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To cite this version:

Fiona Magliozzi, Guillaume Chollet, Etienne Grau, Henri Cramail. Benefit of the reactive extrusion in the course of polyhydroxyurethane synthesis by aminolysis of cyclic carbonates. ACS Sustainable Chemistry & Engineering, American Chemical Society, 2019, 7 (20), pp.17282-17292. 10.1021/acssuschemeng.9b04098. hal-02366940

HAL Id: hal-02366940
https://hal.archives-ouvertes.fr/hal-02366940
Submitted on 21 Nov 2019

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Benefit of the reactive extrusion in the course of polyhydroxyurethane synthesis by aminolysis of cyclic carbonates

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ABSTRACT: Replacing toxic isocyanates and petro-based reactants currently employed for polyurethanes (PUs) synthesis is nowadays a major concern. Among all the possible routes to isocyanate-free PUs, aminolysis of cyclic carbonates, leading to polyhydroxyurethanes (PHUs) seems to be one of the most promising pathways. Herein, we discuss the added value brought by the reactive extrusion process on PHU synthesis. In order to evaluate the benefit and the versatility of the process, three different bis-cyclic carbonates exhibiting different reactivity (Diglycerol Dicarbonate, Seb-bCC-ester and one bisCC containing amide function, Und-6DA-bisCC), were tested in the course of polymerization with different diamines. The PHUs synthesized through reactive extrusion were then compared with the ones obtained through classical bulk polymerizations in terms of kinetics, PHU molar masses and side reactions, clearly demonstrating the benefit of the extrusion process.

KEYWORDS: Polyhydroxyurethanes, reactive extrusion, solvent-free polymerizations, biobased bis cyclic carbonates, process improvement

First developed in the 1930s by Otto Bayer¹, polyurethanes (PUs) are nowadays specialty polymers found in many markets, such as coatings, paints, elastomers, adhesives and especially, foams. Nonetheless, the current industrial ‘polyol route’ for the synthesis of conventional polyurethanes suffers from the use of toxic isocyanates, which latter made from even more hazardous phosgene gas. Despite the secured industrial setups to handle such reactants, their substitution in the PUs industry has become today a real question.² Aiming at investigating safer alternatives, many research groups have, in recent years, been exploring new routes to non-isocyanates PUs, namely NIPUs.³ Among all these strategies, one of the most promising routes appears to be the polypadition of cyclic carbonates (CC) with pluri-amines, through aminolysis reaction.

In addition, the combination of fossil resources depletion together with the need for isocyanate replacement, push scientists to develop bio-based monomers from renewable resources, including vegetable oils⁴-⁵, isosorbide⁶, sugars⁷, terpenes⁸ and lignin⁹. In this context, a large palette of cyclic carbonates has been produced from fully bio-based synthons.¹⁰-¹³

Most of the cyclic carbonates developed to form PHUs are 5-membered cyclic carbonates, 5-CCs.¹²-¹⁸ In a lesser extent, some PHUs can be also prepared from 6- to 8-membered cyclic carbonates²⁹-²⁶. These larger carbonate rings exhibit a higher reactivity in comparison to the 5-CCs, due to their higher ring strain, but suffer from a lower stability at storage. In order to overcome the rather low reactivity of 5CCs, the introduction of functional groups exhibiting a withdrawing electronic effect in alpha or beta position of the carbonate ring is reported to increase its reactivity towards aminolysis. These so-called ‘activated carbonates’, first developed by Tomita et al.¹, were investigated by many research groups.²⁸-²⁹ In this course, we recently designed biscarbonates from fatty acid substrates bearing either ether, ester or thio-ester linkages, in beta position of the carbonate ring.³⁰

Even if the polyaddition between CCs and pluri-amines seems to be the most promising route to NIPUs, such synthetic pathway still suffers from some drawbacks. As a general trend, notably with 5-CCs, their bulk polymerization exhibits a kinetic which is much slower in comparison to the ‘polyl route’, the reactive functions conversion is incomplete and some side reactions can occur with time. An important consequence of these polymerization features is generally the formation of relatively low molar mass PHUs.¹²-¹³ All these limitations are preventing the CC / amine route to NIPUs to be competitive with the current industrial PU process and thus still requires improvements that we aim at addressing in this work.

Indeed, intending to better control the monomer diffusion and overcome the viscosity issue generally encountered in bulk polymerization, we have been investigating the reactive extrusion process of bisCCs and diamines to evaluate the effect of such process on the kinetic profiles and PHUs features (molar masses and side reactions notably). The implementation of this process has also made possible to handle high melting point bicarbonates, which are challenging to polymerize in conventional bulk polymerization. Indeed, the reactive extrusion process enables a high shearing rate that prevents the use of high temperatures and, of course, solvents. Besides, the process presents the main advantage to significantly reduce the reaction times from days to hours, as short polymerization times and fast molar mass build-up are two crucial criteria for a competitive technical process. The literature data regarding the synthesis of NIPUs through reactive extrusion is rather scarce. Mulhaupt and coll. were the first to
report NIPU synthesis through this process. In 2017, this team reported the polymerization of erythritol bicarbonate and different rigid and flexible diamines, in the presence of DABCO as catalyst. Interestingly, the authors demonstrated that addition of Irgranox 1010 and Irgragos 168, known as antioxidants to prevent degradation of polymers, could lead to higher molecular weights PHUs. More recently, the authors reported the polymerization of different bis-cyclic carbonates through reactive extrusion process, with 1,12 diaminododecane as a co-monomer, to design semi-crystalline PHUs, suitable for 3D-printing applications.

In this study, a series of bio-based bисyclic carbonates, i.e. one ether-activated namely DGDC (Diglycerol Dicarbonate) for which the synthesis and the use for PHUs synthesis has been already described, a second ester-activated, Seb-bCC-ester,(bis(2-oxo-1,3-dioxolan-4-yl)methyl) decanedioate, obtained from Glycerol Carbonate, and a third, non-activated and containing amide linkages, Und-6DA-bisCC, were reacted with the commercial diamines, 1,4-diaminobutane (4DA), 1,6-diaminohexane (6DA), 1,10-diaminododecane (10DA), 1,12-diaminododecane (12DA), m-Xylylenediamine (xy-DA), and L-Lysine, by reactive extrusion. The polyhydroxyurethanes so-formed were analyzed in terms of molecular structures, dimensions and thermal properties.

**EXPERIMENTAL SECTION**

**Materials**

The reactants 1,4-diaminobutane, 1,10-diaminododecane, 1,12-diaminododecane, m-Xylylenediamine, diglycerol, were purchased from TCI, Europe. NaHCO₃, Anhydrous MgSO₄ and Triethylamine, TBABr (tetra butyl ammonium bromide), m-CPBA (meta-chloroperbenzoic acid), and L-Lysine were ordered from Merck. Dimethylcarbonate (DMC, extra dry, 99%), Sebacoyl Chloride and 1,6-diaminohexane were obtained from Acros. Solvents like DMF (for chromatography), dichloromethane (DCM), Methanol and Ethanol were ordered from VWR. Deuterated DMSO and CHCl₃ were purchased from EurisoTop. Und-6DA (methyl undecenoate coupled with hexamethylenediamine) was kindly provided by ITERG company.

**Methods and Instruments**

**NMR.** ¹H and ¹³C-NMR spectra were recorded on a Bruker Advance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.65 MHz for ¹H and 13C, respectively) using DMSO-d6 or CDCl₃ as a solvent at room temperature. The polymerization extent was determined by monitoring the carbonate functions conversion according to NMR spectra, following the disappearance of signals belonging to the carbonate. The peak corresponding to the protons in alpha position of the urethane bond was used as internal reference. No internal or external standard were used for NMR analysis.

**FTIR.** Infrared spectra were obtained on a Bruker-Tensor 27 spectrometer, equipped with a diamond crystal, using the attenuated total reflection mode. The spectra were acquired from 400 to 4000 cm⁻¹ using 64 scans at a resolution of 4 wave-numbers.

**SEC.** Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using dimethylformamide (DMF + lithium bromide LiBr 10g/L) as the eluent. Measurements in DMF were performed on an Ultimate 3000 system from Thermo scientific equipped with diode array detector DAD. The system also includes a multi-angle light scattering detector MALLS and differential refractive index detector dRI from Wyatt Technology. Polymers were separated on two different column systems. The first one was two KD-803 Shodex gel columns with a PolyStyrene Divinylbenzene phase (300 x 8 mm, exclusion limit: 50 000) at a flow rate of 0.8 mL/min. The second system was composed of two GF300-510 Ashai pack columns containing a Polyvinyl alcohol phase (7.5 x 300, exclusion limit: 300 000). Columns temperature was held at 50°C. Polystyrene was used as the standard and the calibration method is conventional.

**TGA.** Thermogravimetric analyses (TGAs) were performed on the TGA-Q500 system from TA Instruments at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere from room temperature to 600 °C, and then under air atmosphere from 600°C to 700°C.

**DSC.** Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA Instruments. For each sample, two cycles were performed, the first from -40 to 180 °C at 10 °C min⁻¹ and a second from -40°C to 180°C. The glass transition and melting temperatures were calculated from the second heating run.

**COMPOUNDER. (twin screw extruder).** The reactive compounding was performed using a Micro 5/14 mm twin-screw compounder from thermos Scientific, in a temperature range between 80 and 100 °C for DGDC and Seb-bCC-ester-based PHUs, and between 120°C and 230°C for Und-6DA-based PHUs. The rotation speed of the twin screw was kept constant at 100 rpm. The gained ΔP – time diagrams were recorded by using Polysoft OS and monitor as software.

**5-membered Cyclic Carbonates synthesis**

**Diglycerol dicarbonate (DGDC) synthesis:** DGDC was synthesized according to previously reported synthesis and especially adapted from the work of Bossion et al. Diglycerol di-carbonate was prepared from diglycerol with a 40 % yield through a one-step procedure. In a round bottom flask, 76g (1eq) of diglycerol were introduced and dried under vacuum during 2h at 90°C. Then nitrogen was flushed into the vessel and 1.24g (0.05eq) of sodium methoxide catalyst were added under stirring. A condenser was set up above the flask and 76ml (3eq) of the second reactant, dimethylcarbonate (DMC) were added. The DMC also plays the role of the reaction solvent. The temperature is then set at 110°C. After 48h reaction, the mixture was filtered to remove the sodium methoxide and concentrated by evaporation before two successive recrystallizations in methanol at -80°C. DGDC was recovered by filtration on paper filters and dried under vacuum at room temperature. ¹H NMR (DMSO-d6, 25°C, 400 MHz), δ (ppm): 4.93 (m, 2H, H₂), 4.52 and 4.23 (t, 4H, H₃), 3.74 (t, 4H, H₃) ¹³C NMR (DMSO-d6, 25°C, 100 MHz), δ (ppm): 154.9 (O=O), 101.6 (O=O), 74.8 (CH₂-CH₂-O-CH₂), 69.8 (CH₂-CH₃-O-CH₂), 66.1 (CH₂-CH₂-O-CH₂). IR (cm⁻¹): 2925, 1773, 1476, 1401, 1165. Tg=69 °C. Detailed ¹H NMR spectrum is shown in Figure S1-I.
Seb-bCC-ester synthesis. This synthesis was adapted from the work of Carré et al. In a round-bottom flask, 2.6 eq. (15g) of glycerol carbonate and 4 eq. (27.24 mL) of triethylamine were diluted in 29.1 mL of dichloromethane. 1 eq. (11.6 g, 16.7 mmol) of sebacoyl chloride was slowly added under an inert atmosphere at 0 °C. The mixture reaction was left for 2 h at room temperature. Afterward, the mixture was diluted in 150 mL of dichloromethane and triethylammonium salts, formed during the reaction, were filtered. The filtrate was then washed three times with 3·100 mL of a 10% mol. HCl solution, then three times with 3·100 mL of saturated NaHCO3 solution and lastly with 3·100 mL of brine. The organic phase was finally dried over anhydrous MgSO4. The Seb-bCC-ester powder was recovered by evaporation and dried under vacuum. Seb-bCC-ester was obtained in 70% yield as a white powder after evaporation. 1H NMR (DMSO, 25 °C, 400 MHz) δ (ppm): 5.01 (m, 2H, H2), 4.56 and 4.25 (t, 4H, H1), 4.20 (t, 4H, H3), 2.31 (t, 4H, H4), 1.53 (m, 4H, H5), 1.25 (8H). 13C NMR (DMSO, 25 °C, 100 MHz) δ (ppm): 173.81 (CONH), 155.27 (CH2), 137.18 (CH2–OCO–CH2), 154.1 (O(OCO)), 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. Tm = 84 °C. Detailed 1H NMR spectrum is shown in Figure SI-11.

Und-6DA-bisCC. 1. Epoxidation reaction. The initial Und-6DA (methyl undecenoate coupled with hexamethylenediamine) (50g, 1eq) and m-CPBA (50.7g, 3 eq) were stirred at room temperature in chloroform. After 1 day, the conversion of the double bonds, monitored by 1H NMR spectroscopy (see figure SI-22), was complete. The purification of the product was done in two steps. First, the organic layer was washed over aqueous Na2SO3 (3×500 mL), aqueous NaHCO3 (4×500 mL), neutralized with water and dried over anhydrous sodium sulfate. Solvent was then removed after filtration. Secondly, the bis-epoxide was dispensed in ethanol and centrifuged. After the removal of the supernatant, the precipitated bis-epoxide was then recovered and dried under vacuum. This procedure allows the correct removal of m-CPBA. 2. Carbonation reaction. The bis-epoxide was first pre-mixed with TBABr (3 wt%). Then the mixture was placed in a reactor and CO2 was slowly introduced into the reactor until 50 bars. The vessels were heated up at 140 °C and left under magnetic stirring. After 24 hours, the reactor was cooled down to room temperature and slowly depressurized to the atmospheric pressure. All the 1H NMR of all products revealed quantitative conversion by the disappearance of the protons of the epoxide. Yield: 95%. 1H NMR (CDCl3, 25 °C, 400 MHz) δ (ppm): 5.83 (s, 2NH), 4.70 (m, 2H), 4.53 (t, 2H), 4.06 (t, 2H), 3.26 (m, 4H), 2.16 (t, 4H), 1.78 (m, 2H), 1.62 (m, 6H), 1.53 (m, 4H), 1.47 (m, 4H), 1.30 (m, 16H). 13C NMR (CDCl3, 25 °C, 100 MHz) δ (ppm): 173.81 (CONH), 155.27 (OCOO), 77.22 (CH–OCOO), 69.54 (CH2–OCOO), 39.20 (CH2–NHCCH), 36.65 (CH2–CONH), 33.94 (CH2–CH2–OCOO), 29.17 (CH2), 26.91 (CH2–CH2–NHCCH), 25.84 (CH2–CH2–CONH), 24.43 (CH2–CH2–OCOO). IR (cm⁻¹): 3309, 2918, 2850, 1778, 1637, 1535. Tm = 114 °C. Detailed 1H NMR spectrum of Und-6DA-bisCC can be seen in Figure SI-23. Procedure summary available in Figure SI-21.

Standard procedure for polymerization by reactive extrusion process. Bis-CCs and diamines monomers, generally both powders, were weighed in a stoichiometric ratio of 1 and manually premixed for one minute. Then, the mixture was slowly injected in the micro compounder, without initial pressure. The solvent-free polymerizations were performed from 80°C to 95°C, depending on the diamine nature. The reactants injection usually lasts 5 minutes and was done manually, without pushing the monomers to avoid losses. The twin-screw rotation speed was set at 100 rpm and kept steady during the whole reaction. Torque, actual temperature and pressure measured inside the reactor were followed by PolySoft monitor software. When a liquid diamine was used, bisCCs were first injected into the hot reactor in order to be melted, and then the appropriate volume of the diamine was added with a syringe. In the specific case of Und-6DA-bisCC polymerizations, the temperature was started a 120°C with 1DA, 6DA and m-xylene DA and at 220°C in the case of L-Lysine. In order to ensure the good circulation of the materials during the polymerization by reactive extrusion of those amide-type carbonates, a pressure dependent temperature program was created, in order to level the pressure in the channel. If the pressure recorded on pressure sensor number 1 (p-D1) overcome 100 bars, the temperature was increased by 5°C. The temperature increases allowed to reduce the viscosity of the polymer material, reducing the global pressure in reactor. The pressure in the channel, labelled AP is actually the difference between two pressures sensors located at each edge of the circulation channel. For PHUₙ and PHUᵢ, the pressure on p-D1 never overcome 100 bars and, as a consequence, temperature was kept constant. For PHUᵢ, the temperature was increased, but considering the fact that those increases did not have much impact on the pressure (very dense material created), and due to the already high temperature values, 230°C was put as an upper limit.

Standard procedure for polymerization with magnetic or mechanical stirring.

Bis-CCs (1 eq, 2g) were introduced in schlenk tubes and heated at the desire temperature (oil bath). Then the stirring tool, either magnetic stirrer or the blade for mechanical stirring is added in the schlenk. For mechanical stirring the stirring blade is screwed to a IKA RW20 Digital instrument. The bis-CCs are melted and stirred during 5 min and the appropriate amount of diamine is added (1 eq) under stirring. This method allow the immediate mixing of the diamine with the melted bisCC, preventing its sublimation. After the appropriate reaction time, the stirring is stopped, the schlenk tube is immediately cooled down at room temperature and samples analyzed.

RESULTS AND DISCUSSION

DGDC-based PHUs synthesis through reactive extrusion

Polyhydroxyurethanes were first synthesized from DGDC and two aliphatic diamines, respectively hexamethylene diamine (6DA, PHU₆), and 1,10 diaminodecane (10DA, PHU₁₀), as displayed in Figure 1.
In both cases, the polymers were extruded after 4h and cooled down at room temperature. The polymerization rate was followed by monitoring the pressure drop (ΔP), recorded over time by two pressure sensors located at each end of the circulation channel.

Figure 2. Scheme of the extruder reactor (Inside view). Orange circles represent the two pressure sensors.

The scheme presented in Figure 2 shows in black the hollow part of the extruder where the polymer is formed and circulates during the polymerization. The two orange circles at each edge of the circulation channel represent the two pressure sensors. As clearly understandable from the scheme, when the polymer reaches the end of the twin screws, it is re-injected at the entrance of the screws through the circulation channel. Several parameters such as temperature, screws rotation speed and obviously residence time can be tuned, thus affecting the chemistry itself but also the rheology within the extruder. In this sense, the final properties and mainly the homogeneity of the PHUs so-formed deeply depend on these parameters.

Benyahya et al. have shown that optimal temperature for PHU synthesis is around 80°C and should not be over 120°C. Indeed, several works demonstrated that the formation of urea moieties, the major by-product in poly(hydroxyurethane)s synthesis, occurs when the temperature gets close to 100°C and above. Polymerization temperatures were chosen according to those observations, added to the fact that bulk polymerizations require temperature higher than the melting point of monomers. In the case of DGDC polymerization with 6DA, the reaction temperature was kept at 80°C. As semi-crystalline PHUs were obtained with DGDC/10DA polymerization, the reactive extrusion process was adapted to ensure a good homogeneity of the blend. The time vs temperature program was as follows: start at 80°C/45min, then 85°C/15min, 90°C/15min and finally 95°C/165min (see Figure 3) to guarantee the melting of the entire polymer chains. In this specific case, the reaction was started at the lowest temperature possible for three main reasons: lowering the formation of urea moieties, ensure the efficient circulation of the polymer in the channel and preventing the sublimation of rather low vapour pressure 10DA. Indeed, a higher starting temperature would lead to a partial loss of diamine through sublimation, compromising stoichiometry compliance. Besides, when the substance within the reactor is too liquid (which is the case when the reaction is started at 95°C), the pressure induced by the screws is less efficient, compromising the correct circulation of the polymer within the extruder. Figure 3 shows ΔP recorded over time during PHU₁ synthesis at constant temperature (top) and the ΔP profile obtained during PHU₂ synthesis (bottom). In the case of PHU₁, the plateau reached after 4 hours of reaction shows that the viscosity of the system was no longer increasing, behavior attributed to the completion of the reaction. For PHU₂, even if the ΔP was still increasing during the last two hours, it was decided to stop the polymerization after 4 hours, in order to keep short reaction times. As can be observed for PHU₂, the pressure, and so the viscosity, drastically decreased when the temperature was increased from 80°C to 95°C. This behaviour is obviously characteristic of the thermoplastic feature of the obtained PHUs.

After extrusion, PHU₁ and PHU₂ were analysed by proton NMR, in order to quantify the conversion of reactive functions. In both cases, the carbonate conversion was over 99%, as shown by the stacked ¹H NMR spectra displayed in Figure 4. In order to confirm the high conversion, additional ¹H NMR spectra were recorded with 1024 scans (see Figure SI-2 and Figure SI-3) and FTIR spectroscopy was performed (see Figure SI-4). Carbonate conversion was calculated by integrating the remaining peak of carbonate ring between 4.2 and 4.3 ppm.
Besides, \(^1\)H NMR spectra show that no urea was formed when 6DA was polymerized with DGDC at 80°C, whereas the appearance of a small peak (1.1%) at 5.7 ppm can be noticed on PHU\(_2\), in the case of DGDC / 10DA polymerization.

This peak can be undoubtedly attributed to urea functions according to previous studies. A zoom of this spectrum zone is displayed in Figure 4.

Finally, the thermal properties of the PHUs were determined by DSC and TGA analysis. PHU\(_1\), synthesized from DGDC and 6DA was obtained as an amorphous material. In the case of 10DA, a semi-crystalline polymer was obtained for PHU\(_2\), with crystallization and melting temperature respectively at 94.6°C and 103°C. This temperature found for crystallization confirms the necessity to increase the temperature up to 95°C during polymerization (temperature program previously described) to overcome the crystallisation of the so-created PHU in this extruder. Besides, TGA traces showed thermal stabilities until 204°C and 216°C for PHU\(_1\) and PHU\(_2\) respectively, according to the T\(_{5\%}\) measurement. The second heating cycle of DSC analysis displayed T\(_{g}\)s of 16°C and 5°C respectively.
Comparison with bulk PHU synthesis using magnetic and mechanical stirring.

In order to evaluate the real benefit brought by the reactive extrusion process on the PHU synthesis, comparative bulk-polymerizations were performed using magnetic or mechanical stirrings. As shown in Table 1, PHU$_3$ and PHU$_4$ have been synthesized from DGDC and 6DA or 10DA respectively, in a Schlenk tube under magnetic stirring.

The polymerization temperatures were the same as previously tested by reactive extrusion, meaning 80°C with 6DA and the established temperature ramp (from 80°C to 95°C) for PHU$_4$. The polymers were recovered after 4h of polymerization and analyzed by $^1$H NMR and SEC. PHU$_3$ and PHU$_4$ showed a conversion of carbonate functions of only 48.72% and 40.9% respectively, demonstrating the extremely poor efficiency of magnetic stirring for PHU bulk polymerizations. Detailed $^1$HNMR spectra are displayed in Figures SI-5. Simultaneously, a series of bulk polymerizations were then performed under mechanical stirring, following the conditions already described (see Table 1, PHU$_3$ and PHU$_6$). In both last cases, the carbonate conversions were found very high after 4h reaction time, comparable to the results obtained by reactive extrusion ($^1$H NMR displayed in Figure SI-6). For comparison, SEC traces in DMF of PHU$_3$, PHU$_3$ and PHU$_3$ are displayed in Figure 5. Same comparison with PHU$_3$, PHU$_4$ and PHU$_6$ made from 10DA, is available in Figure SI-7.

The red SEC trace corresponding to PHU$_3$ prepared at 80°C with magnetic stirring, shows the presence of oligomers in significant amount. With magnetic stirring (PHU$_5$, black curve), the amount of oligomers is still detectable but drastically decreased. In agreement with NMR analysis, the polymerization performed by reactive extrusion (blue curve), at 80°C after 4h reaction time, enables the apparent total consumption of carbonate functions, leading to minimum quantities of visible oligomers, and the formation of higher molar masses. All these data confirm that an efficient mixing is essential to ensure the monomer diffusion during the polymerization.

PHU molar mass determination

PHUs molar masses were determined using size exclusion chromatography in DMF, with two different systems of columns. In both cases, molecular weights were calculated with the universal method, related to polystyrene standards. The first series of columns were filled with a gel of PS (Shodex). With this chromatographic system, the molar masses of PHU$_3$ and PHU$_4$ were respectively equal to 37400 g/mol and 35600 g/mol with dispersions values around 1.2 to 1.3. Such dispersity values are not in agreement with high conversion values measured by NMR (Figure 4 and Table 1). Considering this observation, PHUs were also analyzed with a second set of columns filled with a polyvinyl alcohol gel (Ashapack). In this case, the molar masses obtained for PHU$_3$ and PHU$_4$ were equal to 5000 g/mol with $D = 2.5$ and 5600 g/mol with $D = 1.96$, respectively. In this latter case, dispersity values are more consistent with Carothers theory and in agreement with the complete carbonate conversion. However, the relative molar masses appear, in this case, underestimated. Indeed, considering these values, the calculated polymerization degrees would be around 16 both for PHU$_3$ and PHU$_4$. These size exclusion chromatography analyses confirm how it is difficult to estimate the relative molar masses of polyhydroxyurethanes based on polystyrene calibrations, as already discussed in literature data. However, despite this issue, one could compare the SEC data of the prepared PHUs with respect to the process implemented, reactive extrusion vs conventional bulk polymerization.

Versatility of the reactive extrusion process for PHU synthesis.

In order to further investigate the potential of the reactive extrusion process to produce PHU materials, another type of activated bisCC, named Seb-bCC-ester, was tested. Seb-bCC-ester was synthesized in one step from sebacoyl-chloride and glycerol carbonate. To ensure the good melting of the Seb-bCC-ester ($T_m = 84^\circ$C), the polymerization temperature was set at 90°C and the twin screws rotation speed fixed at 100 rpm. Thanks to the ester bond in beta position of the carbonate ring, the reactivity of Seb-bCC-ester towards aminolysis is high, compared to that of DGDC. However, one issue with this monomer is the possibility to form amide linkages within the PHU backbone. As already described, this secondary reaction between ester and amine reactive groups can occur till 70°C. Due to these particularities, the protocol for reactive extrusion polymerization involving Seb-bCC-ester as bis-carbonate monomer was slightly different than the one for DGDC-based PHUs. Indeed, the PHUs so-formed quickly became highly viscous materials, leading to a drastic increase in terms of torque and pressure ($\Delta P$) within the channel.
The polymerizations were let until the blocking of the extruder, due to high threshold torque and/or ΔP reached. The Seb-bCC-ester-based PHUs were taken out directly molded into the circulation channel to obtain brown rubbery materials with a bar-like shape (Figure 6). Consequently, the polymerization duration was comprised between 21 minutes and one hour and a half depending on the monomer systems (Seb-bCC-ester/various aliphatic diamines). The temperature was not increased higher than 90°C in order to minimize the above mentioned secondary reactions. Different aliphatic diamines were tested as co-monomers with Seb-bCC-ester; 1.4-diaminobutane (4DA, PHU9), 1.6-diaminohexane (6DA, PHU10), 1.10-diaminodecane (10DA, PHU11), and 1.12-diaminododecane (12DA, PHU12) as detailed in Table 2.

Figure 6. Synthesis of PHU9-12 from Seb-bCC-ester with different diamines, and pictures of PHUs directly taken out from the extruder.

As these PHUs were insoluble in most classical organic solvents, such as DMSO or DMF for instance, their characterization by NMR and SEC was not easily feasible. However, FTIR spectroscopy analyses have been performed. The FTIR spectra presented in Figure 7 show the expected bands corresponding to urethane bond (ν = 1685 cm⁻¹), in which the slightly visible shoulder (ν = 1733 cm⁻¹) is representative of the ester moieties in beta position of the urethane.

| Process            | PHU | P | H | U | Temperature (°C) | Duration | CC conversion (%) | Ratio Urea / Urethane | Mn [D] (g/mol) | Tg (°C) | Td5% (°C) |
|--------------------|-----|---|---|---|------------------|----------|-------------------|-----------------------|---------------|---------|-----------|
| MAGNETIC STIRRING  | 3   | 6 | DA| 80| 4h               | 49       | 0 / 100           | 16 100 [1.5]          | 2 100 [2.6]   | 8       | Nd        |
|                    | 4   | 10| DA| RP| 4h               | 41       | 0 / 100           | 16 300 [1.3]          | 1 700 [1.9]   | 5       | 189       |
| MECHANICAL STIRRING| 5   | 6 | DA| 80| 4h               | > 99     | 0 / 100           | 22 800 [1.3]          | 3 700 [2.3]   | 19      | 207       |
|                    | 6   | 10| DA| RP| 4h               | > 99     | 0.3 / 99.7        | 17 100 [1.4]          | 3 100 [2.0]   | 5       | 209       |
| REACTIVE EXTRUSION | 1   | 6 | DA| 80| 4h               | > 99     | 0 / 100           | 34 400 [1.4]          | 5 000 [2.5]   | 16      | 206       |
|                    | 2   | 10| DA| RP| 4h               | > 99     | 1.1 / 98.9        | 35 600 [1.3]          | 5 600 [1.9]   | 5       | 219       |

a: Obtained by 'H NMR b: Obtained from SEC analysis in DMF, with LiBr salts, Toluene as flow marker and the KD803 Shodex Columns with PS Divinyl benzene phase. c: Obtained from SEC analysis in DMF, with LiBr salts, Toluene as flow marker and the Asahipack Columns with Polyvinyl Alcohol phase. d: DSC second heating cycle. e: TGA, RT to 600°C under N2 flow. RP: Ramp Protocol: 80°C/85°C/90°C/95°C: 45min/15min/15min/65min. Nd : Not Determined.
The band corresponding to NH and OH vibrations (ν = 3400 cm⁻¹) is also visible. Interestingly, this analysis confirms the complete conversion of carbonate functions, as attested by the absence of remaining band at ν = 1782 cm⁻¹, corresponding to the carbonyl of the cyclic carbonate ring. This result confirms the good homogenization of the reactive medium within the extruder until it is blocked. As expected, the extrusion process contributes to shortening the reaction times drastically thus limiting the occurrence of secondary reactions. In addition, and more importantly, the conversion of carbonate functions was complete without requiring any catalysts. Regarding the amount of by-products contained in the so-created PHUs, the ratio amide/urethane/urea was calculated, as example, for PHU₉. HR-MAS and ¹H NMR analysis were performed respectively on the insoluble and soluble fractions, in DMSO-d₆ (see Figure SI-12). The integration of NMR signals gave the following ratios: 5.4/92.8/1.7 for the insoluble part, and 5.6/94.4/0 for the soluble fraction of PHU₁₀. These results demonstrate that the amount of by-products in Seb-bCC-ester based PHUs remains very low, discharging side reactions from the insolubility issues. Besides, PHU₉₋₁₂ were found to be completely soluble in 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), proving the absence of cross-linking in the material. It was finally hypothesized that the insoluble fraction in DMSO might contain high molar masses chains. This feature will be further discussed.

Thermal properties of Seb-bCC-ester based PHUs

PHUs thermal stabilities (T_d5%) and T_gₜₜ were determined by TGA and DSC, respectively. These values are affected by the diamine chain length: the longer the diamine (from 4DA to 12DA), the lower the glass transition temperature. Indeed, a longer diamine chain length leads to an increase of chain mobility, decreasing the energy needed to induce the glass transition temperature phenomenon. This observation was already made by Benyaha et al., demonstrating the relation between diamine structure and final polymer properties. In addition, the thermal stability of the PHUs is directly correlated to the thermal stability of the diamine. The longer the aliphatic diamine, the higher the PHU thermal stability (see Figure 8). Seb-bCC-ester based PHUs were then obtained with relatively high thermal stability up to 250°C, with a range of T_gₜₜ from -0.9°C to 19°C. TGA and DSC second heating cycle curves can be seen in Figures SI-13 and SI-14.

The above-mentioned results demonstrate that the reactive extrusion process can be efficiently applied to PHUs synthesis and adapted to a wide range of monomers keeping the consistency of the expected final polymer properties.

| PHU | DA  | Polymerization Time | T_gₜₜ (°C) | T_d5% (°C) | T_m(s) (°C) |
|-----|-----|---------------------|-----------|-----------|-------------|
| 9   | 4DA | 1h26                | 8.1       | 217       | --          |
| 10  | 6DA | 1h                  | 3.8       | 220       | --          |
| 11  | 10DA| 21min               | 0         | 239       | 54/78       |
| 12  | 12DA| 1h05                | -0.9      | 250       | 58/89       |

Table 2: Thermal properties of Seb-bCC-ester based PHUs synthesized at 90°C through Reactive Extrusion.
Finally, in order to confirm the results previously demonstrated on DGDC regarding the efficiency of reactive extrusion compared to classical polymerization, the synthesis of PHU$_{10}$ (DGDC/6DA/90°C/1h) was reproduced, using magnetic and mechanical stirring (PHU$_{13}$ and PHU$_{14}$, see Table 3).

As a rapid mean of comparison, stacked curves obtained after DSC second heating cycle for PHU$_{10,13,14}$ are presented in Figure 9. As expected, the highest $T_g$ was obtained for PHU$_{10}$, synthesized through extrusion and the second highest was with mechanical stirring.

Additionally, the Seb-bCC-ester based PHUs prepared from magnetic and mechanical stirring were found to be soluble in classical organic solvents. $^1$H NMR spectra, FTIR spectra and SEC chromatograms are presented in Figures SI-15, SI-17 and SI-18. According to those data, the carbonate function conversion was found to be incomplete. Despite the fact that SEC traces did not allow accurate molar mass calculation, the solubility of those compounds in DMF and DMSO could be related to their lower molar mass, in comparison to PHUs synthesized by reactive extrusion.

**Table 3.** Seb-bCC-ester based PHUs synthesized at 90°C by mechanical or magnetic stirring and associated thermal properties.

| Process | PHU | DA | Polymerization time | $T_{d5\%}$ ($°C$) | $T_g$ ($°C$) |
|---------|-----|----|---------------------|-------------------|------------|
|         |     |    |                     |                   |            |
**Magnetic Stirring**

| 13 | 6DA | 1h | 235 | -10 |

**Mechanical Stirring**

| 14 | 6DA | 1h | 242 | -3 |

This observation is consistent with the above discussed, $T_g$ trend, according to Flory Fox relation between $M_n$ and $T_g$ for a given polymer.

The above results show that an efficient blending and homogenization of the reaction medium is required during the whole polymerization to reach a full carbonate conversion. Indeed, in the case of bulk polymerization between bisCCs and amines, the highly viscous systems require an efficient shearing along with the polymerization in order to ensure the diffusion of reactive species.

In addition to the excellent mixing capacity brought by the reactive extrusion process on highly viscous systems like Seb-bCC-ester based PHUs, allowing short reaction time and minimizing side reactions, the second added value to such process is the capacity to produce “ready to use” materials.

**Toward reactive extrusion for 'Non-Activated' bisCC: a step further**

Finally, the reactive extrusion process was tested on a non-activated (bis)amide-carbonate. This bisCC was synthesized from methyl undecenoate and 6DA, leading to Und-6DA and then to Und-6DA-bisCC by CO$_2$ fixation, after an epoxidation step (Und-6DA-bisEpox), according to the protocol published by Maisonneuve et al.$^{46}$. Detailed $^1$H NMR spectra of Und-6DA, Und-6DA-bisEpox intermediate and final Und-6DA-bisCC, as well as detailed synthetic procedures, can be found in Figures SI-21, SI-22, SI-23. In the case of this bisCC, the cyclic carbonate is substituted by a long alkyl chain. As demonstrated by Garipov et al., the aliphatic chain in alpha position of the carbonate ring exhibits an electron releasing effect which decreases the electrophilicity of the carbonyl and thus reduces the reactivity of the monomer.$^{28}$ Besides, the presence of two amide groups which are interesting moieties to bring mechanical properties to the PHUs, turn these reactants in very hard to process materials. Indeed, the carbonate monomer exhibits high melting points (114°C) and is difficult to solubilize in common solvents.$^{46}$. Polymerizing by reactive extrusion Und-6DA-bisCC with 6DA, 10DA, m-xylylene diamine or L-Lysine as comonomers, led to PHU$_{15-18}$, as reported in Table 4 and Figure 10. Due to the melting points of amide-based CCs, polymerizations were performed over 120°C in order to ensure a complete melting (220°C for PHU$_{18}$). No catalysts were added and the screw rotation speed was kept at 100 rpm.

As the final PHUs so-formed were found very difficult to solubilize in classical solvents, FTIR spectroscopy was used to analyze their structure. The stacked spectra displayed in Figure 11 show that complete conversion of cyclic carbonate functions was obtained for PHU$_{18}$ synthesized obtained with 10DA as co-monomer, and very low amount of carbonate functions are remaining in the other cases (small remaining band at $\nu = 1782$ cm$^{-1}$). Besides, on these spectra, is also visible the band corresponding to urethane moiety ($\nu = 1685$ cm$^{-1}$) and the one appearing at $\nu = 1632$ cm$^{-1}$ attributed to the amide bond.

![Figure 10](image-url)
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Figure 11. Stacked FTIR spectra of PHU$_{17}$ (Grey), PHU$_{16}$ (blue), PHU$_{15}$ (Red) and PHU$_{18}$ (black).

Figure 12 displays the $\Delta P = f(t)$ profiles, obtained for each system during the polymerizations. As clearly visible on the Figure, the pressure values reached in the specific case of Und-6DA-bisCC were extremely high, up to 40 bars for PHU$_{15,16,17}$ and even to 120 bars in the case of L-Lysine-based PHU (PHU$_{18}$). These very high pressures demonstrate the drastic increase in viscosity, correlated with the fast molar mass build-up and the extremely cohesive feature of this amide type bisCC. Temperature and time-related $\Delta P$ profiles can be seen in Figure SI-24. In the cases

Figure 12. $\Delta P = f(t)$ profiles of PHU$_{17}$ (Red), PHU$_{16}$ (Blue), PHU$_{15}$ (Black) and PHU$_{18}$ (Orange). (Drops in pressure corresponds to polymerization temperature increase)

Thermal properties of Und-6DA-bisCC based PHUs

As previously mentioned, the Und-6DA-bisCC based PHUs were found difficult to solubilize in classical solvents, preventing size exclusion chromatography analysis. Furthermore, a recent study published by Zhang et al. explained that segmented PHUs containing amide linkages may interact with common SEC columns, thus making molar masses characterization by SEC not feasible. Nevertheless, thermal analysis (DSC and TGA) have been performed on these PHUs and results are reported in Table 4. Delebecq et al. demonstrated that electronic effects of $\alpha$-$\beta$ substituents on cyclic carbonates not only increase their reactivity but also impact the thermal degradation of the final PU, in a negative way. This relevant conclusion explains the higher thermal stabilities, up to 325$^\circ$C, measured for the non-activated Und-6DA-bisCC based PHUs, compared to previous PHUs synthesized from ether and ester activated carbonates. TGA and DSC curves of PHU$_{15-18}$ can be seen in Figure SI-25 and SI-26.

Table 4. Und-6DA-based PHUs and associated thermal properties.

| PHU | Diamines | Time (h) | $T_g$ (°C) | $T_m$ (°C) | $T_{d5\%}$ (°C) |
|-----|-----------|----------|-------------|-------------|-----------------|
| 15  | 10DA      | 3h30     | 17          | 100/140$^b$ | 263             |
| n  | monomer | time | COOH | T<sub>5%</sub> | T<sub>d5%</sub> |
|----|---------|------|------|---------------|--------------|
| 16 | 6DA     | 3h   | 22   | 95<sup>b</sup> | 266          |
| 17 | m-xyylene | 6h   | 32   | --            | 265          |
| 18 | L-Lysine | 7h15 | 36   | --            | 325          |

* Determined by DSC second heating cycle at 10°C/min.  
  b With crystallization upon heating.  
  c Determined by TGA at 10°C/min under N<sub>2</sub>.

As expected, amide linkages bring rigidity to the materials and T<sub>5%</sub> values for Und-6DA-bisCC based PHUs, were found to be higher than those of DGDC and Seb-bCC-ester based PHUs (up to 36°C).

![Image of PHU15, PHU16, PHU17, and PHU18](image)

**Figure 13.** Pictures of PHU<sub>15-18</sub>, directly obtained from the reactor of the extruder.

Furthermore, the highest thermal stability (T<sub>5%</sub> = 325°C) was achieved with safe, biobased, but hard to process L-Lysine (mp = 215°C). Once again, this result highlights the benefit brought by reactive extrusion on melt polymerizations of high melting points and/or very cohesive derivatives.

Finally, as shown in Figure 13, Und-6DA-based PHUs were extruded and obtained as homogeneous materials and this in much shorter reaction times compared to results previously published by Maisonneuve *et al.* (5 to 7 hours vs few days).<sup>46</sup> In their study, the authors deal with the synthesis and polymerization of a series of fatty acid-based bis-cyclic carbonates bearing amide linkages. Bulk polymerizations were performed at 120°C or 140°C, allowing the relevant comparison with PHU<sub>15</sub>, PHU<sub>16</sub>, and PHU<sub>17</sub>. In order to reach high carbonate functions conversion, reactions times within between 5h and 7 days were needed. The low reaction rate is due to the very slow mobility of reactants, trapped in the very viscous and cohesive hydroxyurethane-amide systems. The above results thus demonstrate that even non-activated carbonates can be polymerized in short reaction times with a palette of diamines exhibiting various structures.

**Conclusion**

Different PHUs have been synthesized from bio-based activated and non-activated bicyclic carbonates, Seb-bCC-ester, DGDC and Und-6DA-bisCC, through reactive extrusion process.

Complete conversions of reactive carbonate functions were obtained in the case of DGDC and Seb-bCC-ester monomers, in short reaction times (hours instead of days), without the need of excessive heating. Those mild conditions and the shorter reaction times prevent the formation of by-products, as no urea was created with DGDC and very low amounts of urea and amide were detected in the case of Seb-bCC-ester based PHUs. Regarding these last polymers, the consistency of T<sub>5%</sub> and thermal stabilities obtained with different diamines prove the versatility of the process with respect to different monomer structures.

Besides, the processability brought by this system is making possible the synthesis of very dense PHUs materials, even from highly viscous precursors. Finally, this study demonstrates the possibility to polymerize non-activated and amide based bisCCs (such as Und-6DA-bisCC), in reasonable conditions of time and directly leading to rigid materials. Reactive extrusion process stands for a promising tool to push PHU synthesis a bit closer to a viable industrial process.

Finally, one can notice that the mini-extruder equipped with conic twin screws and circulation channel used in this work is not fairly representative of the machines used in industries. Industrial systems are composed of single or twin several meters long coaxial screws.<sup>49</sup> This means that generally residence times are relatively shorts, whereas in this study the polymerizations times last until 7 hours. Nevertheless, the results discussed in this publication are intended to prove the benefit that can be brought by this kind of solvent-free technique on PHU synthesis. Even if polymerization times modulate the final properties and as a consequence...
can be adjusted according to targetted applications, further optimization is needed to fit with industrials equipments. As a perspective, the polymerization by reactive extrusion of thermosets PHUs will be investigated, in order to evaluate possible shorter polymerization times.

**ASSOCIATED CONTENT**

Additional $^1$H NMR spectra, FTIR spectra of PHUs and/or bis-cyclic carboantes. Thermal analysis (DSC and TGA) traces of PHUs. SEC comparison of DGDC-2DA-based PHUs synthesized through magnetic stirring, mechanical stirring and reactive extrusion. Additonal analysis (HNMR, FTIR, SEC) on Seb-bCC-ester-based PHUs synthesizez through magnetic and mechanical stirring. \((\Delta P, T) = f(t)\) profiles for Und-6DA-based PHUs.

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**ACKNOWLEDGEMENTS**

The authors gratefully acknowledge the financial support from Region Nouvelle Aquitaine and ITERG. The authors sincerely thank ITERG (French Institute for Fats and Oils) for providing chemical samples.

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Benefit of the reactive extrusion in the course of poly(hydroxy)urethanes synthesis by aminolysis of cyclic carbonates

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Figure SI-17  FTIR spectra of Seb-bCC-ester-based PHUs. PHU$_{13}$ (6DA, magnetic stirring), PHU$_{14}$ (6DA, mechanical stirring), PHU$_{19}$ (10DA, magnetic stirring) and PHU$_{20}$ (10DA, mechanical stirring).

Figure SI-18  SEC traces in DMF of Seb-bCC-ester-based PHUs synthesized through mechanical stirring from 6DA and 10DA

Figure SI-19  Overlay of DSC second heating cycles of PHU$_{13}$ (Seb-bCC-ester/6DA, magnetic stirring) and PHU$_{14}$ (Seb-bCC-ester/6DA, mechanical stirring)

Figure SI-20  Overlay of DSC second heating cycle of PHU$_{19}$ (Seb-bCC-ester/10DA, magnetic stirring) and PHU$_{20}$ (Seb-bCC-ester/10DA, mechanical stirring)

III. Und-6DA-based PHUs

Figure SI-21  Epoxidation and carbonation steps leading to Und-DA-bisCC from Und-6DA

Figure SI-22  Stacked $^1$HNMR Spectra of Und-6DA and Und-6DA-bisEpoxide
**Figure SI-23**  
$^1$HNMR spectrum of Und-6DA-bisCC

**Figure SI-24**  
$\Delta P = f(t)$ profiles obtained during synthesis of Und-6DA-based PHUs.

**Figure SI-25**  
Overlay of TGA traces of Und-6DA-bisCC-based PHUs

**Figure SI-26**  
Overlay of DSC second heating cycles of Und-6DA-bisCC-based PHUs
I. DGDC Based PHUs

Figure SI-1. ¹H NMR spectrum of DGDC, in DMSO-d6, RT, 64 scans
Figure S1-2. $^1$H NMR spectrum of PHU$_1$, DGDC/6DA/Reactive Extrusion, in DMSO-$d_6$, RT, 1024 scans

Figure S1-3. $^1$H NMR spectrum of PHU$_2$, DGDC/10DA/Reactive Extrusion, in DMSO-$d_6$, RT, 1024 scans
Figure SI-4: FTIR spectra of PHU₁ (red) and PHU₂ (black)

Figure SI-5. Stacked ¹H NMR spectra of DGDC-based PHUs synthesized from 6DA and 10DA through magnetic stirring. PHU₁ (top), PHU₄ (bottom). *Residual cyclic carbonates
Figure SI-6 Stacked $^1$H NMR spectra of DGDC-based PHUs synthesized from 6DA and 10DA through mechanical stirring. PHU$_5$ (top), PHU$_6$ (bottom). *Residual cyclic carbonates

Figure SI-7. SEC traces in DMF, DGDC and 10DA based PHUs synthesized through different processes: PHU$_2$ (reactive extrusion), PHU$_4$ (magnetic stirring) and PHU$_6$ (mechanical stirring)
Figure SI-8. Overlay of TGA traces of DGDC/10DA-based PHUs, synthesized through magnetic stirring (PHU$_{4}$, black), mechanical stirring (PHU$_{6}$, red) and reactive extrusion (PHU$_{2}$, blue)

Figure SI-9. Overlay of DSC second heating cycle of DGDC/6DA-based PHUs. PHU$_{1}$ (reactive extrusion, black), PHU$_{5}$ (magnetic stirring, red), PHU$_{3}$ (mechanical stirring, blue)
II. Seb-bCC-ester based PHUs

Figure SI-10. Overlay of DSC second heating cycle of DGDC/10DA-based PHUs. PHU$_2$ (reactive extrusion, black), PHU$_4$ (magnetic stirring, red), PHU$_6$ (mechanical stirring, blue)

Figure SI-11. $^1$H NMR spectrum of Seb-bCC-ester, in DMSO-d6, RT, 64 scans
A. Seb-bCC-ester based PHUs from reactive extrusion

Seb-bCC-ester based PHUs synthesized from reactive extrusion were found to be partially insoluble in classical solvents such as DMSO, leading to a soluble fraction (analyzed by classical NMR analysis) and to an insoluble fraction, which swells in DMSO-d6 and which can be characterized by the HR-MAS technique. The analysis was performed as follow:

The HR-MAS analysis was performed by the CESAMO (ISM-UMR5255, Université de Bordeaux). The polymer was dissolved in small amount of DMSO and 20 µL of the solution was introduced into a HRMAS-NMR 4 mm zirconia rotor, fitted with a perforated Teflon insert and sealed with a Kel-F cap. All NMR experiment were recorded at 25 °C on Bruker Avance III 600 equipped with a Bruker $^1$H,$^{13}$C HRMAS probe working at $^{13}$C and $^1$H frequencies of 150.93 and 600.16 MHz, respectively. The rotor was inserted into the HR-MAS probe and MAS rate of 2500 Hz. All NMR spectra were phased and baseline-corrected.

![HR-MAS spectrum](image)

Figure SI-12. Zoom between 5.6 and 8.1ppm on $^1$H NMR spectrum, of the soluble fraction of PHU$_{ins}$ in DMSO-d6 at RT (top), Zoom between 5.6 and 8.1ppm on $^1$H HR-MAS spectrum, of the insoluble and swollen fraction of PHU$_{ins}$ in DMSO-d6 at RT (bottom)
Figure S1-13. Overlay of TGA traces of Seb-bCC-ester-based PHUs synthesized through reactive extrusion. PHU₉ (4DA, Red), PHU₁₀ (6DA, Black), PHU₁₁ (10DA, Grey) and PHU₁₂ (12DA, Blue)

Figure S1-14. Overlay of TGA traces of Seb-bCC-ester-based PHUs synthesized through reactive extrusion. PHU₉ (Red), PHU₁₀ (Black), PHU₁₁ (Grey) and PHU₁₂ (Blue)
B. From magnetic and mechanical stirring

In order to compare reactive extrusion and classical polymerization stirring devices, four Seb-bCC-ester based PHUs were synthesized with 10DA and 6DA, through mechanical stirring and magnetic stirring. Synthesis details and associated thermal properties are summarized in Table 1. Seb-bCC-ester based PHUs synthesized with mechanical stirring were found to be soluble in classical solvents such as DMSO or DMF, making possible NMR and SEC analysis. Results are presented in Figure 10 and 11. Given the shape of the chromatograms, meaning the spreading of the curves on the whole retention time scale, $M_n$ values were not calculated. Indeed, we are firmly convinced that those values, added to the dispersities, integrated on the so broad scale and would have been meaningless.

Table SI-1. Seb-bCC-ester-based PHUs synthesized from 6DA and 10DA, through mechanical and magnetic stirring, and associated thermal properties

| PHU | Process          | Diamine | Duration | $T_g$ (°C) | $T_{d5\%}$ |
|-----|------------------|---------|----------|------------|------------|
| 13  | Magnetic Stirring| 6DA     | 1h       | -9.5       | 235        |
| 14  | Mechanical Stirring| 6DA   | 1h       | -2.5       | 242        |
| 19  | Magnetic Stirring| 10DA    | 21min    | -3.3       | Nd         |
| 20  | Mechanical Stirring| 10DA  | 21min    | -3.3       | 246        |

Figure SI-15. $^1$H NMR spectrum of PHU14, Seb-bCC-ester/6DA/Mechanical stirring (top) and magnetic stirring (bottom), in DMSO-d$_6$, RT, 64 scans. *Residual cyclic carbonate. Ratio Amide/Urethane/Urea - Conversion: 1.7/98.3/0 – 89.4% (PHU$_{14}$), 5.9/94.1/0 - 76.5% (PHU$_{13}$).
Figure S16. $^1$H NMR spectrum of PHU19, Seb-bCC-ester/10DA/Mechanical stirring (top) and magnetic stirring (bottom), in DMSO-d6, RT, 64 scans. *Residual cyclic carbonate. Ratio Amide/Urethane/Urea - Conversion: 2.2/97.8/0 – 85.9 % (PHU19), 1.7/98.3/0 – 90.0%

Figure S17. FTIR spectra of Seb-bCC-ester-based PHUs. PHU13 (6DA, magnetic stirring), PHU14 (6DA, mechanical stirring), PHU19 (10DA, magnetic stirring) and PHU20 (10DA, mechanical stirring).
Figure SI-18. SEC traces in DMF of Seb-bCC-ester-based PHUs made through mechanical stirring from 6DA (PHU\textsubscript{13}, top), and 10DA (PHU\textsubscript{19}, bottom)
Figure SI-19. Overlay of DSC second heating cycles of PHU\textsubscript{13} (Seb-bCC-ester/6DA, magnetic stirring) and PHU\textsubscript{14} (Seb-bCC-ester/6DA, mechanical stirring)

Figure SI-20. Overlay of DSC second heating cycle of PHU\textsubscript{19} (Seb-bCC-ester/10DA, magnetic stirring) and PHU\textsubscript{20} (Seb-bCC-ester/10DA, mechanical stirring)
III. Und-6DA-based PHUs

Und-6DA

Und-6DA-bisEpoxide

Und-6DA-bisCC

Figure SI-21. Epoxidation and carbonation steps leading to Und-DA-bisCC from Und-6DA
Figure SI-22. Stacked $^1$H NMR Spectra of Und-6DA (top) and Und-6DA-bisEpoxyde (bottom), in CDCl$_3$, RT

Figure SI-23. $^1$H NMR spectrum of Und-6DA-bisCC in CDCl$_3$, RT, 64 scans. * TBABr traces
Figure SI-24. ∆P = f(t) profiles obtained during synthesis of Und-6DA-based PHUs. Top: PHU_{16} (6DA, left), PHU_{17} (m-xylylene-DA, right). Bottom: PHU_{15} (10DA, left), PHU_{18} (L-Lysine, right)
Figure SI-25. Overlay of TGA traces of Und-6DA-bisCC-based PHUs, 10°C/min, under azote until 600°C and under air until 700°C.

Figure SI-26. Overlay of DSC second heating cycles of Und-6DA-bisCC-based PHUs, 10°C/min, from -40°C to 180°C.