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

Lise Maisonneuve,^[a, b] Anne-Laure Wirotius,^[a, b] Carine Alfos,^[c] Etienne Grau,^[a, b] and Henri Cramail*^[a, b]

(Bis) 6-membered cyclic carbonates were prepared from methyl 10-undecenoate, which is produced from ricinoleic acid, a main constituent of castor oil. Kinetics on these new fatty acid-based 6-membered cyclic carbonates revealed that they are much more reactive than their homolog 5-membered ones (30 times). Poly(hydroxyurethane)s (PHUs) were then synthesized from these bis 6 membered cyclic carbonates at a temperature as low as room temperature and in solvent or bulk. Unexpectedly, chemical gels were obtained. The latter were the consequence of side reactions of carbonate ring-opening with the hydroxyl groups of the formed poly(hydroxyurethane)s. Quenching with a large excess of hexylamine enabled the breaking-up of the gel with the formation of urea linkages.

The most explored alternative route to isocyanate free polyurethanes apply to vegetable oils is based on the reaction of 5-membered cyclic carbonates and amines.¹⁻⁴ This strategy has been investigated to prepare cross-linked as well as linear poly(hydroxyurethane)s (PHUs). Besides, the functionalization of triglycerides or derivatives with cyclic carbonates includes almost exclusively the epoxidation followed by carbonation of the double bonds. Therefore, the so-formed 5-membered cyclic carbonates are linked to one or two electron-releasing alkyl chain(s) (if synthesized from methyl undecenoate or methyl oleate respectively), which deactivate(s) the cyclic carbonate.^{3,5-8} In addition, 5-membered cyclic carbonates are known to be stable over ring opening polymerization.^{1,2,4} Thus, long reaction time, high polymerization temperatures and bulk conditions are necessary to obtain high conversion and subsequent high molar masses. While regarding the literature, few authors have developed PHUs from more reactive fossil-based cyclic carbonates; either with an electro-withdrawing group nearby the cyclic carbonate⁹⁻²⁰ or by using larger size ring cyclic carbonates.²⁰⁻²⁴ For instance, Endo and coll. synthesized petroleum-based 6 and 7-membered cyclic carbonates and their corresponding poly(hydroxyurethane)s.²¹⁻²³

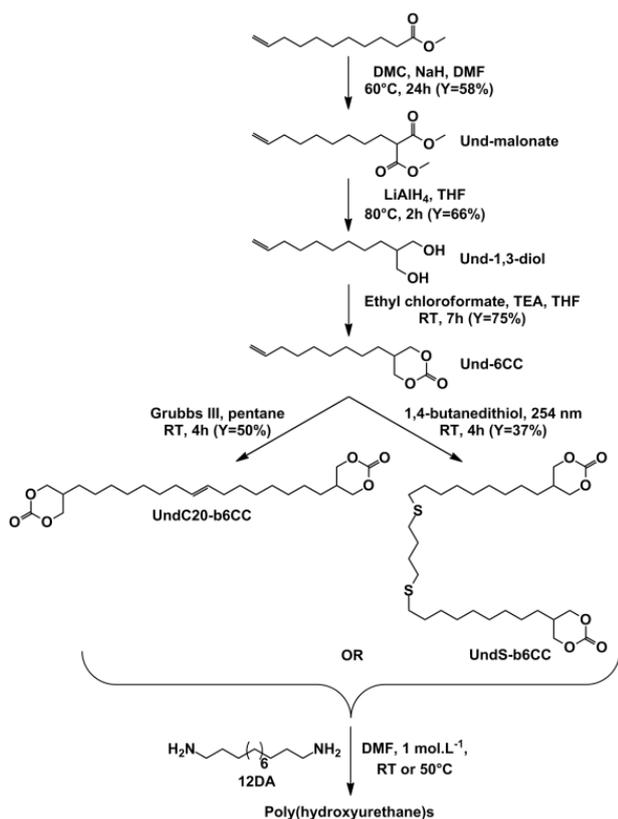
To our knowledge, no literature has been published on the preparation of vegetable oil-based bis 6-membered cyclic carbonates. In the present communication, the synthesis of 6-membered cyclic carbonate from methyl undecenoate (Und-6CC) is reported via malonate and 1,3-diol intermediates. To prepare the fatty acid-based malonate, the approach developed by Meier and coll^{25,26} was preferred due to the use of non-toxic DMC. The coupling of Und-6CC was done under mild conditions, by metathesis or thiol-ene reactions allowing the preparation of bis 6-membered cyclic carbonates: UndC20-b6CC and UndS-b6CC respectively. In addition, a kinetic study on ring opening of carbonates by hexylamine has been performed to demonstrate the high reactivity of Und-6CC. The bis 6-membered cyclic carbonates were then examined in polymerization with dodecane-1,12-diamine

(12DA) in solution. Unexpectedly, network has been obtained due to a side reaction of carbonate opening via hydroxyl functions. The bridge can be broken by urethanization and the released PHUs were then fully characterized.

Bis 6-membered cyclic carbonate (b6CC) synthesis

As illustrated in Scheme 1, the synthesis of Und-6CC involved three steps which are (i) the malonate synthesis from methyl undecenoate (Und-malonate), (ii) the reduction of the malonate into a 1,3-diol (Und-1,3-diol) and finally (iii) the cyclization into a 6-membered cyclic carbonate (Und-6CC). The chemical structures of the synthesized Und-6CC, UndC20-b6CC and UndS-b6CC compounds as well as the different intermediates were assessed by NMR and FTIR-ATR spectroscopies.

After optimization of reported conditions on dimethyl sebacate (see ESI), Und-malonate was synthesized at 60°C for 24 hours from methyl undecenoate using 40 eq. of DMC, 2.5 eq. of NaH and 1 eq. of DMF. The conversion of methyl undecenoate into Und-malonate was confirmed by ¹H NMR spectroscopy. After the work up, the percentage of unreacted methyl undecenoate (26.7%) was determined through ¹H NMR. Moreover, the Claisen-condensation side product was detected in proportion between 2.4% and 3% depending on the batch using the optimized conditions. After purification, Und-malonate was isolated with a yield of 58%. Reduction of Und-malonate was carried out under reflux for 2 hours using 4.1 eq. of LiAlH₄ in dried THF (Yield 66%). In FTIR-ATR, the disappearance of the band corresponding to the carbonyl and the appearance of a large band around 3280 cm⁻¹ clearly indicate the reduction of malonate into diol. The synthesis of Und-1,3-diol was also confirmed by ¹H NMR. Cyclization of the Und-1,3-diol into Und-6CC has been managed using ethyl chloroformate and a stoichiometric amount of TEA at room temperature in THF and diluted conditions. This method was preferred over non-phosgene route due to the compared high conversion obtained. However, non-phosgene routes can be also largely feasible as reported in the literature.²⁷⁻³⁵ After the reaction, remaining ethyl chloroformate and Und-1,3-diol (3%) as well as side products formed (16% of dialkyl carbonate obtained by the reaction of Und-1,3-diol and 1 eq. ethyl chloroformate) were removed by flash chromatography. The purity of the final Und-6CC was 99.5% as determined by GC-FID (Yield 75%).



Scheme 1: General synthetic route to Und-6CC, UndC20-b6CC and UndS b6CC, as well as the poly(hydroxyurethane)s syntheses.

The monofunctional Und-6CC was then “dimerized” thanks to the terminal double bond on its long alkyl chain, by metathesis (UndC20-b6CC) or thiol-ene (UndS-b6CC) reactions. These reactions have gained attention in the last decades as green methodologies³⁶⁻³⁸ and were chosen due to the mild conditions required. The Figures 1-(1) to 1-(3) present the stacked ¹H NMR respectively for the purified Und-6CC, UndC20-b6CC and UndS-b6CC. The metathesis reaction of Und-6CC was performed at room temperature in dried pentane with 3rd generation Grubbs catalyst (1/200). The reaction was driven thanks to the precipitation of the formed product. A conversion of 67% was achieved after 4 hours as estimated by ¹H NMR. The product was then purified with flash chromatography using a mixture of cyclohexane and ethyl acetate as eluent (Yield 50%).³⁹ In the line with the environmentally friendly and high efficiency process, the thiol-ene addition, which has already been valorized with vegetable oil derivatives,³⁸ was also carried out to couple Und-6CC. The thiol-ene reaction was carried out under UV irradiations at room temperature. The reaction was monitored with ¹H NMR spectroscopy with the disappearance of the double bond protons. The poor yield (37%) can be explained by the formation of side products presumably by ring opening of the cyclic carbonate by a nucleophile. Indeed, compounds with higher molar masses were present in the crude mixture as observed in SEC. (see ESI).

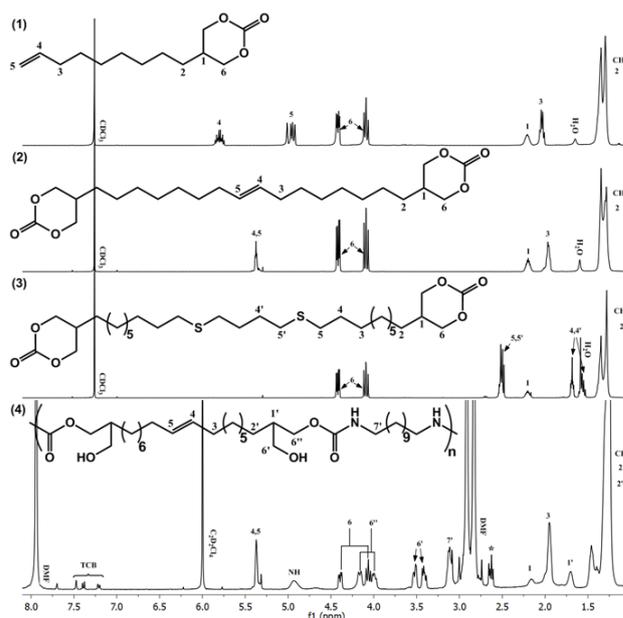


Fig. 2: Stacked ¹H NMR spectra of (1) Und-6CC, (2) UndC20-b6CC, (3) UndS-b6CC (analyses in CDCl₃) and (4) PHU-2 after 6 hours of polymerization (conversion of 76.6%) (analysis in C₂D₂Cl₄). (*) Remaining 12DA.

Cyclic carbonates reactivity toward hexylamine

In order to identify precisely the difference in reactivity between 6-membered and 5-membered cyclic carbonates, the monitoring of the kinetic of the reaction was followed *in situ* by NMR spectroscopy. Various cyclic carbonate substrates such as trimethylene carbonate (6CC), Und-6CC, ethylene carbonate (5CC) and Dec-5CC (obtained by carbonation of 1,2-epoxy-9-decene as a 5-membered ring cyclic carbonate equivalent of Und-6CC) have been investigated on the reaction with hexylamine at 50°C and 1 mol.L⁻¹ in DMSO-d₆, using TCB as internal reference. Otherwise mentioned, the ratio between cyclic carbonate and amine was 1:1 and confirmed by ¹H NMR. In the case of Und-6CC for instance, as the reaction was going, the signals for the protons CH₂-O of the cyclic carbonate at 4.40 ppm and 4.09 ppm decreased. Moreover, three signals at 3.94 ppm (CH₂-OCONH), 3.41 ppm (CH₂-OH) and 2.98 ppm (CH₂-NHCOO), corresponding to the formation of the urethane appeared. Regarding the kinetic reaction order, best fits were obtained considering a second order in all cases (see ESI), as mostly reported in the literature.^{23,40-42} Table 1 gives the estimated initial apparent reaction rate constants (k_{app}) obtained for the different cyclic carbonates.

As reported in the literature,²¹⁻²³ trimethylene carbonate appeared much more reactive than ethylene carbonate (k_{6CC}/k_{5CC}=2.5). In a similar way, Und-6CC demonstrated a higher reactivity than Dec-5CC, with reaction rate constants of 0.93 L.mol⁻¹.h⁻¹ and 0.03 L.mol⁻¹.h⁻¹ respectively (k_{Und-6CC}/k_{Dec-5CC}=31). In the case of 6-membered cyclic carbonate, the effect of an alkyl group with +I inductive effect in β position appears limited since the difference in reactivity between trimethylene carbonate and Und-6CC is quite low. However, the difference between the kinetic curves of ethylene carbonate and Dec-5CC clearly demonstrated the effect of a +I inductive effect substituent in α position on the reactivity of the 5-membered cyclic group. This observation underlined the low reactivity of the usually prepared fatty acid-based 5-membered cyclic carbonates.^{1,2,4} An acceleration (deviation from the 2nd order) was observed with the 6-membered cyclic carbonates

after a certain time (see ESI). On the opposite, a deceleration was observed for the 5-membered cyclic carbonates. These behaviours may be due to the interaction of the formed hydroxy groups with the reactant.

Table 1: Reaction rate constants obtained for the different model reactions at 50°C in DMSO

Cyclic carbonate (CC)	[CC] (mol.L ⁻¹)	T (°C)	k _{app} (L.mol ⁻¹ .h ⁻¹) ^[a]
Und-6CC	1	30	0.46
	1	50	0.93
	1	70	1.92
	0.2	50	0.15
	5	50	1.77
trimethylene carbonate 6CC	1	50	1.41
ethylene carbonate 5CC	1	50	0.56
Dec-5CC	1	50	0.03

[a] Calculated from the kinetics performed in NMR using a second order law. (see ESI for the equations)

The kinetic of the reaction between Und-6CC and hexylamine increases with the reactant concentration and temperature (see ESI). The reaction rate constants are 0.15, 0.93 and 1.77 L.mol⁻¹.h⁻¹ at 0.2, 1 and 5 mol.L⁻¹ respectively. This again testified a complex behavior and additional interactions between amines and/or carbonates with H donors appear to impact the kinetic rate. The reaction rate constants at 30, 50 and 70°C, are 0.46, 0.93 and 1.92 L.mol⁻¹.h⁻¹ respectively for an initial concentration of 1 mol.L⁻¹. From the Arrhenius plot, the activation energy (E_a) can be estimated as 21 kJ.mol⁻¹ for Und-6CC. Moreover, a slight deviation from the 2nd order can be noticed at 5 mol.L⁻¹ and at 70°C. One should note that no urea formation was observed in all these experiments.

Finally the amine ratio has also an influence on the reaction kinetic between Und-6CC and hexylamine. As the starting concentration of amine is higher, the reaction rates increase. (see ESI) This underlines the positive effect of the amine on the kinetic.

Isocyanate free poly(hydroxyurethane)s

PHUs were synthesized from the two bis 6-membered cyclic carbonates: UndC20-b6CC or UndS-b6CC and dodecane-1,12-diamine (12DA) as comonomer. (see Scheme 1) The polymerizations were performed in DMF⁴³ at 1 mol.L⁻¹, at RT or 50°C. PHU formation was confirmed by FTIR-ATR by the appearance of bands at 1686 cm⁻¹ and 1534 cm⁻¹, which correspond to the urethane linkage C=O and CN vibrations respectively. Besides, a large band at 3620 cm⁻¹-3158 cm⁻¹ was attributed to the NH and OH vibrations. The chemical structures of the PHUs were also supported by NMR analyses, as illustrated in Figure 1-(4) for PHU-2. The signals for the protons corresponding to the opening of the 6-membered cyclic carbonate appeared in the ranges 4.00-4.15 ppm and 3.42-3.50 ppm. The formation of the urethane linkage was confirmed by the presence of the signal at 3.11 ppm, which corresponds to the protons CH₂-NHC(O)O of the urethane function.

SEC data in Table 2, indicate the formation of PHUs with molar masses in the range 9 000 to 23 000 g.mol⁻¹ after one day in solvent. As expected, higher molar masses were obtained at 50°C compared to room temperature, which is coherent with the different conversion. Besides, the reactivities of UndC20-b6CC and UndS-b6CC are similar as can be seen in the Table 2. The dispersities were in the range 1.4-1.7 while in step-growth polymerization, the dispersity must theoretically reach 2. Thus by improving the reaction conditions, the molar masses could still be improved. In conclusion, we successfully polymerized in mild conditions (solvent and at low

temperature: RT-50°C) fatty acid-based bis 6-membered cyclic carbonates.

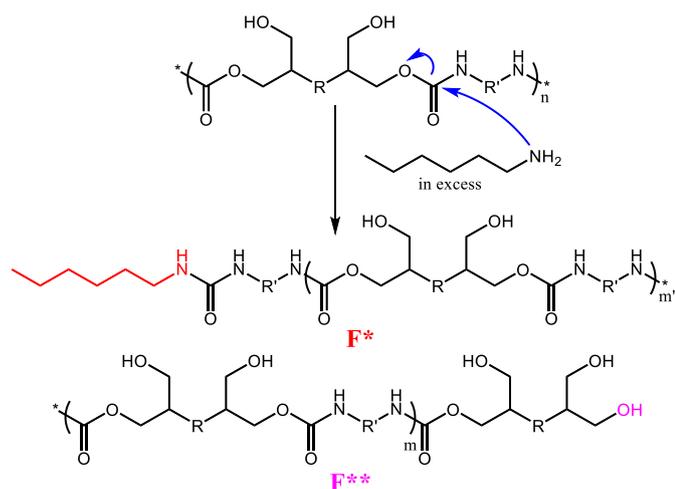
Table 2: Molar masses and dispersity of the PHUs from 6-membered cyclic carbonate polymerized in DMF (1mol.L⁻¹).

PHU	b6CC	T °C	Time	Conv. (%) ^[a]	\bar{M}_n (g.mol ⁻¹) ^[c]	Đ
1	UndC20-b6CC	30	30min	0	3 400	1.0
			4h	1.3	6 700	1.0
			6h	3.3	9 600	1.1
			1d	43.4	8 900 ^[d]	1.2
			2d	89.3	14300 ^[d]	1.4
2	UndC20-b6CC	50	30min	14.0	6 700	1.0
			4h	66.5	9 300 ^[d]	1.2
			6h	76.6	11500 ^[d]	1.2
			8h	83.2	12 800 ^[d]	1.4
			1d	90.3 ²	21600	1.5
2d	-	22300	1.3			
3	UndS-b6CC	50	30min	8.2	7 000	1.0
			4h	46.9	8200 ^[d]	1.0
			6h	63.3	6500	1.0
			8h	73.5	11100 ^[d]	1.2
			1d	90.0 ^[b]	22600	1.7
2d	-	20000	1.4			

[a] Calculated by ¹H NMR. [b] Calculated by FTIR-ATR. [c] SEC in DMF with 1wt% LiBr - calibration PS standards. [d] Multi modal molar masses.

After one day at 50°C, the polymerization mixtures appeared as gels and were not soluble anymore, which can be explained by the formation of side reactions between the hydroxyl groups present in the polymer backbone and the remaining cyclic carbonates. This hypothesis has been confirmed for model compounds trimethylene carbonate and hexylamine, by the detection of side products thanks to ESI-TOF MS, showing the carbonate ring-opening by alcohol (see ESI). Similar side products were detected with the Und-6CC. These carbonate linkages between PHU chains explain the 3D network formation during the bis-carbonate / bisamine polymerization.

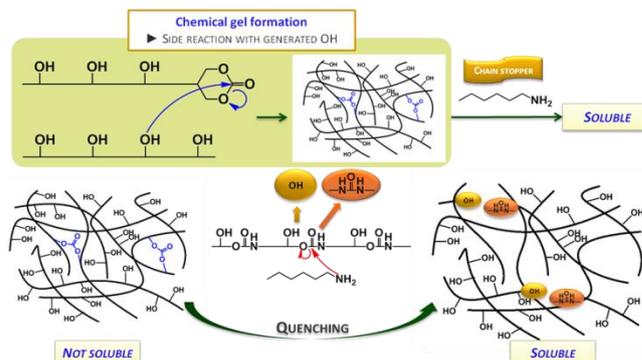
After quenching, the polymerization medium with a large excess of hexylamine, the polymers were surprisingly fully soluble again and MALDI-TOF MS analyses were carried out on the PHUs (Figure 2), (see also ESI for MALDI-TOF MS of quenched PHU-2 and detailed explanations). While analyzing the different signals, three PHU families (F1-3) were detected (see ESI): (F1) terminated with two cyclic carbonates quenched, (F2) with one cyclic carbonate quenched and one amine and (F3) with two amines. In the particular case of PHU-2, the isomerizations that have taken place during the metathesis were clearly visible with peaks sets separated by 14. The repeated unit was clearly visible for both PHU-2 ($M_{unit}=624 + x^*M_{CH_2}$ g.mol⁻¹) and PHU-3 ($M_{unit}=775$ g.mol⁻¹). Moreover, smaller signals assignable to urea side reactions (see Scheme 2) were also observable, corresponding both to the formation of urea (F*) and the generation of the alcohol (F**) from F1 and F2 families. The fact that F3* was not visible confirmed that the side reactions occur during the quenching of the sample and not during the polymerization. These side reactions of trans-urethanization and/or urea formation explained the breaking-up of the chemical gel formed during the polymerization (see Scheme 3).



Scheme 2: Generation of F* and F** from F2 PHU family during the quenching with an excess of hexylamine.

Finally, the PHUs from UndC20-b6CC were amorphous and present glass transition temperatures around 0°C determined by DSC (see

ESI). The PHU from UndS-b6CC was amorphous as well, with a glass transition temperature of -20°C. This lower T_g can be explained by the presence of the sulfur atom, which is known to impart flexibility to the polymer chains. PHUs exhibited degradation temperature up to 310°C under N₂ (see ESI).



Scheme 3: Hypothesis of chemical gel formation and reactions occurring during the quenching allow solubility.

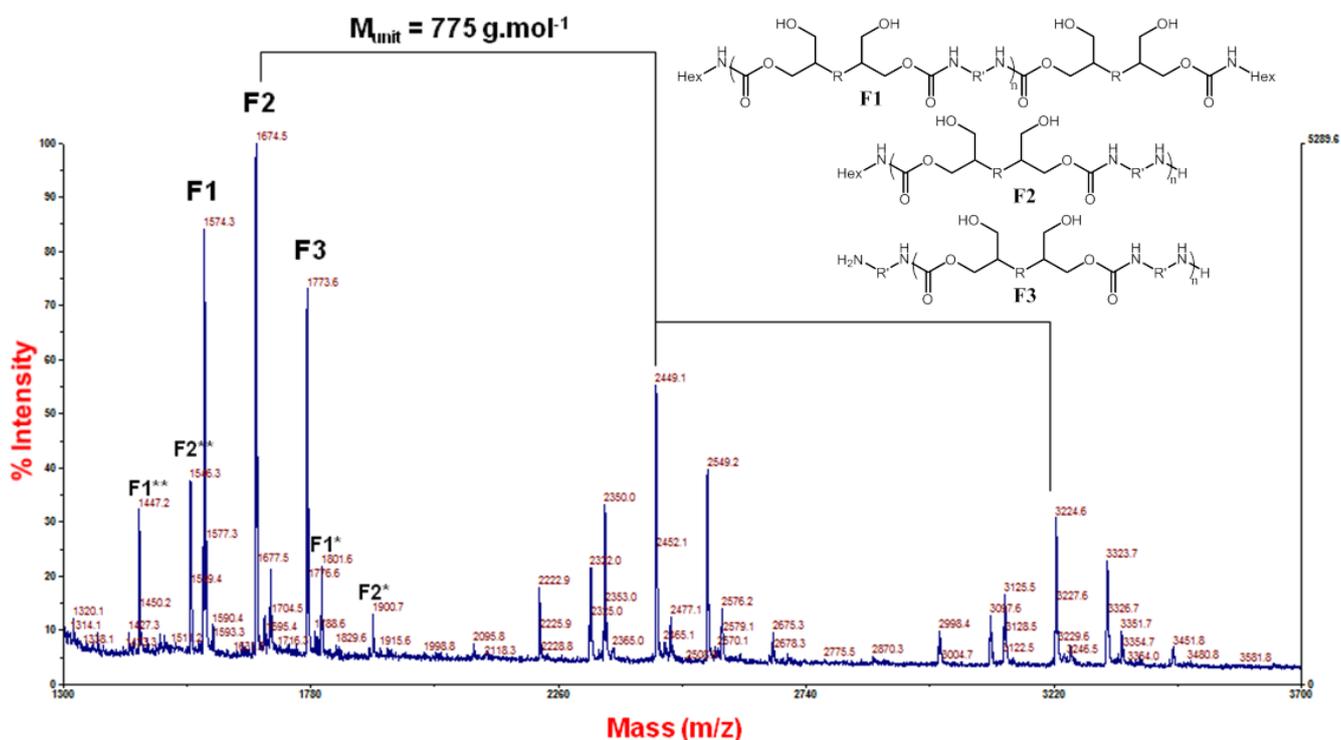


Fig.2: MALDI-TOF MS analysis of the PHU-3 between UndS-b6CC and 12DA. (Matrix trans-3-indoleacrylic acid). (F1) terminated with two cyclic carbonates quenched, (F2) with one cyclic carbonate quenched and one amine and (F3) with two amines

Conclusions

In conclusion, two bis 6-membered cyclic carbonates were synthesized from methyl undecenoate via malonate, 1,3-diol and monofunctional 6-membered cyclic carbonate intermediates. The latter was coupled by metathesis or thiol-ene reactions to produce the two bis 6-membered cyclic carbonates, one with an internal double bond (UndC20-b6CC) or one with sulfur atoms (UndS-b6CC). The model reaction kinetics were performed to validate the higher

reactivity ($k_{\text{Und-6CC}}/k_{\text{Dec-5CC}}=31$) of the fatty acid-based 6-membered cyclic carbonate compared to the 5-membered ones.

The synthesized bifunctional 6-membered cyclic carbonates were effectively used as building blocks for thermoplastic isocyanate free PHUs in combination with dodecane-1,12-diamine as comonomer. Molar masses up to 23 000 g.mol⁻¹ (dispersity of 1.7) were obtained after only one day in DMF (1 mol.L⁻¹) at 50°C. At higher conversion, a chemical gel is obtained probably due to cyclic carbonate ring opening by the formed hydroxide. Finally, results

demonstrated the possibility to break-down this network by adding in second step a mono-amine via urea formation.

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Notes and references

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kinetic was performed in deuterated DMF and showed no dramatic solvent effect on the kinetic (see ESI)

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	page 1
2- Measurements	page 1
3- Experimental protocols	page 4
4- Graphical data	page 9

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 (LiAlH₄) (95%), sodium hydride (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 ¹³C-NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ¹H and ¹³C, respectively) by using CDCl₃ as a solvent at room temperature, except otherwise mentioned. Two-dimensional analyses such as ¹H-¹H COSY (COrrrelation SpectroscopY) and ¹H-¹³C 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 *Iteq* 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 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. 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 Structurale 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

6CC syntheses and characterizations

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%. ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 170.12 (C=O), 139.28 (C=C), 114.32 (C=C), 52.57 (C=O), 51.87 (C-O), 33.89 (C=C), 29.27-27.46 (CH₂). 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 LiAlH₄ (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%. ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 25°C, 100 MHz) δ (ppm): 139.42 (C=C), 114.41 (C=C), 67.02 (C-OH), 42.18 (C-OH), 34.02 (C=C), 30.05-27.44 (CH₂). 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%. ^1H 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 ($\text{C}=\text{CH}_2$), 114.42 ($\text{CH}=\text{C}$), 72.24 ($\text{C}-\text{CH}_2-\text{OCOO}$), 33.84 ($\text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$), 31.39 ($\text{C}-\text{CH}-\text{CH}_2-\text{OCOO}$), 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 driven thanks 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%. ^1H 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 ($\text{CH}=\text{CH}$), 72.22 ($\text{CH}-\text{CH}_2-\text{OCO}$), 32.55 ($\text{C}-\text{CH}_2-\text{CH}=\text{CH}$), 31.32 ($\text{C}-\text{CH}-\text{CH}_2-\text{OCO}$), 29.25-26.68 (CH_2). IR (cm^{-1}): 2918, 2850, 1726. $T_m=59^\circ\text{C}$.

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 ^1H 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%. ^1H 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 (CDCl₃, 25°C, 100 MHz) δ (ppm): 148.71 (OCOO), 72.24 (CH-CH₂-OCO), 32.31 and 31.90 (CH₂-S-CH₂), 31.42 (CH-CH₂-OCO), 29.78 and 26.72 (CH₂-CH₂-S-CH₂-CH₂), 29.60-26.72 (CH₂). IR (cm⁻¹): 2922, 2850, 1750, 1727. T_m=82°C.

Kinetic experiments monitored by ¹H 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 CaH₂ 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 μ L, 0.1 mmol, 0.2 eq.) were added into an NMR tube. The hexylamine (66 μ L, 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. 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. ¹H NMR, ¹³C NMR and IR detail are given below only for the reaction between Und-6CC+hexylamine.

Product of the reaction between Und-6CC+hexylamine: ¹H 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). ¹³C NMR (DMSO-d₆, 70°C, 100 MHz) δ (ppm): 148.72 (OCOO), 139.14 (CH=CH₂), 114.62 (CH=CH₂), 64.62 (CH-CH₂-OCONH), 61.80 (CH-CH₂-OH), 41.83 (OH-CH₂-CH-CH₂-OCONH), 40.8 (CH₂-NHCOO), 33.50 (CH₂-CH=CH₂), 33.65-22.40 (CH₂), 13.94 (CH₃). 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, CO₂ 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 ^1H 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:** ^1H 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 ($\underline{\text{C}}\text{H}=\text{CH}_2$), 114.54 ($\text{CH}=\underline{\text{C}}\text{H}_2$), 77.36 ($\underline{\text{C}}\text{H}-\text{OCOO}$), 69.51 ($\underline{\text{C}}\text{H}_2-\text{OCOO}$), 34.02 ($\underline{\text{C}}\text{H}_2-\text{CH}-\text{OCOO}$), 33.78 ($\underline{\text{C}}\text{H}_2-\text{CH}=\text{CH}_2$), 29.11-28.80 (CH_2), 24.48 ($\underline{\text{C}}\text{H}_2-\text{CH}_2-\text{CH}-\text{OCOO}$). 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]: ^1H 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.

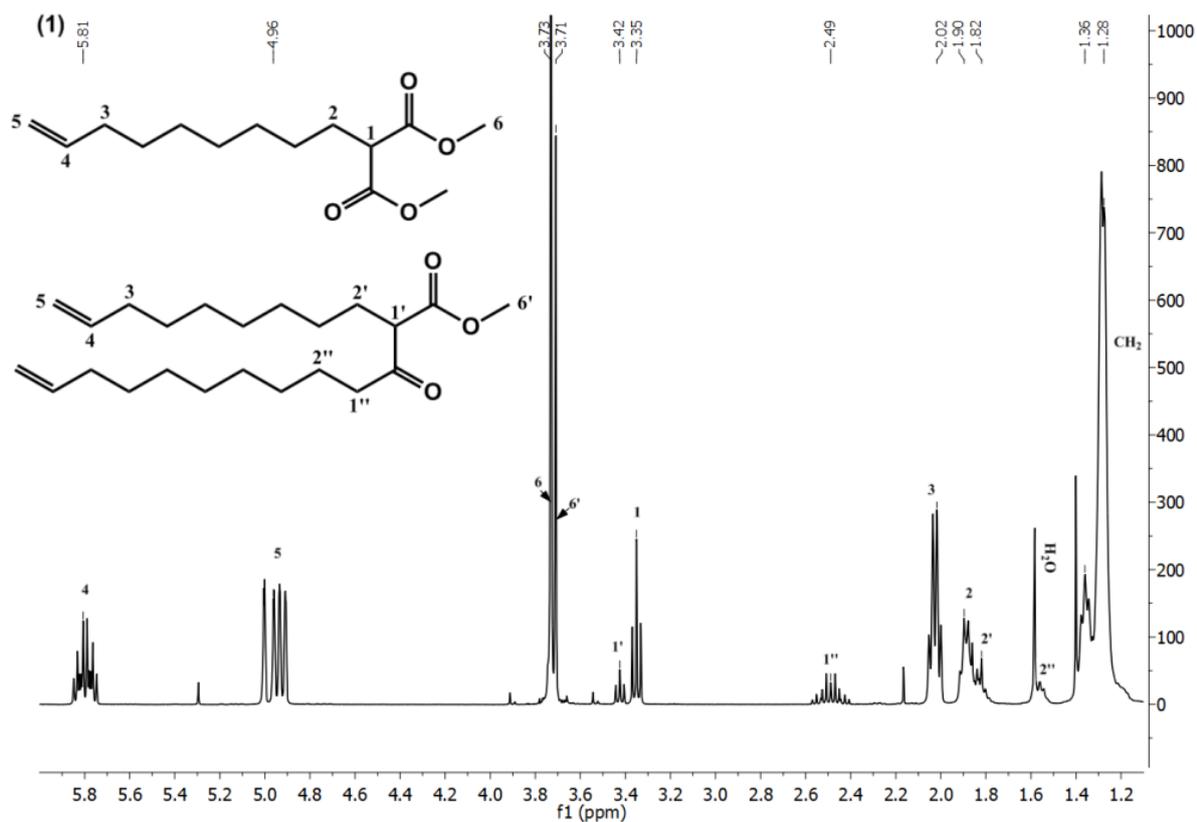
PU-3 [UndS-b6CC+12DA]: ^1H NMR (TCE-d₂, 25°C, 400 MHz) δ (ppm): 4.89 (s, 2.NH), 4.23-4.09 (m, 4H), 3.58-3.49 (m, 4H), 3.17 (m, 4H), 2.57 (m, 8H), 1.77-1.72 (m, 6H), 1.62 (m, 4H), 1.51-1.33 (m, CH_2). IR (cm^{-1}): 3620-3158, 2925, 2852, 1686, 1534.

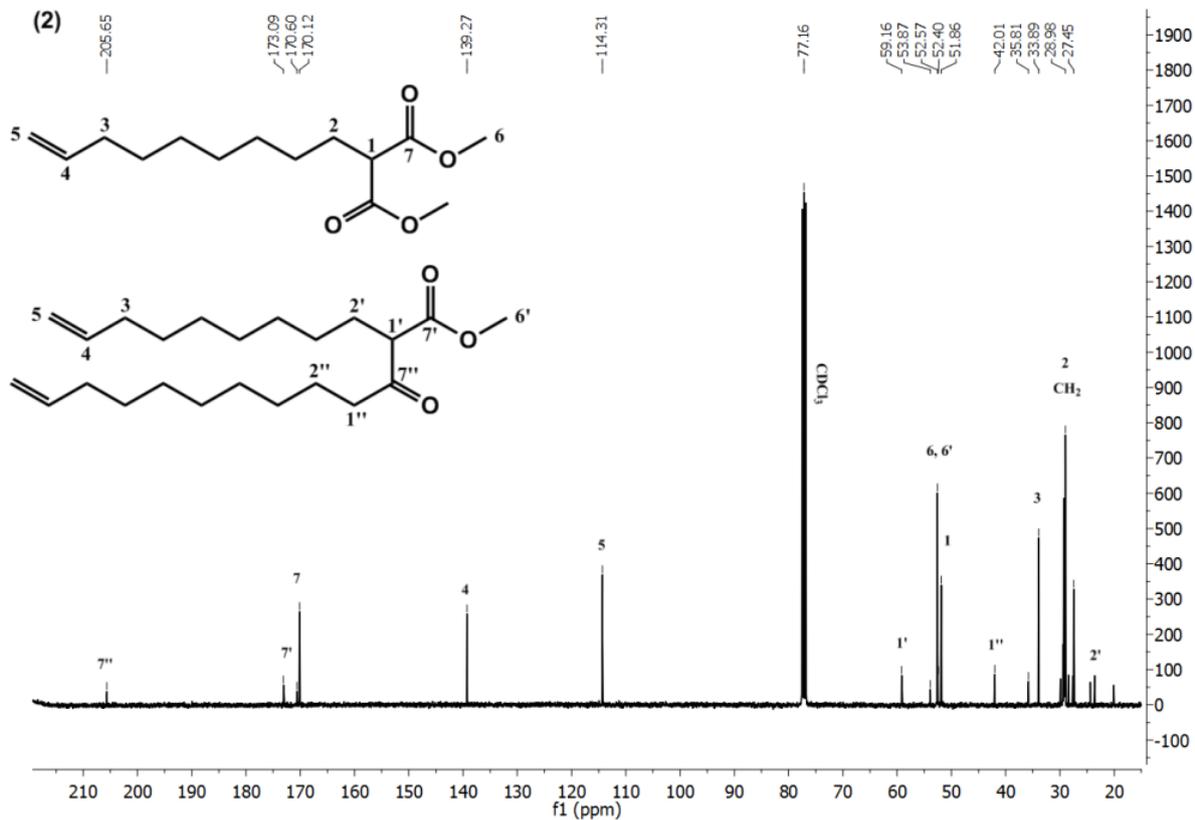
4- Graphical data

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

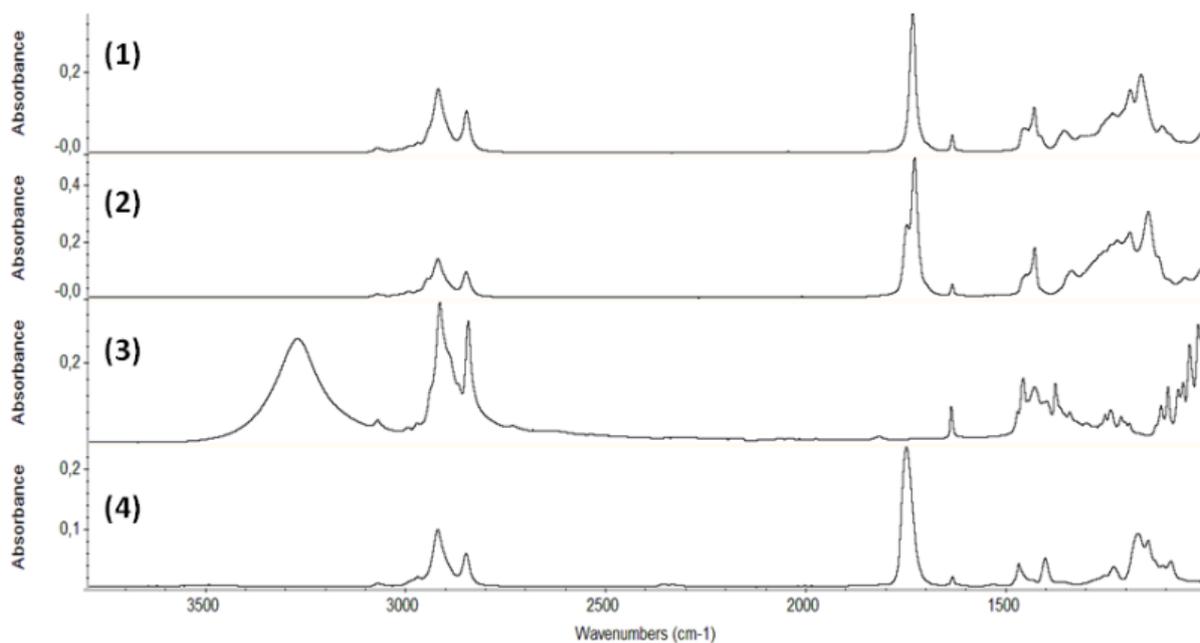
SebDE (eq.)	DMC (eq./ester)	NaH _{60%} disp. (eq.)	DMF (eq./ester)	Time (h)	Malonate conversion ¹
1	20	2.5	1	10	26
1	30	2.5	1	15	50*
1	40	2.5	1	24	80
1	40	2.5	1	40	71

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

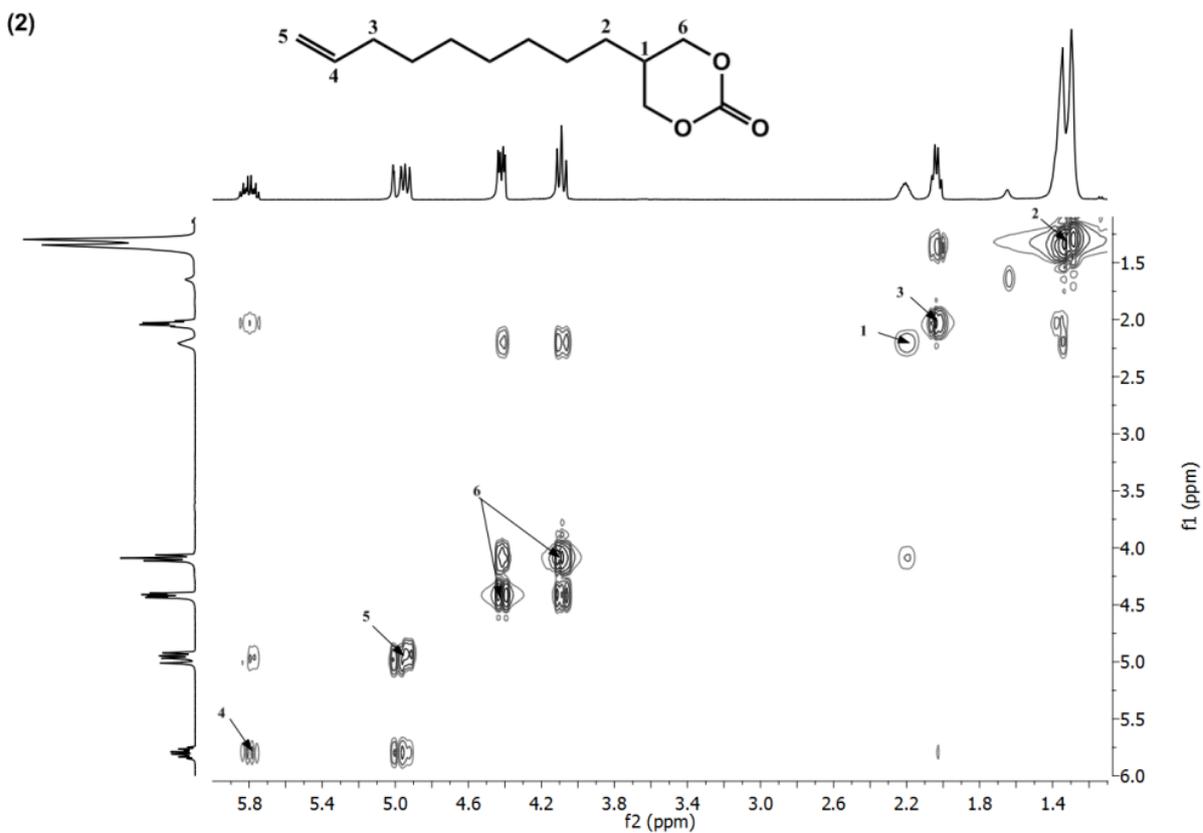
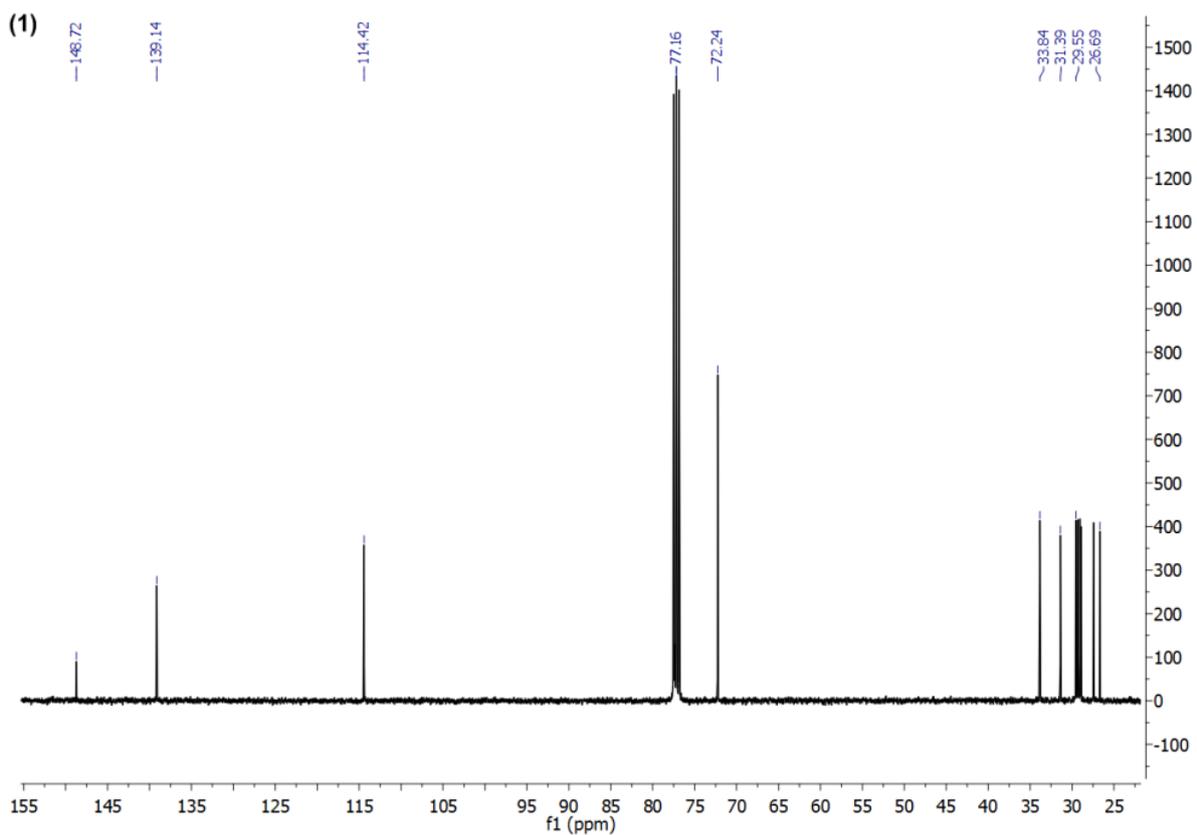




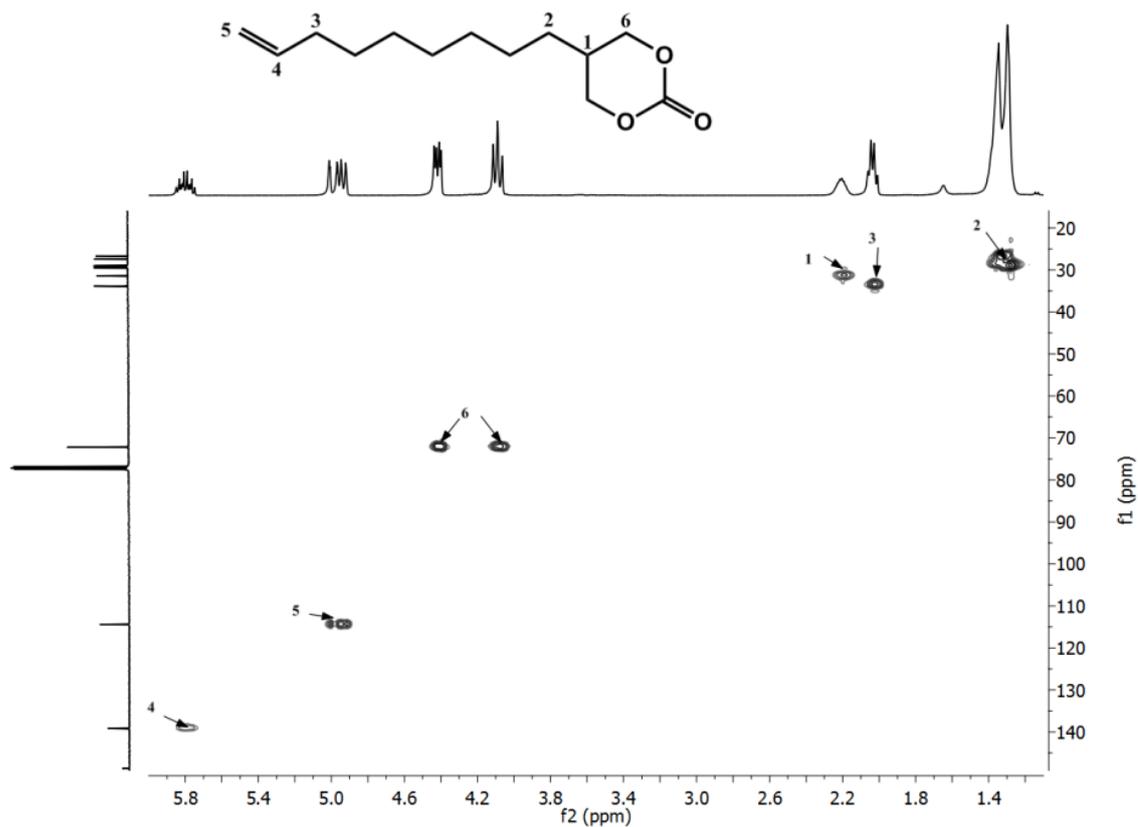
ESI Figure 1- Evidence of the formation of the Claisen-condensation product in a chromatography aliquot: (1) ^1H NMR and (2) ^{13}C NMR.



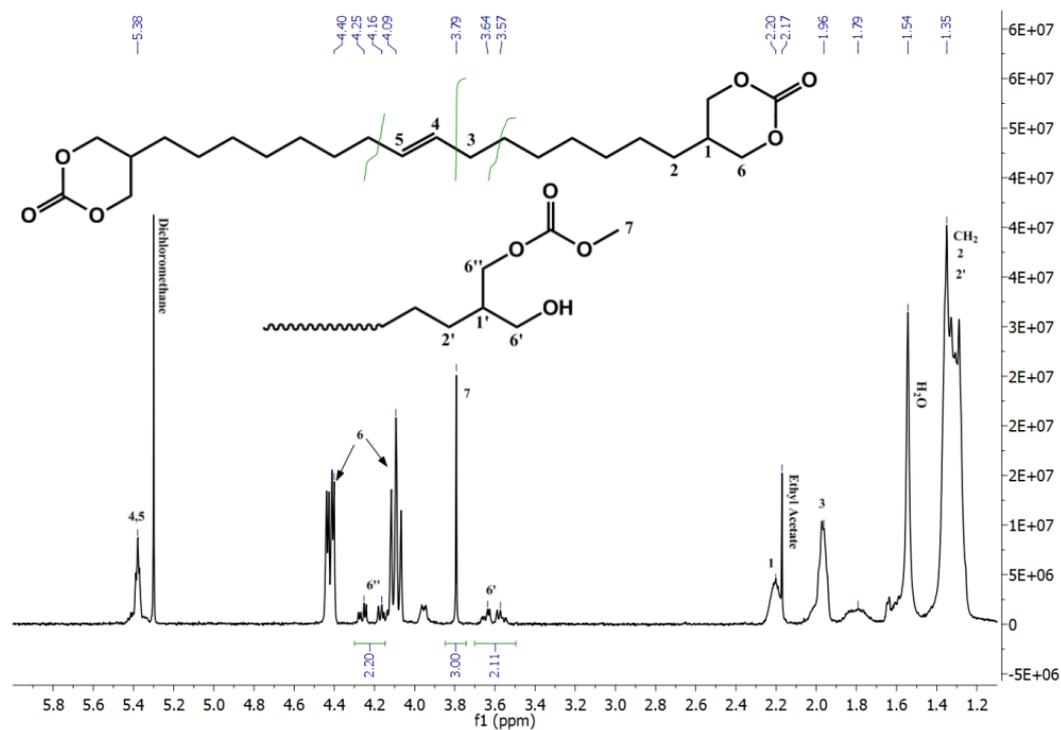
ESI Figure 2- Stacked FTIR-ATR spectra of (1) methyl undecanoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC.



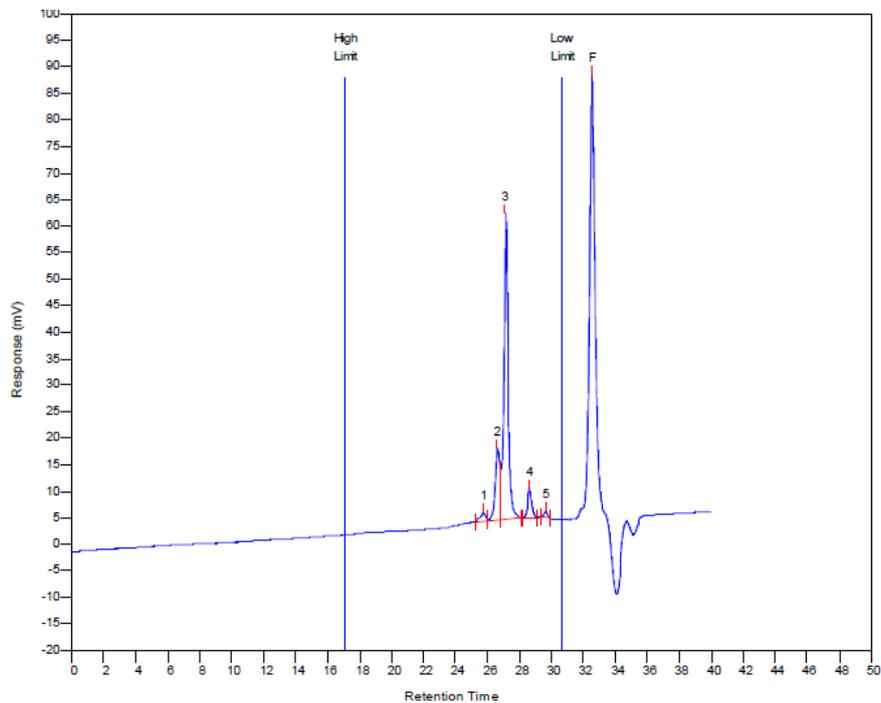
(3)



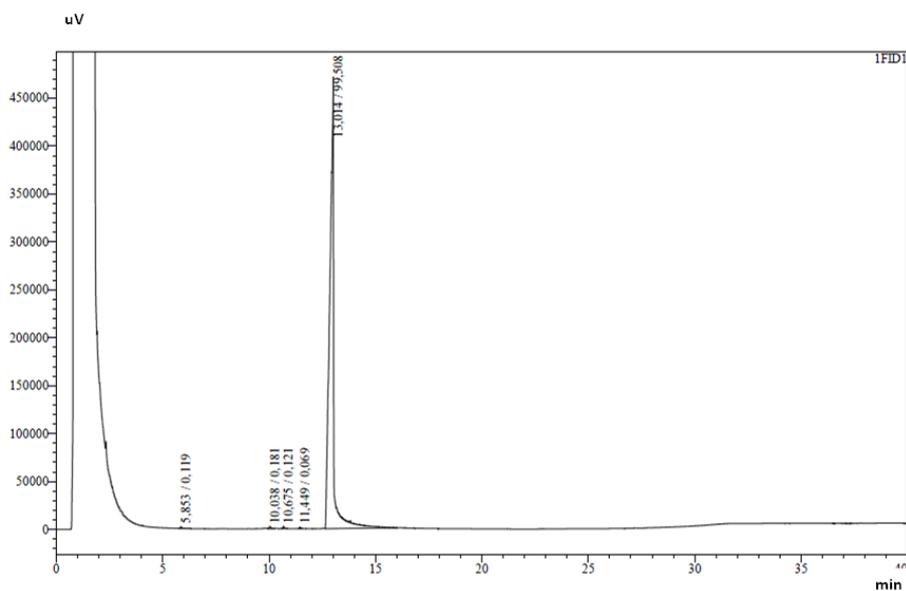
ESI Figure 5- NMR analyses of purified Und-6CC: (1) ^{13}C NMR, (2) ^1H - ^1H COSY 2D-NMR and (3) ^1H - ^{13}C HSQC-NMR.



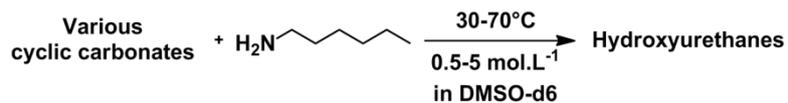
ESI Figure 6- Evidence for the ring opening of the 6-membered cyclic carbonates of UndC20-b6CC while a test of recrystallization in methanol. (Analysis performed in CDCl_3 .)



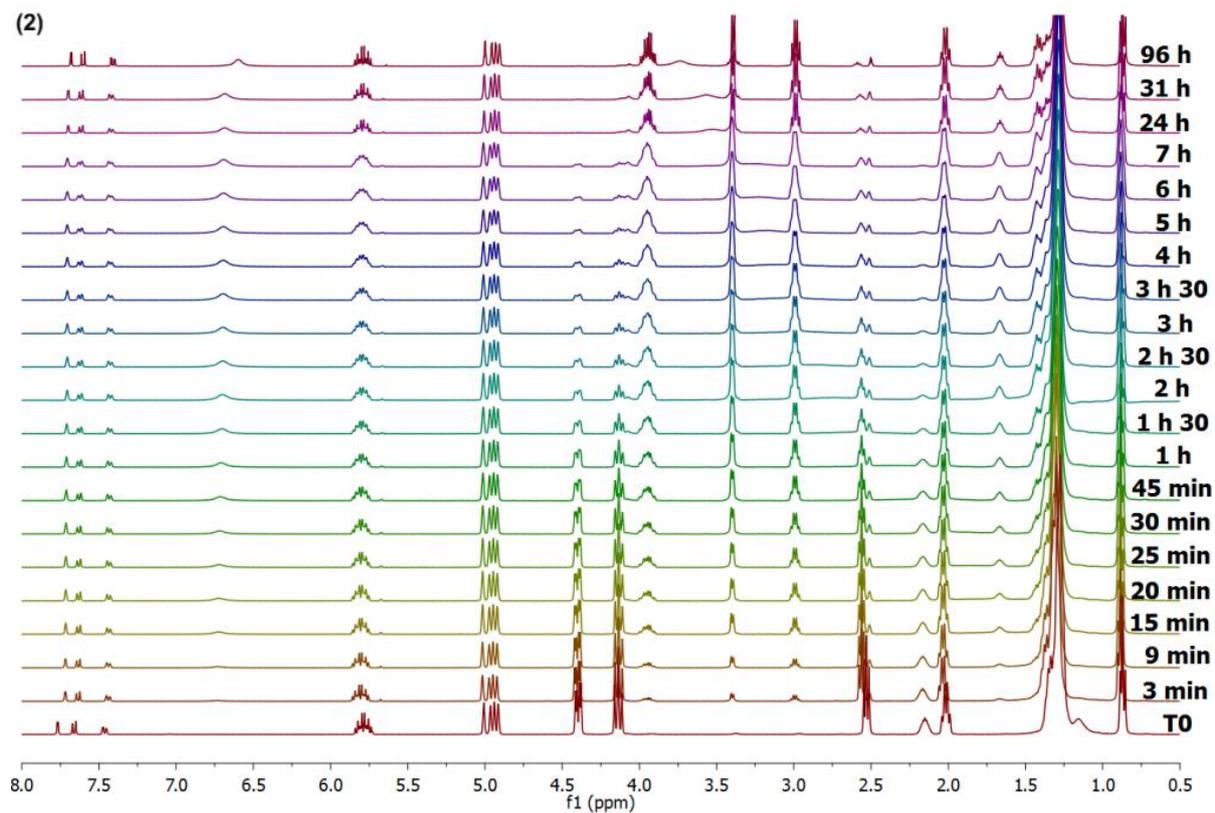
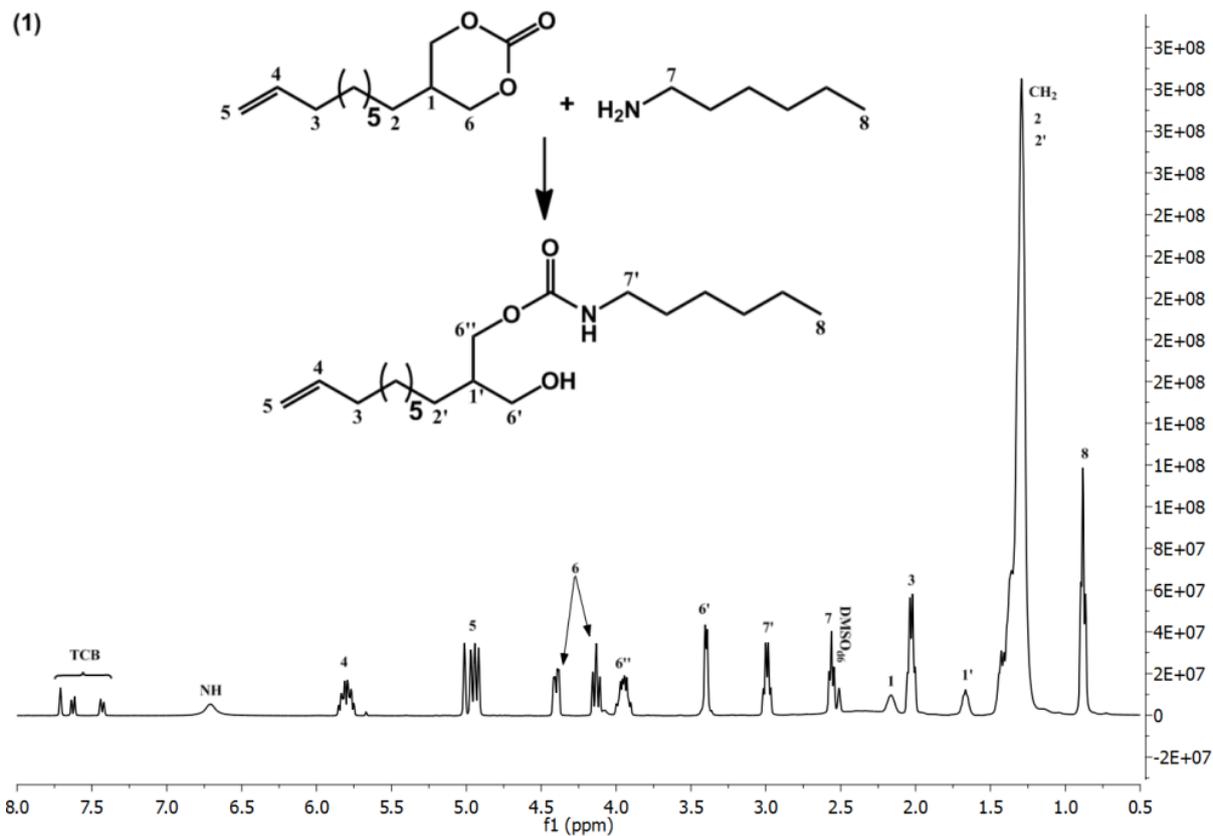
ESI Figure 7- SEC analyses of a flash chromatography aliquot, collected while a test of purification of UndS-b6CC by flash chromatography.



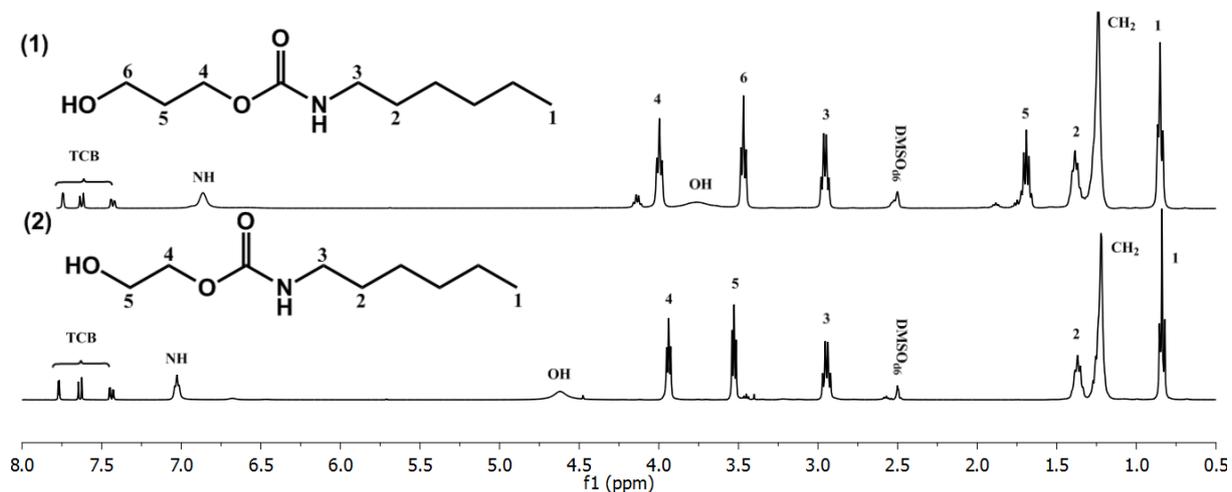
ESI Figure 8- Gas chromatography of Und-6CC.



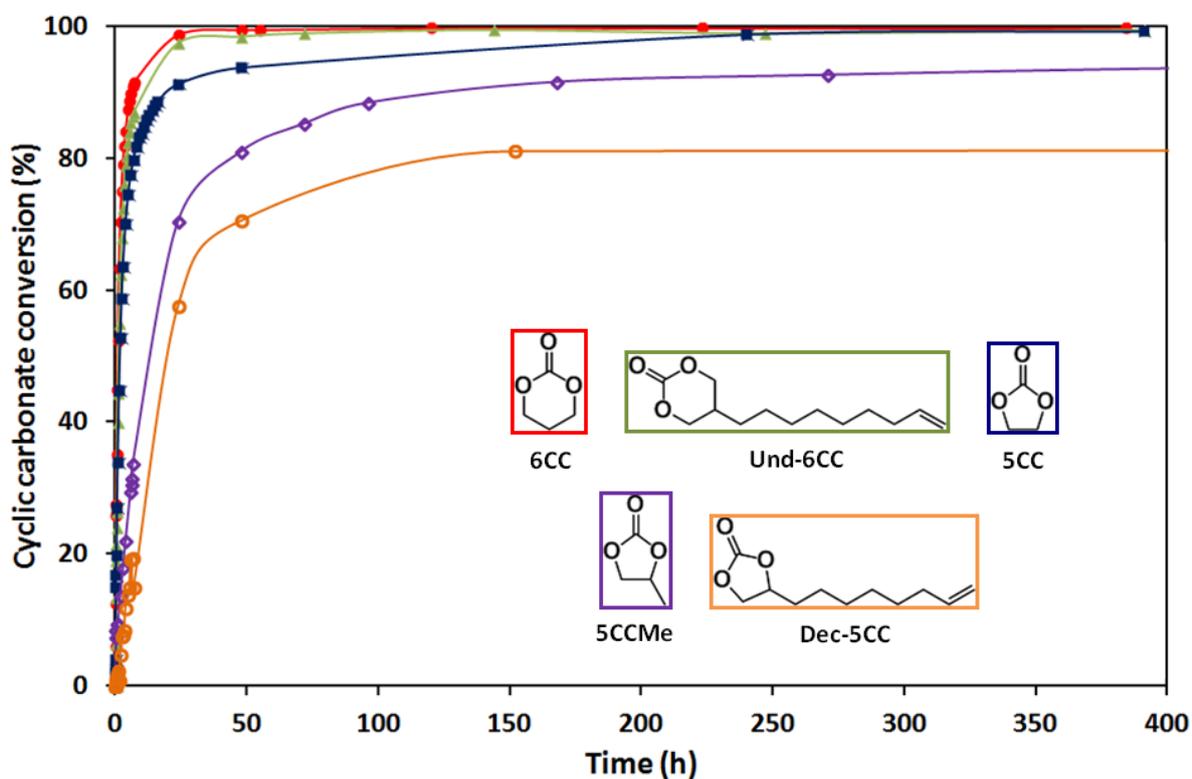
ESI Scheme 1- Model reaction of various cyclic carbonates with hexylamine in different conditions.



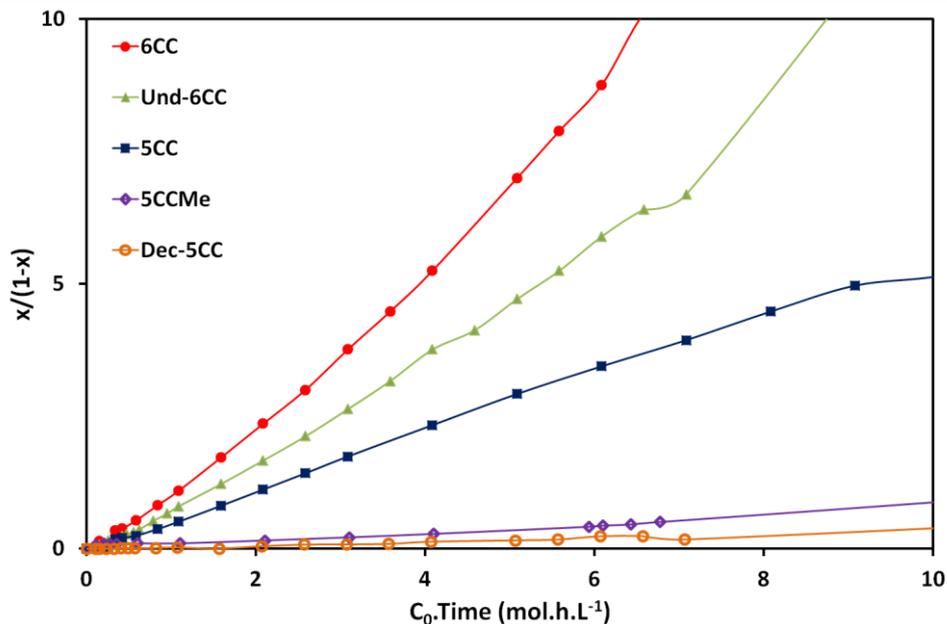
ESI Figure 9- Reaction between Und-6CC and hexylamine at 70°C in DMSO-d₆ at 1 mol.L⁻¹, with a ratio 1:1. (1) ^1H NMR after 1 hour and (2) Stacked ^1H NMR monitoring.



ESI Figure 10- Stacked ^1H NMR of the different model reaction performed with hexylamine at 50°C in DMSO-d_6 at 1 mol.L^{-1}
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-d_6 , 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).

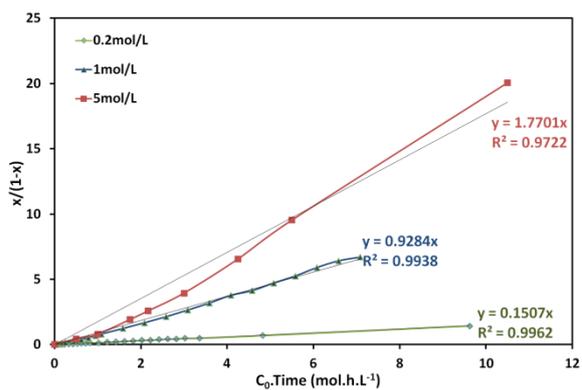
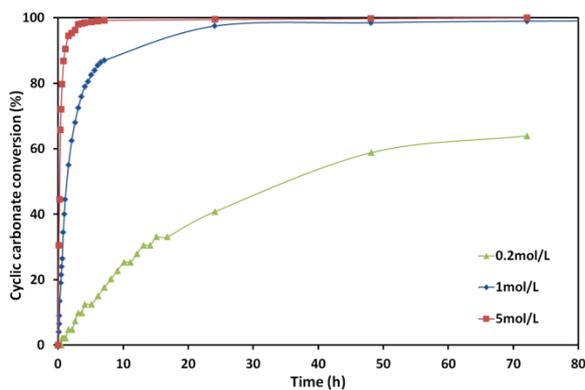
$$-\frac{d[CC]}{dt} = k_{app}[CC][A] = k_{app}[CC]^2 \quad (E1)$$

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

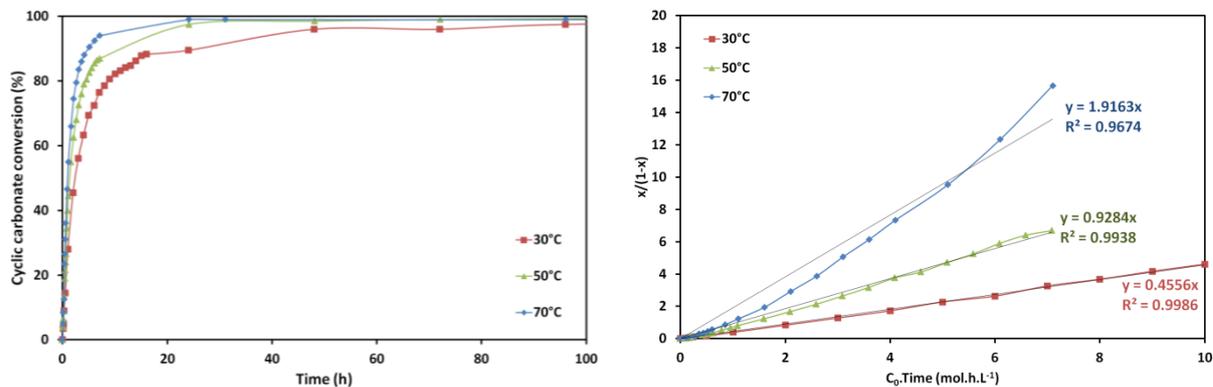
$$\frac{1}{[CC]} - \frac{1}{c_0} = k_{app}\Delta t \quad (E3)$$

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

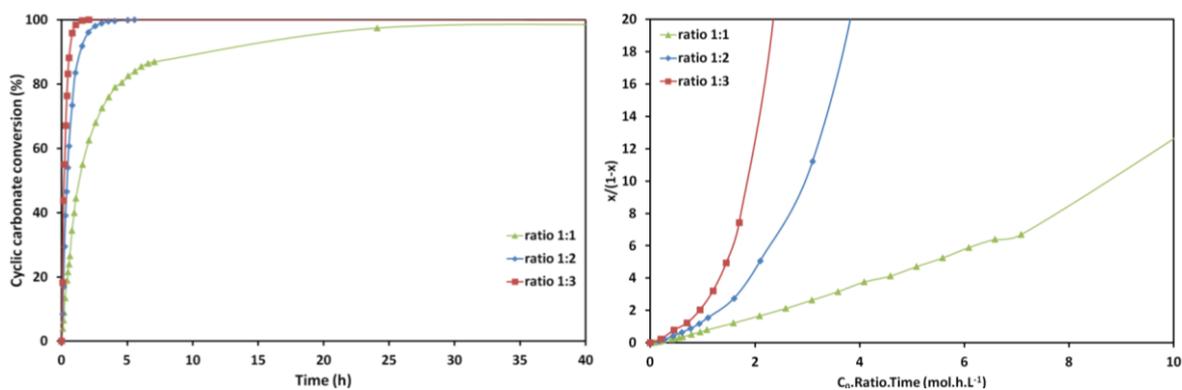
$$\frac{x}{1-x} = k_{app}C_0\Delta t \quad (E5)$$



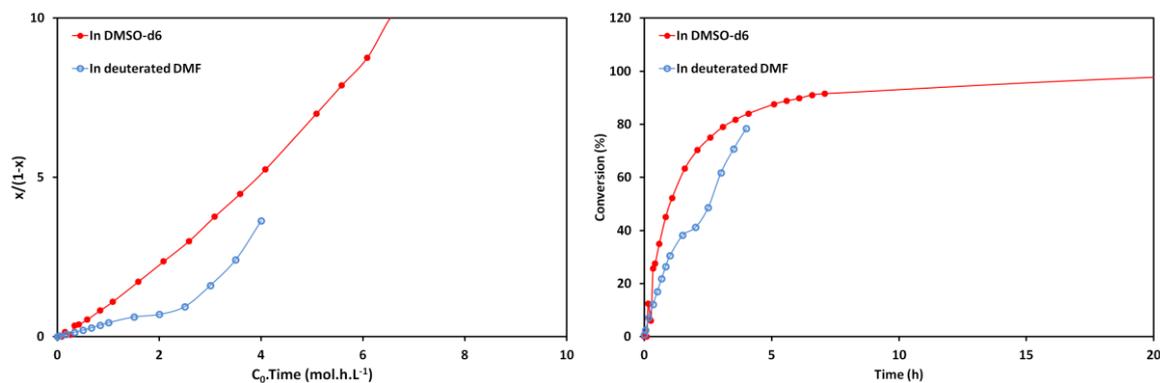
ESI Figure 13- Effect of the reactant concentrations on the kinetic of the reactions between Und-6CC and hexylamine. (50°C, in DMSO-d6, ratio 1:1)



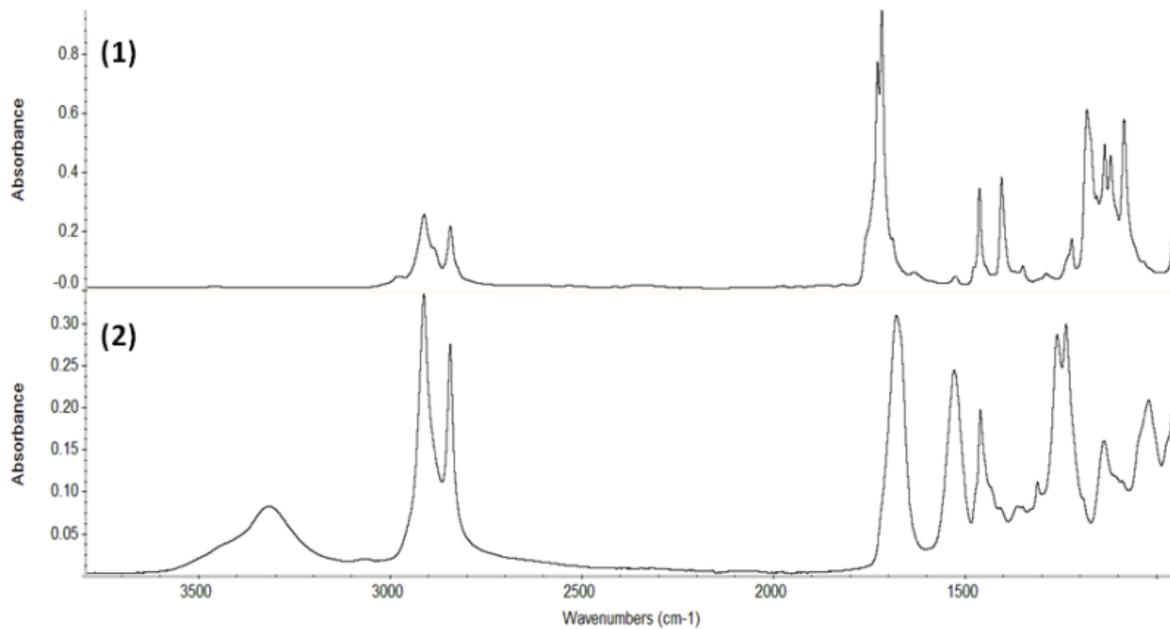
ESI Figure 14- Effect of the temperature on the kinetic of the reactions between Und-6CC and hexylamine. (1 mol.L⁻¹ in DMSO-d₆, ratio 1:1)



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)

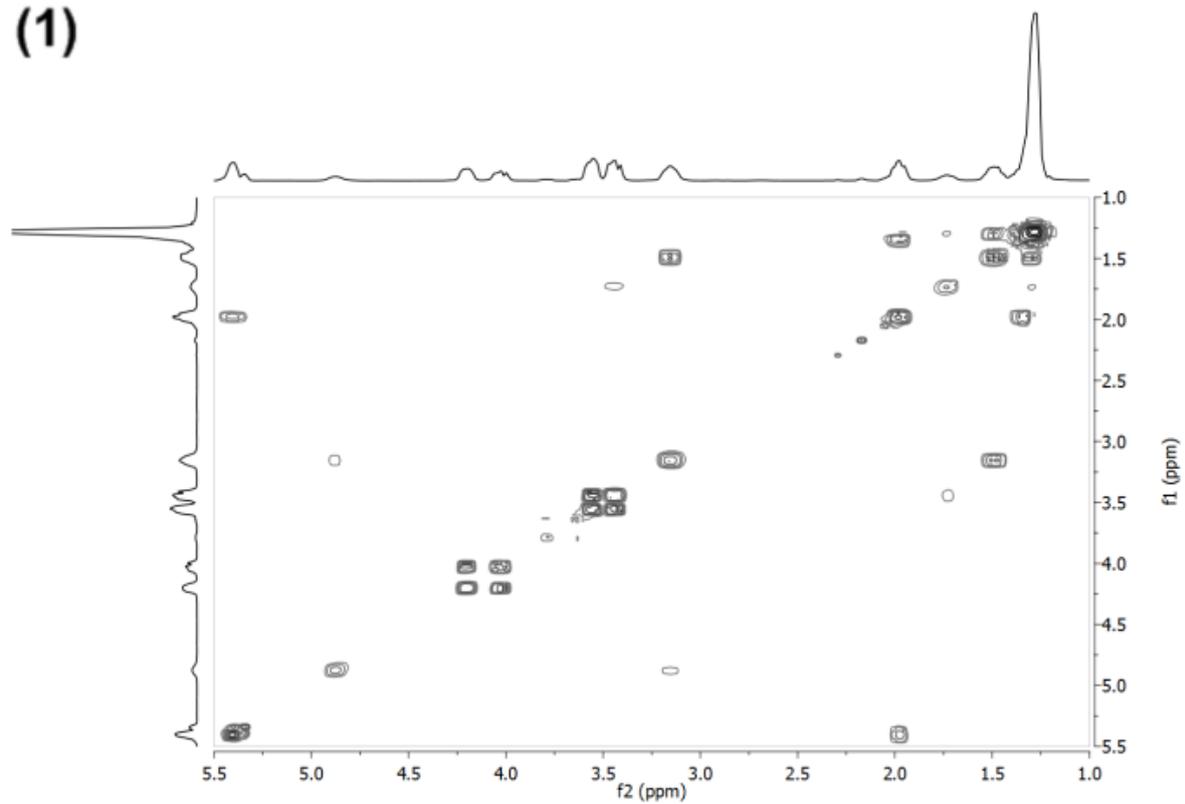


ESI Figure 16- No dramatic solvent effect on the kinetics as demonstrated from the reactions between trimethylene carbonate (6CC) and hexylamine in deuterated DMSO or DMF.

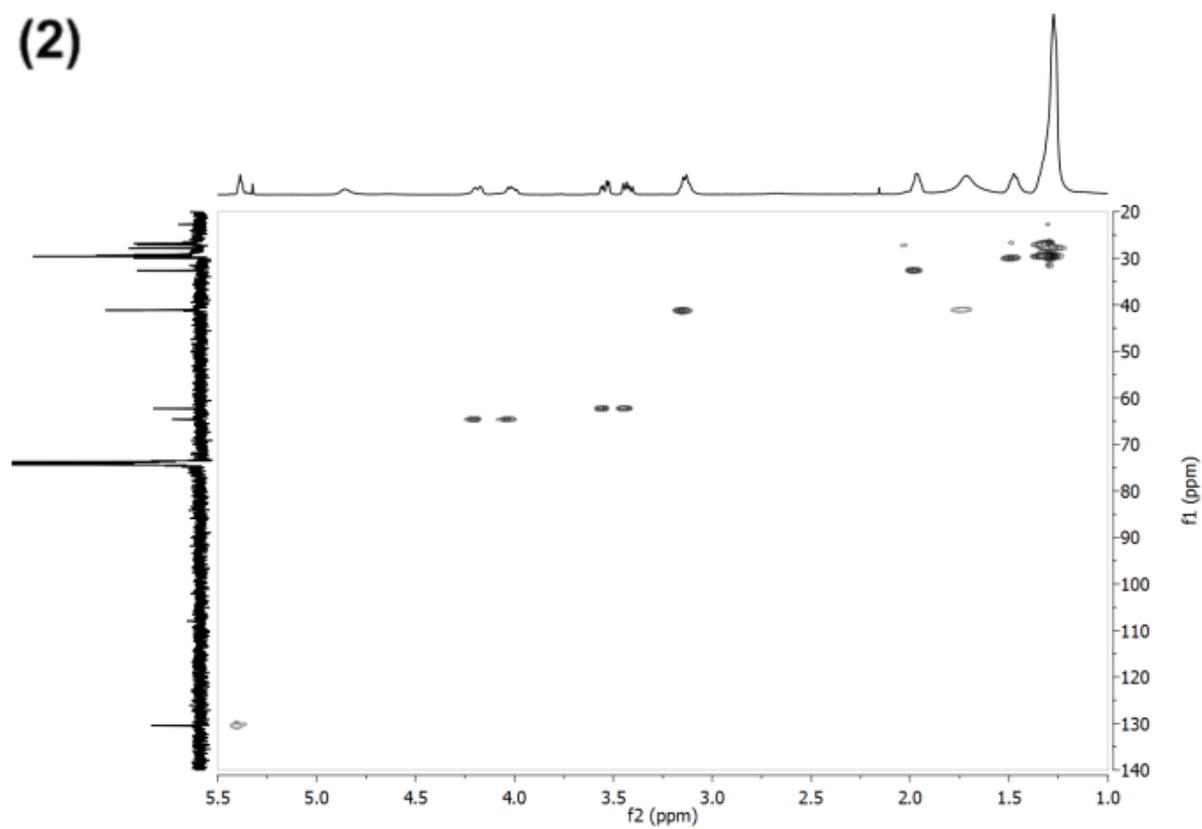


ESI Figure 17- Stacked FTIR-ATR spectra of (1) UndC20-b6CC and (2) the corresponding poly(hydroxyurethane)s with dodecane-1,12-diamine (PHU-2).

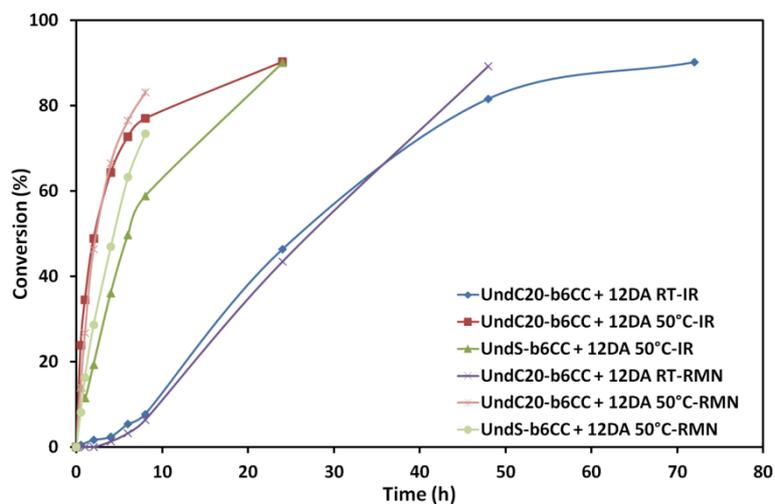
(1)



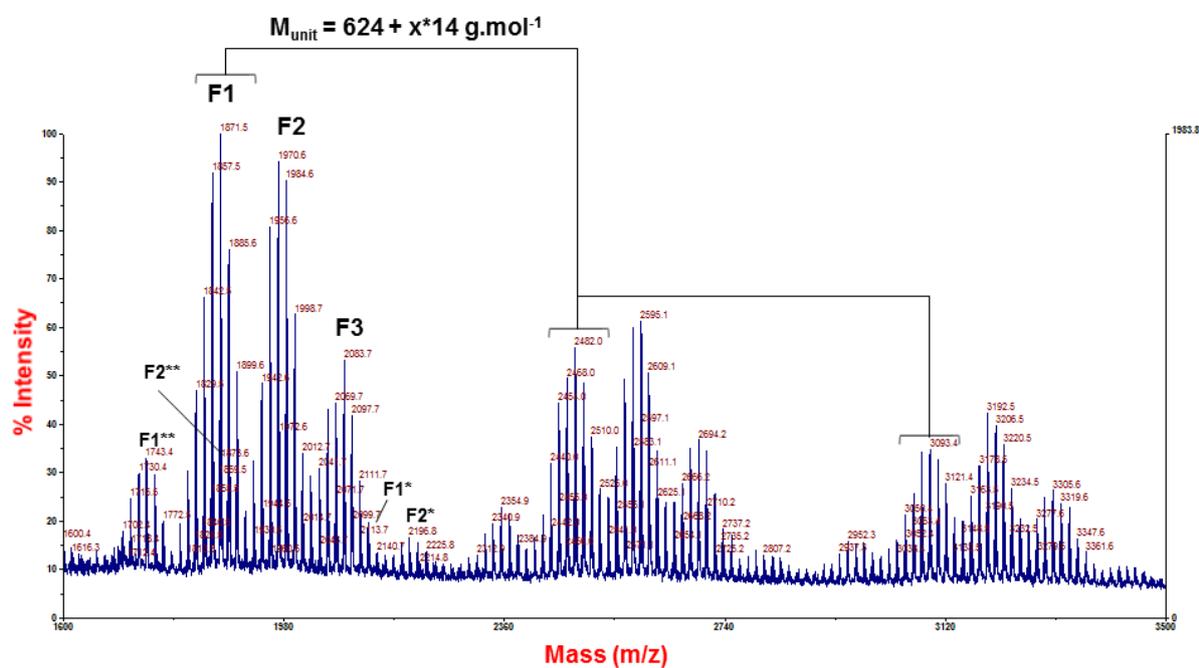
(2)



ESI Figure 18-(1) ^1H - ^1H COSY and (2) ^1H - ^{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 ¹H NMR for UndC20-b6CC and UndS-b6CC with dodecane-1,12-diamine.

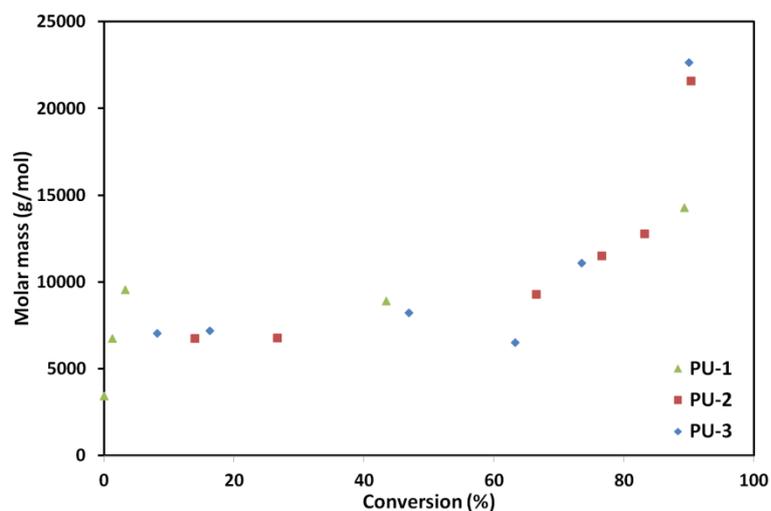


ESI Figure 20- MALDI-TOF MS analysis of PHU-2 between UndC20-b6CC and 12DA. (Matrix trans-3-indoleacrylic acid)

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

PHU families	Description	For PHU-2 ($M_{\text{unit}} = 624 + x \cdot M_{\text{CH}_2} \text{ g.mol}^{-1}$) {M th vs M exp}	For PHU-3 ($M_{\text{unit}} = 775 \text{ g.mol}^{-1}$) {M th vs M exp}
F1	hex-C-(C _{n-1} -A _n)-C-hex	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{Na}}$ {n=3 no isomerization (1898,53 vs 1899.6)}	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{Na}}$ {n=2 (1574.14 vs 1574.3)}
F2	hex-C-(C _n -A _n)-A	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{Na}}$ {n=3 no isomerization (1997,64 vs 1998.7)}	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{Na}}$ {n=2 (1673.25 vs 1674.3)}
F3	A-(C _{n+1} -A _n)-A	$(n+1) \cdot (M_{\text{unit}}) + M_{12\text{DA}} + M_{\text{Na}}$ {n=3 no isomerization (2096,75 vs 2097.7)}	$(n+1) \cdot (M_{\text{unit}}) + M_{12\text{DA}} + M_{\text{Na}}$ n=2 (1772.36 vs 1773.6)
F1*	hex-C-(C _{n-1} -U ^A -A _n)-C-hex	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$ {n=3 minus 1 CH ₂ (2110,73 vs 2113.7)}	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-b6CC}} + 2 \cdot M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$ n=2 (1800.34 vs 1801.6)
F2*	hex-C-(C _n -U ^A -A _n)-A	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$ {n=3 no isomerization (2223,84 vs 2225.8)}	$(n+1) \cdot (M_{\text{unit}}) + M_{\text{hex}} + M_{\text{urea}} + M_{\text{Na}}$ n=2 (1899.45 vs 1900.7)
F1**	hex-C-(C _{n-1} -A _n)-C ^{OH}	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-6CC/OH}} + M_{\text{hex}} + M_{\text{Na}}$ {n=3 no isomerization (1770,42 vs 1772.5)}	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-6CC/OH}} + M_{\text{hex}} + M_{\text{Na}}$ n=2 (1446.03 vs 1447.2)
F2**	C ^{OH} -(C _n -A _n)-A	$n \cdot (M_{\text{unit}}) + M_{\text{UndC20-CC/OH}} + M_{12\text{DA}} + M_{\text{Na}}$ {n=3 no isomerization (1869,53 vs 1871.5)}	$n \cdot (M_{\text{unit}}) + M_{\text{UndS-6CC/OH}} + M_{12\text{DA}} + M_{\text{Na}}$ n=2 (1545.14 vs 1546.3)

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



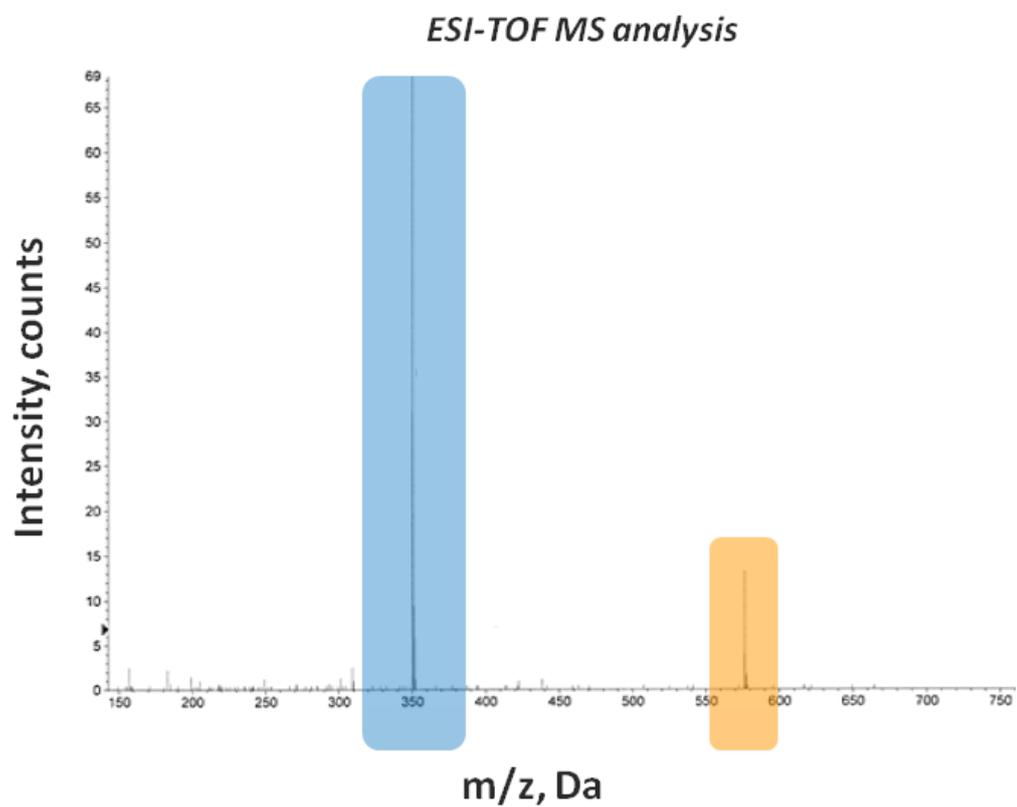
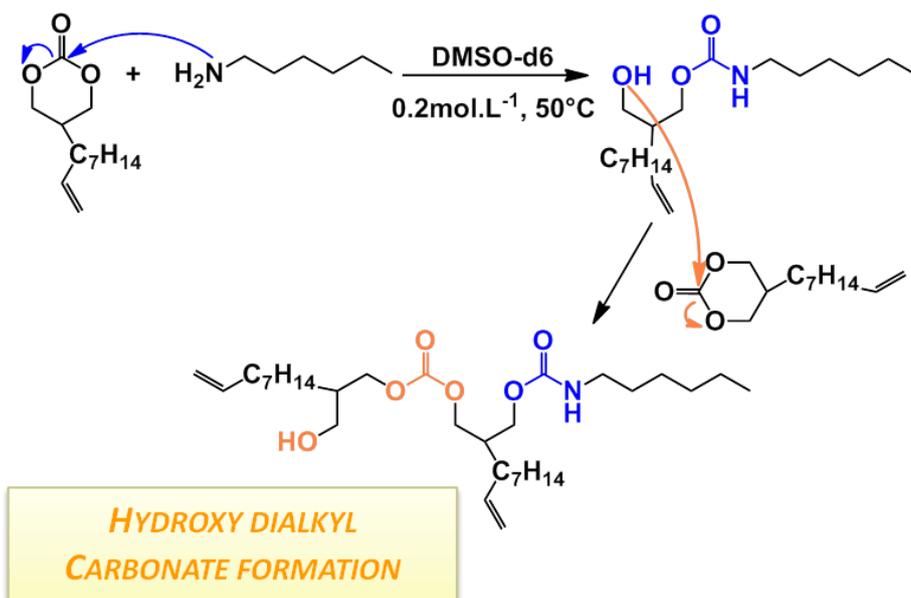
ESI Figure 21- Evolution of the molar masses with the conversion for PHU-1, PHU-2 and PHU-3.

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

Sample	T_g ($^{\circ}\text{C}$) ¹	$T_{5\%}$ ($^{\circ}\text{C}$) ²
PHU-1	-0.3	254
PHU-2	-0.6	271
PHU-3	-20	313

(1) Determined by DSC at $10^{\circ}\text{C}\cdot\text{min}^{-1}$.

(2) Determined by TGA at $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen.



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