Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPLEMENTARY INFORMATION

Fatty acid-based (bis) 6-membered cyclic carbonates as efficient isocyanate free poly(hydroxyurethane)s precursor

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Supplemental Information Contents

1- Materials

Methyl 10-undecenoate (>96.0%), dodecane-1,12-diamine (12DA, >98%) and 1,3-dioxane-2-one (trimethylene carbonate, >98%) were supplied by TCI, Europe. N,N-dimethylformamide (DMF, anhydrous grade), lithium aluminum hydride ($LiAlH_4$) (95%), sodium hydrate (NaH) (60 % dispersion in mineral oil), ethyl chloroformate (97%), 1,4-butanedithiol (>97%), ethylvinyl ether (99%), Grubbs 2nd and 3rd generation metathesis catalyst, hexylamine (99%) and ethylene carbonate (5CC, 98%) were obtained from Sigma-Aldrich. The dimethyl carbonate (DMC, 99%), triethyl amine (TEA, 99%) and 1,2-epoxy-9-decene (96%) were purchased from Alfa Aesar. The propylene carbonate (5CCMe, 99.5%) was obtained from Fisher. 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.

2- Measurements

2.1- Nuclear Magnetic Resonance (NMR) analysis

^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 $CDCl_3$ as a solvent at room temperature, except otherwise mentionned. Two-dimensional analyses such as ^1H-^1H COSY (COrrelation SpectroscopY) and ^1H-^{13}C HSQC (Heteronuclear Single Quantum Spectroscopy) were also performed on the monomers.

2.2- Fourier Transformed Infra-Red-Attenuated Total Reflection (FTIR-ATR)

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.

2.3- Gas chromatography (GC-FID)

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.

2.4- Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) analyses of PUs were performed in DMF with 1wt% LiBr (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 5µm Guard (guard column 7.5 mm ID x 5.0 cm L); PLgel 5µm MIXED-D (7.5 mm ID x 30.0 cm L) and PLgel 5µm 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.

2.5- Differential Scanning Calorimetry (DSC)

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 (or 200 °C for higher melting point polyurethanes) at 10 °C.min^{-1} were performed and then the glass transition and crystallization temperatures were calculated from the second heating run.

2.6- Thermogravimetric analysis (TGA)

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.

2.7- Time-of-flight mass spectrometer with electrospray ionization (ESI-TOF MS)

Mass spectra were performed by the *Centre d'Etude Stucturale 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. Samples were dissolved in THF at 1 mg/ml, and then 10 µl of this solution was diluted in 1 ml of methanol.

2.8- Time-of-flight mass spectrometer with matrix-assisted laser desorption/ionization (MALDI-TOF MS)

MALDI-MS spectra were performed by the *Centre d'Etude Stucturale et d'Analyse des Molécules Organiques* (*CESAMO*) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV.

Samples were dissolved DMF at 10 mg/ml. The IAA matrix (trans-3-Indoleacrylic acid) solution was prepared by dissolving 10 mg in 1 ml of DMF. A methanol solution of cationisation agent (NaI, 10 mg/ml) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

3- Experimental protocols

<u>6CC syntheses and characterizations</u>

1- Malonate (Und-Malonate) synthesis

The optimizations were first performed on dimethyl sebacate varying the number of equivalents of DMC and the reaction times by using the same strategy. The methyl undecenoate (20 g, 100.9 mmol) was stirred with DMC (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 water, dried over anhydrous sodium sulfate, filtered and then the remaining DMC was removed on rotary evaporator. The compound ***Und-malonate*** was purified by flash chromatography using a mixture of cyclohexane and ethyl acetate and obtained as a viscous liquid. Yield=58%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz) δ (ppm): 5.79 (m, 1H), 4.95 (m, 2H), 3.73 and 3.71 (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): 170.12 ($\underline{C}OOCH_3$), 139.28 ($\underline{C}H=CH_2$), 114.32 ($CH=\underline{C}H_2$), 52.57 ($C=OO\underline{C}H_3$), 51.87 ($\underline{C}H-(C=OOCH_3)_2$), 33.89 ($\underline{C}H_2-CH=CH_2$), 29.27-27.46 ($CH_2$). IR (cm^{-1}): 2924, 2854, 1734.

2- Reduction of the malonate: 1,3-diol (Und-1,3-diol) synthesis

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 distilled water followed by hydrochloric acid solution (2N) was added dropwise. The product was then extracted three times with ethyl acetate. The organic layer was washed twice with 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. Yield=66%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz) δ (ppm): 5.81 (m, 1H), 4.93 (m, 2H), 3.78-3.63 (m, 4H), 2.96 (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): 139.42 ($\underline{C}H=CH_2$), 114.41 ($CH=\underline{C}H_2$), 67.02 ($CH-\underline{C}H_2-OH$), 42.18 ($\underline{C}H-CH_2-OH$), 34.02 ($\underline{C}H_2-CH=CH_2$), 30.05-27.44 (CH_2). IR (cm^{-1}): 3277, 2919, 2850.

3- Cyclization: 6-membered cyclic carbonate synthesis (Und-6CC)

The optimizations were first carried out on 1,3-propanediol varying the additive, carbonation agent and the concentration by using the same procedure. 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 and obtained as a viscous liquid with 99.5% purity determined by GC-FID. Yield=75%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz) δ (ppm): 5.81 (m, 1H), 4.96 (m, 2H), 4.40 (m, 2H), 4.09 (m, 2H), 2.21 (m, 1H), 2.05 (m, 2H), 1.35-1.30 (m, 12H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz) δ (ppm): 148.72 (OCOO), 139.14 ($\underline{C}H=CH_2$), 114.42 ($CH=\underline{C}H_2$), 72.24 ($\underline{C}H_2$-OCOO), 33.84 ($\underline{C}H_2-CH=CH_2$), 31.39 ($\underline{C}H-CH_2$-OCOO), 29.53-26.69 (CH_2). IR (cm^{-1}): 2924, 2856, 1753.

4- Coupling reaction

4.1- Metathesis reaction: Bis 6-membered cyclic carbonate synthesis (UndC20-b6CC)

Into a round-bottom flask equipped with a mineral oil bubbler, the Und-6CC (4 g, 17.7 mmol) was charged with dried pentane (40mL) and 3rd generation Grubbs catalyst (78.2 mg, 0.088 mmol). The contents were vigorously stirred at room temperature for 4 hours. Afterwards, 3.8 mL of ethylvinyl ether was added to deactivate the Grubbs catalyst. The equilibrium was drived thank to the precipitation of the formed product. The product was then purified with flash chromatography using a mixture of cyclohexane and ethyl acetate as eluent. ***UndC20-b6CC*** was obtained as a grey solid. Yield=51.5%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz) δ (ppm): 5.37 (m, 2H), 4.41 (m, 4H), 4.09 (m, 4H), 2.20 (m, 2H), 1.97 (m, 4H), 1.35-1.28 (m, 22H). ^{13}C NMR ($CDCl_3$, 25°C, 100 MHz) δ (ppm): 148.71 (OCOO), 130.46 (CH=CH), 72.22 ($CH-\underline{C}H_2$-OCO), 32.55 ($\underline{CH_2}$-CH=CH), 31.32 ($\underline{C}H-CH_2$-OCO), 29.25-26.68 (CH_2). IR (cm^{-1}): 2918, 2850, 1726. T_m=59°C.

4.2- Thiol-ene reaction: Bis 6-membered cyclic carbonate synthesis (UndS-b6CC)

The Und-6CC (4 g, 17.7 mmol) and 1,4-butanedithiol (2.38 g, 19.4 mmol, 1.1 eq.) were weighed into a flask. The reaction mixture was then UV-irradiated (254 nm) at room temperature. The reaction was monitored with ^{1}H NMR spectroscopy with the disappearance of the double bond. After completion of the reaction, ***UndS-b6CC*** was purified by recrystallization in a mixture of cyclohexane and ethyl acetate (70:30) and obtained as a white solid. Yield=37%. ^{1}H NMR ($CDCl_3$, 25°C, 400 MHz) δ (ppm): 4.40 (m, 4H), 4.09 (m, 4H), 2.52 (m, 8H), 2.20 (m, 2H), 1.68 (m, 4H), 1.57 (m, 4H), 1.35-1.28 (m, 28H). ^{13}C

NMR ($CDCl_3$, 25°C, 100 MHz) δ (ppm): 148.71 (OCOO), 72.24 (CH-$\underline{C}H_2$-OCO), 32.31 and 31.90 ($\underline{C}H_2$-S-$\underline{C}H_2$), 31.42 ($\underline{C}$H-CH_2-OCO), 29.78 and 26.72 ($\underline{C}H_2$-CH_2-S-CH_2-$\underline{C}H_2$), 29.60-26.72 (CH_2). IR (cm^{-1}): 2922, 2850, 1750, 1727. T_m=82°C.

Kinetic experiments monitored by ^{1}H NMR

The kinetic experiments were performed in NMR tube at 50°C and 1 mol.L^{-1} in DMSO-d6 and with a ratio 1:1 between cyclic carbonate and hexylamine. All reagents were dried before the reaction: on CaH_2 for hexylamine and on molecular sieves otherwise. For instance; a pre-solution of trimethyl carbonate (153 mg, 1.5 mmol, 3 eq.) and DMSO-d6 (1.5 mL) is first prepared. Then, one third of this solution and trichlorobenzene as internal reference (12.5 μL, 0.1 mmol, 0.2 eq.) were added into an NMR tube. 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 ^{1}H NMR spectroscopy with the disappearance of the cyclic carbonate protons. After 7 hours or 15 hours, if the reaction was not completed, the NMR tube was placed in an oil bath at the desired temperature and reanalyzed later. For some experiments, the concentration (0.5 mol.L^{-1} and 5 mol.L^{-1}), the temperature (30°C and 70°C) and the amine ratio (1:2 and 1:3) were modulated. ^{1}H NMR, ^{13}C NMR and IR detail are given below only for the reaction between Und-6CC+hexylamine.

Product of the reaction between Und-6CC+hexylamine: ^{1}H NMR (DMSO-d6, 70°C, 400 MHz) δ (ppm): 6.71 (NH), 5.79 (m, 1H), 4.97 (m, 2H), 3.94 (m, 2H), 3.41 (m, 2H), 2.98 (m, 2H), 2.02 (m, 2H), 1.66 (m, 1H), 1.29 (m, 20H), 0.88 (t, 3H). ^{13}C NMR (DMSO-d6, 70°C, 100 MHz) δ (ppm): 148.72 (OCOO), 139.14 ($\underline{C}H=CH_2$), 114.62 (CH=$\underline{C}H_2$), 64.62 (CH-$\underline{C}H_2$-OCONH), 61.80 (CH-$\underline{C}H_2$-OH), 41.83 (OH-CH_2-$\underline{C}$H-CH_2-OCONH), 40.8 ($\underline{C}H_2$-NHCOO), 33.50 ($\underline{C}H_2$-CH=CH_2), 33.65-22.40 (CH_2), 13.94 (CH_3). IR (cm^{-1}): 3384, 2924, 2858, 1705.

Synthesis of Dec-5CC: 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, CO_2 was slowly introduced into the reactor until 50 Bar. After 24 hours, the reactor was cooled down to RT and slowly depressurized to the atmospheric pressure. The ^{1}H NMR of the final mixture revealed a conversion of 94.5%. The Dec-5CC was purified by flash chromatography using a mixture of cyclohexane: ethyl acetate with 0% to 30% of ethyl acetate. Y=50%. ***Dec-5CC:*** ^{1}H NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 25°C, 100 MHz) δ (ppm): 155.18 (OCOO), 138.99 ($\underline{C}H{=}CH_2$), 114.54 ($CH{=}\underline{C}H_2$), 77.36 ($\underline{C}H$-OCOO), 69.51 ($\underline{C}H_2$-OCOO), 34.02 ($\underline{C}H_2$-CH-OCOO), 33.78 ($\underline{C}H_2$-$CH{=}CH_2$), 29.11-28.80 (CH_2), 24.48 ($\underline{C}H_2$-CH_2-CH-OCOO). IR (cm^{-1}): 2924, 2856, 1786.

Polymer syntheses and characterizations

PHUs were prepared from the bis 6-membered cyclic carbonates (UndC20-b6CC and UndS-b6CC) and dodecane-1,12-diamine (12DA). PHU syntheses were performed in DMF at room temperature or at 50°C into a schlenk tube under magnetic stirring and nitrogen atmosphere for 2 days. TCB was used as a reference. No catalysts were added for the polymerization reactions. The recovered polymer samples were quenched by a large excess of hexylamine which was then removed by vacuum distillation prior to solubilize the polymer for SEC analyses.

PU-2 [UndC20-b6CC+12DA]: ^{1}H NMR (TCE-d2, 25°C, 400 MHz) δ (ppm): 5.39 (s, 2H), 4.86 (s, 2.NH), 4.17-4.02 (m, 4H), 3.52-3.45 (m, 4H), 3.13 (m, 4H), 1.96 (m, 4H), 1.71 (m, 2H), 1.48-1.27 (m, CH_2). IR (cm^{-1}): 3620-3158, 2925, 2852, 1686, 1534.

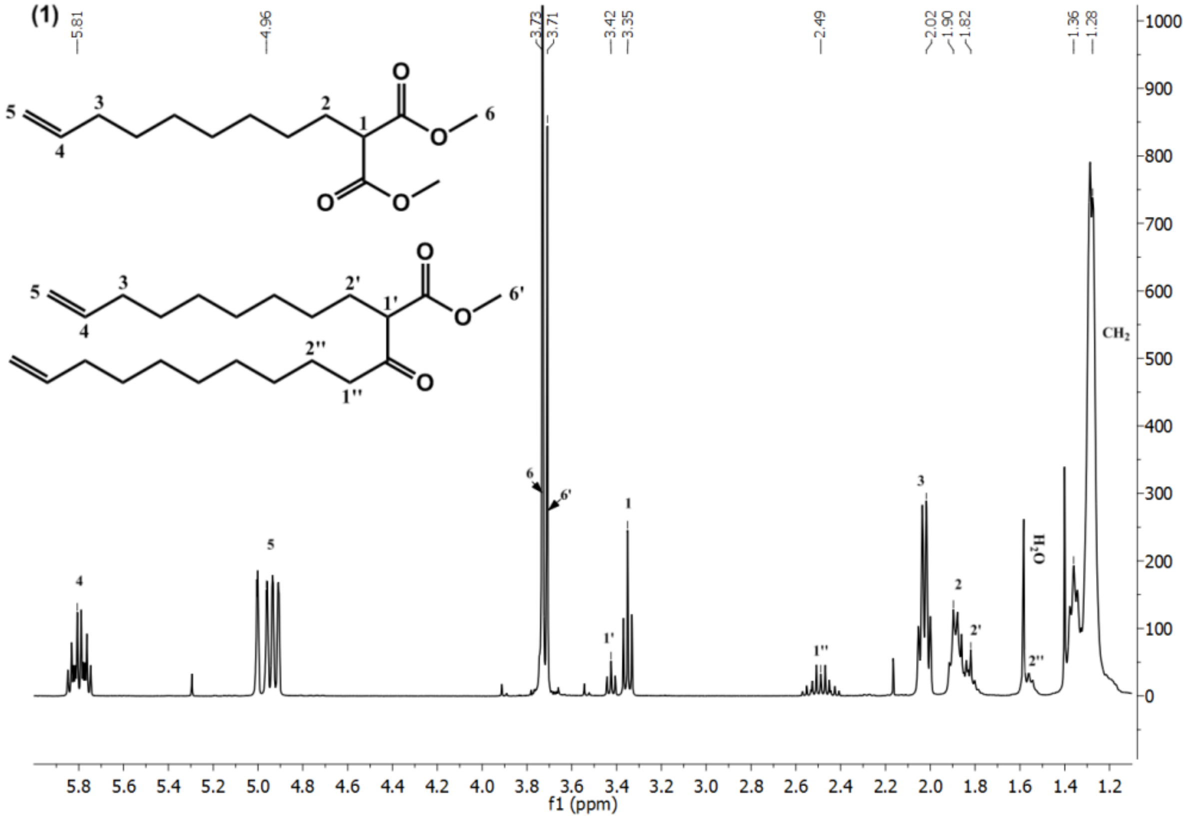
PU-3 [UndS-b6CC+12DA]: ^{1}H NMR (TCE-d2, 25°C, 400 MHz) δ (ppm): 4.89 (s, 2.NH), 4.23-4.09 (m, 4H), 3.58-3.49 (m, 4H), 3.17 (m, 4H), 2.57 (m, 8H), 1.77-1.72 (m, 6H), 1.62 (m, 4H), 1.51-1.33 (m, CH_2). IR (cm^{-1}): 3620-3158, 2925, 2852, 1686, 1534.

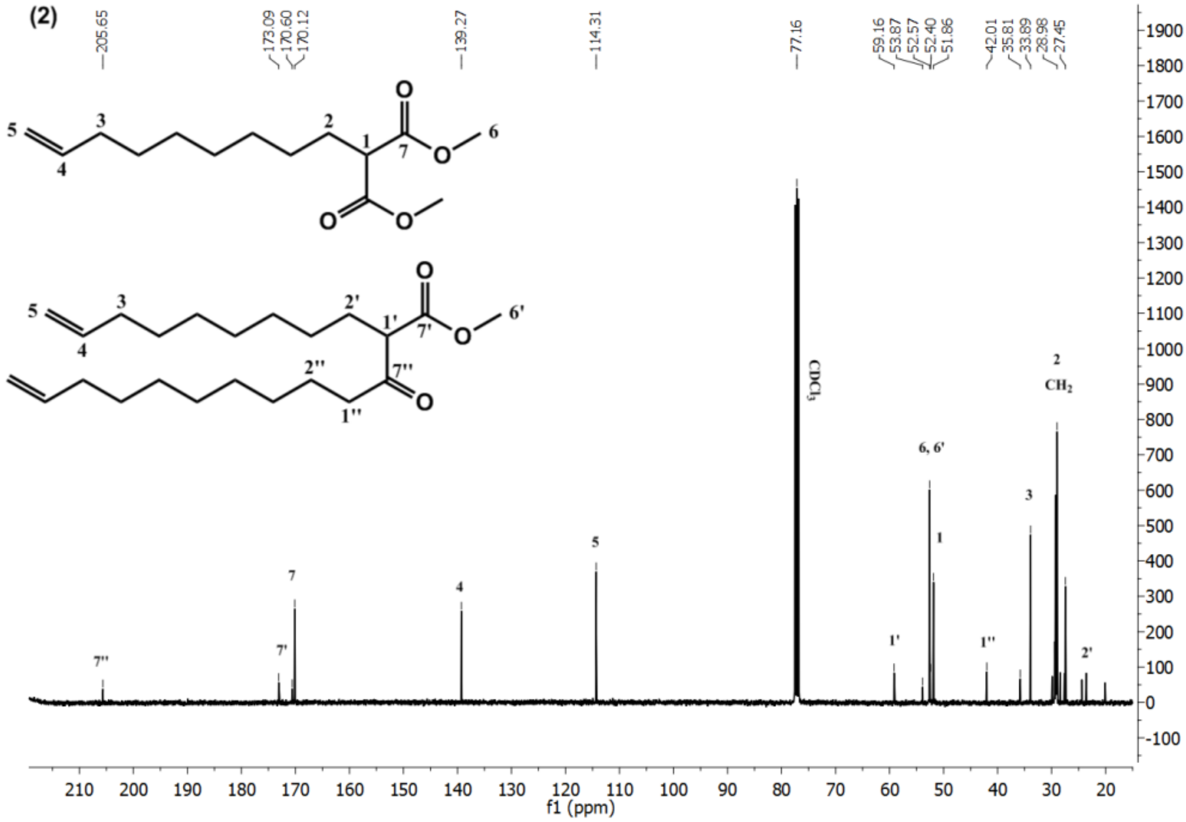
4- Graphical data

ESI Table 1- Optimization of the conditions for the malonate synthesis at 60°C on dimethyl sebacate (SebdE).

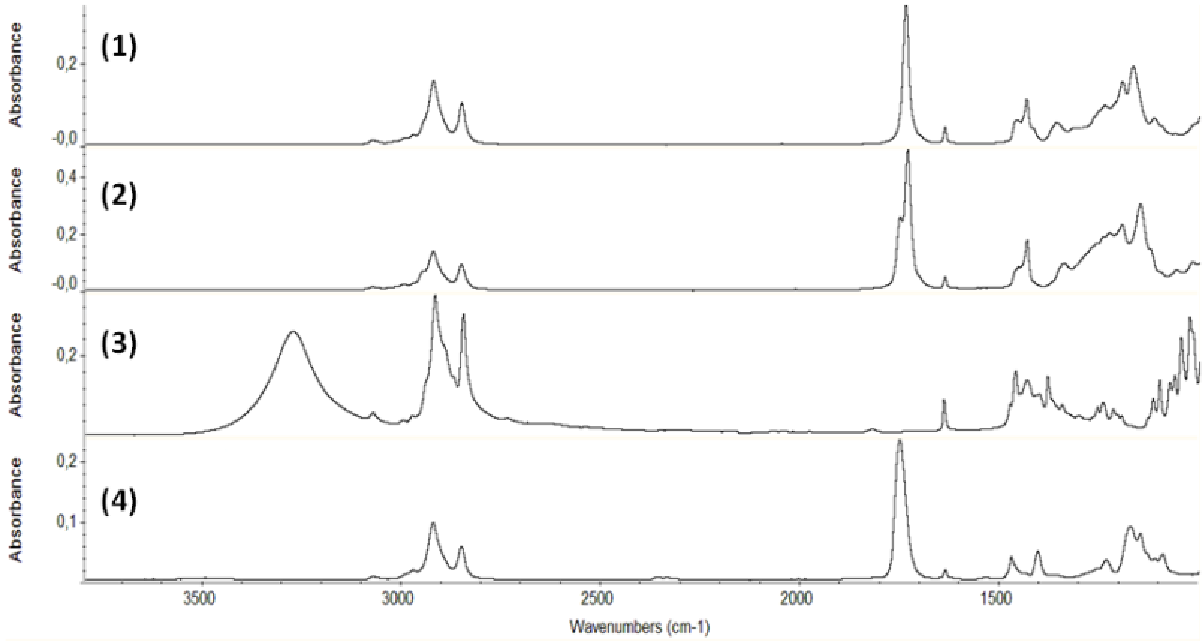
SebdE (eq.)	DMC (eq./ester)	NaH $_{60\% \text{ disp.}}$ (eq.)	DMF (eq./ester)	Time (h)	Malonate conversion[1]
1	20	2.5	1	10	26
1	30	2.5	1	15	50*
1	40	2.5	1	24	80
1	40	2.5	1	40	71

(1) Estimated by ^{1}H NMR. (*) Claisen side products.

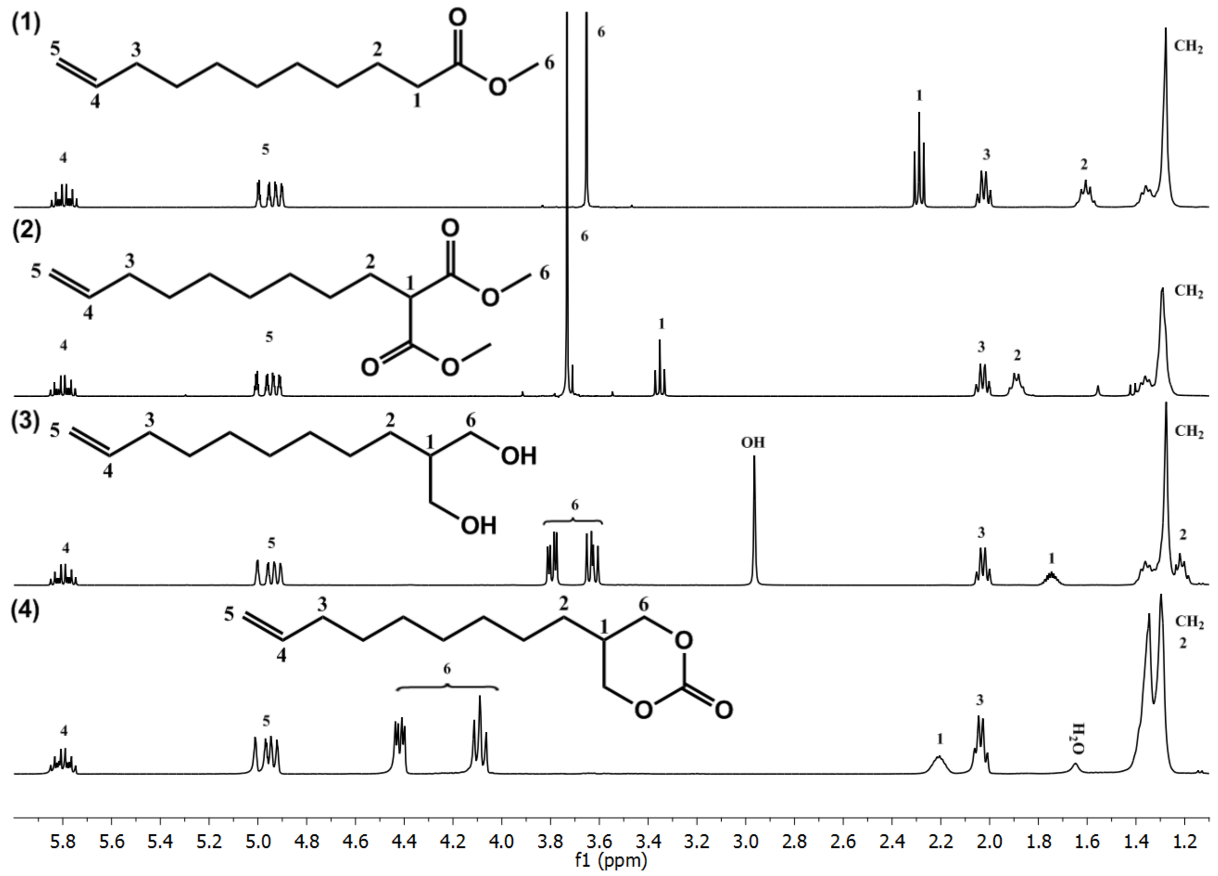




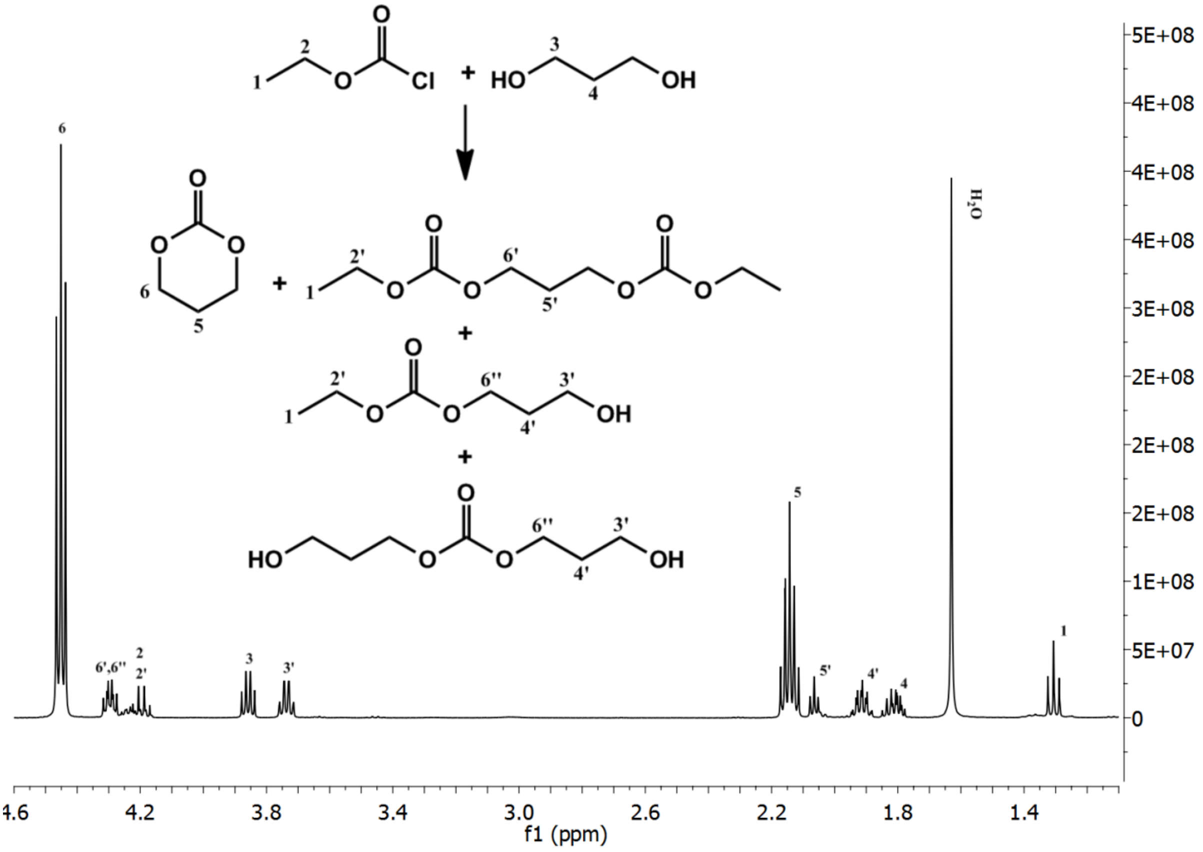
ESI Figure 1- Evidence of the formation of the Claisen-condensation product in a chromatography aliquot: (1) ^{1}H NMR and (2) ^{13}C NMR.



ESI Figure 2- Stacked FTIR-ATR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC.

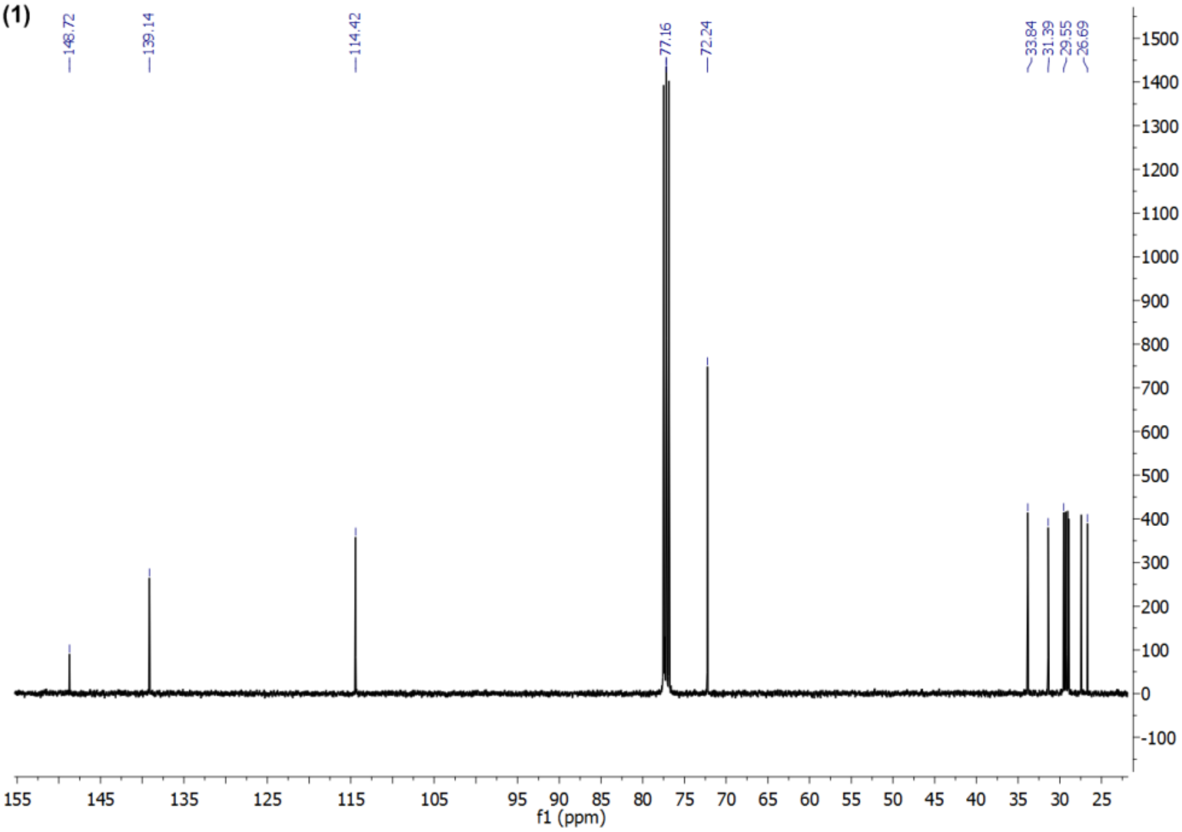


ESI Figure 3- Stacked ^{1}H NMR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC. (All analyses were performed in CDCl$_3$.)



ESI Figure 4- Synthesis of 6-membered cyclic carbonate from 1,3-propanediol. (Analysis in CDCl$_3$)

(1)



148.72
139.14
114.42
77.16
72.24
33.84
31.39
29.55
26.69
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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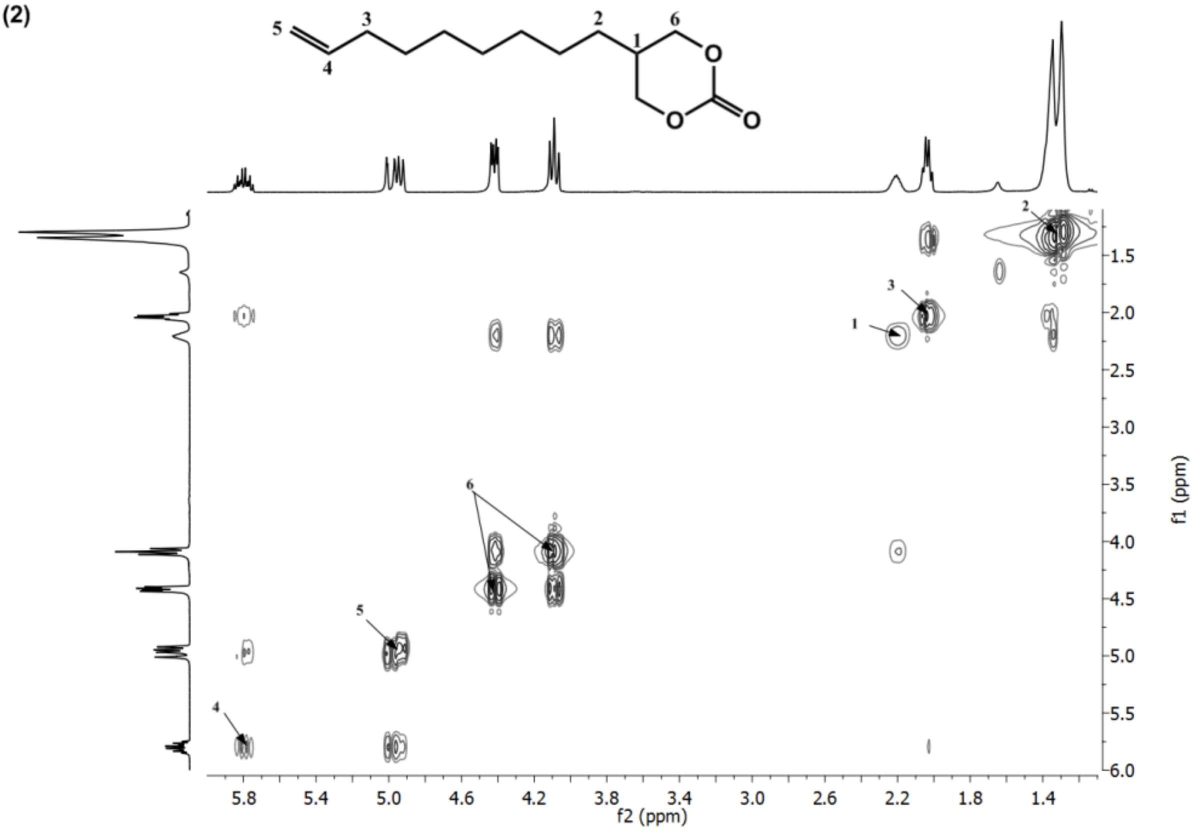
f1 (ppm)

(2)



5
4
3
2
1
6
O
O
O
5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4
f2 (ppm)
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3.5
4.0
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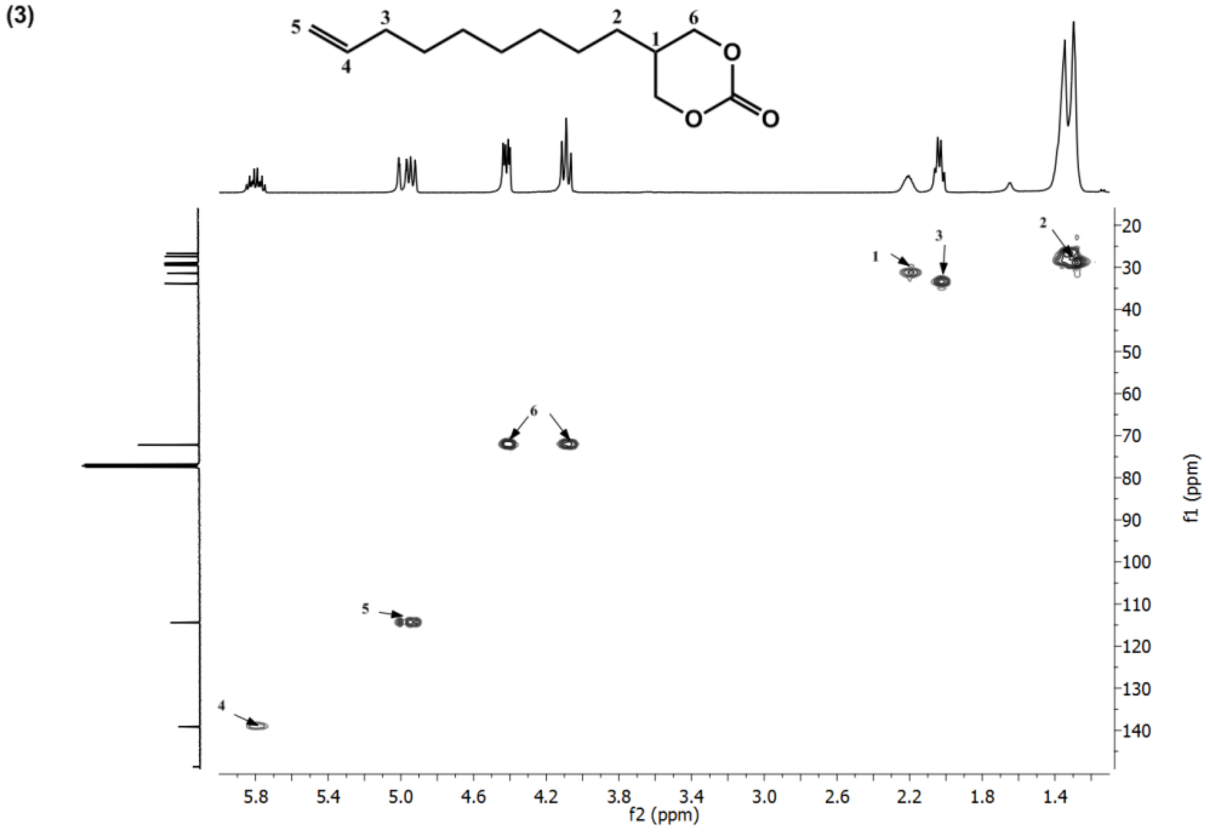
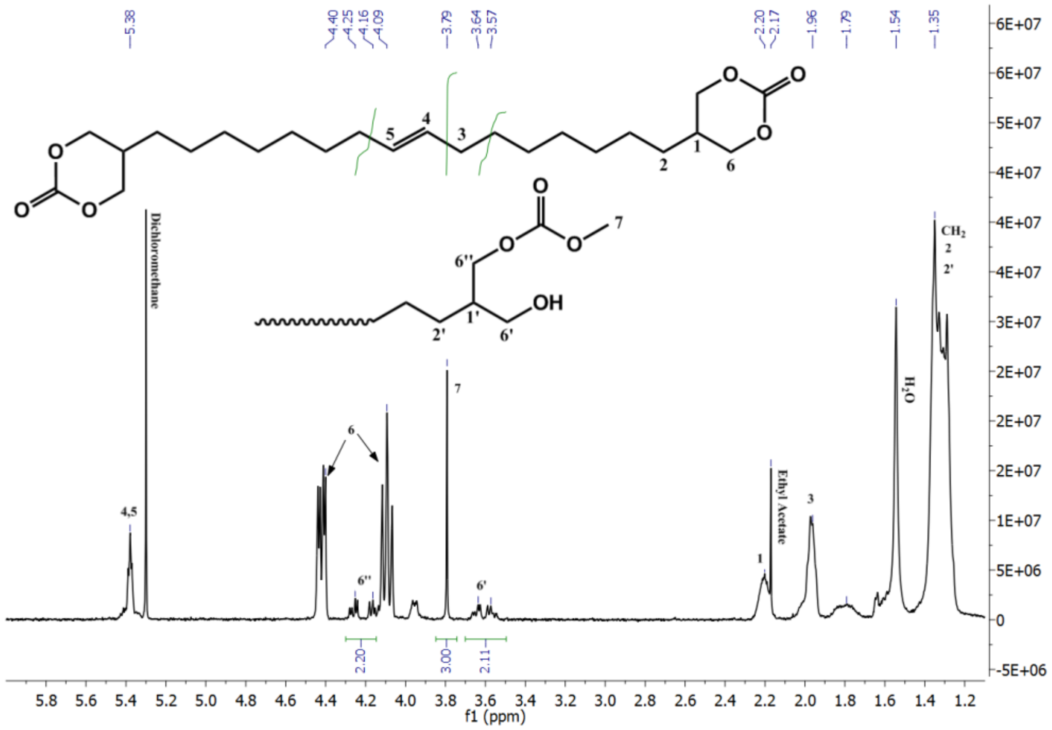
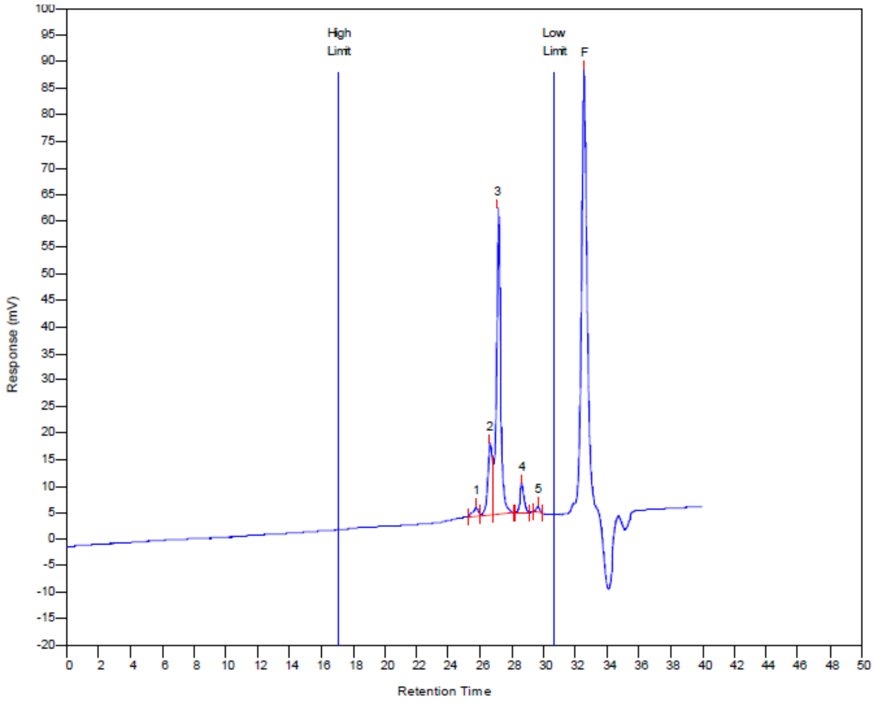
6.0
f1 (ppm)



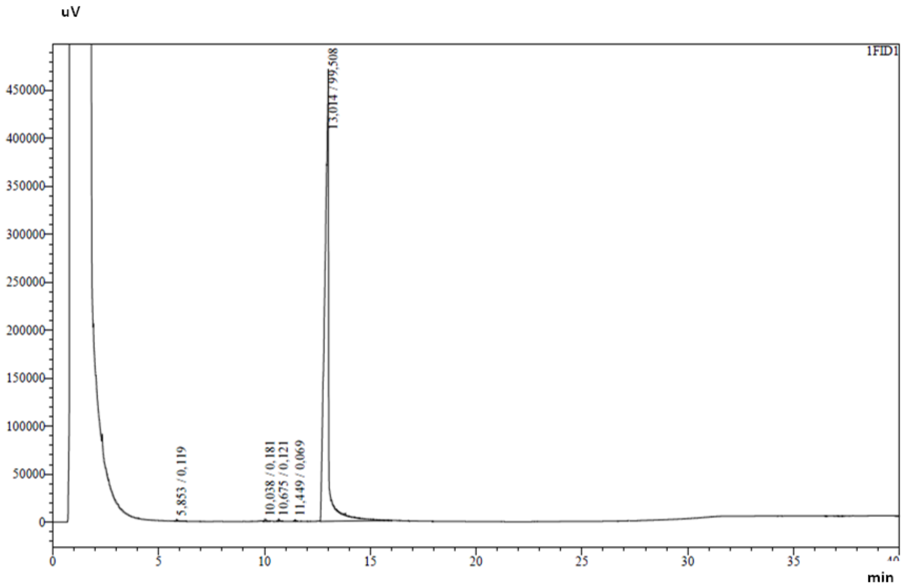
ESI Figure 5- NMR analyses of purified Und-6CC: (1) ^{13}C NMR, (2) ^{1}H-^{1}H COSY 2D-NMR and (3) ^{1}H-^{13}C HSQC-NMR.



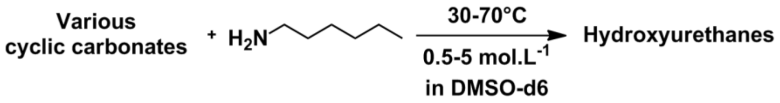
ESI Figure 6- Evidence for the ring opening of the 6-membered cyclic carbonates of UndC20-b6CC while a test of recrystalization in methanol. (Analysis performed in CDCl$_3$.)



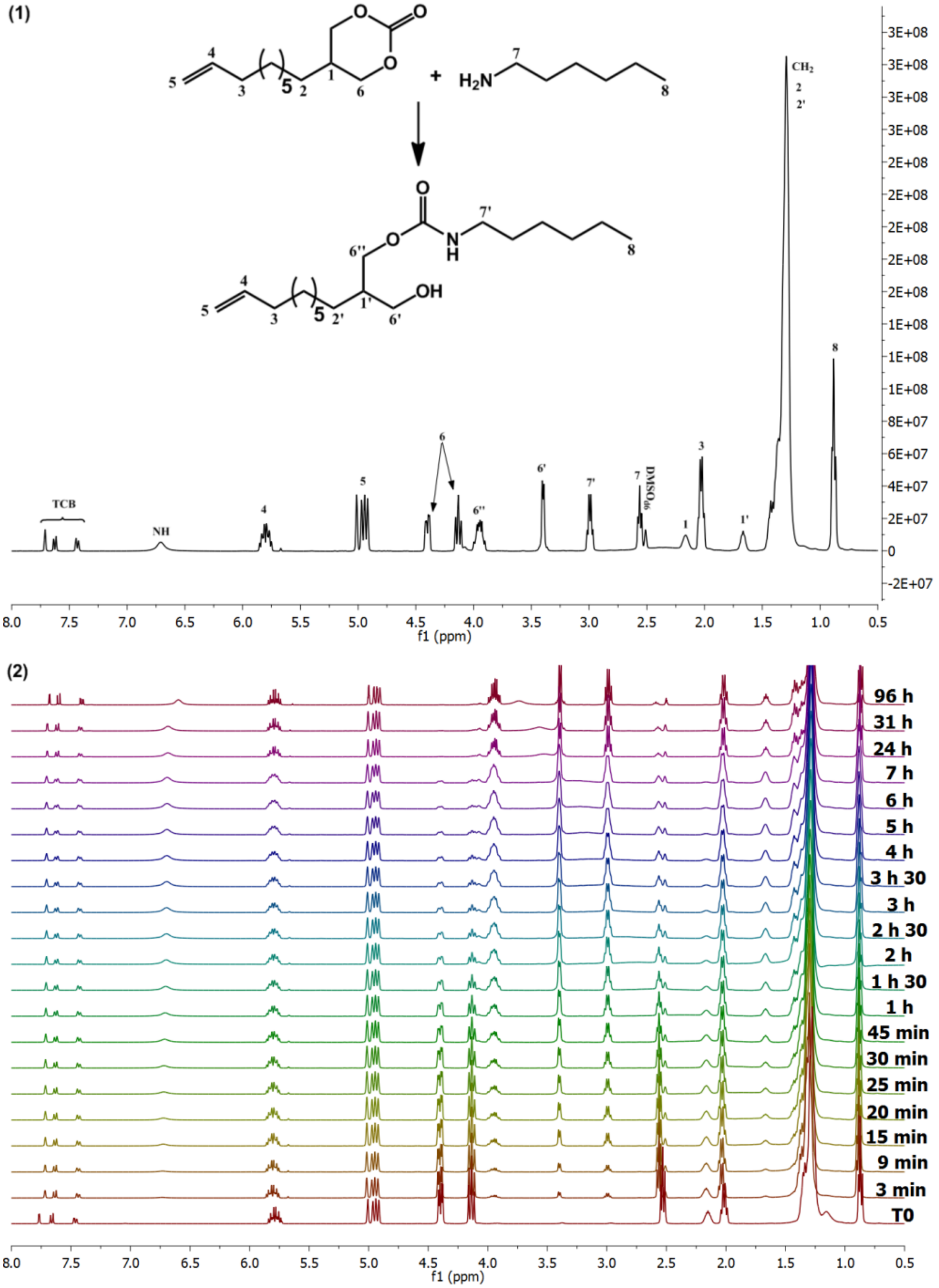
ESI Figure 7- SEC analyses of a flash chromatography aliguot, collected while a test of purification of UndS-b6CC by flash chromatography.



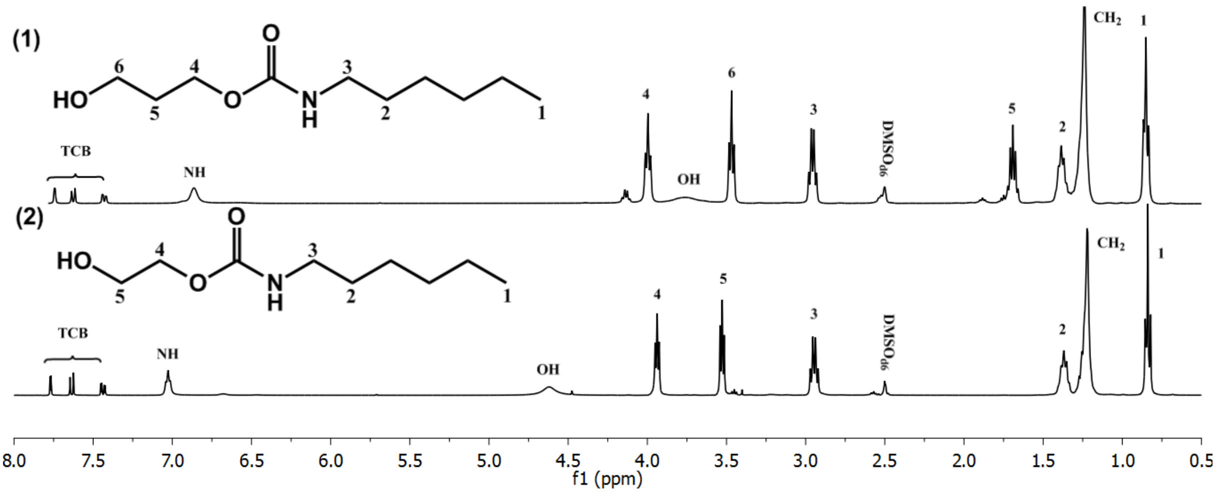
ESI Figure 8- Gas chromatography of Und-6CC.



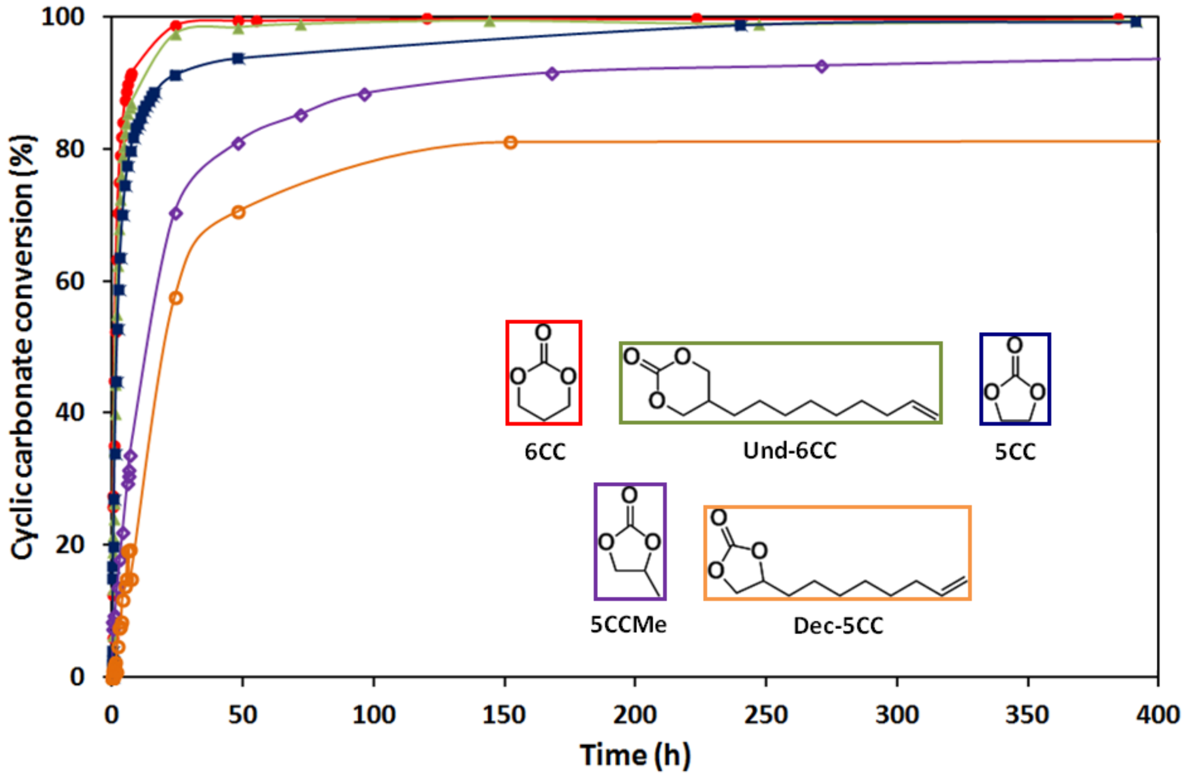
ESI Scheme 1- Model reaction of various cyclic carbonates with hexylamine in different conditions.



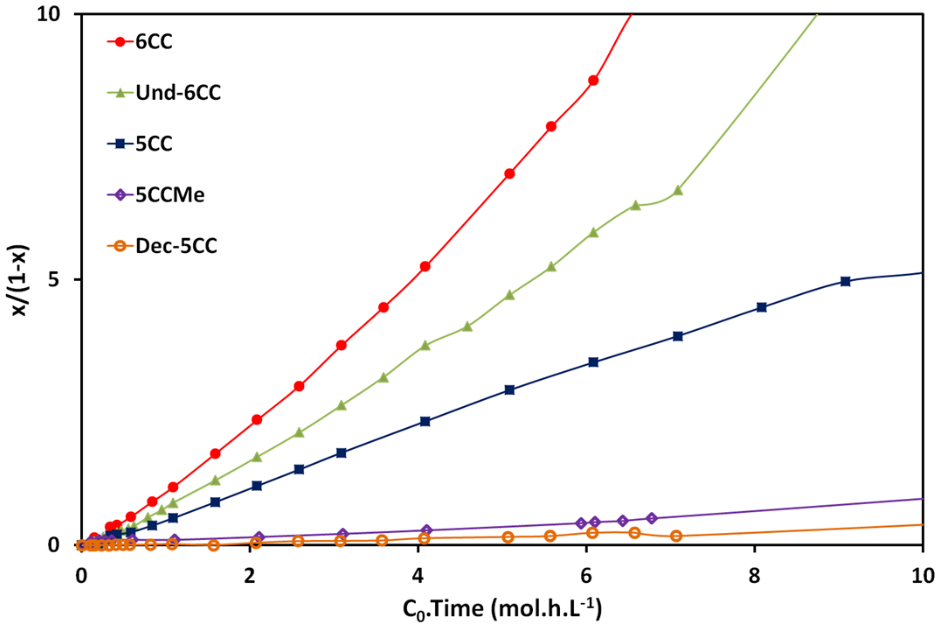
ESI Figure 9- Reaction between Und-6CC and hexylamine at 70°C in DMSO-d6 at 1 mol.L^{-1}, with a ratio 1:1. (1) ^{1}H NMR after 1 hour and (2) Stacked ^{1}H NMR monitoring.



ESI Figure 10- Stacked ^{1}H NMR of the different model reaction performed with hexylamine at 50°C in DMSO-d6 at 1 mol.L^{-1}. (1) from trimethylene carbonate and (2) from ethylene carbonate.



ESI Figure 11- Effect of various cyclic carbonates chemical structures on the kinetic of the reactions with hexylamine. (50°C, 1 mol.L^{-1} in DMSO-d6, ratio 1:1)



ESI Figure 12- Verification of the second 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}).

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

(E1)

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

(E2)

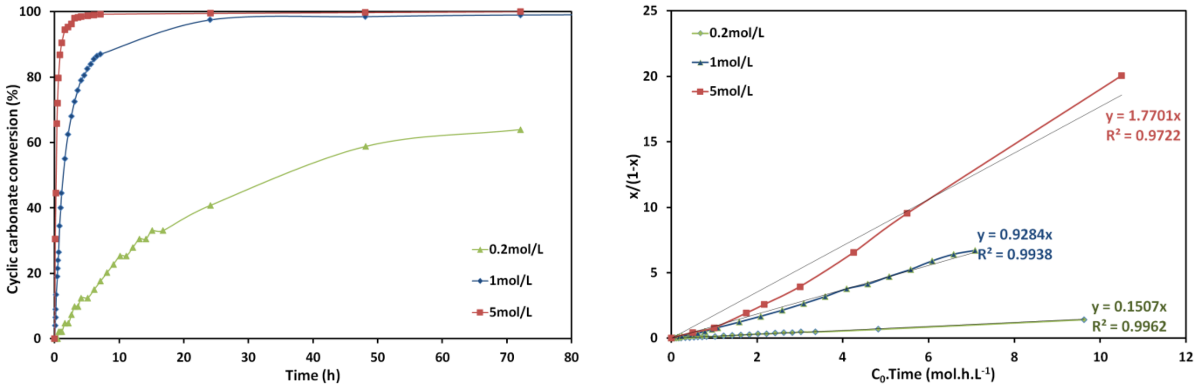
$$\frac{1}{[CC]} - \frac{1}{C_0} = k_{app}\Delta t$$

(E3)

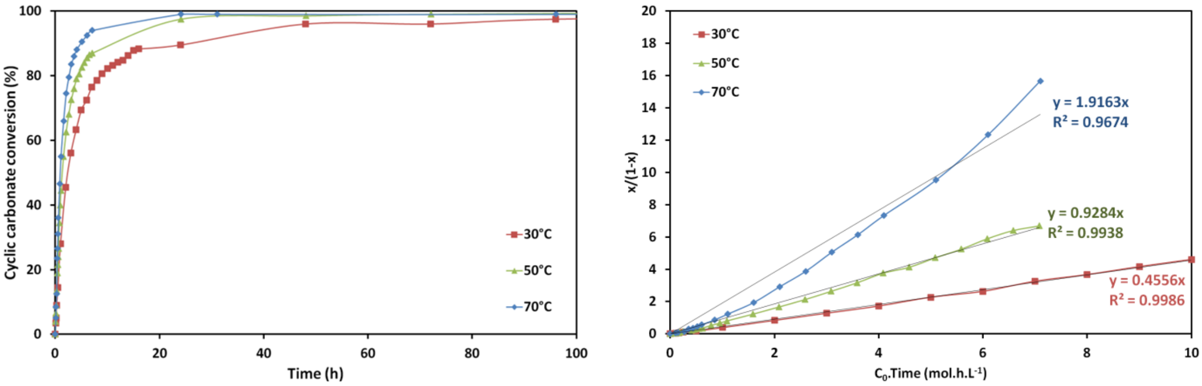
or $[CC] = C_0 - C_0x = C_0(1-x)$ (E4)

$$\frac{x}{1-x} = k_{app}C_0\Delta t$$

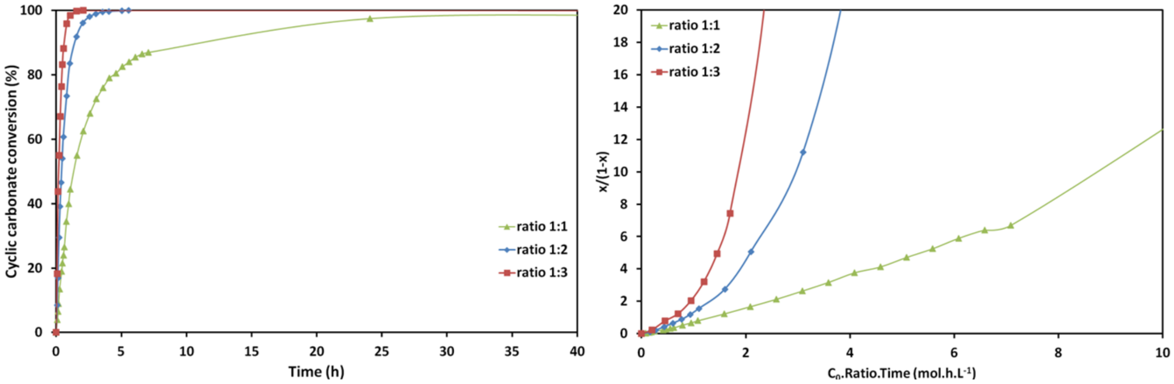
(E5)



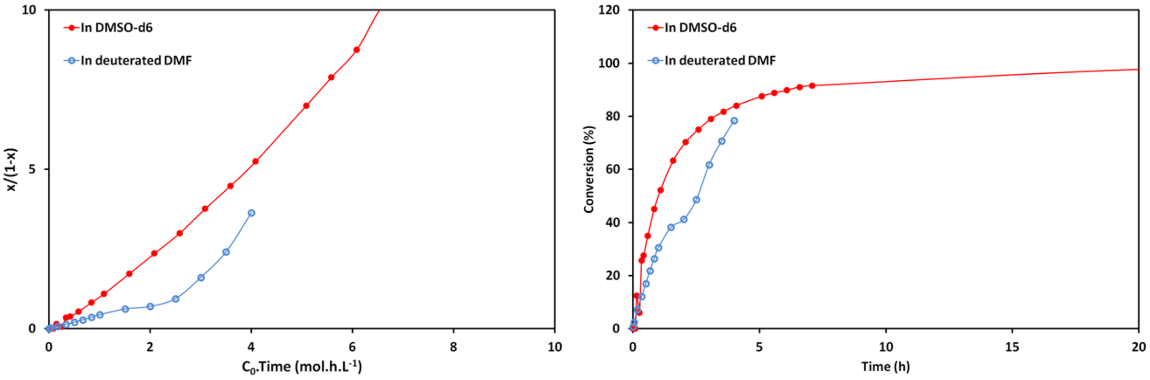
ESI Figure 13- Effect of the reactant concentrations on the kinetic of the reactions between Und-6CC and hexylamine. (50°C, in DMSO-d6, ratio 1:1)



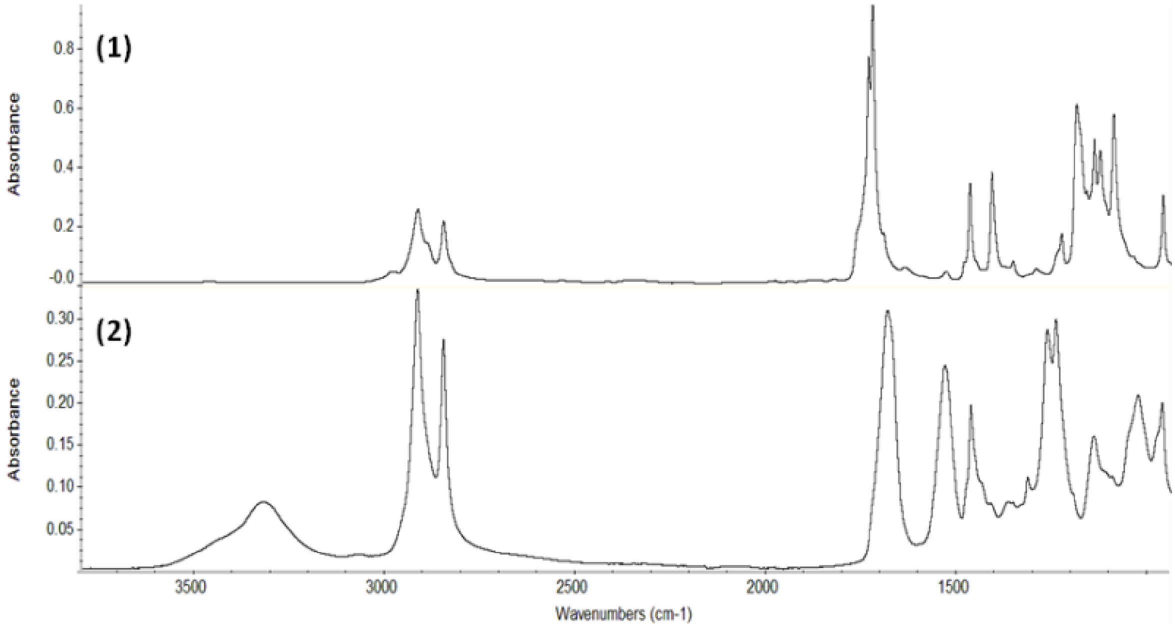
ESI Figure 14- Effect of the temperature on the kinetic of the reactions between Und-6CC and hexylamine. (1 mol.L^{-1} in DMSO-d6, ratio 1:1)



ESI Figure 15- Effect of the cyclic carbonate to hexylamine ratio on the kinetic of the reactions with Und-6CC. (50°C, 1 mol.L^{-1} in DMSO-d6)

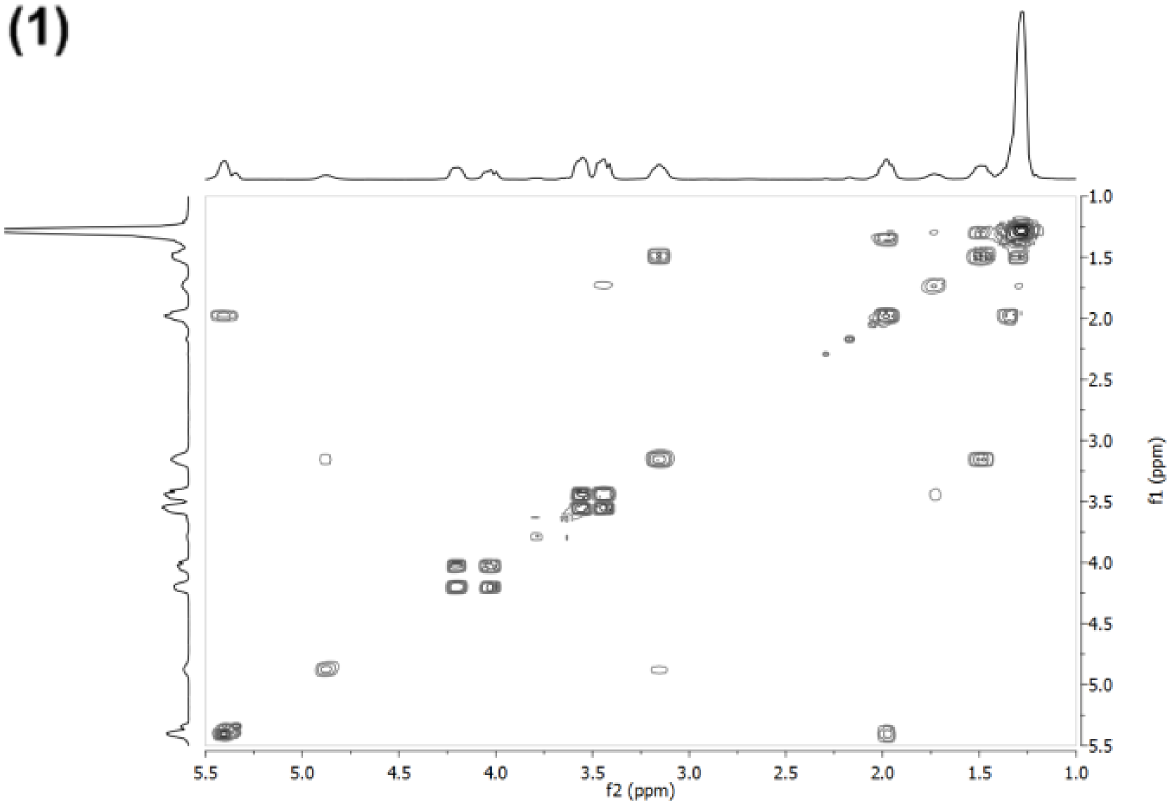


ESI Figure 16- No dramatic solvent effect on the kinetics as demonstrated from the reactions between trimethylene carbonate (6CC) and hexylamine in deuterated DMSO or DMF.

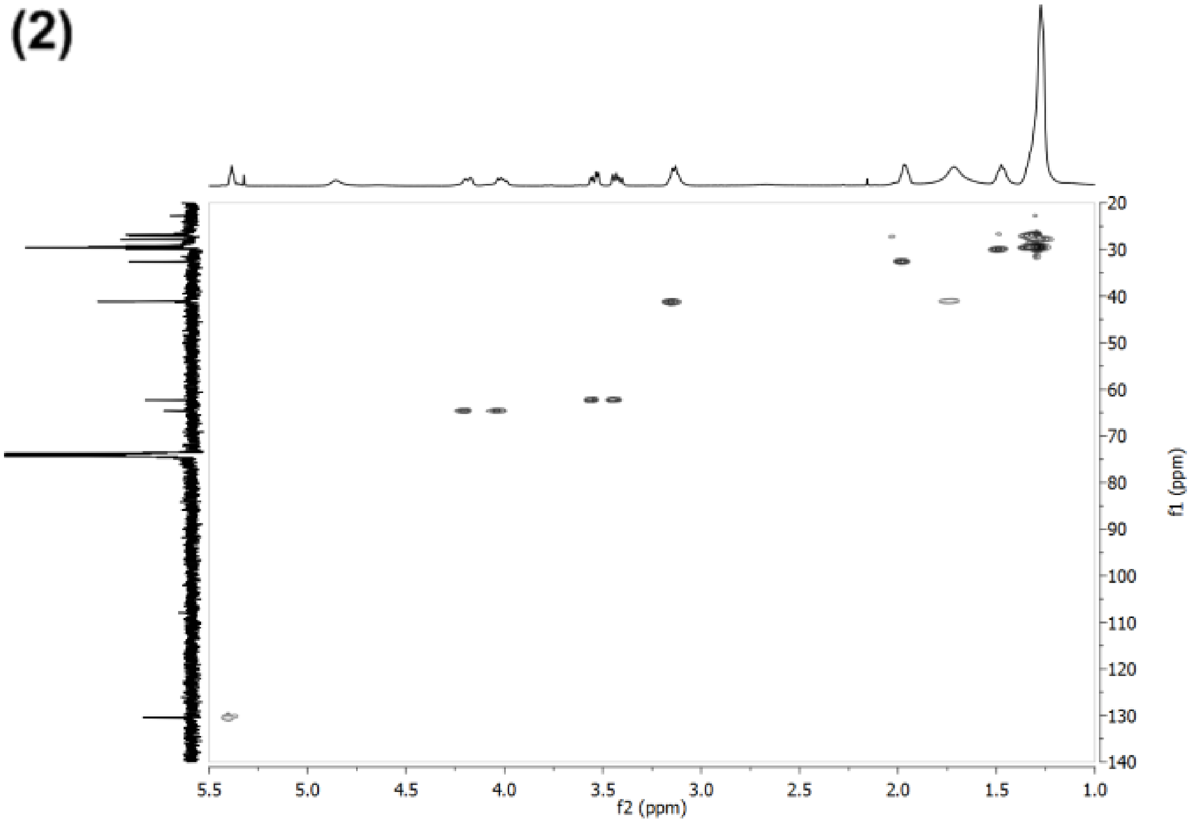


ESI Figure 17- Stacked FTIR-ATR spectra of (1) UndC20-b6CC and (2) the corresponding poly(hydroxyurethane)s with dodecane-1,12-diamine (PHU-2).

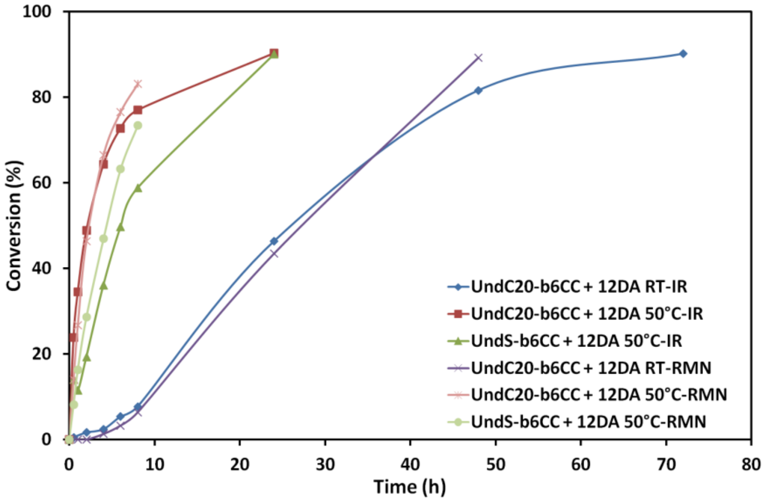
(1)



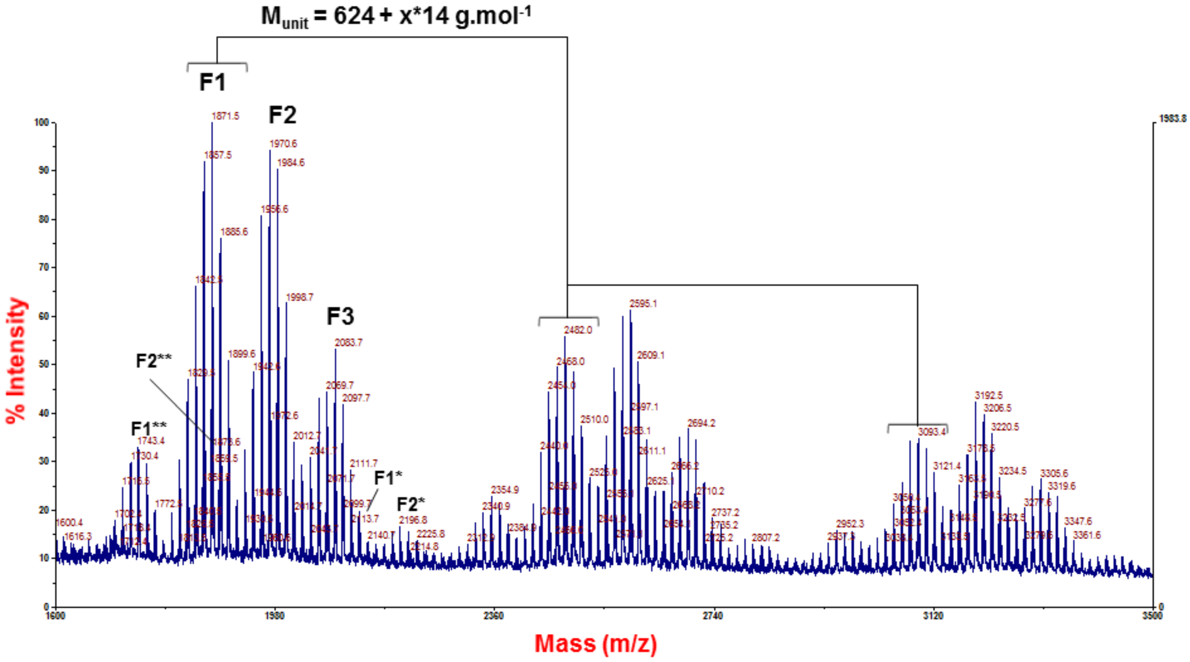
(2)



ESI Figure 18-(1) ^{1}H-^{1}H COSY and (2) ^{1}H-^{13}C HSQC-NMR spectra of PHU-2 from UndC20-b6CC and 12DA after quenching and DMF evaporation. (Analyses in TCE)



ESI Figure 19- Evolution of the polymerization kinetics at room temperature and 50°C by FTIR-ATR and ^{1}H NMR for UndC20-b6CC and UndS-b6CC with dodecane-1,12-diamine.

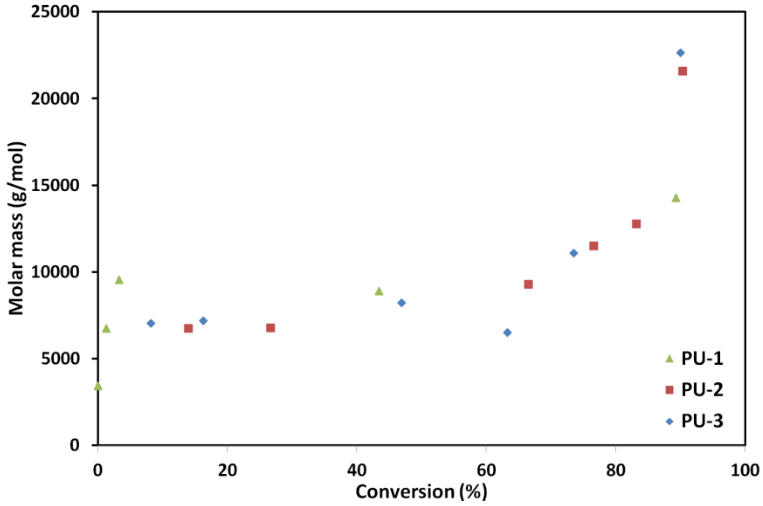


ESI Figure 20- MALDI-TOF MS analysis of PHU-2 between UndC20-b6CC and 12DA. (Matrix trans-3-indoleacrylic acid)

ESI Table 2- Different PHU families visible in MALDI-TOF MS.

PHU families	Description	For PHU-2 (M_{unit}= 624 + x*M_{CH2} g.mol^{-1}) {M th vs M exp}	For PHU-3 (M_{unit}= 775 g.mol^{-1}) {M th vs M exp}
F1	hex-C-(C_{n-1}-A_n)-C-hex	$n*(M_{unit})+M_{UndC20\text{-}b6CC}$ $+2*M_{hex}+M_{Na}$ {n=3 no isomerization (1898,53 vs 1899.6)}	$n*(M_{unit})+M_{UndS\text{-}b6CC}+2*M_{hex}+M_{Na}$ {n=2 (1574.14 vs 1574.3)}
F2	hex-C-(C_n-A_n)-A	$(n+1)*(M_{unit})+M_{hex}+M_{Na}$ {n=3 no isomerization (1997,64 vs 1998.7)}	$(n+1)*(M_{unit})+M_{hex}+M_{Na}$ {n=2 (1673.25 vs 1674.3)
F3	A-(C_{n+1}-A_n)-A	$(n+1)*(M_{unit})+M_{12DA}+M_{Na}$ {n=3 no isomerization (2096,75 vs 2097.7)}	$(n+1)*(M_{unit})+M_{12DA}+M_{Na}$ n=2 (1772.36 vs 1773.6)
F1*	hex-C-(C_{n-1}-U^A-A_n)-C-hex	$n*(\ M_{unit})+$ $M_{UndC20\text{-}b6CC}+2*M_{hex}+M_{urea}+M_{Na}$ {n=3 minus 1 CH_2 (2110,73 vs 2113.7)}	$n*(\ M_{unit})+$ $M_{UndS\text{-}b6CC}+2*M_{hex}+M_{urea}+M_{Na}$ n=2 (1800.34 vs 1801.6)
F2*	hex-C-(C_n-U^A-A_n)-A	$(n+1)*(M_{unit})+M_{hex}+M_{urea}+M_{Na}$ {n=3 no isomerization (2223,84 vs 2225.8)}	$(n+1)*(M_{unit})+M_{hex}+M_{urea}+M_{Na}$ n=2 (1899.45 vs 1900.7)
F1**	hex-C-(C_{n-1}-A_n)-C^{OH}	$n*(M_{unit})+M_{UndC20\text{-}6CC/OH}+M_{hex}+M_{Na}$ {n=3 no isomerization (1770,42 vs 1772.5)}	$n*(M_{unit})+M_{UndS\text{-}6CC/OH}+M_{hex}+M_{Na}$ n=2 (1446.03 vs 1447.2)
F2**	C^{OH}-(C_n-A_n)-A	$n*(M_{unit})+M_{UndC20\text{-}CC/OH}$ $+M_{12DA}+M_{Na}$ {n=3 no isomerization (1869,53 vs 1871.5)}	$n*(M_{unit})+M_{UndS\text{-}6CC/OH}+M_{12DA}+M_{Na}$ n=2 (1545.14 vs 1546.3)

Abbreviations are as followed: hex=hexylamine with M_{hex}= 101.12 g.mol^{-1}; C=UndC20-b6CC or UndS-b6CC with $M_{UndC20\text{-}b6CC}$= 424.51+x*14 g.mol^{-1} and $M_{UndS\text{-}b6CC}$= 774.57 g.mol^{-1}; A=dodecane-1,12-diamine with M_{12DA}= 200.23 g.mol^{-1}; U^A=urea linkage on 12DA with M_{urea}= $M_{12DA}+M_{CO}-2*M_H$= 226.2 g.mol^{-1}; C^{OH}=C-CO+H with $M_{UndC20\text{-}6CC/OH}$= 424.51+x*14-$M_{CO}+M_H$ g.mol^{-1} and $M_{UndS\text{-}6CC/OH}$= 774.57-$M_{CO}+M_H$=747.58 g.mol^{-1}.



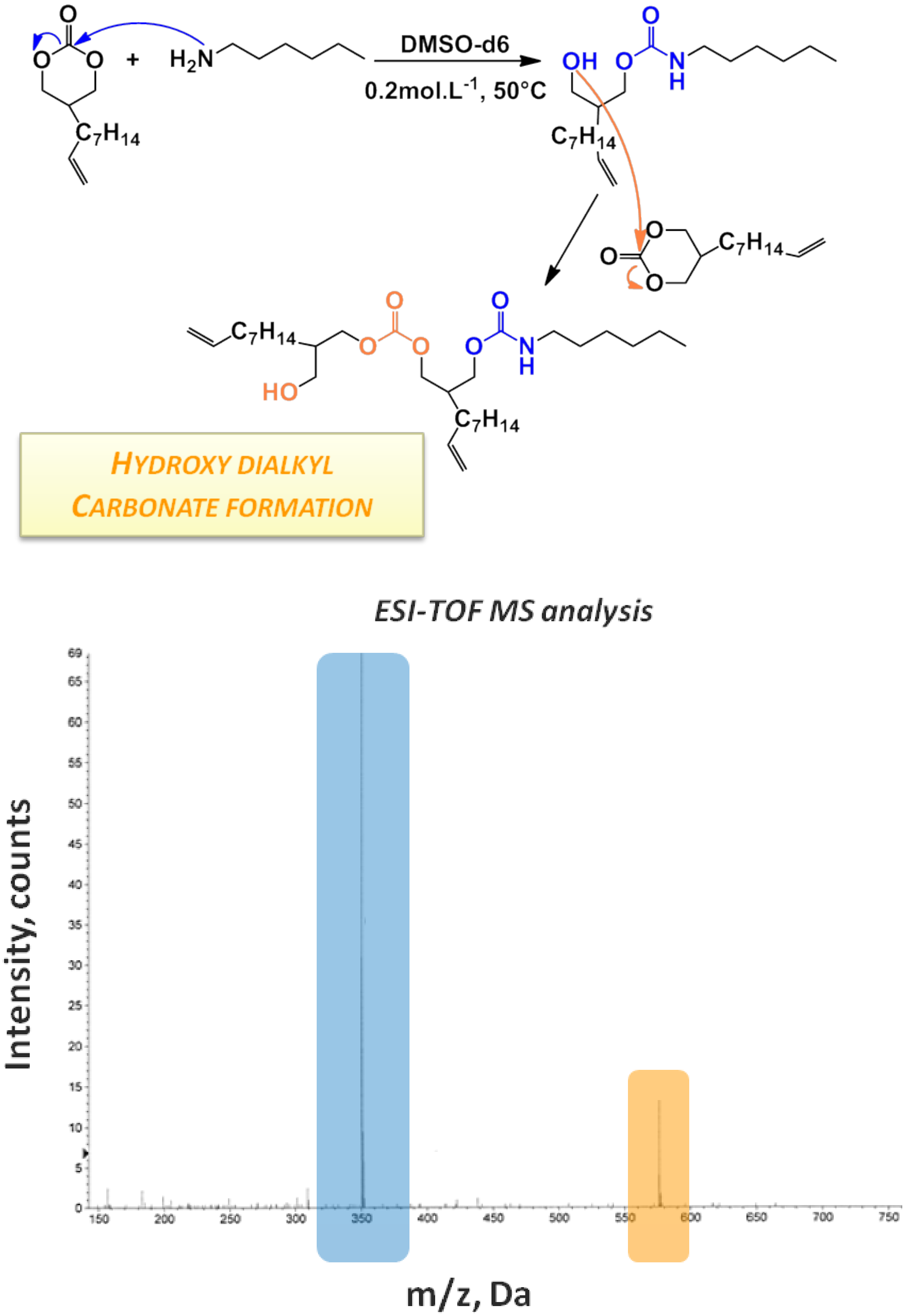
ESI Figure 21- Evolution of the molar masses with the conversion for PHU-1, PHU-2 and PHU-3.

ESI Table 3- Thermal stability and thermo-mechanical properties of the synthesized PHUs.

Sample	T_g (°C)[1]	$T_{5\%}$ (°C) [2]
PHU-1	-0.3	254
PHU-2	-0.6	271
PHU-3	-20	313

(1) Determined by DSC at 10°C.min^{-1}.

(2) Determined by TGA at 10°C.min^{-1} under nitrogen.



ESI Figure 22- Evidence of hydroxyl dialkyl carbonate formation by ESI-TOF MS analysis.