SUPPLEMENTARY INFORMATION

Novel green fatty acid based-bis cyclic carbonates to isocyanate free poly(hydroxyurethane amide)s

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Supplemental Information Contents

1- Materials

Methyl 10-undecenoate (>96.0%), butane-1,4-diamine (4DA, 99%) and 1,3-bis[3,5-bis(trifluoromethyl)phenyl]thiourea (Schreiner catalyst, >98%) were supplied by TCI, Europe. The 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), 3-chloroperbenzoic acid (≤77%), tetrabutylammonium bromide (TBABr, >98%) and poly(propylene glycol) bis(2-aminopropyl ether) (Jeffamine, $\bar{M}_n$=400 g.mol^{-1}) were obtained from Sigma-Aldrich. The 1,3-propanediol (99%), dimethyl, piperazine (Pip, anhydrous, 99%), N,N'-dimethylpropane-1,3-diamine (PMe, 97%), sebacoyl chloride (97%) and 1,4-butanediol (99%) were purchased from Alfa Aesar. Isophorone diamine (IPDA, >99%) was obtained from Fisher. The dimer fatty acid-based diamine (Priamine 1075) was purchased from CRODA. The catalyst 1-methyl-3-methylimidazolium iodide salt (MMII) was purchased from Solvionic and the 1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide (TBD.HBr) was synthesized by our partners from the research group of Landais and coll. (S. Foltran, J. Alsarraf, F. Robert, Y. Landais, E. Cloutet, H. Cramail and T. Tassaing, *Catalysis Science & Technology*, 2013, **3**, 1046-1055.) 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

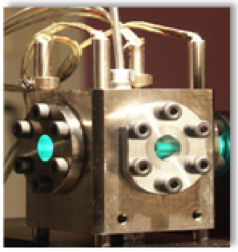
2.1- Nuclear Magnetic Resonance (NMR) analysis

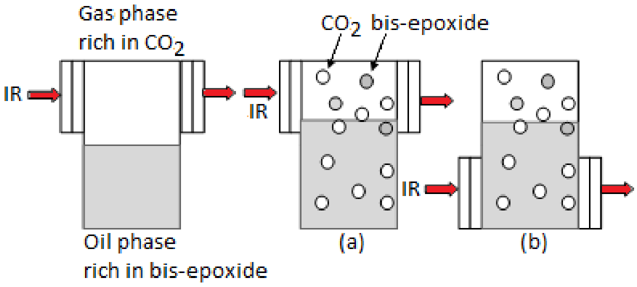
^{1}H and ^{13}C-NMR spectra were recorded on Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ^{1}H and ^{13}C, respectively) by using $CDCl_3$ as a solvent at room temperature, except otherwise mentionned. Two-dimensional analyses such as ^{1}H-^{1}H COSY (Homonuclear correlation Spectroscopy) and ^{1}H-^{13}C HSQC (Heteronuclear single quantum coherence) 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- Kinetic experiments monitored by in-situ FTIR of the carbonation reaction (ISM)





The in situ infrared absorption measurements were performed at the *Institut des Sciences moléculaires (ISM)* on a Biorad interferometer (type FTS-60A) equipped with a globar as the infrared source, a KBr/Ge beam splitter and a DTGS (deuterated triglycine sulfate) detector in order to investigate the spectral range 400–6000 cm^{-1}. Single beam spectra recorded with a 2 cm^{-1} resolution were obtained after the Fourier transformation of 50 accumulated interferograms. The kinetic studies of the carbonation reaction were performed using the ISM home-made stainless steel cell equipped with two cylindrical germanium windows with a path length of 100 µm in order to measure the infrared spectra in the wavenumber range extending from 700 to 5000 cm^{-1}. Heating was achieved by using four cartridge heaters distributed throughout the body of the cell. Two thermocouples were used, the first one located close to a cartridge heater for the temperature regulation and the second one close to the sample area to measure the temperature of the sample with an accuracy of about 2°C. The cell was connected *via* a stainless steel capillary to a hydraulic pressurizing system which allows the pressure to be raised up to 50 MPa with an absolute uncertainty of ± 0.1 MPa and a relative error of ±0.3%.

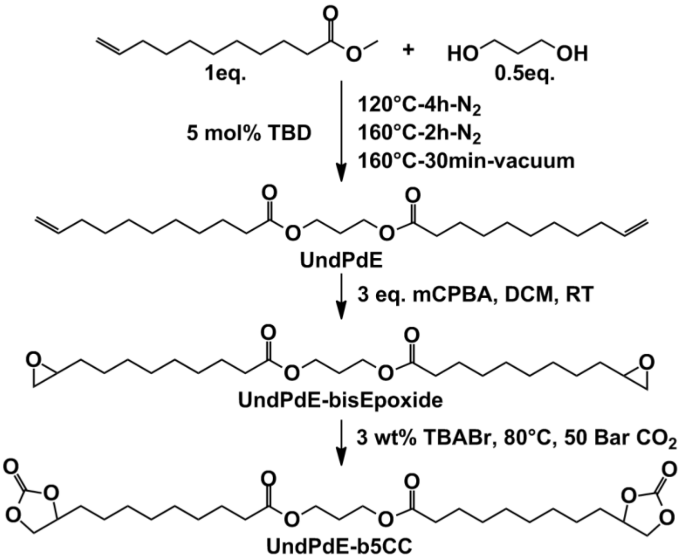
2.4- Size exclusion chromatography (SEC)

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 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)). The elution times of the filtered samples were monitored using RI detectors.

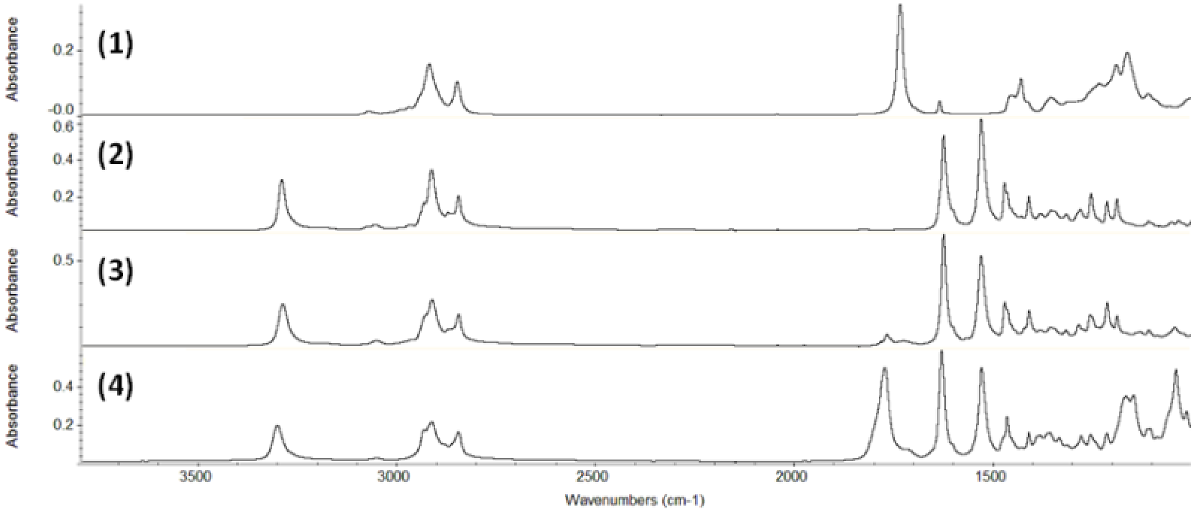
2.5- Differential Scanning Calorimetry (DSC)

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.

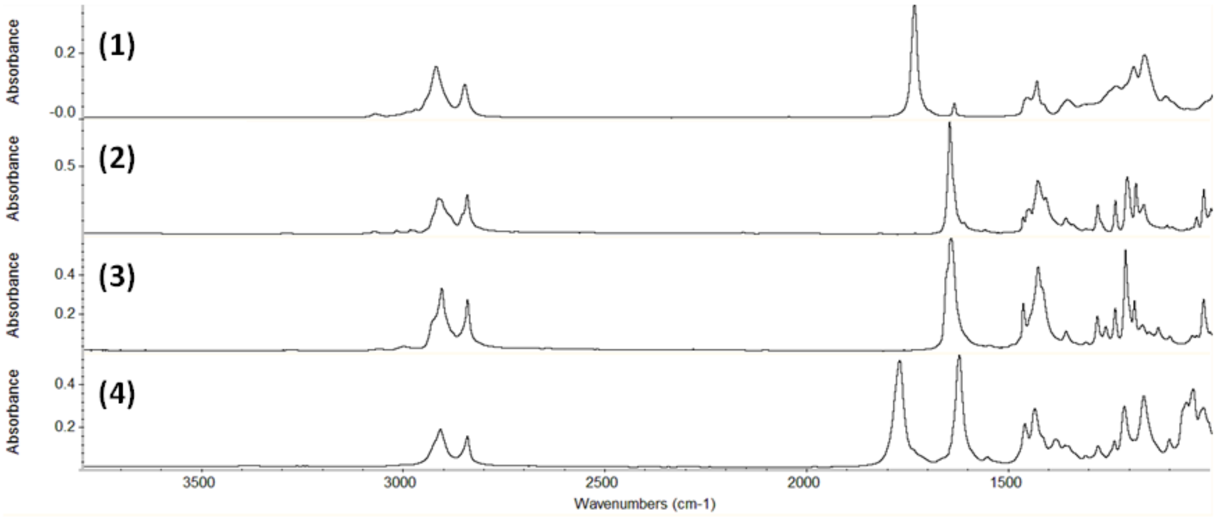
3- Graphical data



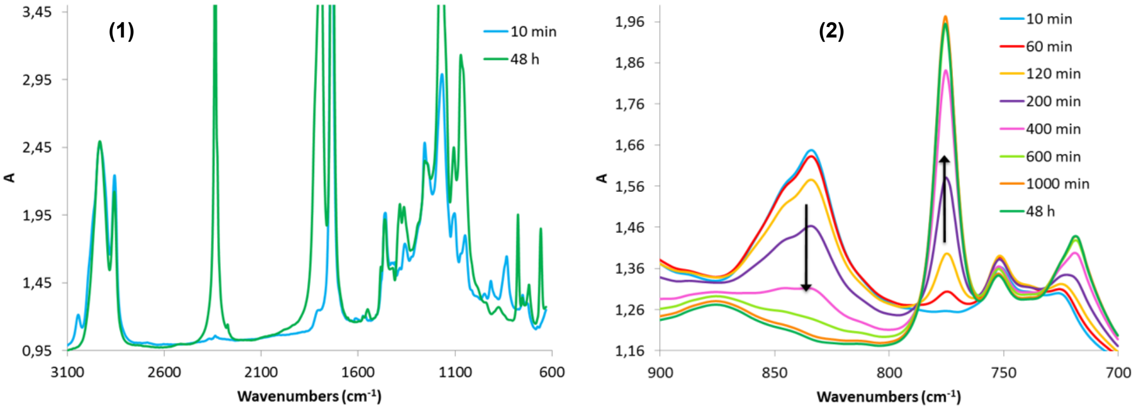
ESI Scheme 1- Synthetic pathway to UndPdE-b5CC from methyl undecenoate, 1,3-propanediol and CO_2.



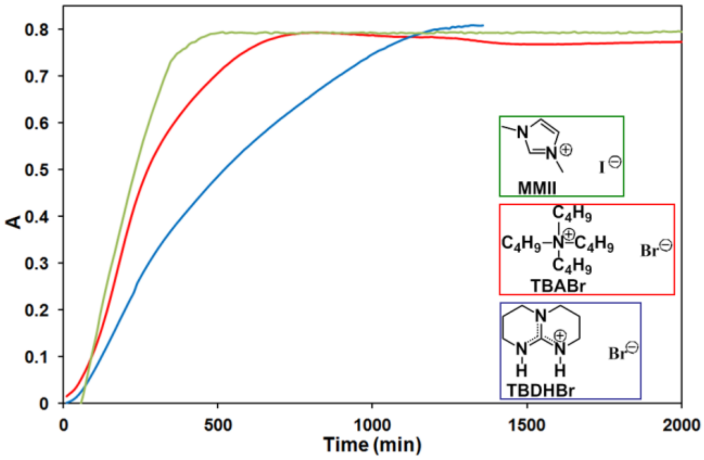
ESI Figure 1- Stacked FTIR-ATR spectra of (1) Methyl undecenoate, (2) UndBdA, (3) UndBdA-bisEpoxide and (4) UndBdA-b5CC.



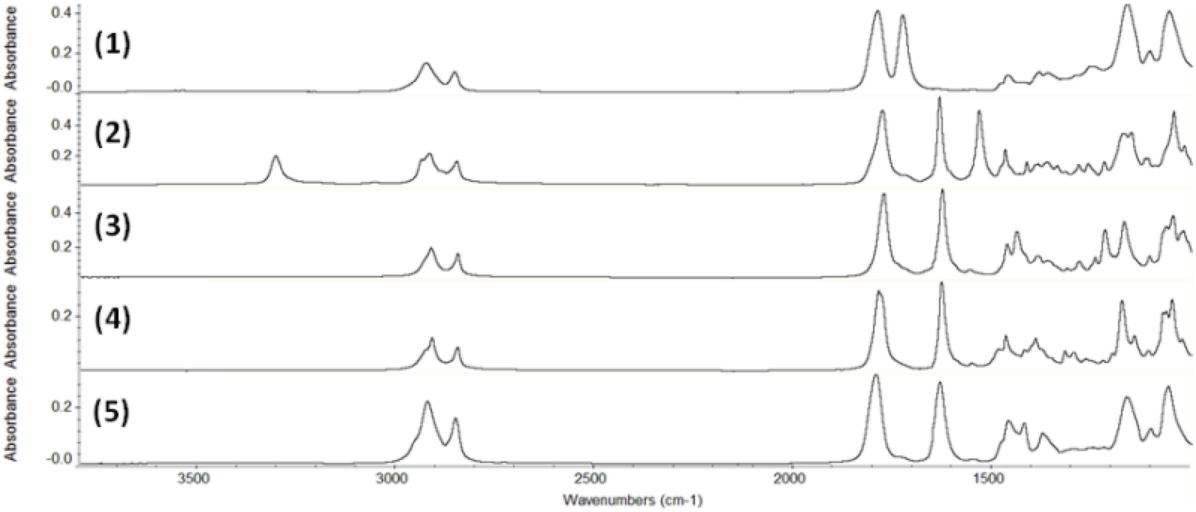
ESI Figure 2- Stacked FTIR-ATR spectra of (1) Methyl undecenoate, (2) UndPipdA, (3) UndPipdA-bisEpoxide and (4) UndPipdA-b5CC.



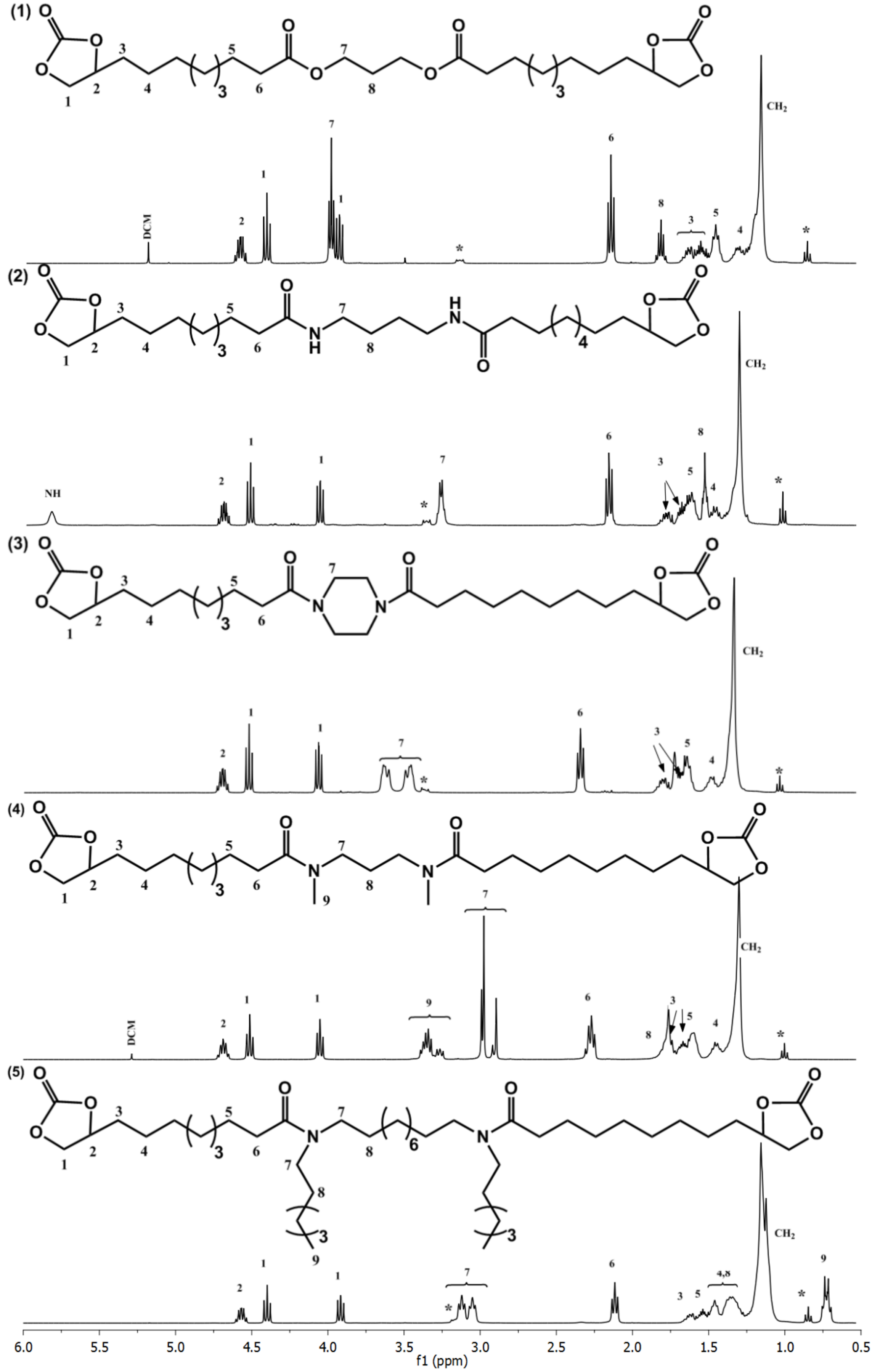
ESI Figure 3- Stacked FTIR spectra of the carbonation reaction of UndPdE-bisEpoxide at 80°C with 50 Bar of CO_2 and 3 wt% TBABr (1) at 10 min and 48 hours and (2) at different reaction times with a focus between 900 cm^{-1} and 700 cm^{-1}.



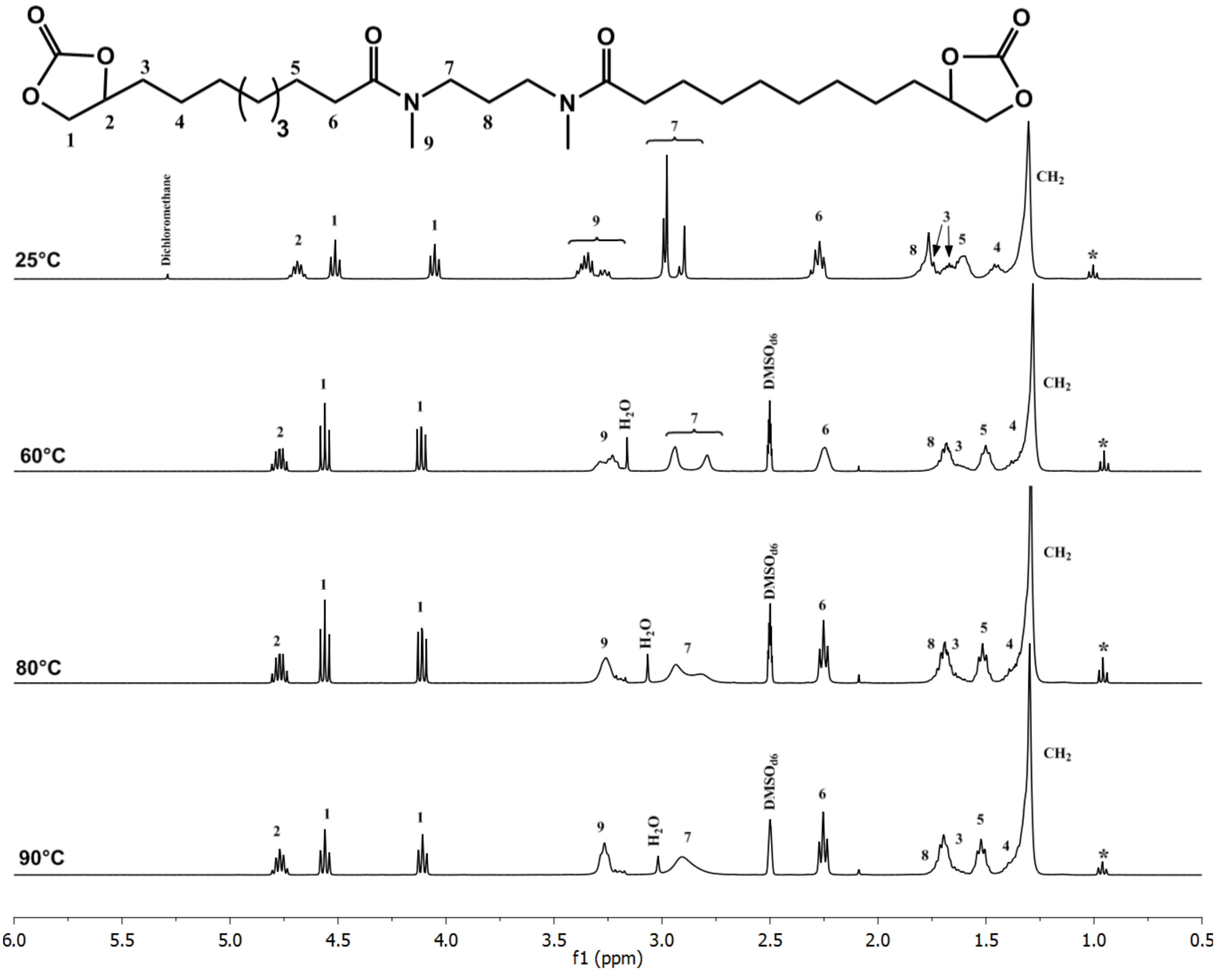
ESI Figure 4- Evolution of the absorbance of the band at 775 cm^{-1} during the carbonation reaction of UndPdE-bisEpoxide at 80°C with 50 Bar of CO_2 and 3 wt% catalyst.



ESI Figure 5- Stacked FTIR-ATR spectra of (1) UndPdE-b5CC, (2) UndBdA-b5CC, (3) UndPipdA-b5CC, (4) UndPMedA-b5CC and (5) UndDHexdA-b5CC.



ESI Figure 6- Stacked ^{1}H NMR spectra of (1) UndPdE-b5CC, (2) UndBdA-b5CC and (3) UndPipdA-b5CC, (4) UndPMedA-b5CC and (5) UndDHexdA-b5CC. (*) TBABr. (Analyses in $CDCl_3$)

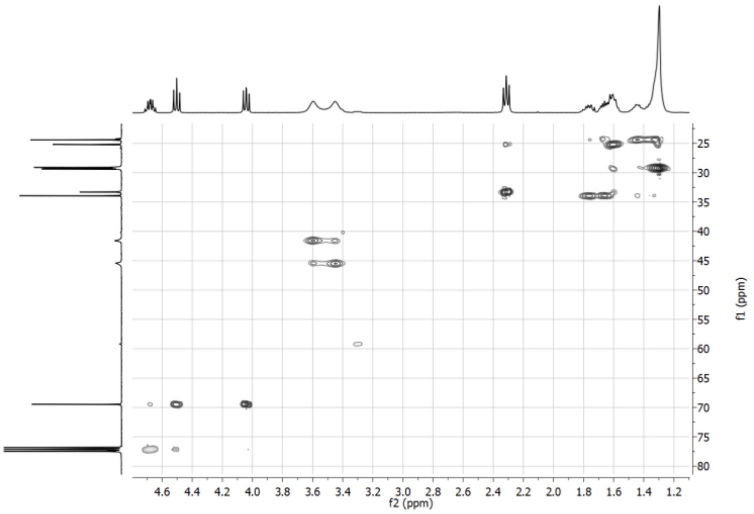


ESI Figure 7- ^{1}*H NMR of UndPMedA-b5CC at 25°C (in CDCl*$_3$*), 60°C, 80°C and 90°C. (in DMSO-d6)*

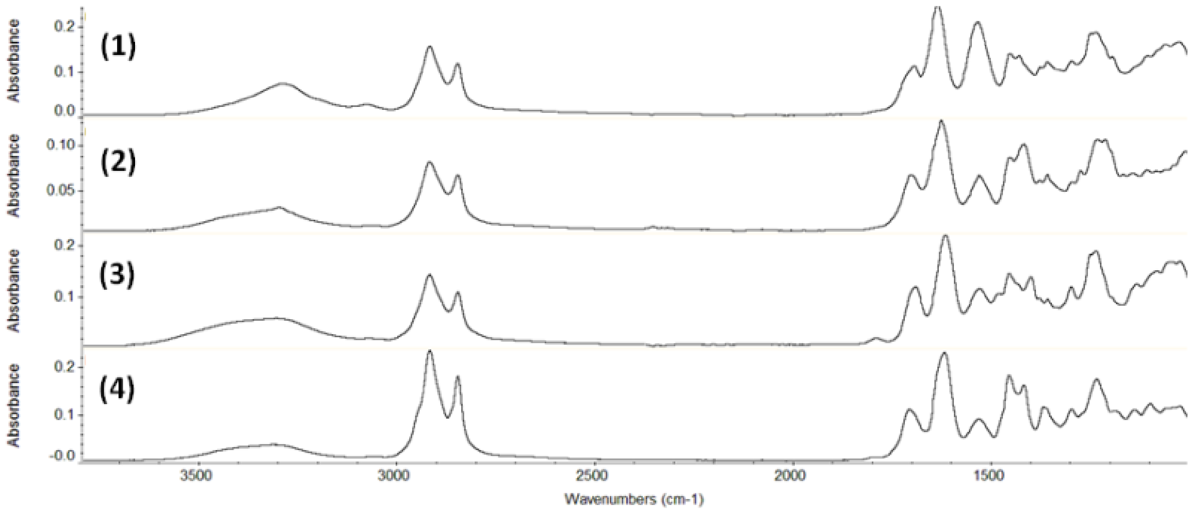
ESI Table 1- Characterizations of the synthesized bis cyclic carbonates.

Synthesized b5CC	Total yield (%)	%purity	T$_m$ (°C)[3]
UndPdE-b5CC	68	99.1[1]	L
UndBdA-b5CC	76	nd	137.4
UndPipdA-b5CC	56	nd	132.6
UndPMedA-b5CC	64	88.6[2]	102.5[4]
UndDHexdA-b5CC	44	nd	L

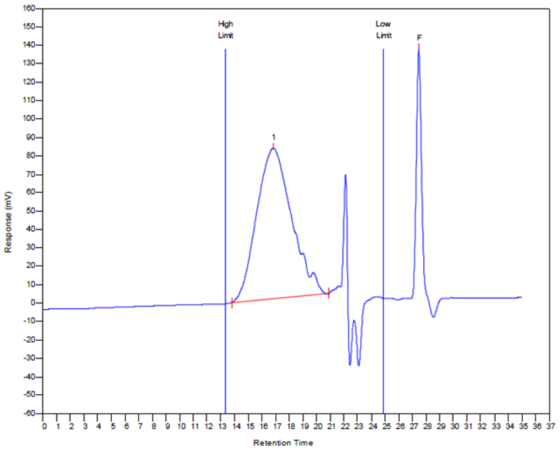
(1) Determined by SEC, (2) Determined by GC-FID and (3) Determined by DSC 10°C/min under N$_2$, (4) Crystallization while heating, nd=not determined, L=liquid at room temperature.



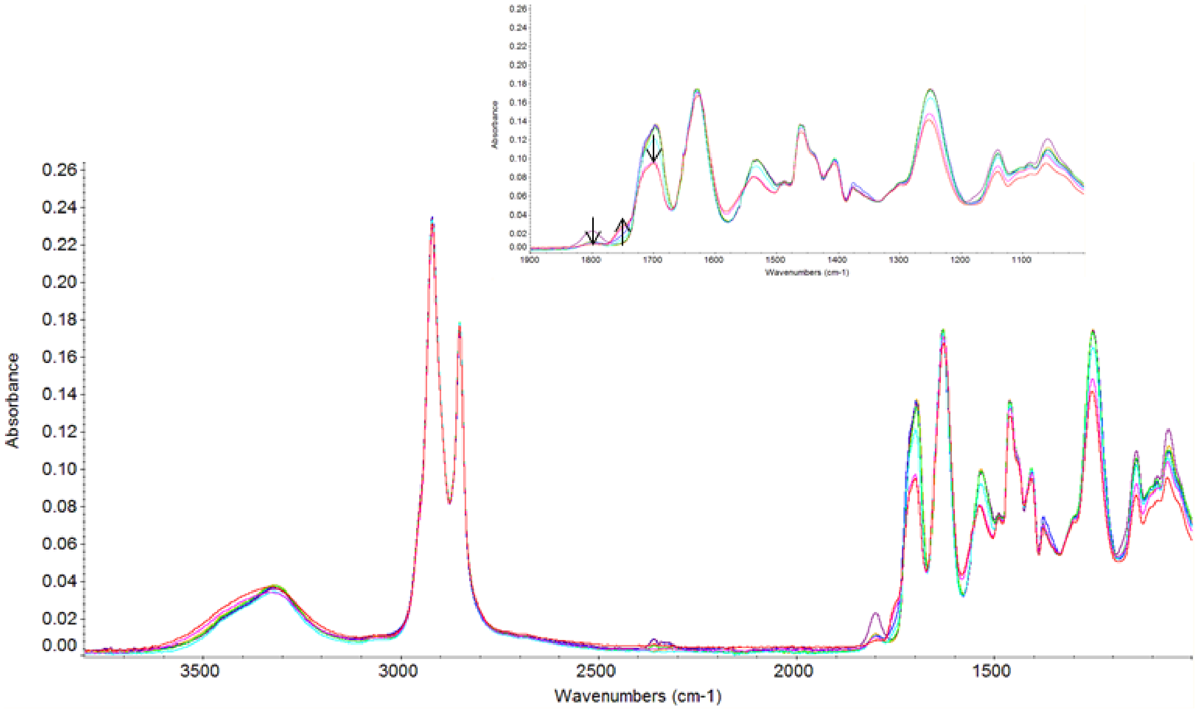
ESI Figure 8- ^1H-^{13}C HSQC-NMR of UndPipdA-b5CC. (Analysis in $CDCl_3$)



ESI Figure 9- Stacked FTIR-ATR spectra of PHU-BdA-1, PHU-PipdA-1, PHU-PMedA-1 and PHU-DHexdA-1.



ESI Figure 10- SEC analysis of PHU-PMedA-2 (SEC in DMF with 1 wt% LiBr - calibration PS standards).

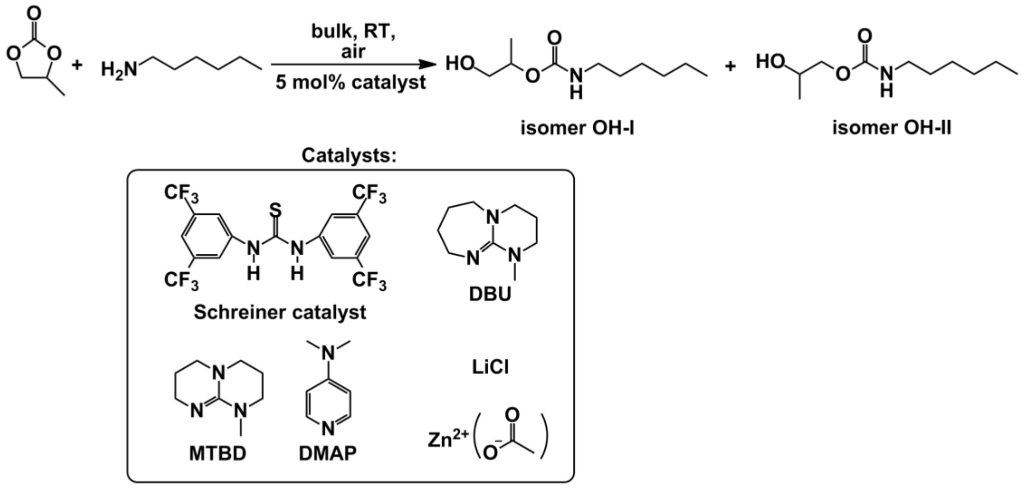


ESI Figure 11- FTIR-ATR evidence of the presence of side reactions during the polymerization in bulk at high temperature of PU-PMedA-2.

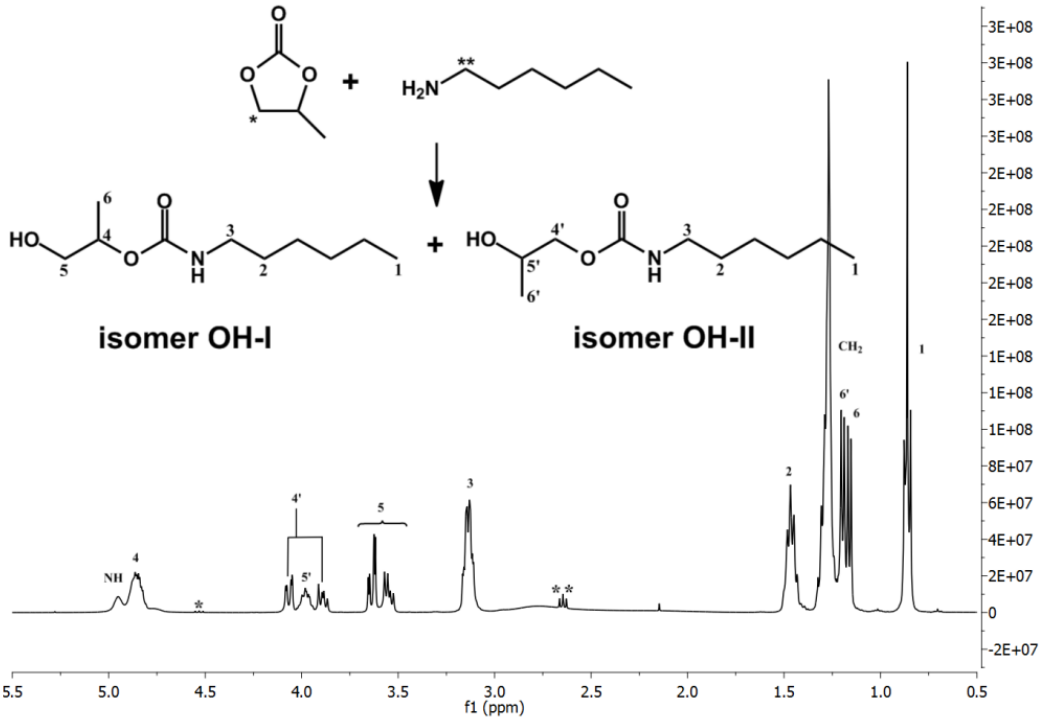
ESI Table 2- Decrease of the molar mass and of the glass transition temperature during the polymerization in bulk at high temperature of PU-PMedA-2.

Time (d)	$\bar{M}_n$ (g.mol^{-1})	$\bar{M}_w$ (g.mol^{-1})	Đ	Tg (°C)
1d	28 100	41 400	1.47	-4.5
6d	28 700	47 500	1.66	nd
15d	17 200	27 800	1.61	-11.5

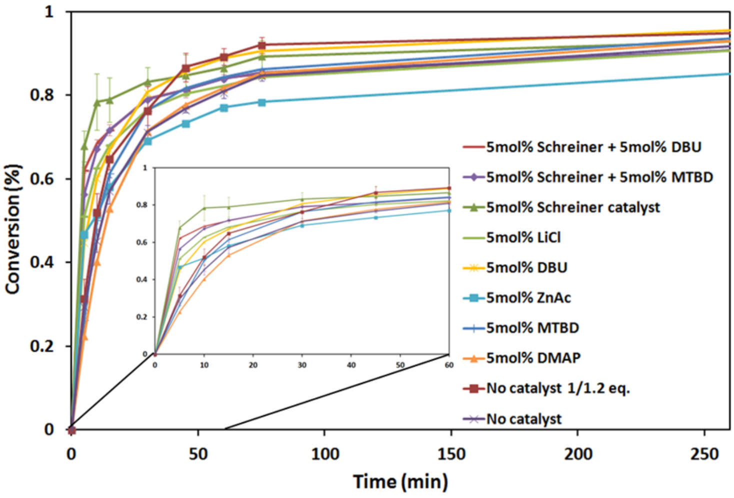
SEC in DMF with 1 wt% LiBr - calibration PS standards.



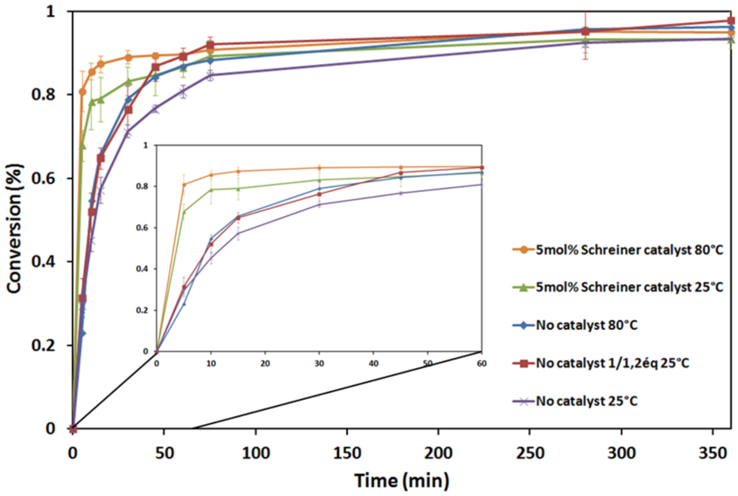
ESI Scheme 2- Model reaction of propylene carbonate and hexylamine as well as the various catalysts used.



ESI Figure 12- ^{1}*H NMR of the reaction between propylene carbonate and hexylamine without catalyst at RT after 11 days. (Analysis in* $CDCl_3$*)*



ESI Figure 13- Kinetic data of the model reaction with various catalysts at 25°C in bulk.



ESI Figure 14- Kinetic data of the model reaction with Schreiner catalyst at 25°C and 80°C in bulk.

ESI Table 3- Analyses of the reactions between 5CCMe and hexylamine with different catalysts in bulk at RT.

Catalyst used	Catalyst quantity (mol%)	Ratio OH I : OH
No	/	58:42
DMAP	5	57 :43
MTBD	5	58 :42
ZnAc	5	60 :40
DBU	5	53 :47
LiCl	5	58 :42
Schreiner catalyst	5	59 :41
Schreiner catalyst + MTBD	5+5	57 :43
Schreiner catalyst + DBU	5+5	50 :50

(1) Calculated by ^1H NMR using the equation: $\% OH\ I = \frac{I_{OH\ I}}{I_{OH\ I} + I_{OH\ II}} * 100$, where % OH I, $I_{OH\ I}$ and $I_{OH\ II}$ are the % of the product with primary hydroxyl and the integrations of the peaks corresponding to the product with primary and secondary hydroxyl respectively.