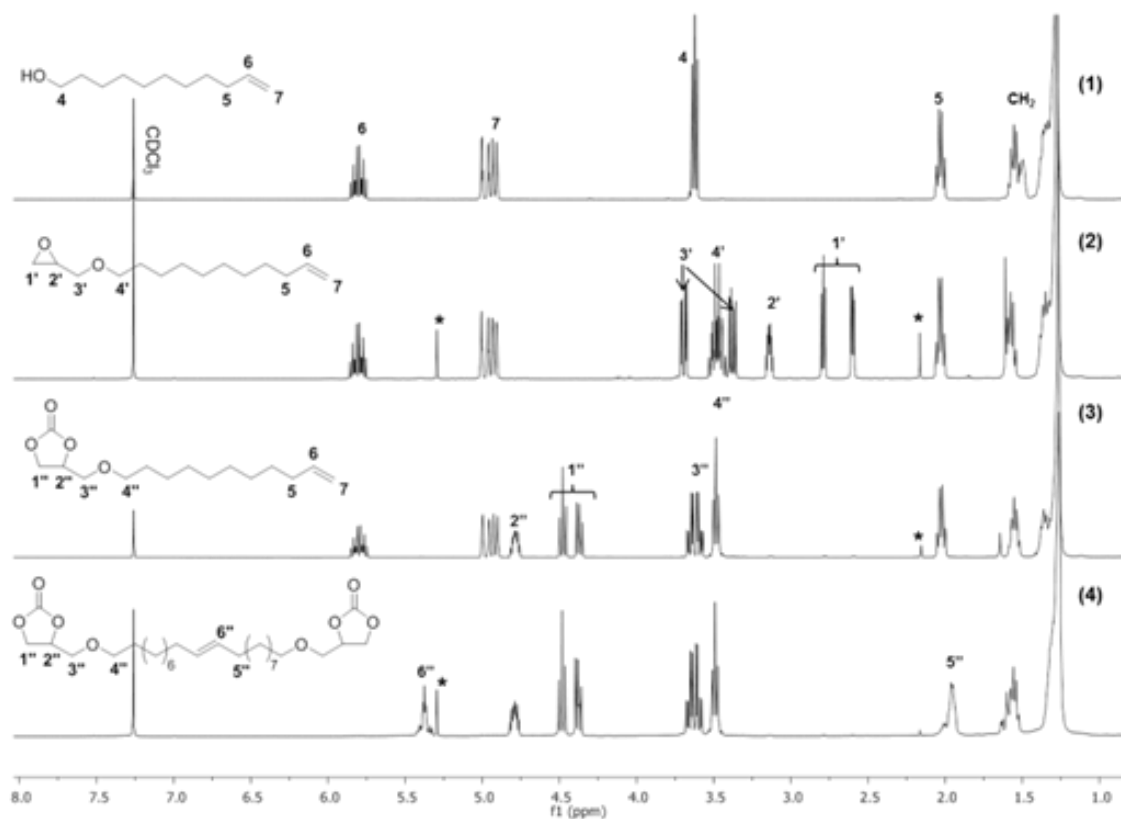


ESI Figure 1- Abbreviations and structures of epoxides, mono-cyclic carbonates, bis-cyclic carbonates and diamines.

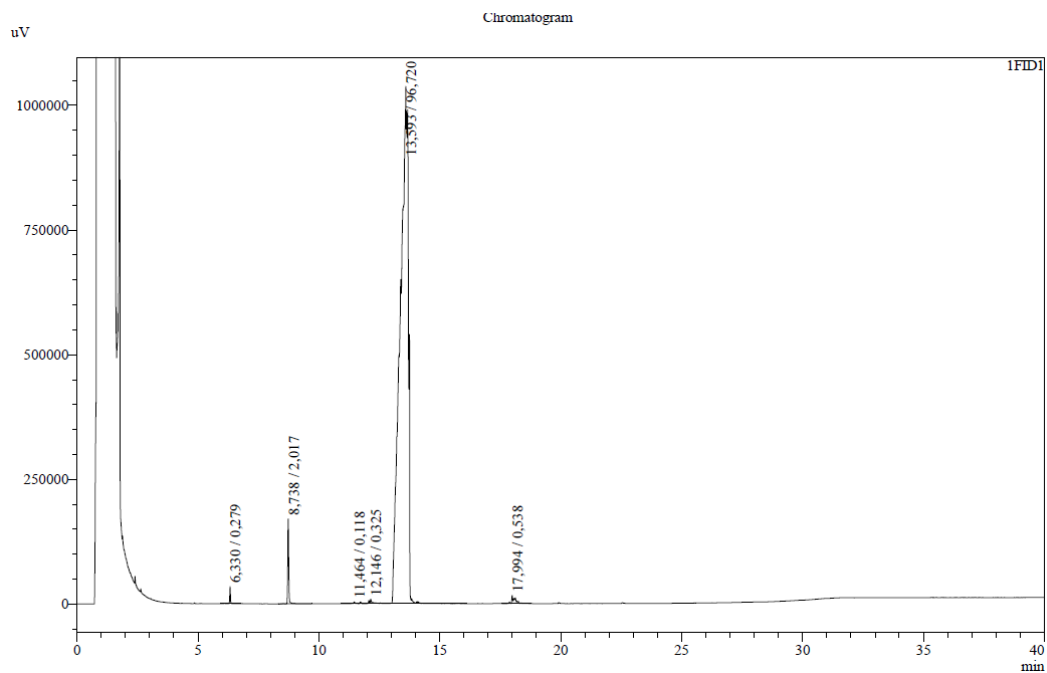




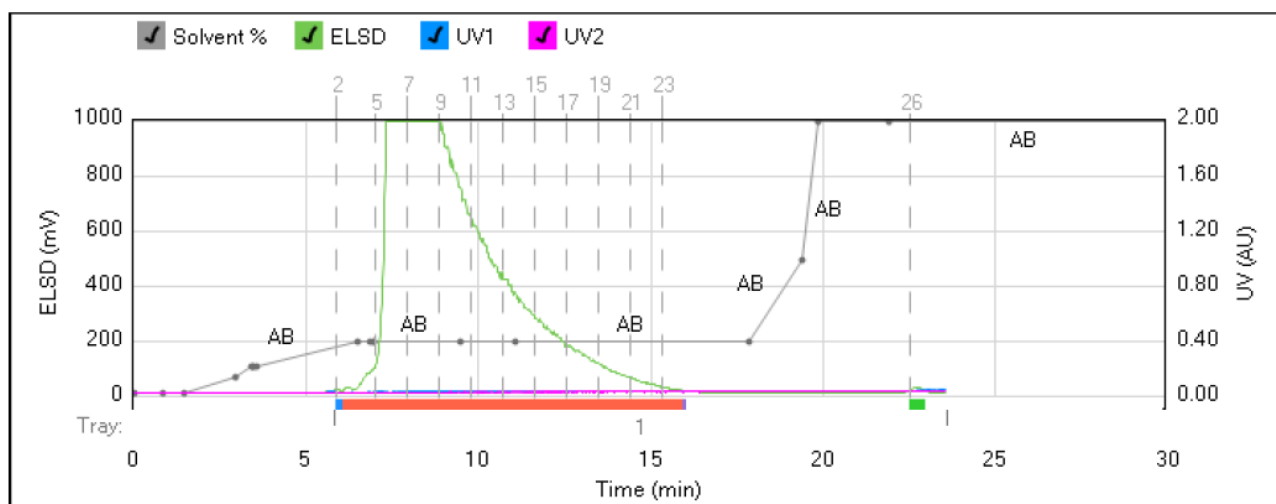
ESI Figure 3 - NMR analysis of purified UndCC-ether: (1) ^{13}C NMR, (2) ^1H - ^1H COSY NMR and (3) ^1H - ^{13}C HSQC-NMR. (Analysis performed in CDCl_3 .)



ESI Figure 4 - Stacked ^1H NMR spectra of (1) undecen-1-ol, (2) Und-epoxide, (3) UndCC-ether and (4) Und-bCC-ether (All analyses were performed in CDCl_3 .) (* : residual solvents)

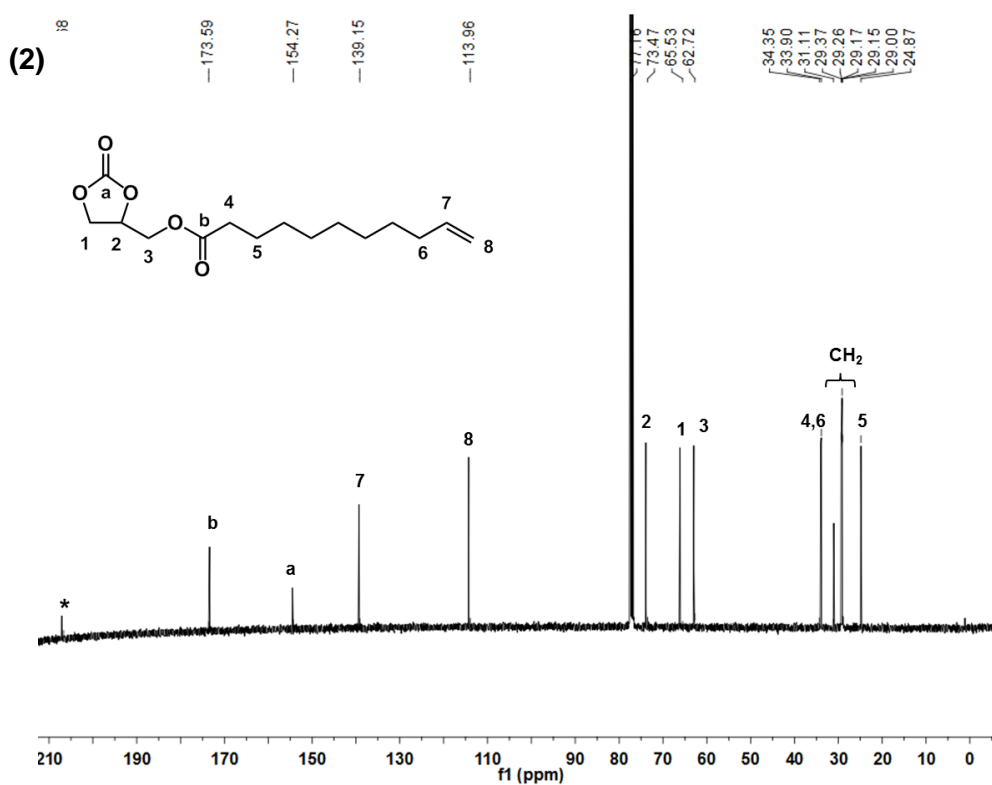
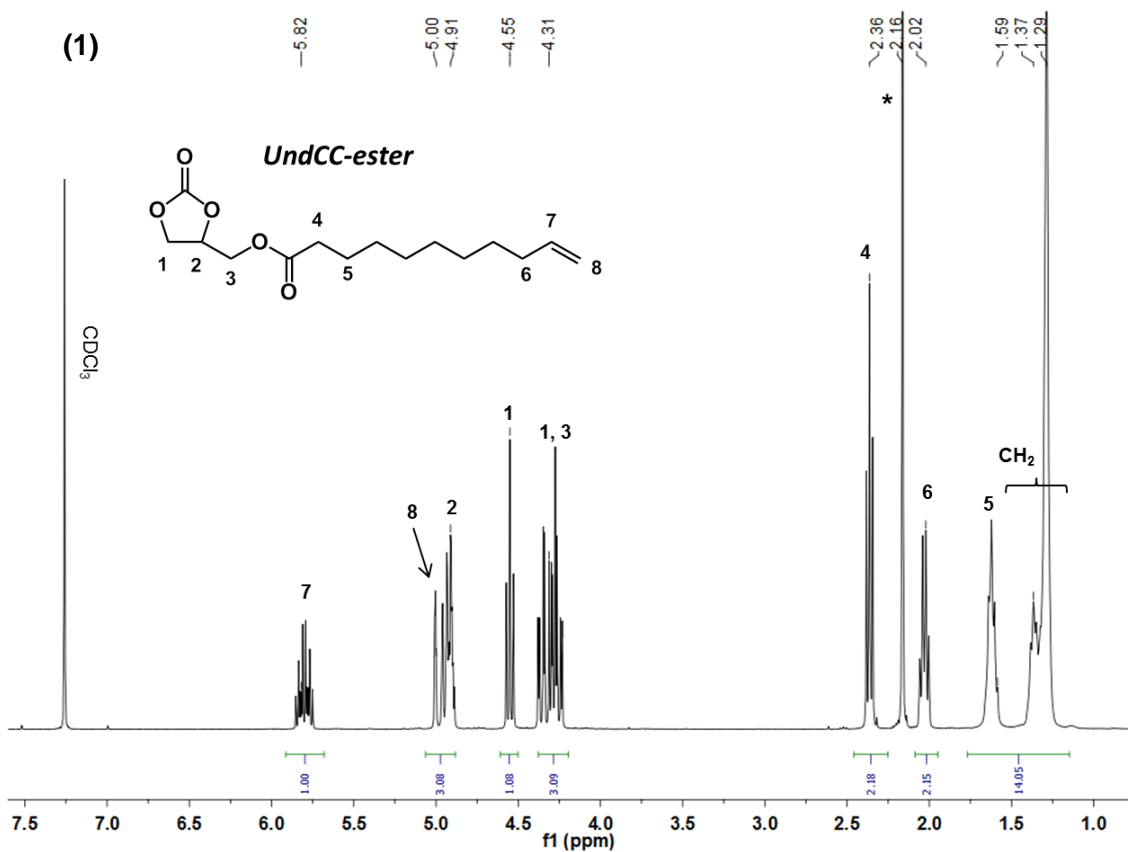


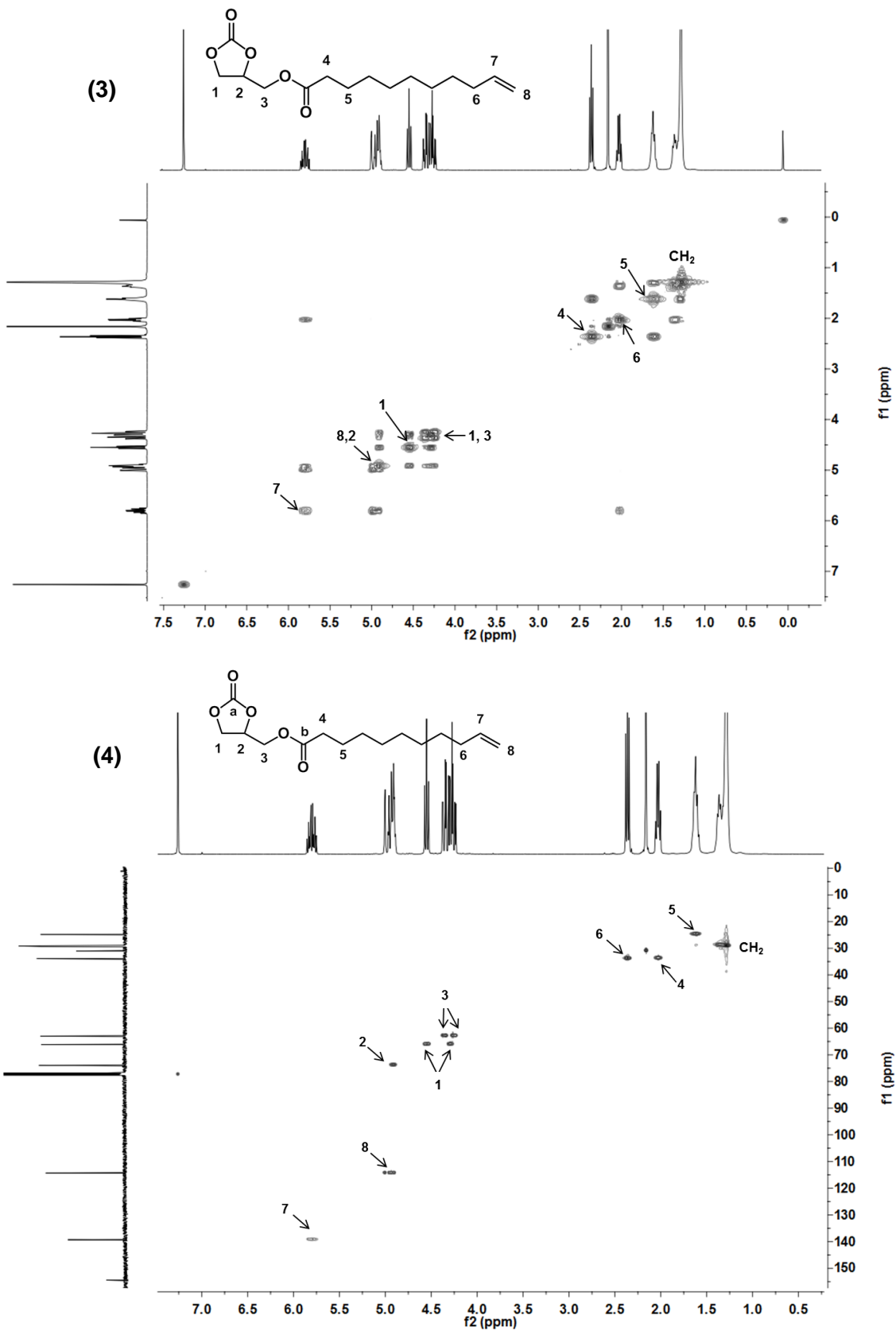
ESI Figure 5- Gas chromatography of UndCC-ether (96,7% purity).



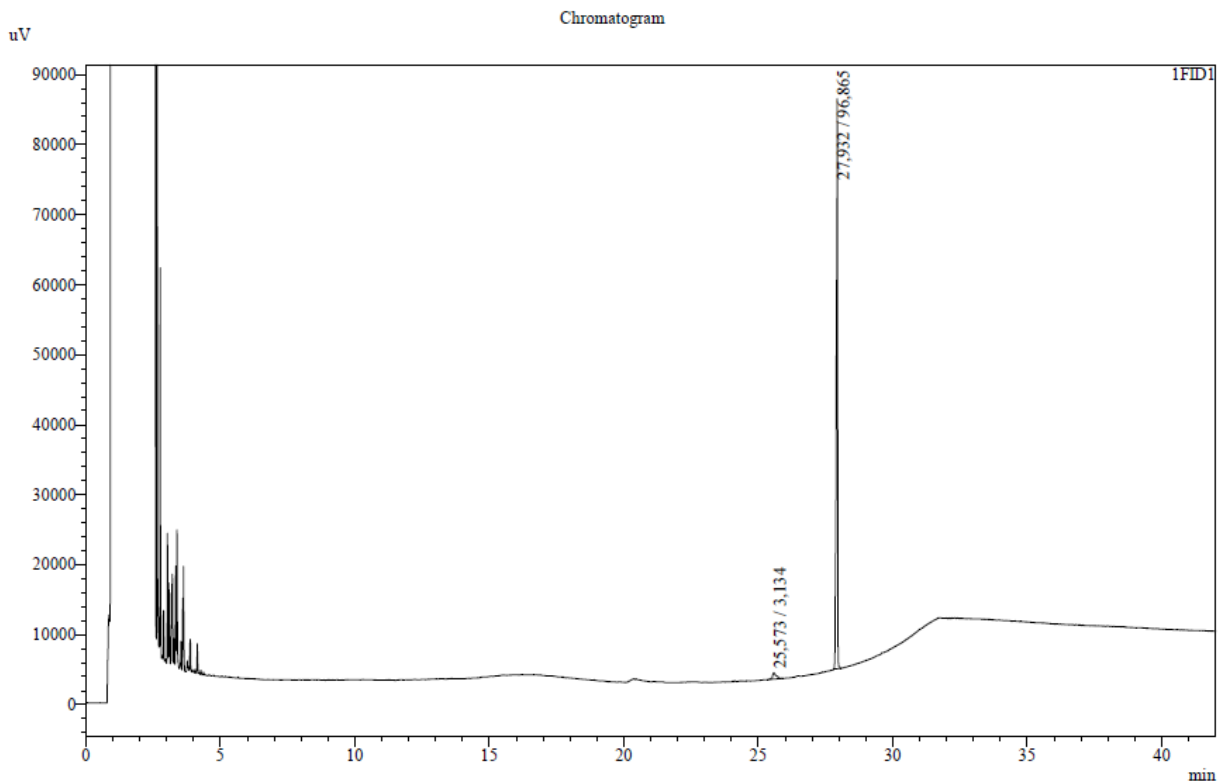
ESI Figure 6- Flash chromatogram of UndCC-ether.

1.2. Und-bCC-ester synthesis



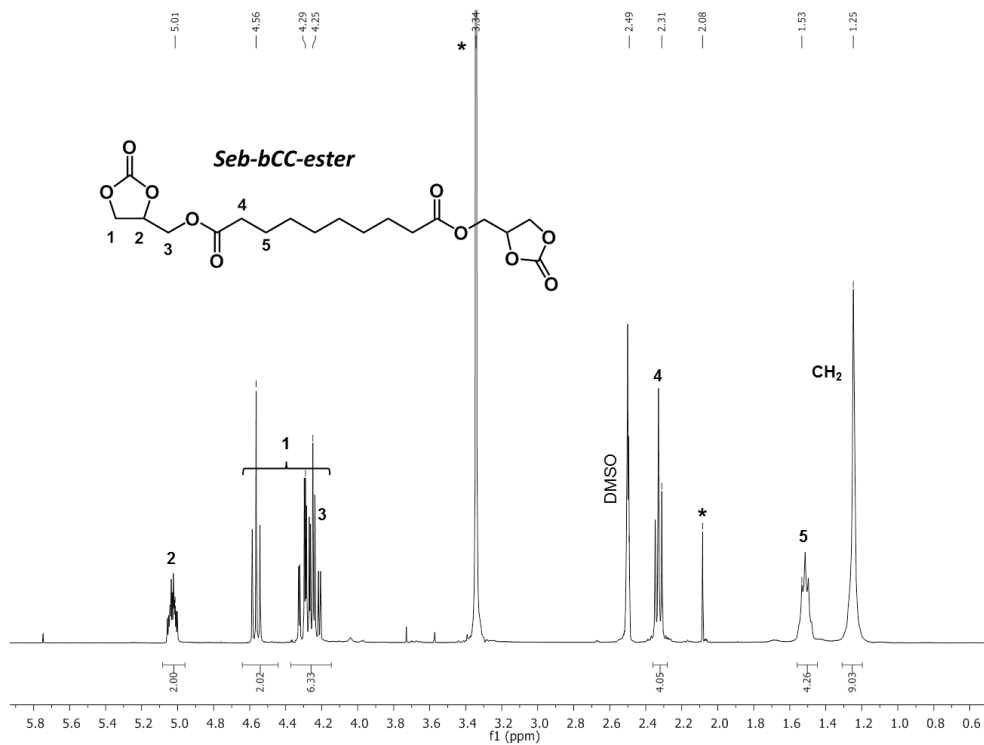


ESI Figure 7- NMR analysis of purified UndCC-ester (1) ^1H NMR, (2) ^{13}C NMR, (3) ^1H - ^1H COSY NMR and (4) ^1H - ^{13}C HSQC-NMR.
(Analysis performed in CDCl_3) (* : residual solvents)



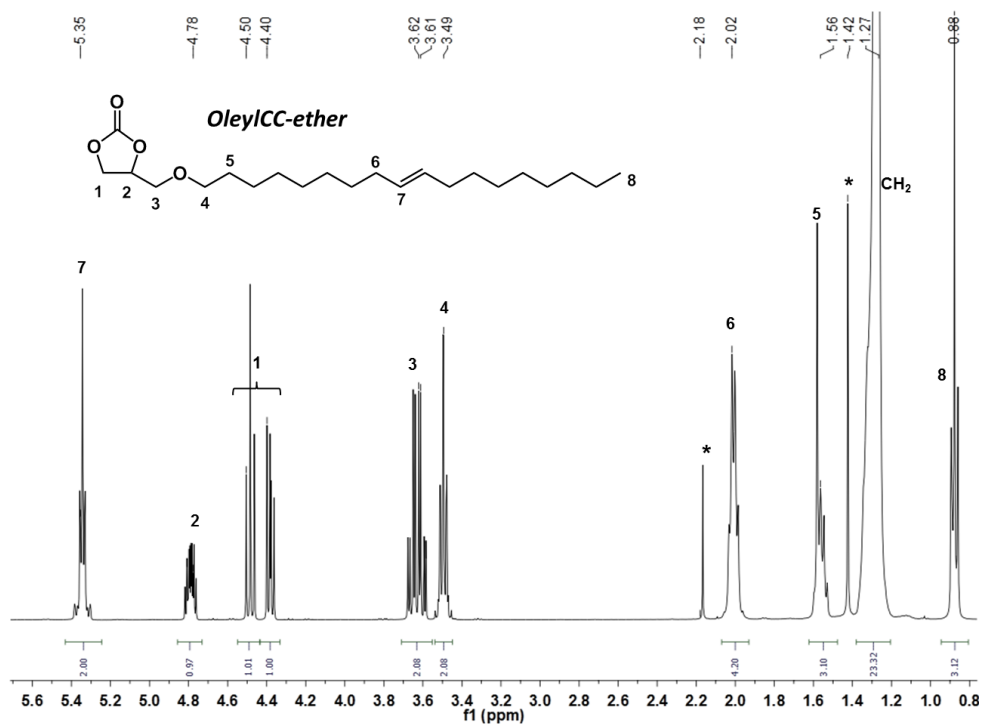
ESI Figure 8- Gas chromatography of UndCC-ester (96.8 % purity).

1.3. Seb-bCC-ester synthesis



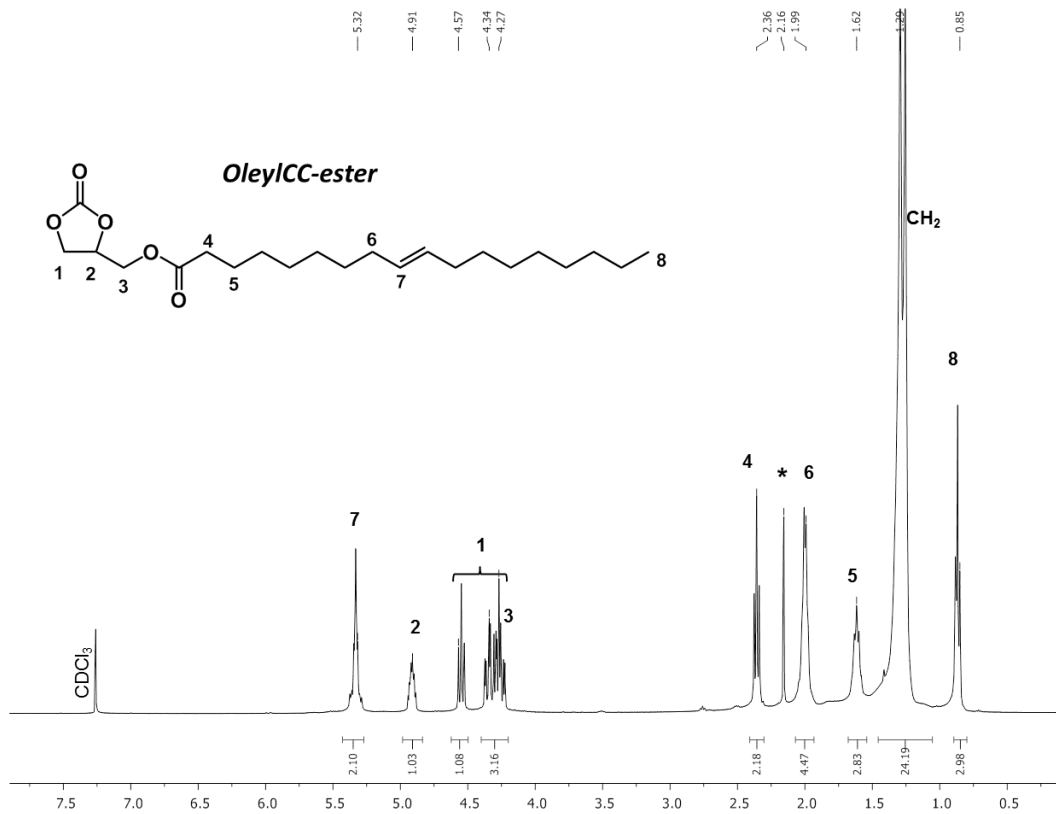
ESI Figure 9- ¹H NMR spectrum of Seb-bCC-ester (Analysis performed in DMSO-d₆.) (: residual solvents)*

1.4. OleylCC-ether synthesis



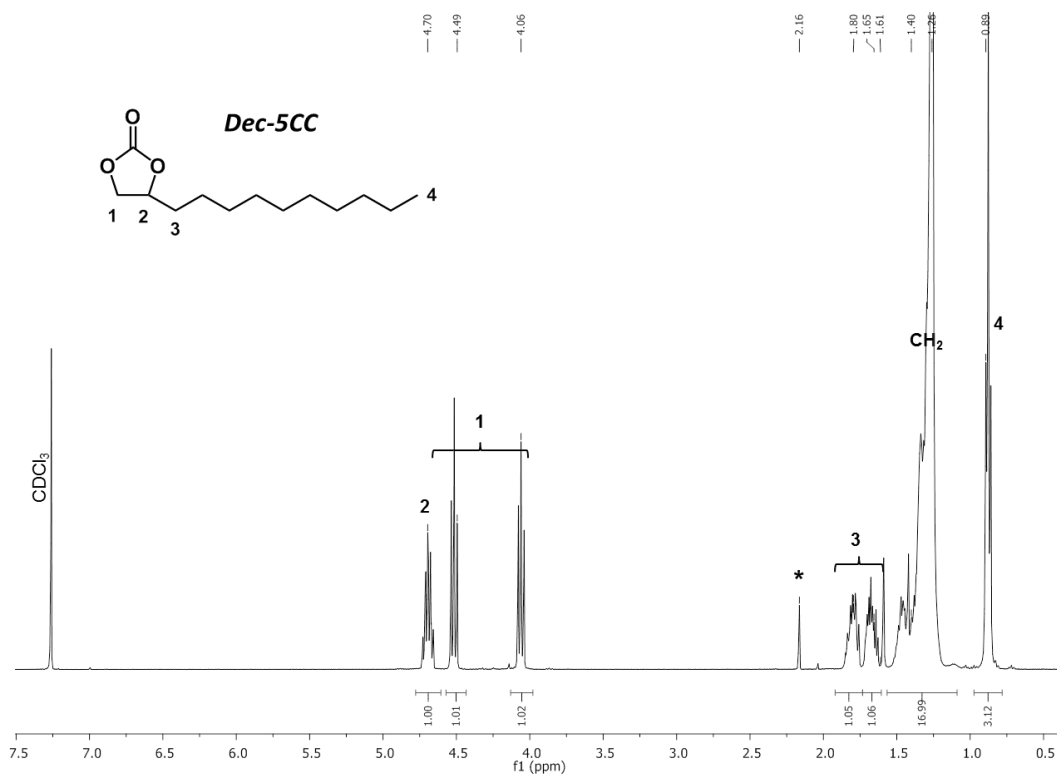
ESI Figure 10- ¹H NMR spectrum of OleylCC-ether (Analysis performed in CDCl₃) (* : residual solvents)

1.5. OleylCC-ester synthesis



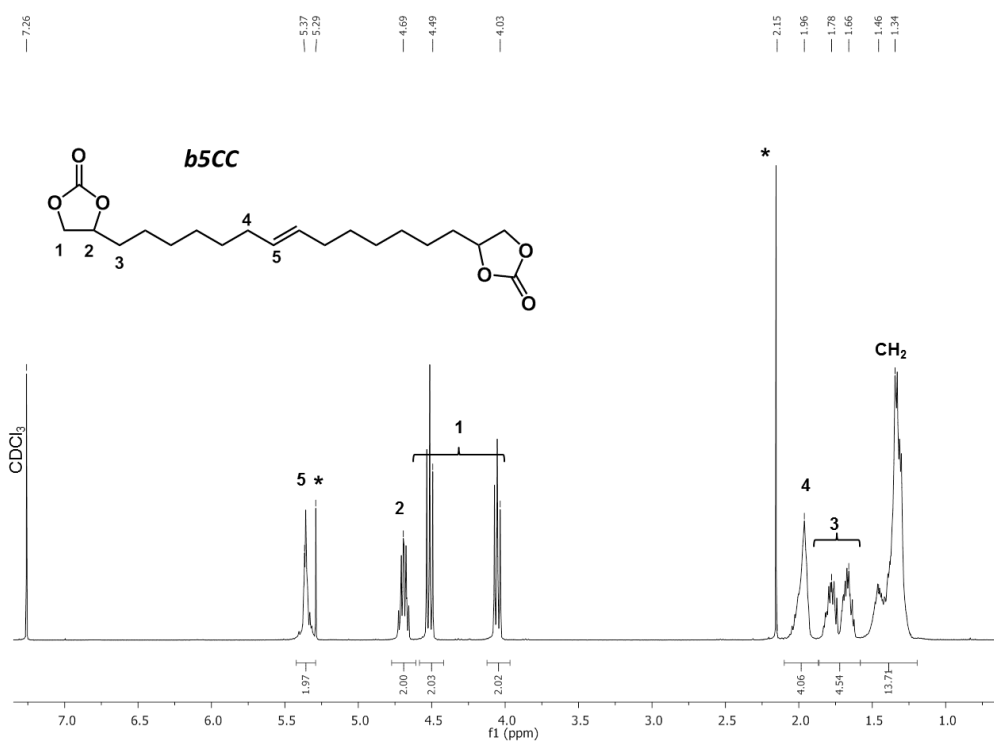
ESI Figure 11- ¹H NMR spectrum of OleylCC-ester (Analysis performed in CDCl₃)

1.6. OleylCC-ester synthesis



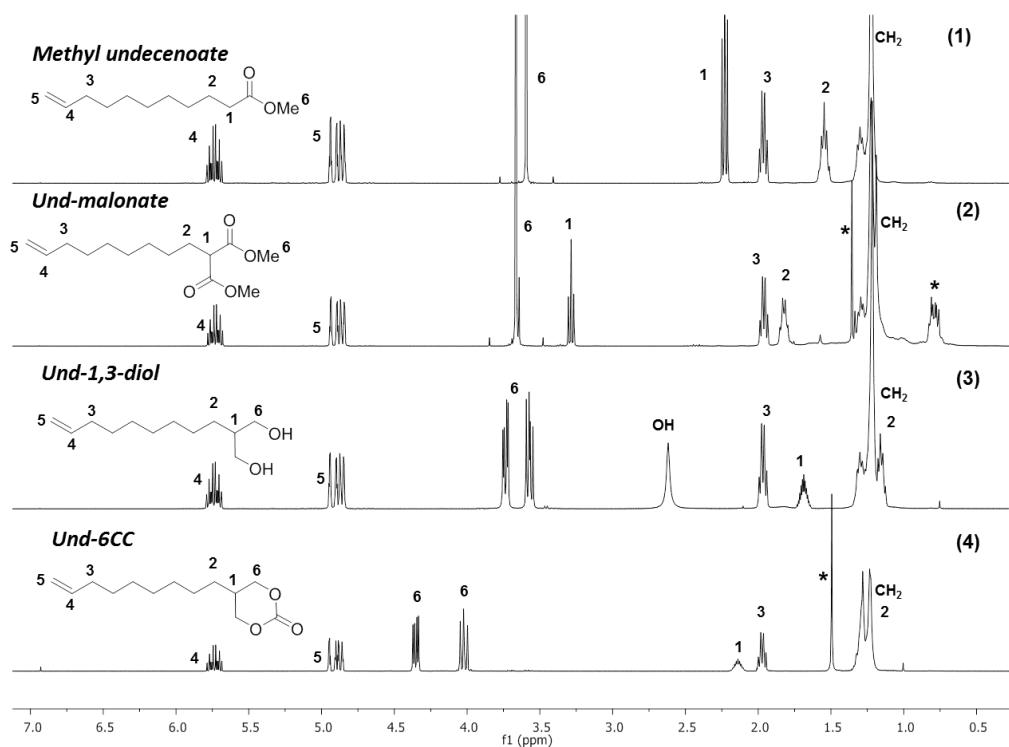
ESI Figure 12- ¹H NMR spectrum of Dec-5CC (Analysis performed in CDCl₃.) (* : residual solvents)

1.7. b5CC synthesis



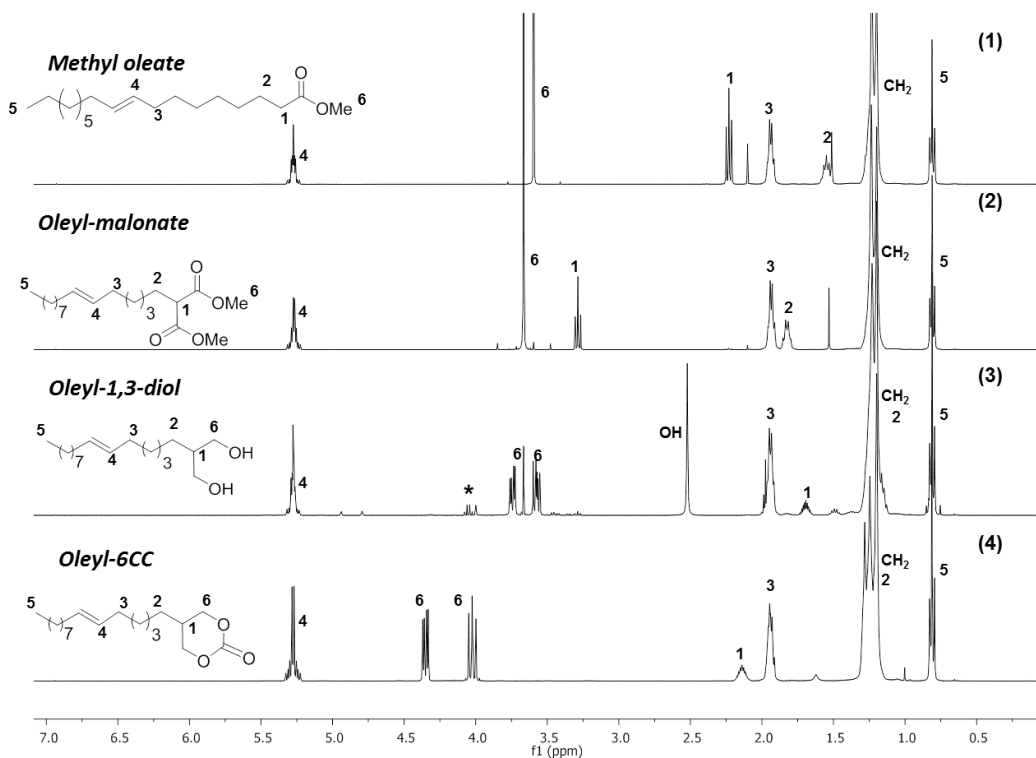
ESI Figure 13- ¹H NMR spectrum of b5CC (Analysis performed in CDCl₃.)(* : residual solvents)

1.8. Und-6CC synthesis



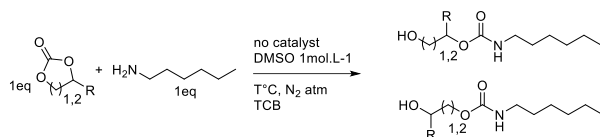
ESI Figure 14- Stacked ^1H NMR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC. (All analyses were performed in CDCl_3)(* : residual solvents)

1.9. Oleyl-6CC synthesis

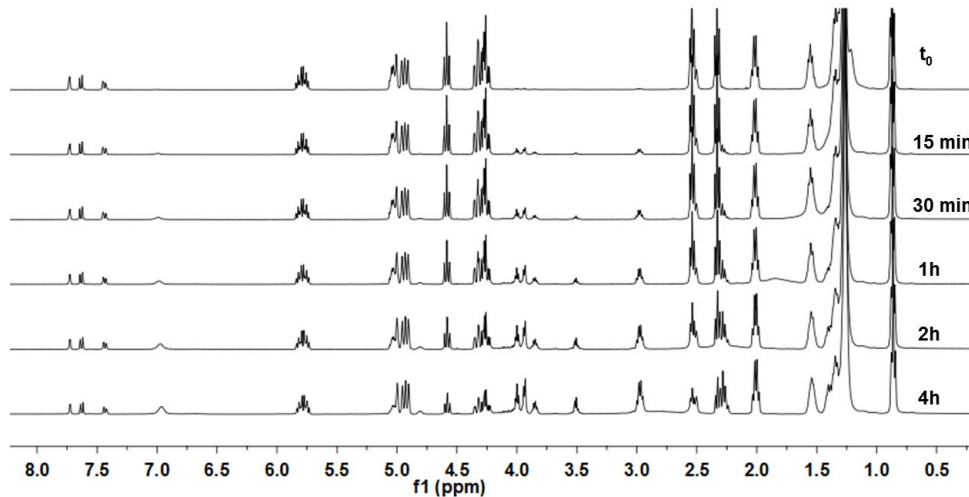


ESI Figure 15- Stacked ^1H NMR spectra of (1) methyl oleate, (2) Oleyl-malonate, (3) Oleyl-1,3-diol and (4) Oleyl-6CC. (All analyses were performed in CDCl_3)(* : impurities).

2. Graphical data of kinetic measurements

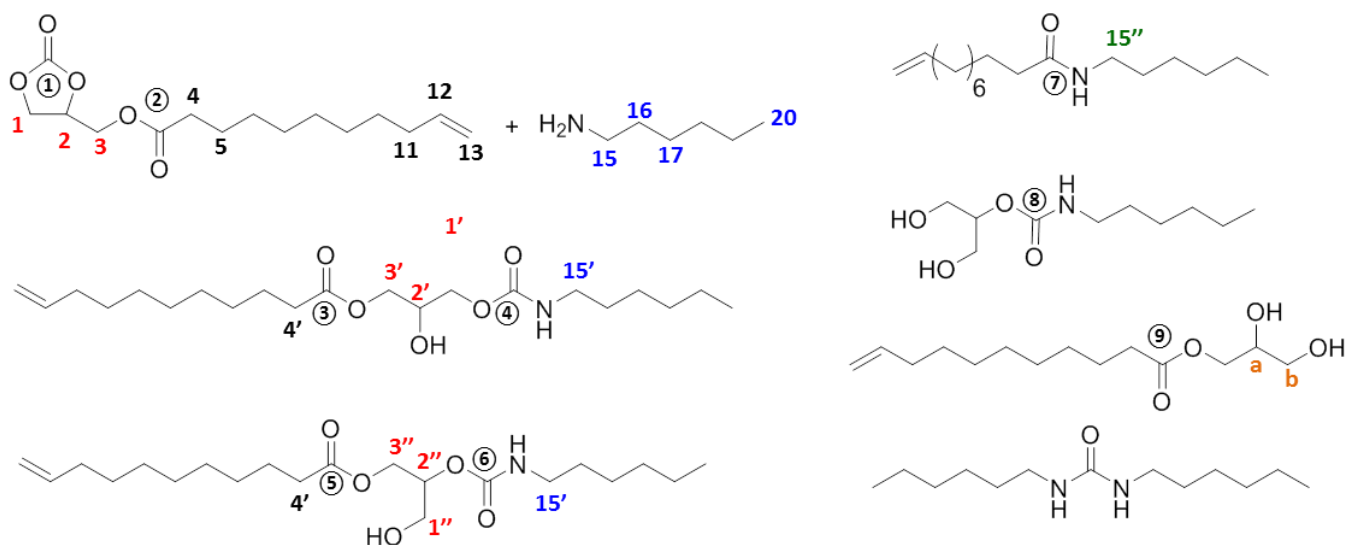


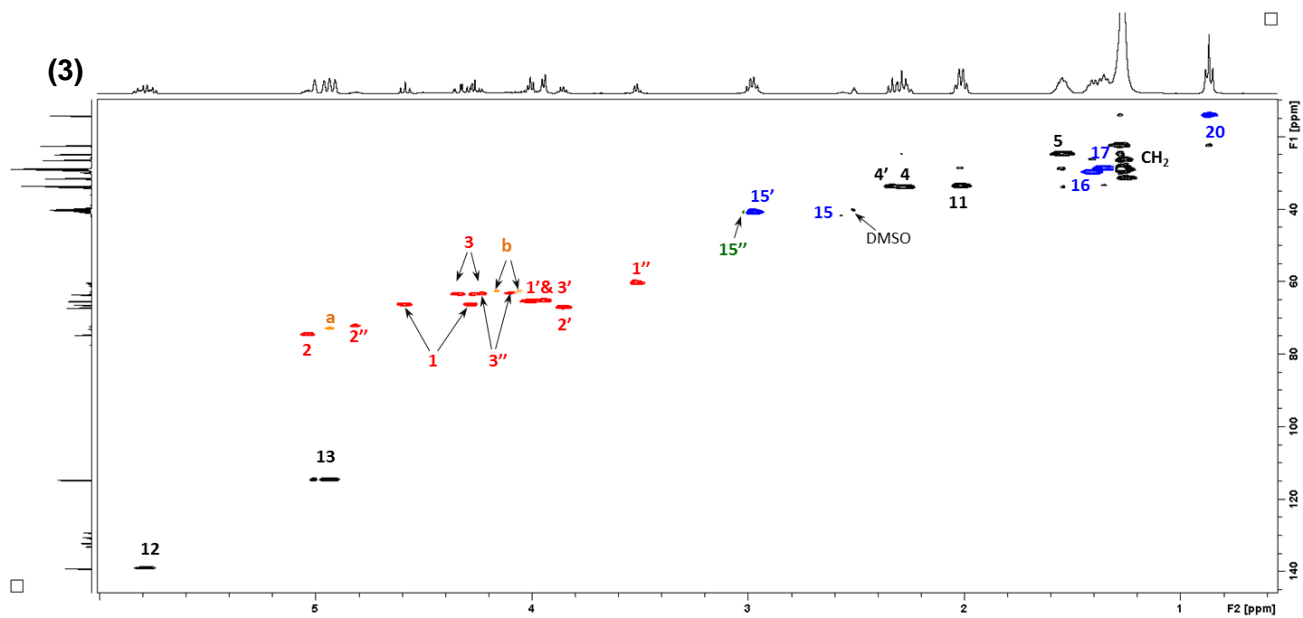
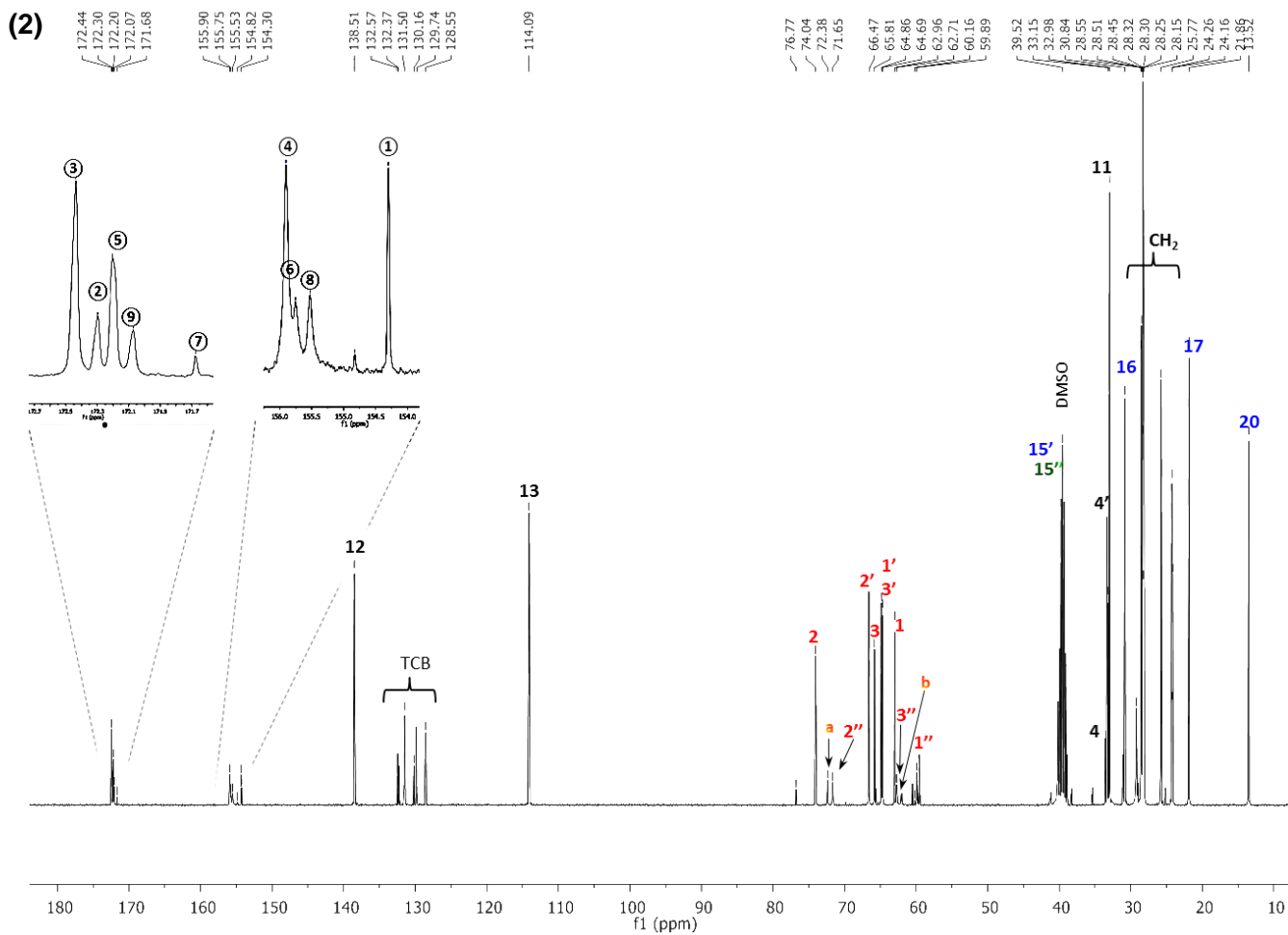
ESI Scheme 1- Model reaction of various cyclic carbonates with hexylamine in different conditions.



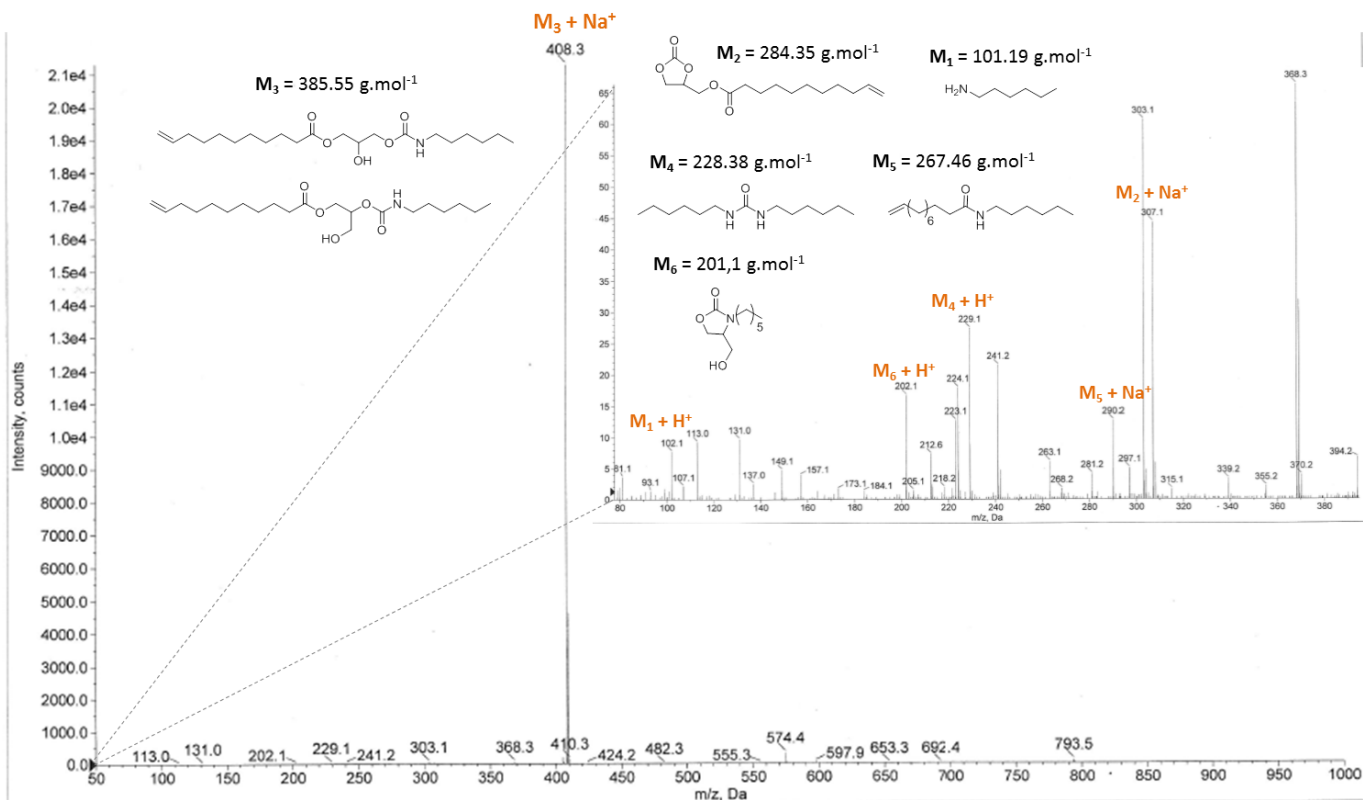
ESI Figure 16- Stacked ^1H NMR monitoring of the reaction between UndCC-ester and hexylamine with a ratio 1:1, at 50°C in DMSO-d_6 at 1 mol.L^{-1} .

(1)

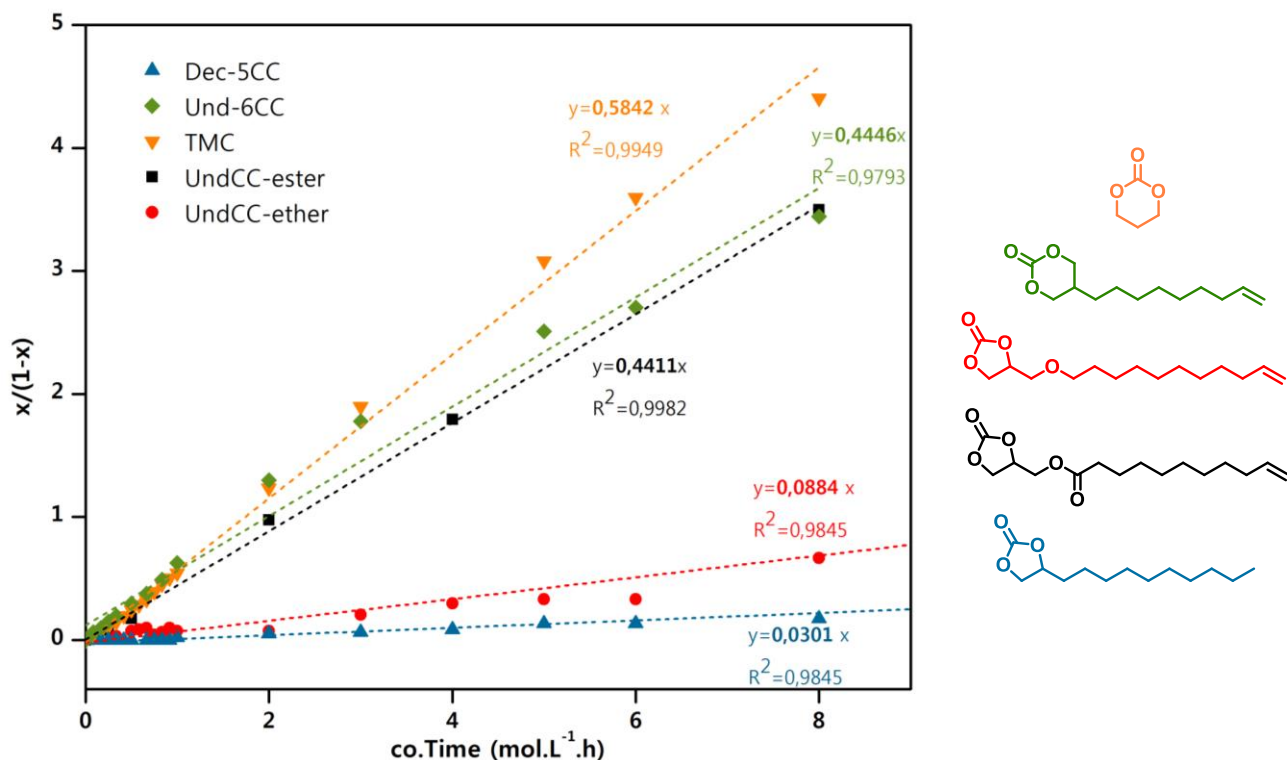




ESI Figure 17 – (1) Scheme of the different molecules identified by (2) ^{13}C and (3) ^1H - ^{13}C HSQC during the model reaction between UndCC-ester and hexylamine (ratio 1:1, in DMSO- d_6 at 50°C).



ESI Figure 18 – ESI analysis of the reaction between UndCC-ester and hexylamine at 50°C in bulk, with a ratio 1:1.



ESI Figure 19- 2nd order Kinetic law: Time- $(x/(1-x))$ relationships for the reactions of cyclic carbonates with hexylamine, at 50°C and in DMSO-d₆ (1 mol.L⁻¹).

$$-\frac{d[CC]}{dt} = k_{app}[CC][A] = k_{app}[CC]^2 \quad (E1)$$

$$-\frac{d[CC]}{[CC]^2} = k_{app}dt \quad (E2)$$

$$\frac{1}{[CC]} - \frac{1}{C_0} = k_{app}\Delta t \quad (E3)$$

$$\text{or } [CC] = C_0 - C_0x = C_0(1-x) \quad (E4)$$

$$\frac{x}{1-x} = k_{app}C_0\Delta t \quad (E5)$$

ESI Formula 1 - 2nd order Kinetic law formula: Time-(x/(1-x))

$$\% \text{ Urea} = \frac{\int H_{urea}}{\int H_{urea} + \int H_{amide} + \int H_{urethane}} \quad (E)$$

$$\% \text{ Amide} = \frac{\int H_{amide}}{\int H_{urea} + \int H_{amide} + \int H_{urethane}} \quad (E')$$

$$\% \text{ Urethane} = \frac{\int H_{urethane}}{\int H_{urea} + \int H_{amide} + \int H_{urethane}} \quad (E'')$$

ESI Formula 2 - Formula used for the calculation of % of urea, amide and urethane formed during kinetic measurements and polymerization, using ¹H NMR integrations of labile protons (H_{urea} , H_{amide} and $H_{urethane}$) in DMSO-d6 .

$$k_{app} = A_{app} \cdot e^{\frac{-E_a}{RT}}$$

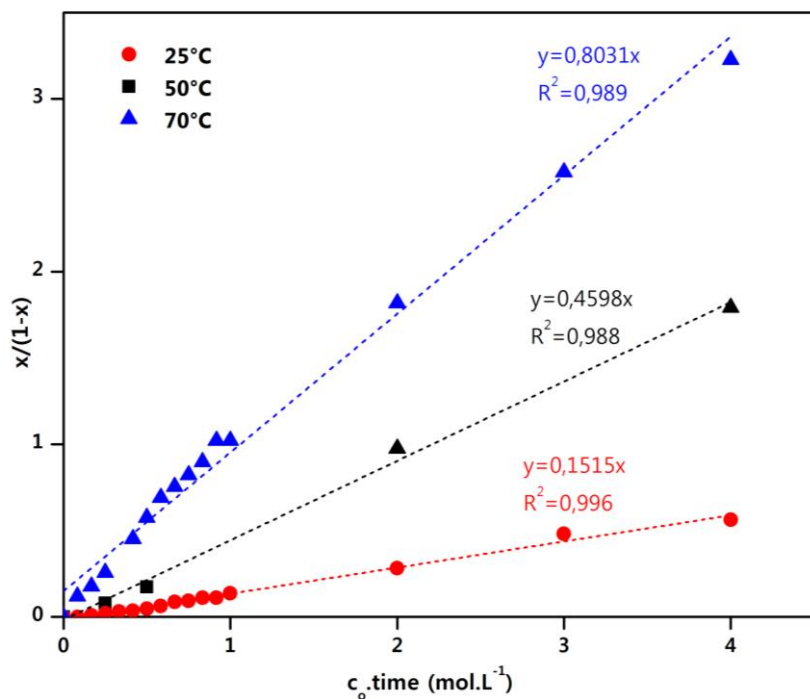
Note : The activation energy is not the only parameter to take into account in kinetic analysis. In the Arrhenius equation, A_{app} is the pre-exponential factor that indicates the rate of efficient collision. The bigger A_{app} , the more reactive the monomer is. A_{app} was calculated for 5CC and 6CC synthesized by Endo and coll.(reference 13) and for **UndCC-ester**.

A_{app} (6CC) = 13570 L.mol⁻¹.h⁻¹;

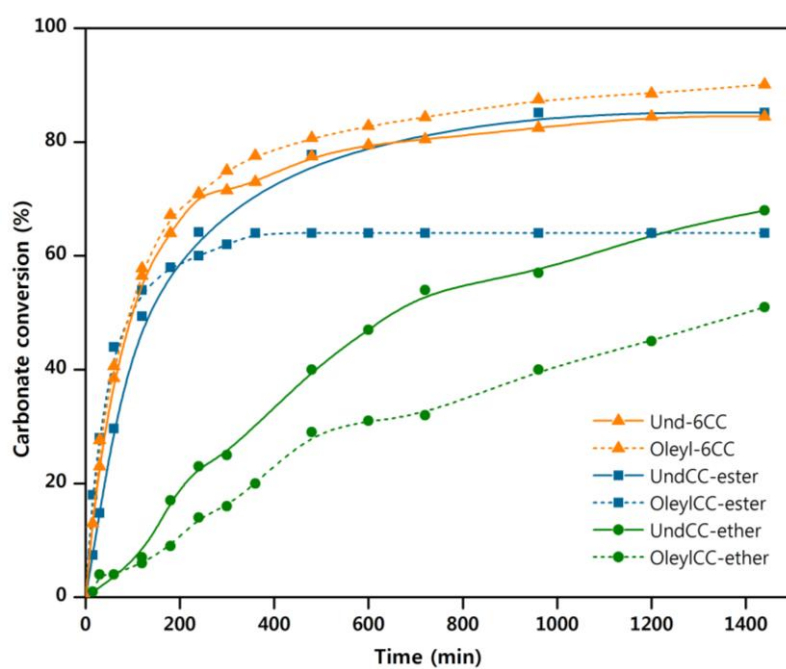
A_{app} (5CC) = 1.72 L.mol⁻¹.h⁻¹;

A_{app} (**UndCC-ester**) = 10282 L.mol⁻¹.h⁻¹.

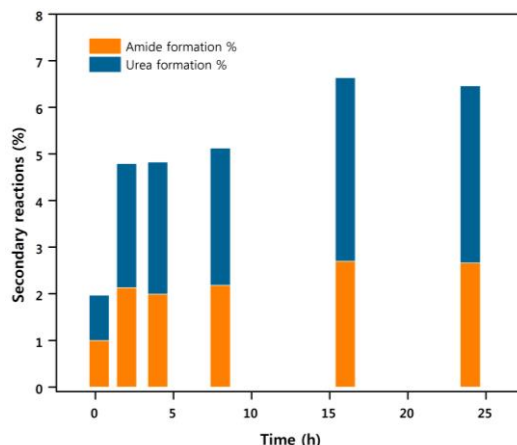
ESI Formula 3 – Arrhenius equation and calculation of A_{app} for 5CC, 6CC (Endo and coll.) and **UndCC-ester**.



ESI Figure 20 - Effect of the temperature on the kinetic of the reactions between UndCC-ester and hexylamine. (1 mol.L⁻¹ in DMSO-d₆, ratio 1:1)



ESI Figure 21 - Chain length effect on the kinetic of the reactions between reactive cyclic carbonates and hexylamine (1 mol.L⁻¹ in DMSO-d₆, ratio 1:1, 25°C)



ESI Figure 22 - Proportions of side reactions obtained during the reactions between UndCC-ester and hexylamine over 24h (1 mol.L⁻¹ in DMSO-d₆, 50°C, ratio 1:1).

3. Graphical data of Poly(hydroxyurethane)s

PHU-1[b5CC + 10DA] : ¹H NMR (DMSO-d₆, 25°C, 400 MHz) δ (ppm): (see ESI†). IR (cm⁻¹): 3600-3100, 2920, 2848, 1685, 1532.

PHU-2 [Und-bCC-ether + 10DA]: ¹H NMR (DMSO-d₆, 25°C, 400 MHz) δ (ppm): (see ESI†). IR (cm⁻¹): 3600-3100, 2928, 2853, 1663, 1505, 1093.

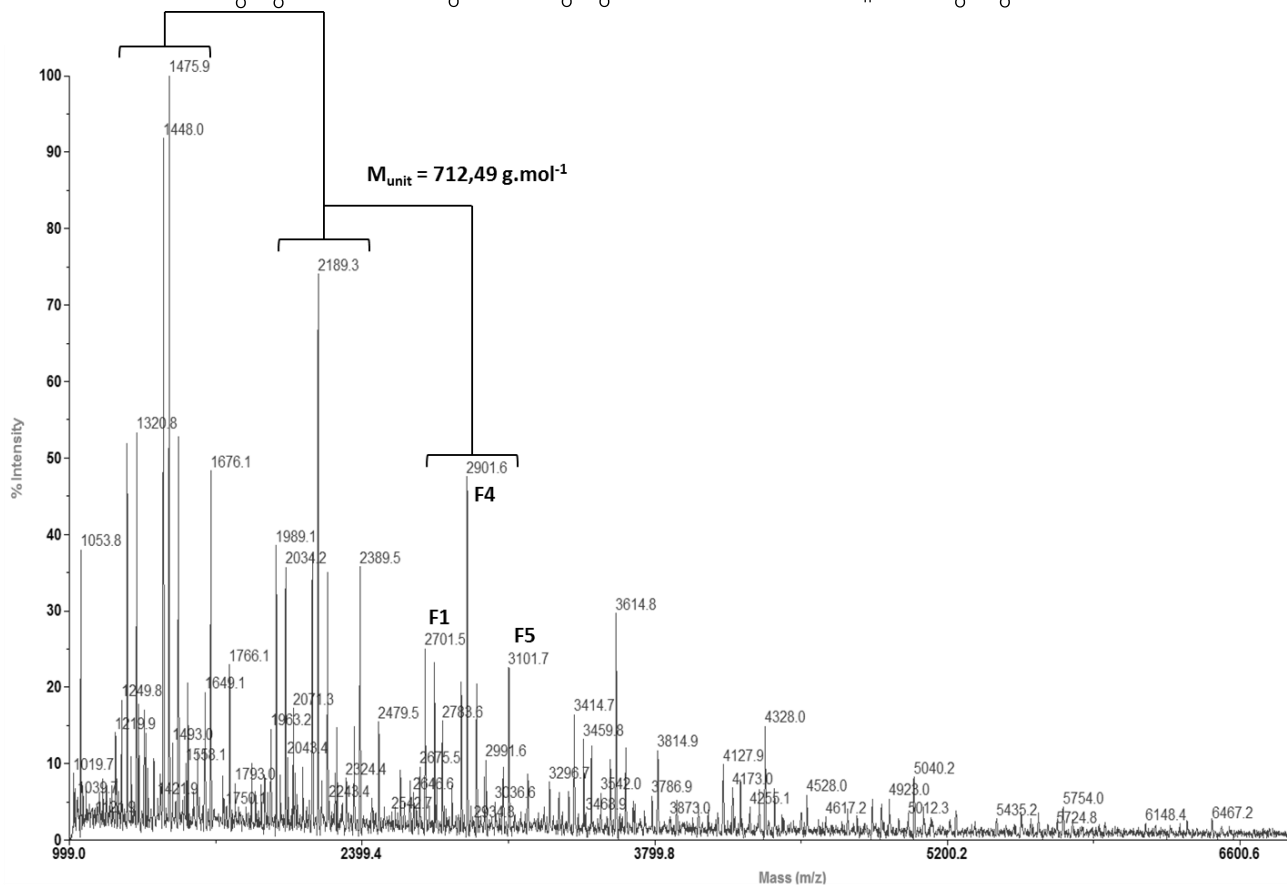
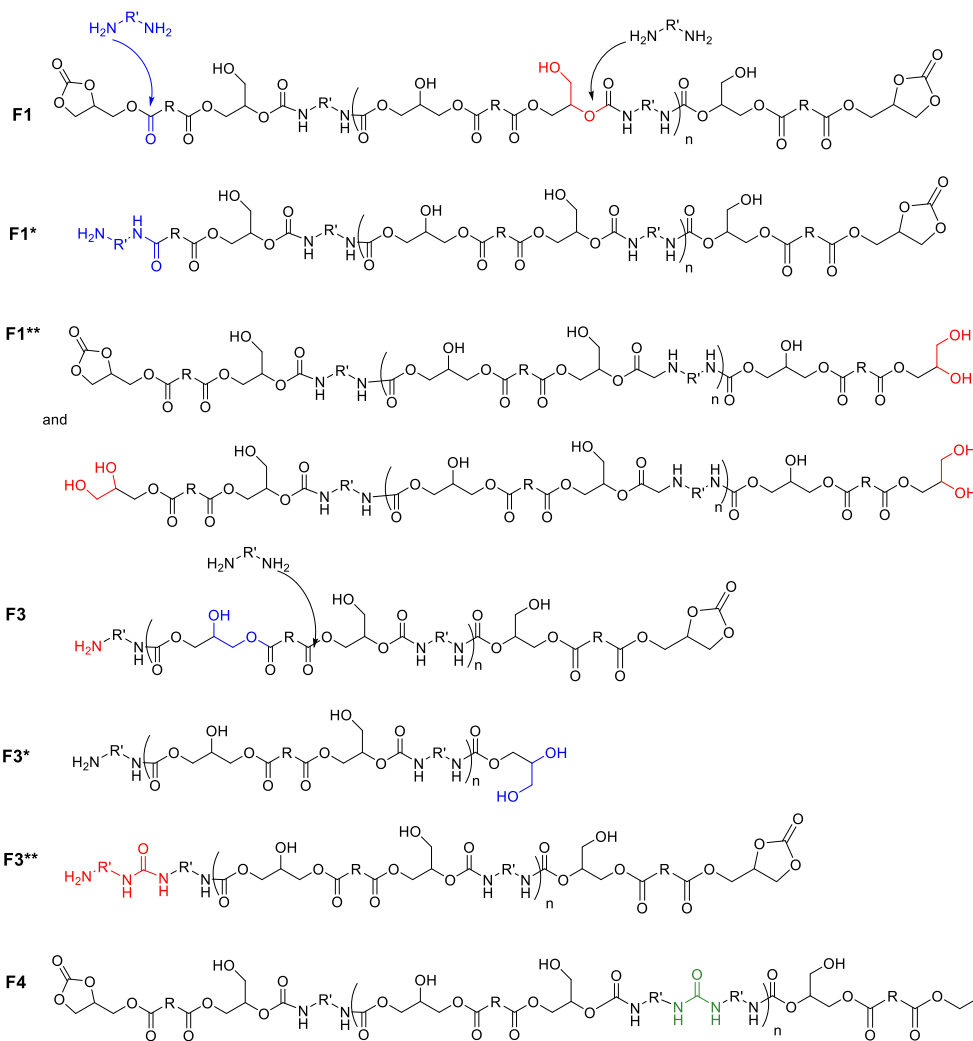
PHU-3 [Und-bCC-ester + 10DA]: ¹H NMR (DMSO-d₆, 25°C, 400 MHz) δ (ppm): (see ESI†). IR (cm⁻¹): 3600-3100, 2923, 2848, 1709, 1663, 1545.

PHU families	Description	Reaction	PHU 1 (M _{unit} = 712.49 g.mol ⁻¹)
F1	C-(C _{n-1} -A _n)-C	Polyaddition : urethane formation	n*(M _{unit})+M _C +M _{Na}
F2	C-(C _n -A _{n-1})-A	Polyaddition : urethane formation	n*(M _{unit})+M _A +M _{Na}
F3	A-(C _n -A _n)-C	Polyaddition : urethane formation	(n+1)*(M _{unit})+M _{Na}
F4	C-(C _{n-1} -U ^A -A _n)-C	1 Urea linkage within the chain	n*(M _{unit})+M _C +M _{urea} +M _{Na}
F5	C-(C _{n-1} -U ^A -U ^A -A _n)-C	2 Urea linkages within the chain	n*(M _{unit})+M _C + 2M _{urea} +M _{Na}
F1*	A _{amide} -(C _{n-1} -A _n)-C	Transamidification at the chain end or by cyclisation	n*(M _{unit})-M _{GC} +M _{amine} +M _{Na}
F3*	A-(C _n -A _n)-C _{GC}	Transamidification intra-chain	(n+1)*(M _{unit})+ M _{GC} +M _{Na}
F1**	C-(C _{n-1} -A _n)-C ^{OH}	Urea formation intra-chain resulting in the formation of hydroxyl groups at the chain-end	n*(M _{unit})+M _C -M _{C=O} +2M _H +M _{Na}
	C ^{OH} -(C _{n-1} -A _n)-C ^{OH}		n*(M _{unit})+M _C -2M _{C=O} +4M _H +M _{Na}
F3**	U ^A -(C _n -A _n)-C	Urea formation at the chain end	(n+1)*(M _{unit})+M _{urea} +M _{Na}

*amide formation

** urea formation

Abbreviations are as followed: C=**Und-bCC-ester** with M_C= 540.29 g.mol⁻¹; A=decane-1,10-diamine with M_A= 172.19 g.mol⁻¹; U^A=urea linkage on A with M_{urea}= M_A+M_{C=O}-2M_H= 198.19 g.mol⁻¹; GC=glycerol carbonate and equivalents in mass , with M_{GC}= 118.3 g.mol⁻¹; C^{OH} : chain end produced by urea formation : M_{COH}= M_C-M_{C=O}+2M_H=514.29 g.mol⁻¹



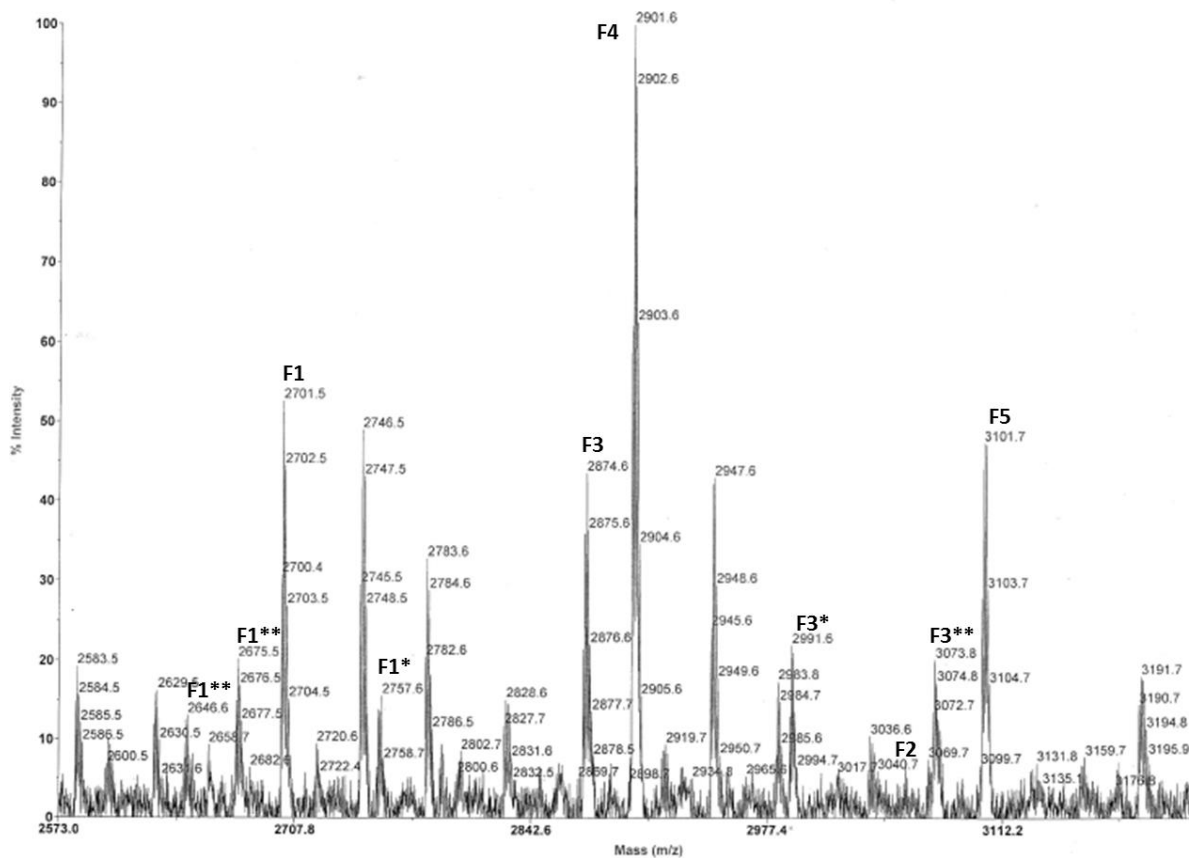


Figure 23 – Different PHU families in the sample PHU1 visible in MALDI-TOF MS

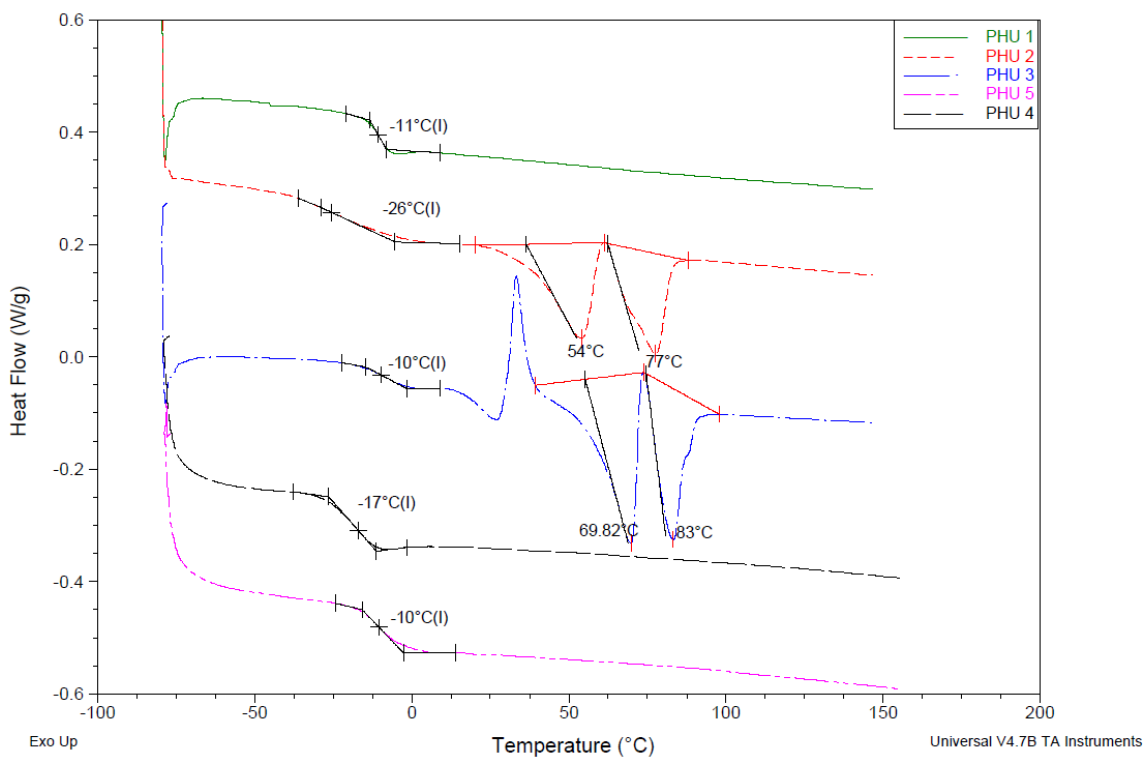


Figure 24 – DSC curves of the synthesized PHU (PHU 1-PHU 5).

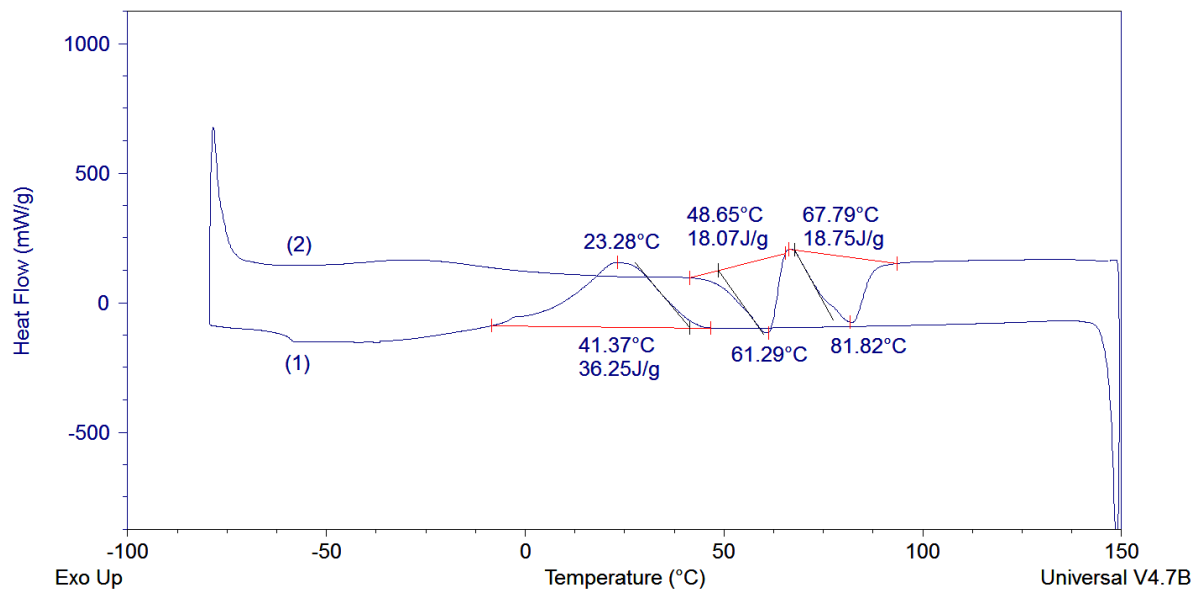


Figure 25 – DSC curves of the synthesized PHU 2 showing (1) the first cooling run and (2) the 2nd heating run.

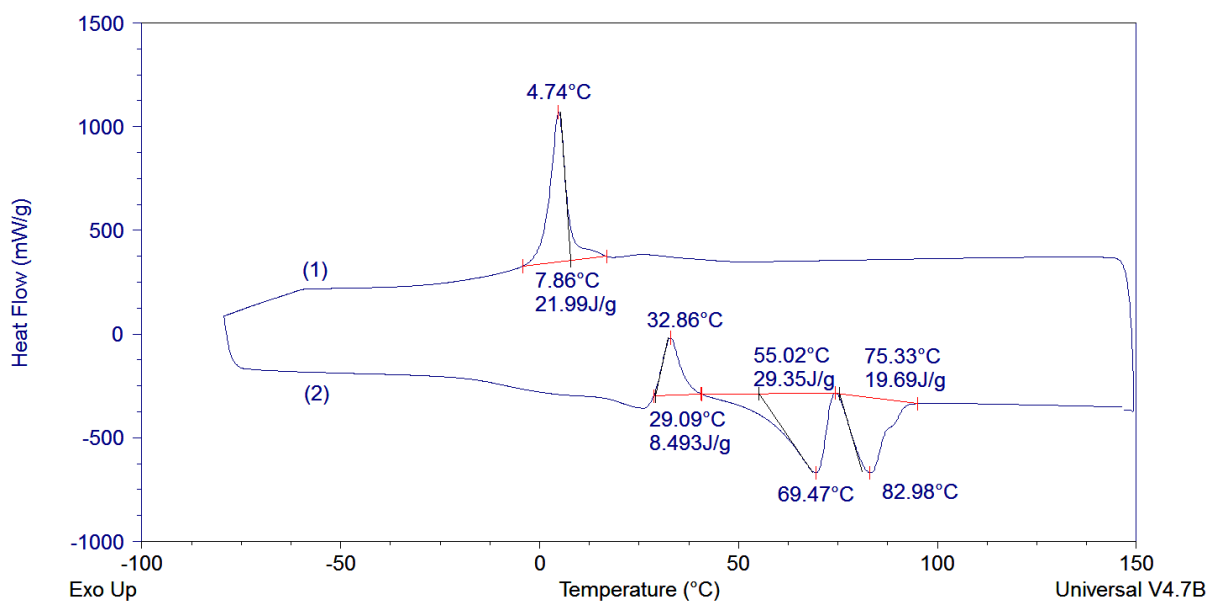


Figure 26 – DSC curves of the synthesized PHU 3 showing (1) the first cooling run and (2) the 2nd heating run.

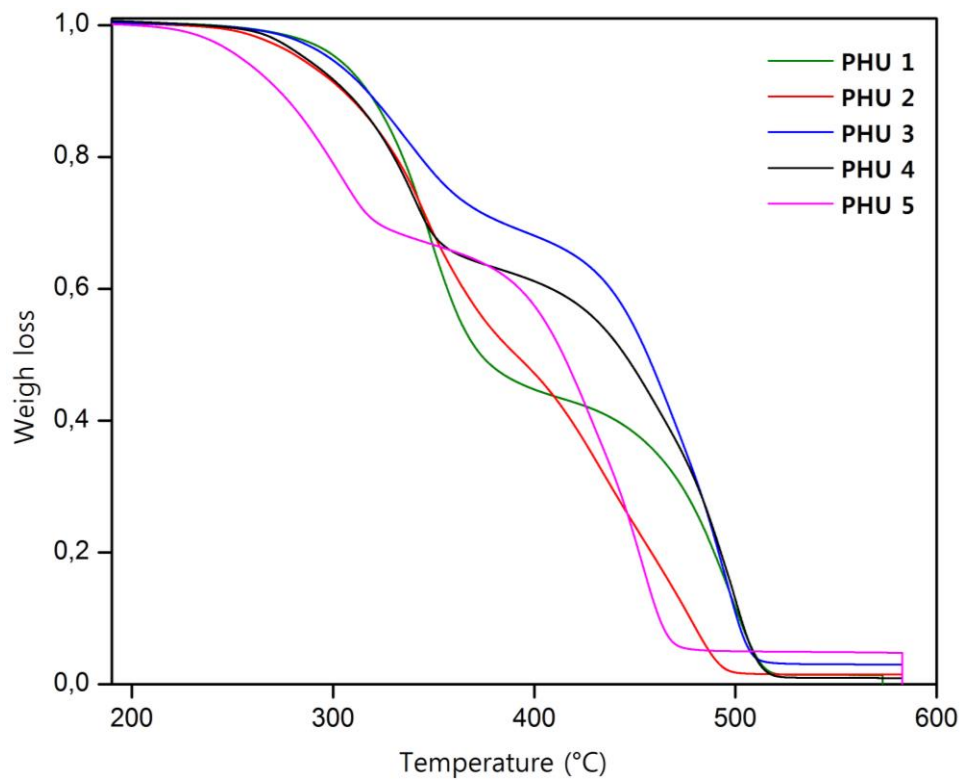


Figure 27 – TGA curves of the synthesized PHU (PHU 1-PHU 5) from 200°C (after DMF removal) to 600°C.