



HAL
open science

Synthesis of fatty acid-based Non-Isocyanate Polyurethanes, NIPUs, in bulk and mini-emulsion

Estelle Rix, Etienne Grau, Guillaume Chollet, Henri Cramail

► **To cite this version:**

Estelle Rix, Etienne Grau, Guillaume Chollet, Henri Cramail. Synthesis of fatty acid-based Non-Isocyanate Polyurethanes, NIPUs, in bulk and mini-emulsion. *European Polymer Journal*, 2016, 84, pp.863-872. 10.1016/j.eurpolymj.2016.07.006 . hal-01373137

HAL Id: hal-01373137

<https://hal.science/hal-01373137>

Submitted on 26 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis of fatty acid-based Non-Isocyanate Polyurethanes, NIPUs, in bulk and mini-emulsion

Estelle Rix^{a,b}, Etienne Grau^{a,b}, Guillaume Chollet^c, Henri Cramail^{a,b*}

^a Centre National de la Recherche Scientifique, Laboratoire de Chimie des Polymères Organiques, UMR 5629, F-33607 Pessac Cedex, France.

^b Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, ENSCBP Bâtiment A, 16, Avenue Pey-Berland, F-33607 Pessac Cedex, France

^c ITERG, 11 rue Gaspard Monge, Parc Industriel, Pessac Cedex, F-33600, France

*corresponding author: cramail@enscbp.fr

Abstract

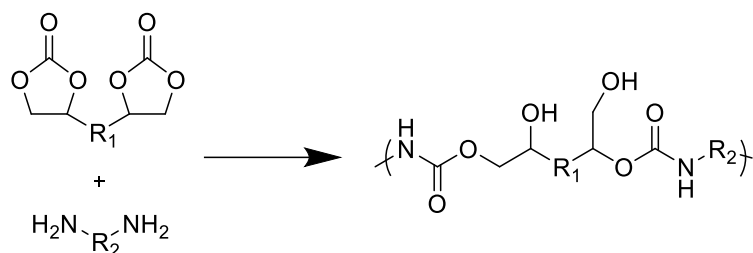
The synthesis of fatty acid-based poly(hydroxy urethane)s, PHUs, was investigated. Bulk polymerization of fatty acid-based bis-carbonates with fatty acid diamine, Priamine® 1075, was first studied, allowing us to prepare non-isocyanate polyurethanes, NIPUs, at low temperature (60°C) and in few hours. Water-borne NIPUs latexes were then prepared with the same monomers through mini-emulsion process. Different surfactants and hydrophobic additives were tested in order to obtain stable emulsions and polymer particles. NIPUs latexes with solid content up to 30 wt.% could be achieved. As a general trend, NIPUs prepared in mini-emulsion exhibited lower molar masses than the ones formed in bulk, phenomenon explained by the partial hydrolysis of cyclic carbonates.

Keywords

Poly(hydroxy urethane), mini-emulsion, latex, fatty acids, water-borne, NIPUs

Introduction

Polyurethanes (PUs) are commodity polymers used in a wide range of applications. The latter are industrially produced by polyaddition of polyols and polyisocyanates in the presence of catalysts. Due to the toxicity of isocyanate derivatives and to some of the catalysts used, alternative sustainable routes to PUs have been developed.[1] One of the most promising strategy thoroughly investigated nowadays is the polyaddition of bis-cyclic carbonates with polyamines yielding poly(hydroxy urethane)s, PHUs (Scheme 1).



Scheme 1: Synthesis of poly(hydroxy urethane)s, PHUs

In addition, due to the depletion of fossil resources, the synthesis of PUs and PHUs from bio-based resources have been carried out, especially from vegetable-based derivatives.[1-7] Polyurethanes can be prepared under various forms depending on the application, such as foams, fibers, TPUs, latexes, etc. Water-borne PU dispersions are generally used for coating or adhesive applications. There is today an increasing interest for water-borne PU dispersions as the latter release less organic volatile compounds (VOCs) than solvent-borne systems. There are many examples of PU aqueous dispersions in the literature [8-10], while PHUs aqueous dispersions are barely discussed. In 2008, Rhodia patented glycerol carbonate-based aqueous dispersions of low molar mass PHUs, that were, in a second step, cross-linked with water-soluble isocyanates.[11] Ochiai *et al.* investigated the polyaddition of bis-cyclic carbonates and diamines in water, without any surfactant; the authors tested two bis-cyclic carbonates derived from bisphenol-A and 1,4-butanediol with 1,6-hexanediamine and 4,4'-methylenebis(cyclohexylamine) as di-amines.[12] The authors obtained PHUs of relatively low molar masses ($M_n < 4.5 \text{ kg}\cdot\text{mol}^{-1}$, $D=1,8-2,2$).

In this study, we performed aqueous dispersions of PHUs by mini-emulsion polymerization. This process has already been described to prepare water-borne PUs dispersions, [13-15] and, more recently, bio-based PUs, [16, 17] following the classical reaction of diisocyanates with diols. In this study, we extended the mini-emulsion polymerization process to the polyaddition of hydrophobe fatty acid-based bis-cyclic carbonates and diamines to design NIPUs latexes.

Experimental section

Materials

The dimer diamine, so-called DDA, was kindly provided by CRODA® under the tradename Priamine® 1075, as well as the dimer diacid Pripol® 1009. The poly(ricinoleic acid) diacid E1450 and olive oil were supplied by ITERG. 4-(dimethylamino)pyridine (DMAP, >99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%) and hexadecane (>99%) were supplied by Sigma-Aldrich. Tween® 80 was supplied by Fisher Scientific. 1,3-Dicyclohexylcarbodiimide (DCC, 99%) was

supplied by ABCR. 4-vinyl-1,3-dioxolan-2-one (vinyl ethylene carbonate, 99%) was supplied by Alfa-Aesar. 4-(hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate, >90%) was supplied by TCI. All solvents were reagent grades and used as received.

Methods

Synthesis of BCC

In a round-bottomed flask equipped with a magnetic stirrer, 1,4-butanethiol (1 eq., 26 g), vinyl ethylene carbonate (2 eq., 48.5 g), dichloromethane (10 mL) and 2,2-dimethoxy-2-phenylacetophenone (0.001 eq., 110 mg) are introduced. The flask is introduced in a water bath at ambient temperature under UV light at 365nm (6 W). The reaction is followed by ¹H NMR; complete conversion is achieved in 8 h. After removal of the dichloromethane by vacuum evaporation, the product BCC is obtained as a colourless viscous liquid, with a yield of 100%. The structure of BCC is confirmed by ¹H NMR analysis, with characteristic peaks at 4.1, 4.6 and 4.9 ppm.

Synthesis of BGC-C₃₆

In a three-necked round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet and an addition funnel, reactants are introduced: glycerol carbonate (2 eq., 7.7 g), Pripol® 1009 (1 eq., 18.7 g), 4-dimethylaminopyridine (0.5 eq., 2 g) and dichloromethane (180 mL). The flask is introduced in an ice bath under magnetic stirring. The addition funnel is filled with a solution of N,N'-dicyclohexylcarbodiimide (2 eq., 13.5 g) in 25 mL of dichloromethane. This solution is introduced drop-wise in the flask in approximately 15 min. The reaction medium is left under magnetic stirring at ambient temperature for 24 h, then filtered on sintered glass and the dichloromethane is removed by vacuum evaporation. 150 mL of chloroform is then introduced, and the organic phase is washed three times over a 0.1 M HCl aqueous solution and three times over a saturated solution of Na₂CO₃. After removal of chloroform under vacuum, the product BGC-C₃₆ is obtained as a viscous liquid. The structure of BGC-C₃₆ is confirmed by ¹H NMR analysis and FTIR: characteristic peaks at 4.2-4.4, 4.55 and 4.95 ppm are visible in ¹H NMR spectrum and characteristic absorbance bands of ester and cyclic carbonate in FTIR spectrum, respectively at 1740 and 1800 cm⁻¹ (see Figure S1).

Synthesis of BGC-E₁₄₅₀

In a three-necked round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet and an addition funnel, reactants are introduced: glycerol carbonate (2 eq., 3.25 g), α,ω-COOH poly(ricinoleic acid) E₁₄₅₀ (1 eq., 20 g), 4-dimethylaminopyridine (0.5 eq., 840 mg) and

dichloromethane (100 mL). The flask is introduced in an ice bath under magnetic stirring. The addition funnel is filled with a solution of N,N'-dicyclohexylcarbodiimide (2 eq., 5.68 g) in 20 mL of dichloromethane. This solution is introduced drop-wise in the flask in approximately 15 min. The reaction medium is then left under magnetic stirring at ambient temperature for 24 h. The reaction medium is then filtered on sintered glass and the dichloromethane is removed by vacuum evaporation. 150 mL of chloroform is then introduced and the organic phase is washed three times over a 0.1 M HCl aqueous solution and three times over a saturated solution of Na₂CO₃. After removal of chloroform under vacuum, the product BGC-E₁₄₅₀ is obtained as a viscous liquid. The structure of BGC-E₁₄₅₀ is confirmed by ¹H NMR analysis and FTIR: characteristic peaks at 4.2-4.4, 4.55 and 4.95 ppm are visible in ¹H NMR spectrum and absorbance bands in FTIR spectrum at 1740 and 1800 cm⁻¹ (see Figure S2).

Bulk polymerization: general procedure

In a tubular Schlenk flask equipped with a magnetic stirrer, the bis-cyclic carbonate and the diamine are introduced (total mass~500 mg). The Schlenk is placed in an oil bath under magnetic stirring and maintained at a chosen temperature. The polymerization is monitored by ¹H NMR spectroscopy by following the disappearance of the signals characteristic of the cyclic carbonate (using, as internal reference, the CH₂ protons in alpha of the ester function).

Emulsification: general procedure

Material: The ultra-sound probe used is a Bioblock Scientific VibracellTM at 750 W, with an amplitude of 40%.

Typical emulsification process for a solid content of 20 wt.%:

Aqueous phase (12 g): the surfactant is dissolved in distilled water under magnetic stirring.

Organic phase (3 g): it is composed of the bis-cyclic carbonates and diamines and a hydrophobic agent. The latter are quickly mixed in an ice bath prior to emulsification.

First, the aqueous phase is introduced in a beaker under magnetic stirring. The organic phase is then introduced drop-wise over 1 min to obtain the dispersion. The latter is then placed in an ice bath and emulsified with the ultra-sound probe during 120 s or 240 s.

Mini-emulsion polymerization: general procedure

The mini-emulsion (15 g) is introduced in a round-bottomed flask equipped with an anchor stirrer. The mini-emulsion is then heated at 60°C with a heating plate (Carousel 6 Plus reaction StationTM), while under mechanical stirring at 300 rpm.

Nuclear magnetic resonance (NMR)

^1H and ^{13}C NMR were obtained with a Bruker Avance I 400 spectrometer at 25°C (100.2 MHz and 100.6 MHz for ^1H and ^{13}C analysis respectively). CDCl_3 and DMSO-d_6 were used as solvents. Two-dimension analyses were also performed: ^1H - ^1H COSY, ^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC.

Fourier Transform Infra-Red spectroscopy (FTIR)

FTIR spectra were obtained with a Nicolet iS10 spectrometer from ThermoScientific by attenuated total reflectance. The spectra are the result of 16 scans with a resolution of 4 cm^{-1} .

Size exclusion chromatography (SEC)

SEC analyses were performed in THF at 40°C with a « PL-GPC 50 plus integrated GPC » of Polymer Laboratories-Varian equipped with a series of four columns TOSOH: TSKgel TOSOH :HXL-L (guard column 6,0 mm ID x 4,0 cm L) ; G4000HXL (7,8 mm ID x 30,0 cm L) ; G3000HXL (7,8 mm ID x 30,0 cm L) ; et G2000HXL (7,8 mm ID x 30,0 cm L). The elution flow is $1\text{ mL}\cdot\text{min}^{-1}$ and the elution times controlled by a refractive index detector (RI). The internal reference is trichlorobenzene.

Differential Scanning Calorimetry (DSC)

Thermograms were measured with a DSC Q100 of TA Instruments. For each sample, two heating cycles from -80 to 120°C at $10^\circ\text{C}\cdot\text{min}^{-1}$ were performed. The glass transition temperatures were determined on the second heating cycle.

Dynamic Light Scattering (DLS)

Particle size distributions were measured by DLS with a Zetasizer Nano ZS-90 from Malvern (laser helium-neon 632.8nm, diffused intensity measured at 90°). Mini-emulsions and latex were diluted at 0.01 wt.% in continuous phase (deionized water and surfactant). For each sample, three measurements were performed.

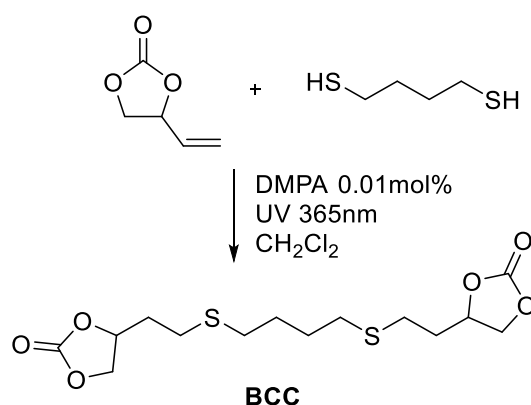
Thermogravimetric Analysis (TGA)

TGA were performed on a TGA-Q50 system from TA instruments at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

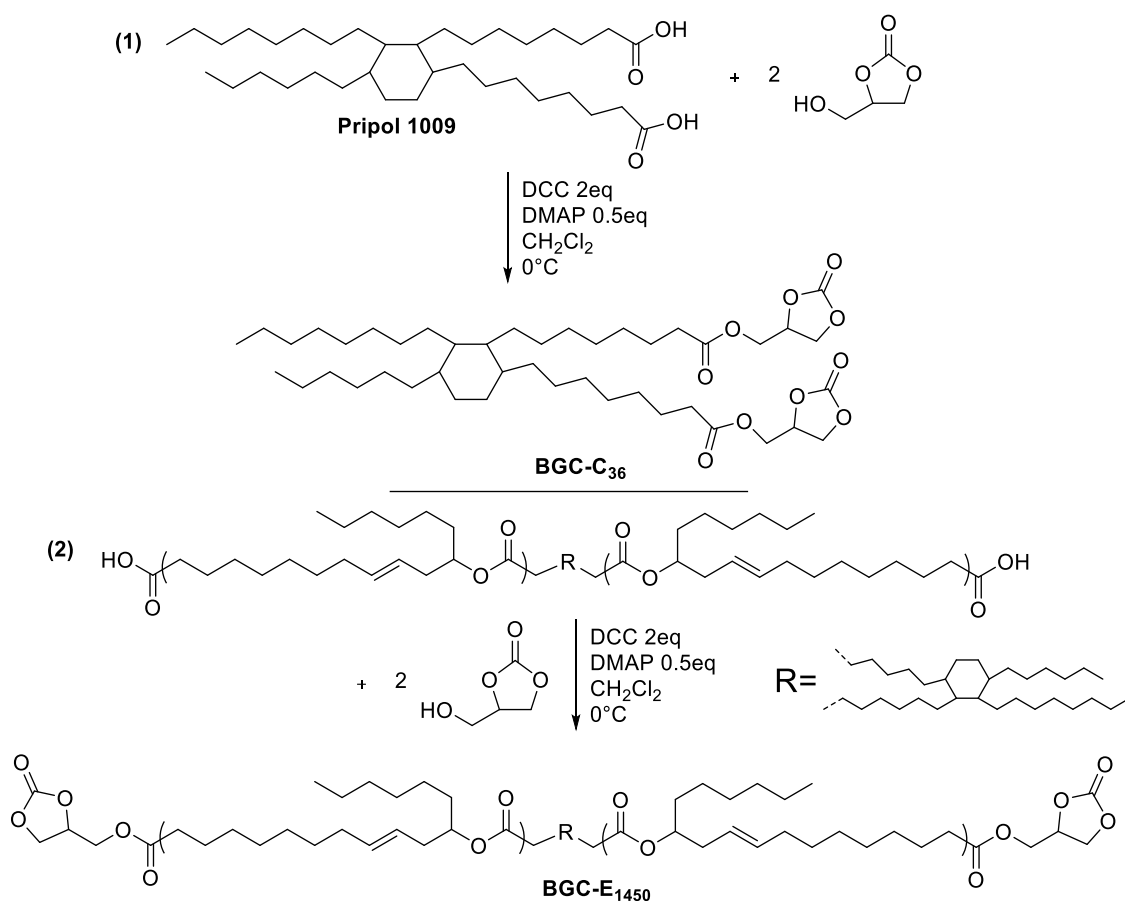
Results and discussion

Bis-cyclic carbonate synthesis

Three bis-cyclic carbonates were synthesized. BCC was obtained by thiol-ene addition between 1,4-butanedithiol and vinyl ethylene carbonate (Scheme 2), while BGC-C₃₆ and BGC-E₁₄₅₀ were synthesized by esterification of bio-based diacids with glycerol carbonate (Scheme 3). BGC-C₃₆ is issued from a bio-based dimer diacids (Pripol® 1009 from CRODA®) containing 36 carbons and BGC-E₁₄₅₀ from E₁₄₅₀, an α,ω -COOH oligo(ricinoleic acid) with a M_n value of 1450 g.mol⁻¹. Indeed, E₁₄₅₀ was obtained by polycondensation of ricinoleic acid in the presence of 0.2 eq. of Pripol® 1009. These three bis-cyclic carbonates were obtained in high yield (over 90%) and their structures confirmed by NMR (see Figures S3, S4 and S5).



Scheme 2: Synthesis of bis-carbonate, BCC



Scheme 3: Synthesis of BGC-C₃₆ (1) and BGC-E₁₄₅₀ (2) (R= Pripol® 1009)

These bis-cyclic carbonates were investigated for their physico-chemical properties. The latter are hydrophobic and liquid at room temperature and are expected to be good candidates for polymerization in mini-emulsion.

The polymerization of these three bis-cyclic carbonates was performed in bulk and in mini-emulsion with a bio-based liquid and hydrophobic fatty acid-based dimer diamine DDA (Figure 1).

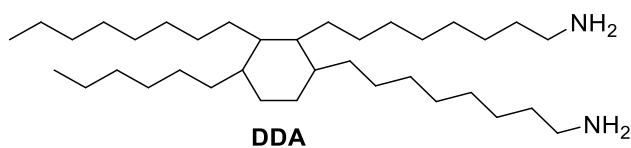
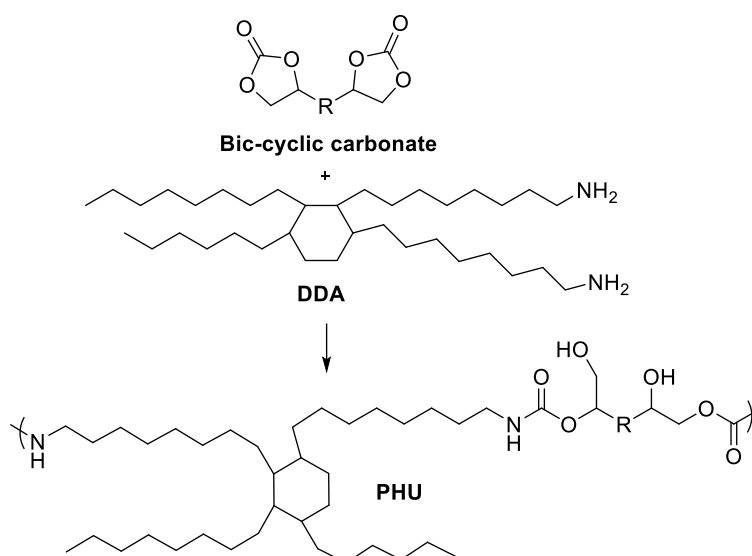


Figure 1: Dimer diamine, DDA (Priamine® 1075 from CRODA®)

Part 1: Bulk polymerization

First, bulk polymerizations of bis-carbonates BCC, BGC-C₃₆ and BGC-E₁₄₅₀ with dimer diamine DDA were investigated (Scheme 4). Due to the uncertainty on the molar mass and carbonate functionality of fatty acid-based monomers BGC-C₃₆ and BGC-E₁₄₅₀, the carbonate/amine ratios were first optimized in order to obtain the highest molar mass PHUs (see Figure S6). The optima

found are 1 eq., 0.75 eq. and 1.3 eq. for BCC, BGC-C₃₆ and BGC-E₁₄₅₀ respectively for 1eq of DDA. These results are understandable since the starting Pripol 1009® contains some trimers and exhibits an apparent functionality over 2, while ricinoleic acid used for E₁₄₅₀ contains traces of oleic acid and thus E₁₄₅₀ exhibits an apparent functionality slightly below 2.



Scheme 4: Bulk synthesis of PHUs from bis-cyclic carbonates with DDA

The polymerizations were monitored by ¹H NMR in CDCl₃ following the disappearance of the signals characteristic of the cyclic carbonates. Results are summarized in Table 1.

Table 1: Polymerization conditions and properties of the PHUs synthesized in bulk polymerization of bis-cyclic carbonate and DDA

Bis-carbonate	Temperature (°C)	Polymerization time (h)	M _w ^a (kg.mol ⁻¹)	Đ ^a	T _g ^b (°C)	T _d ^d (5wt%) (°C)
BCC	60	24	19.6	1.9	-50/ -19	-
	60	14 days	35.5	1.9	-54/ -16	190
BGC-C ₃₆	20	48	10.1	1.7	-23	-
	60	24	14.2	2	-24	232
	90	24	17.7	2.2	-23	-
	130	6	17.6 ^c	2.6	-25	-
BGC-E ₁₄₅₀	20	24	9.3	1.7	-52	-

	60	24	12.1	1.8	-55	228
	90	5	11.4	1.8	-54	-
	130	4	11.6	1.8	-51	-

^a Measured by SEC in THF, PS standard calibration. ^b Measured by DSC at 10°C.min⁻¹ on the second heating cycle. ^c

Only the soluble part was analyzed. ^d Measured by TGA at 10°C/min under nitrogen stream

For each polymerization, the viscosity rises until magnetic stirring becomes impossible, due to the molar mass increase together with the interactions between polymer chains through hydrogen bondings.

In the case of BCC, the PHU obtained at 60°C exhibits a $M_w=19.6 \text{ kg}\cdot\text{mol}^{-1}$ after 24h of polymerization, value that increases to $35.5 \text{ kg}\cdot\text{mol}^{-1}$ after 14 days (see NMR spectrum, Figure S7). The rather slow polymerization together with the relatively low molar mass obtained after 24 h are in agreement with literature data. [18-20]

The polymerizations of BGC-C₃₆ or BGC-E₁₄₅₀ with DDA were performed at 20, 60, 90 and 130°C (see NMR spectra, Figures S8 and S9). The kinetic profiles obtained by ¹H NMR in CDCl₃ for each polymerization temperature and monomer, are displayed in Figure 2. Interestingly, in the case of BGC-C₃₆ and DDA polymerization, the carbonate conversion is rather fast in the first two hours then reaches a plateau between 87 and 99% with respect to the polymerization temperature. For the system BGC-E₁₄₅₀ / DDA, the results are similar, with a full conversion of the carbonate functions reached in only 5 hours at 90°C and 130°C. At lower temperature, a conversion of carbonate functions above 95% can be reached after 24 h. These results demonstrate that polymerization kinetic and conversion of these two bis-carbonates are barely affected by the temperature. It is worth noting that carbonate functions conversion can reach completion in only few hours that makes these monomers of potential interest for industrial purposes. This rather fast kinetics was expected since, in the case of BCC, a thio-ether linkage is located in *gamma* of the cyclic carbonate, while an ester linkage is present in *beta* position for BGC-C₃₆ and BGC-E₁₄₅₀. Indeed, it could be demonstrated that ester or ether functions located nearby the carbonate ring eases its ring-opening by amines. [21]

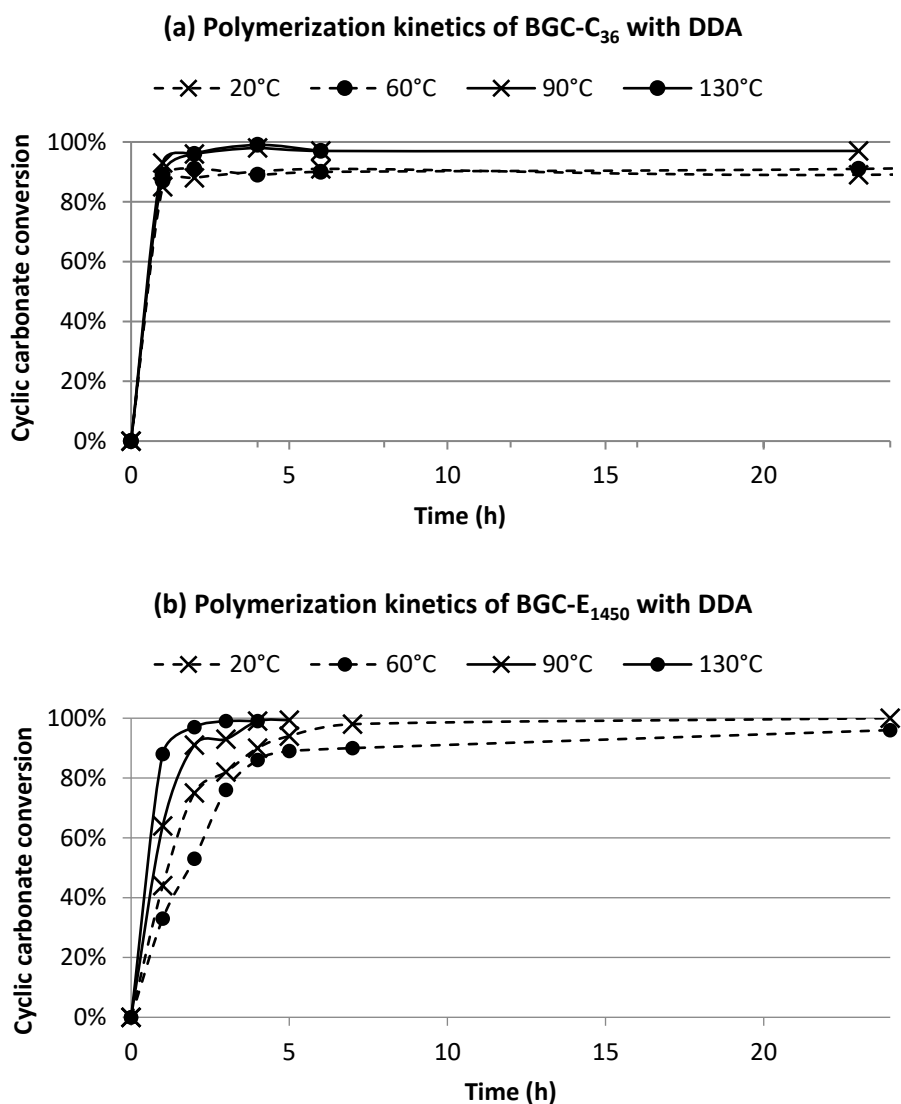


Figure 2: Kinetic profiles of carbonate function conversion followed by ¹H NMR in CDCl₃ for the polymerization of DDA with BGC-C₃₆ (a) or BGC-E₁₄₅₀ (b) at various temperatures

Accordingly, the molar mass of the so-formed PHUs depends on the polymerization temperature. Indeed, the molar mass varies from $M_w=10\text{kg}\cdot\text{mol}^{-1}$, $\bar{D}=1.7$ at 20°C to $17.6\text{ kg}\cdot\text{mol}^{-1}$, $\bar{D}=2.6$ at 130°C for the PHUs synthesized from BGC-C₃₆ and DDA (see Figure S10). One should mention that at 130°C the polymer obtained is not fully soluble in THF that may be due to partial cross-linking of the polymer. To a lesser extent, the same behaviour is observed for the PHUs obtained from BGC-E₁₄₅₀ and DDA; $M_w=9.3\text{ kg}\cdot\text{mol}^{-1}$, $\bar{D}=1.7$ at 20°C to $11.6\text{ kg}\cdot\text{mol}^{-1}$, $\bar{D}=1.8$ at 130°C. As expected, all the PHUs obtained with these monomers bearing dangling alkyl chains are amorphous. PHUs from BCC exhibit two T_gs around $-52^\circ\text{C} \pm 2^\circ\text{C}$ and $-17^\circ\text{C} \pm 2^\circ\text{C}$ while PHUs from BGC-C₃₆ and BGC-E₁₄₅₀ have only one T_g at $-24^\circ\text{C} \pm 1^\circ\text{C}$ and $-53^\circ\text{C} \pm 2^\circ\text{C}$ respectively (see Figures S11, S12 and S13).

The thermal stability of PHUs was investigated by TGA under a nitrogen stream at a heating rate of 10°C/min and the data are summarized in Table 1. Higher thermal stability up to 230°C were obtained with BGC-C₃₆ and BGC-E₁₄₅₀ in comparison to BCC (190°C).

In conclusion to this first part, we could show that polymerizations of BCC, BGC-C₃₆ or BGC-E₁₄₅₀ with DDA can be performed at rather low temperature in a reasonable polymerization time (few hours). In the following section of this manuscript, the mini-emulsion polymerization of these monomers is described.

Part 2: Mini-emulsion polymerization

The mini-emulsion polymerization of BCC and DDA was first investigated. Indeed, the latter monomers are both liquid and hydrophobic monomers and can be easily emulsified in the presence of a surfactant. Tween® 80 appeared to efficiently stabilize the emulsion while SDS (sodium dodecylsulfate) and CTAB (cetyltrimethylammonium bromide) led to sedimentation for emulsion with solid content of 20 wt.%. In Table 2, the droplet size of the mini-emulsions formed with BCC and DDA are displayed for various surfactant concentrations and solid contents up to 30 wt.%. Interestingly, the addition of a hydrophobe was not necessary in this case to stabilise the monomer droplets, as already observed in a previous study also concerning fatty acid-based water-borne dispersions. [17] The polymerizations were then performed at 60°C for 24 h, and the resulting latex particle sizes are given in Table 2.

Table 2: Droplet size diameters of BCC and DDA mini-emulsions with Tween®80, and droplet size diameters of the corresponding PHU latexes after polymerization for 24 h at 60°C

Solid content (wt%)	Surfactant concentration (wt%)	Droplet size^a diameter (nm)	Particle size^a diameter (nm)
20	5	200 ^b	unstable
20	10	100	100
30	10	<i>nd</i>	95 ^b
30	17	<i>nd</i>	75 ^b
40	10	<i>nd</i>	unstable

^a Mean size diameter in number, measured by DLS (Zetasizer NanoZS). ^b A second population of larger size is observed in intensity measurement by DLS. (see Figure S14)

For a solid content of 20 wt.%, a minimal Tween®80 concentration of 10 wt.% was required to obtain stable emulsions. At these concentrations, the mini-emulsion droplet size diameter was found equal to 100 nm according to DLS measurement in number. As expected, after polymerization, the latex obtained has a mean particle size of 100 nm, identical to the one of the starting mini-emulsion. The PHUs formed were characterized by ¹H NMR and compared to the PHUs obtained in bulk in the same condition (60°C, 24 h) (Figure 3). The ¹H NMR spectra appeared to be similar indicating that the polymerization took place in dispersed media without any effect of the water.

When the solid content was increased to 30 wt.%, with the same amount of Tween® 80, the mean particle size diameter slightly decreased to 95 nm and a second population appeared around 500-800 nm, population only visible in intensity size distributions by DLS (see Figure S14). An increase of the surfactant concentration to 17 wt.% enabled a decrease of the mean particle size (75 nm), but the second population of larger particles remained present. Above 30 wt.% of solid content, no stable mini-emulsion or latex could be obtained. Thus, a solid content not exceeding 30 wt.% leads to the more stable and monodisperse mini-emulsions and particle latexes.

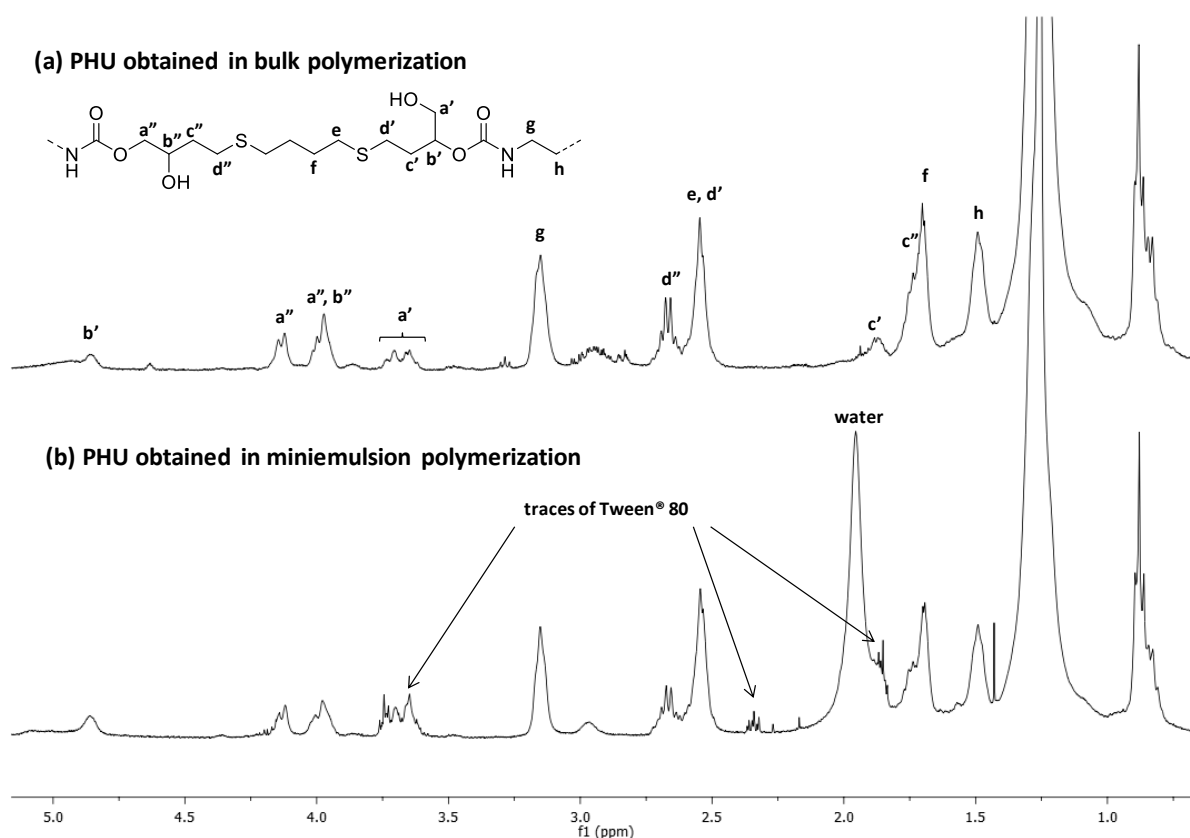


Figure 3: ¹H NMR spectra in CDCl₃ of the PHUs obtained by polymerization of BCC and DDA at 60°C in 24h in bulk (a) and mini-emulsion (b)

The PHUs, obtained by mini-emulsion polymerization, were characterized by SEC and DSC. Results are displayed in Table 3. Interestingly, the molar mass of the PHUs with a same batch of

monomers, obtained after 24 hours, in bulk and mini-emulsion polymerizations are similar and exhibit values of $M_w=10.7-11.2 \text{ kg}\cdot\text{mol}^{-1}$ and $\bar{D}=1.7$. The M_w value of the PHU prepared in bulk was found lower than the one indicated in Table 1; this feature may be explained by the presence of some impurities in this batch of BCC (not detected by NMR) or, more probably, by an uncertainty of the BCC/DDA stoichiometric ratio, sensitive parameter that can affect drastically the molar mass values. The corresponding SEC chromatograms are given in Figure 4.

Table 3: Characteristics of the PHUs obtained after 24 h by polymerization of BCC and DDA at 60°C in bulk and by mini-emulsion polymerization at 20wt% solid content in the presence of Tween®80 (10 wt.%)

	Mini-emulsion polymerization			Bulk polymerization	
	Particle size diameter (nm) ^a	M_w (kg.mol ⁻¹) [\bar{D}] ^b	T_g (°C) ^c	M_w (kg.mol ⁻¹) [\bar{D}] ^b	T_g (°C) ^c
BCC	100	11.2 [1.7]	-21	10.7 [1.7]	-50/-19

^a Mean size in number, measured by DLS (Zetasizer NanoZS). ^b Measured by SEC in THF calibrated with PS standards.

^c Measured by DSC on the second heating cycle at 10°C.min⁻¹ after 24h

The PHUs prepared in mini-emulsion from BCC only exhibit one T_g at -21°C (see Figure S15) in comparison to the PHUs prepared in bulk (-50°C/-19°C). This difference is not explained and may be due to the presence of traces of Tween® 80, present in the former case.

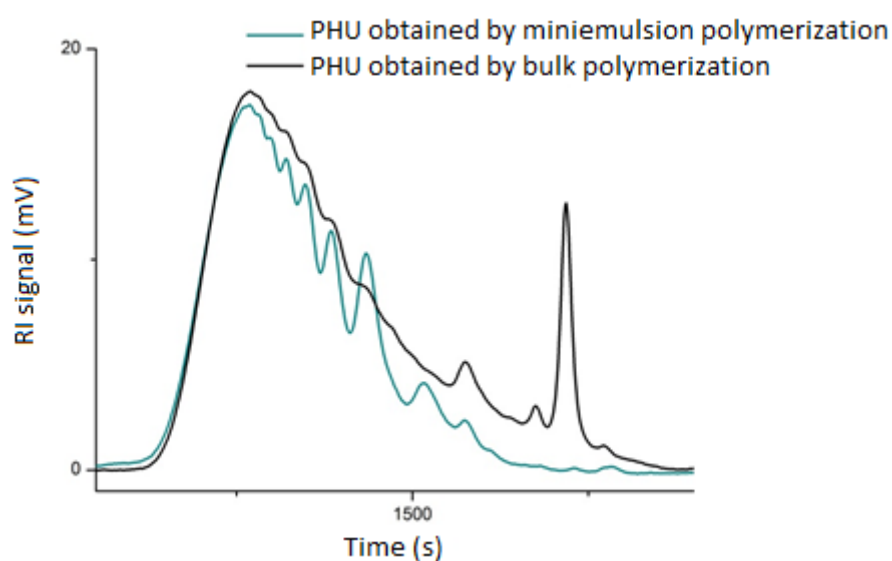


Figure 4: SEC traces in THF of the PHUs obtained by polymerization of BCC and DDA in bulk polymerization (black) and mini-emulsion polymerization (greenish) at 60°C after 24h

polymerization time

These first results obtained with BCC as bis-cyclic carbonate clearly demonstrated that PHUs can be synthesized by mini-emulsion leading to stable latex with a solid content up to 30wt%.

The mini-emulsion polymerizations involving more viscous fatty acid-based carbonates (BGC) and DDA were then performed. In this case, mini-emulsions of BGC-C₃₆ or BGC-E₁₄₅₀ and DDA were obtained by ultrasonication only in the presence of SDS as a surfactant (1.2 wt.% in deionized water). In addition, hydrophobic agents have to be added at a concentration of 3.3 wt.% of the organic phase to prevent creaming. One should note that Tween 80 leads to emulsion creaming with or without hydrophobe even at a solid content as low as 10 wt.%. Table 4 summarizes the various systems tested as well as the characteristics of the PHUs synthesized.

Table 4: Characteristics of the PHUs obtained by polymerization of BGC-C₃₆ or BGC-E₁₄₅₀ and DDA in 24 h by mini-emulsion (in the presence of SDS at 1.2 wt.%)

Bis-cyclic carbonate	T (°C)	Hydrophobe	Mini-emulsion polymerization			
			Droplet diameter (nm) ^a	Particle diameter (nm) ^a	M _w (kg.mol ⁻¹) [Đ] ^b	T _g (°C) ^c
BGC-C ₃₆	20 ^f	Hexadecane	85	95 ^d	6.6 [1.55]	<i>nd</i>
	60	Hexadecane	85	116 ^e	7.1 [1.55]	-28
		Olive oil	85	85 ^d	6.8 [1.7]	<i>nd</i>
		none	120 ^d	74 ^d	5.8 [1.4]	-26
BGC-E ₁₄₅₀	60	Hexadecane	61 ^d	53 ^d	6.6 [1.8]	-55

SDS is the surfactant (1.2wt% of the aqueous phase)

The hydrophobe is introduced in the organic phase at a concentration of 3.3 wt%.

^a Mean size in number, measured by DLS (Zetasizer NanoZS). ^b Measured by SEC in THF calibrated with PS standards.

^c Measured by DSC on the second heating cycle at 10°C.min⁻¹. ^d Polydisperse size distribution. ^e Another population is visible in volume and intensity measurements by DLS around 500 nm. ^f Polymerization performed during 48 h

As can be seen in Table 4, the mean particle diameters remain in rather good agreement with the droplet ones but the particle diameters generally exhibit a broad distribution. In addition, the molar masses of the PHUs prepared in these conditions remain in the range M_w=5,8-7,1 kg.mol⁻¹ with Đ=1.4-1.8. In the case of BGC-C₃₆, the nature of the hydrophobic agent has no effect on the molar mass of the PHUs obtained. Meanwhile, in the absence of hydrophobe, the PHU molar mass is

slightly lower, $M_w=5.8 \text{ kg}\cdot\text{mol}^{-1}$ against $6.8\text{-}7.1 \text{ kg}\cdot\text{mol}^{-1}$ when a hydrophobe is used.

For all the systems tested, the molar masses M_w and dispersities of the PHUs obtained are lower in mini-emulsion polymerization than in bulk (see Table 1). The occurrence of the partial hydrolysis of the carbonates was suspected to explain this phenomenon. This reaction, favoured with temperature [11], would explain the differences in the PHU molar mass obtained in bulk and mini-emulsion at 60°C and 20°C . The analysis of ^1H NMR spectra of the PHUs obtained in mini-emulsion polymerization show several signals at 3.5-4 ppm (Figure 5), which could match the protons of hydrolysed compounds. [22] Further NMR analyses did not allow us to fully confirm such hypothesis, due to the presence of too many signals in this range.

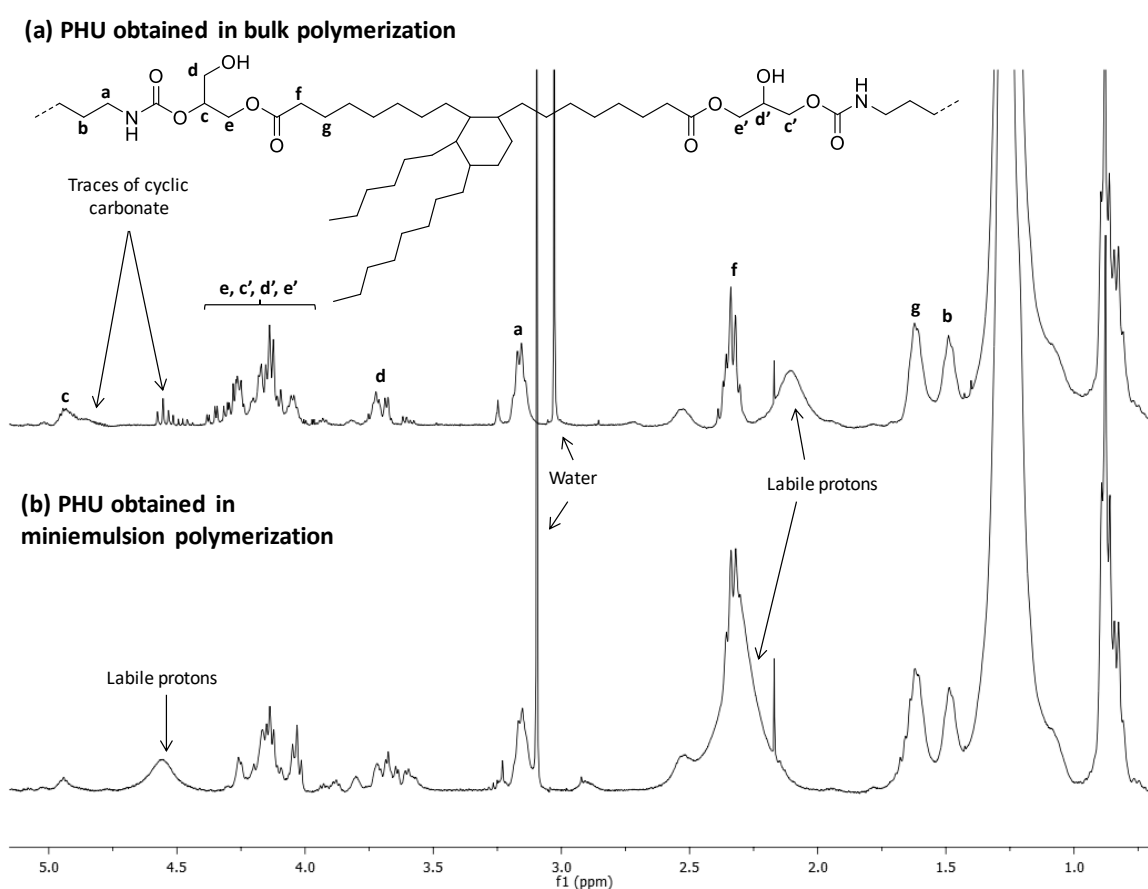


Figure 5: ^1H NMR spectra in CDCl_3 of the PHUs obtained by polymerization of BGC- C_{36} and DDA at 60°C in 24 h in bulk (a) and mini-emulsion (b)

Conclusions

Three new liquid bis-cyclic carbonates were synthesized and polymerized with DDA. The obtained PHUs were obtained in bulk or *via* mini-emulsion polymerization. In bulk, the PHUs with a reasonable molar mass were obtained at low temperature (60°C) in 24 h.

Up to 30 wt.% solid content bio-based poly(hydroxyl urethane) latexes were obtained through mini-emulsion polymerization. Tween 80 as surfactant without any hydrophobic agent was needed in the case of BCC while SDS with an hydrophobic agent were required in the cases of more viscous fatty acid (bis)carbonates, BGC-C₃₆ and BGC-E₁₄₅₀. PHUs of lower molar masses were observed in mini-emulsion in comparison to bulk polymerization, possibly because of the hydrolysis of cyclic carbonates. Finally, all the PHUs obtained exhibited low T_g values (ranging from -55°C to -15°C), values compatible with applications in the fields of adhesives or coatings.

Acknowledgment

The authors are very thankful to ADEME agency for funding this project (DAPUBS project).

References

- [1] L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s, *Chem. Rev.* 115 (2015) 12407-12439.
- [2] O. Kreye, H. Mutlu, M.A.R. Meier, Sustainable routes to polyurethane precursors, *Green Chem.* 15 (2013) 1431–1455.
- [3] A. Boyer, E. Cloutet, T. Tassaing, B. Gadenne, C. Alfos, H. Cramail, Solubility in CO₂ and carbonation studies of epoxidized fatty acid diesters: towards novel precursors for polyurethane synthesis, *Green Chem.* 12 (2010) 2205–2213..
- [4] C. Duval, N. Kébir, R. Jauseau, F. Burel, Organocatalytic synthesis of novel renewable non-isocyanate polyhydroxyurethanes, *J. Polym. Sci. Part A Polym. Chem.* 54 (2015) 758–764
- [5] H. Blattmann, M. Fleischer, M. Bähr, R. Mülhaupt, Isocyanate- and Phosgene-Free Routes to Polyfunctional Cyclic Carbonates and Green Polyurethanes by Fixation of Carbon Dioxide, *Macromol. Rapid Comm.* 35 (2014) 1238–1254
- [6] A. Cornille, J. Serres, G. Michaud, F. Simon, S. Fouquay, B. Boutevin, S. Caillol, Syntheses of epoxyurethane polymers from isocyanate free oligo-polyhydroxyurethane , *Eur. Pol. J.* 75 (2016) 175-189
- [7] L. Poussard, J. Mariage, B. Grignard, C. Detrembleur, C. Jérôme, C. Calberg, B. Heinrichs, J. De Winter, P. Gerbaux, J.-M. Raquez, L. Bonnaud, Ph. Dubois, Non-Isocyanate Polyurethanes from Carbonated Soybean Oil Using Monomeric or Oligomeric Diamines To Achieve Thermosets or Thermoplastics, *Macromolecule* 49 (2016) 2162-2171
- [8] B.K. Kim, Aqueous polyurethane dispersions, *Colloid Polym. Sci.* 274 (1996) 599–611.
- [9] L. Poussard, F. Burel, J.P. Couvercelle, C. Loutelier-Bourhis, C. Bunel, Synthesis of new anionic HTPB-based polyurethane elastomers: Aqueous dispersion and physical properties, *J. Appl. Polym. Sci.* 100 (2006) 3312–3322.

- [10] D. Dieterich, Aqueous emulsions, dispersions and solutions of polyurethanes; synthesis and properties, *Prog. Org. Coatings*. 9 (1981) 281–340.
- [11] J.M. Bernard, Procédé de préparation de polyhydroxy-uréthanes, WO2008107568, 2008.
- [12] B. Ochiai, Y. Satoh, T. Endo, Nucleophilic polyaddition in water based on chemo-selective reaction of cyclic carbonate with amine, *Green Chem.* 7 (2005) 765–767.
- [13] F. Tiarks, K. Landfester, M. Antonietti, One-step preparation of polyurethane dispersions by miniemulsion polyaddition, *J. Polym. Sci. Part A Polym. Chem.* 39 (2001) 2520–2524.
- [14] C.-Y. Li, Y.-H. Li, K.-H. Hsieh, W.-Y. Chiu, High-molecular-weight polyurethanes prepared by one-step miniemulsion polymerization, *J. Appl. Polym. Sci.* 107 (2008) 840–845.
- [15] A. Valério, M. Fortuny, A.F. Santos, P.H.H. Araújo, C. Sayer, Poly(Urea-Urethane) Synthesis by Miniemulsion Polymerization Using Microwaves and Conventional Polymerization, *Macromol. React. Eng.* 9 (2015) 48–59.
- [16] B.G. Zanetti-Ramos, E. Lemos-Senna, V. Soldi, R. Borsali, E. Cloutet, H. Cramail, Polyurethane nanoparticles from a natural polyol via miniemulsion technique, *Polymer* 47(24) (2006) 8080-8087.
- [17] E. Rix, G. Ceglia, J. Bajt, G. Chollet, V. Heroguez, E. Grau, et al., Hydrophobe-free miniemulsion polymerization: towards high solid content of fatty acid-based poly(urethane-urea) latexes, *Polym. Chem.* 6 (2015) 213–217.
- [18] L. Maisonneuve, A.S. More, S. Foltran, C. Alfos, F. Robert, Y. Landais, et al., Novel green fatty acid-based bis-cyclic carbonates for the synthesis of isocyanate-free poly(hydroxyurethane amide)s, *RSC Adv.* 4 (2014) 25795–25803.
- [19] X. Sheng, G. Ren, Y. Qin, X. Chen, X. Wang, F. Wang, Quantitative synthesis of bis(cyclic carbonate)s by iron catalyst for non-isocyanate polyurethane synthesis, *Green Chem.* 17 (2015) 373–379.
- [20] V. Besse, F. Camara, F. Méchin, E. Fleury, S. Caillol, J.-P. Pascault, B. Boutevin, How to explain low molar masses in PolyHydroxyUrethanes (PHUs), *Eur. Polym. J.* 71 (2015), 1-11
- [21] O. Lamarzelle, P.-L. Durand, A.-L. Wirotius, G. Chollet, E. Grau, H. Cramail, Activated lipidic cyclic carbonates for non-isocyanate polyurethane synthesis, *Polym. Chem.* 7 (2016) 1439-1451
- [22] G. Knothe, Glycerol Esters - ¹H-NMR Spectroscopy of Fatty Acids and Their Derivatives, *AOCS Libr.* (2006). <http://lipidlibrary.aocs.org/content.cfm?ItemNumber=40263> (accessed September 28, 2015).

Synthesis of fatty acid-based Non-Isocyanate Polyurethanes, NIPUs, in bulk and mini-emulsion

SUPPLEMENTARY INFORMATIONS

Estelle Rix^{a,b}, Guillaume Chollet^c, Etienne Grau^{a,b}, Henri Cramail^{a,b*}

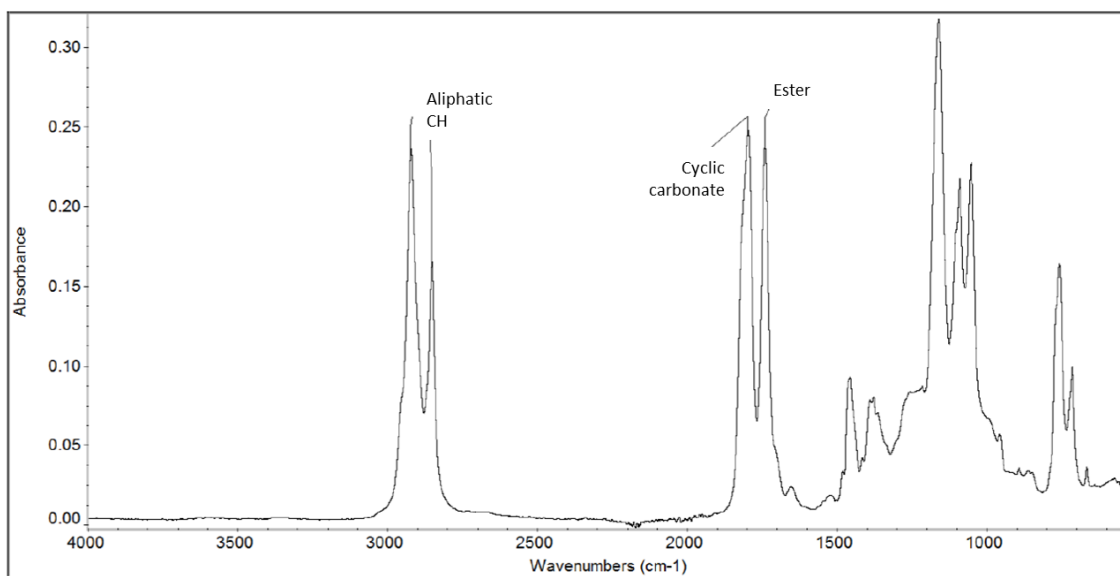


Figure S1: FT-IR spectrum of BGC-C36

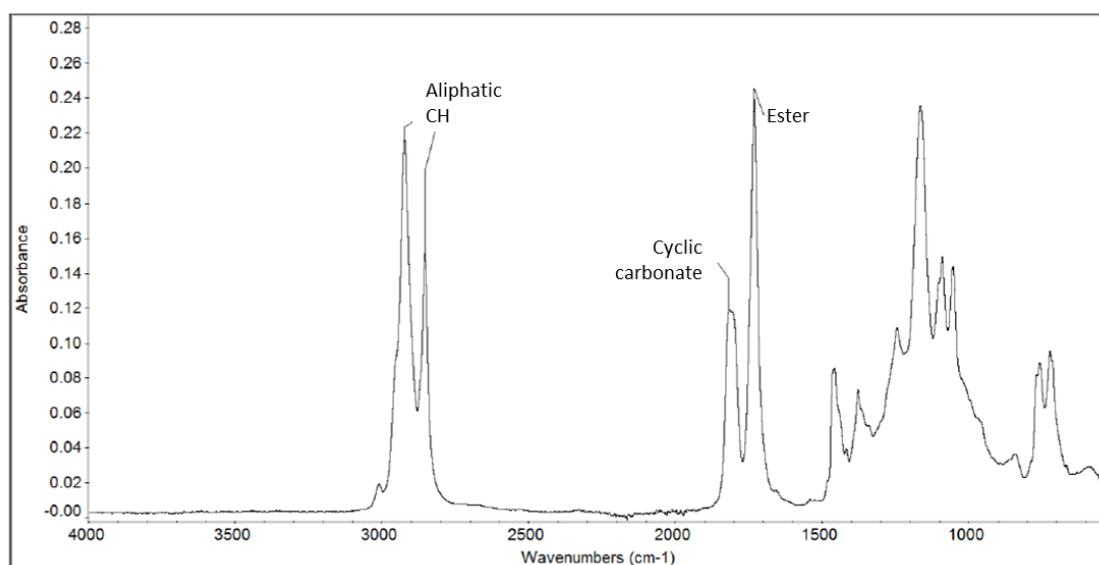


Figure S2: FT-IR spectrum of BGC-E1450

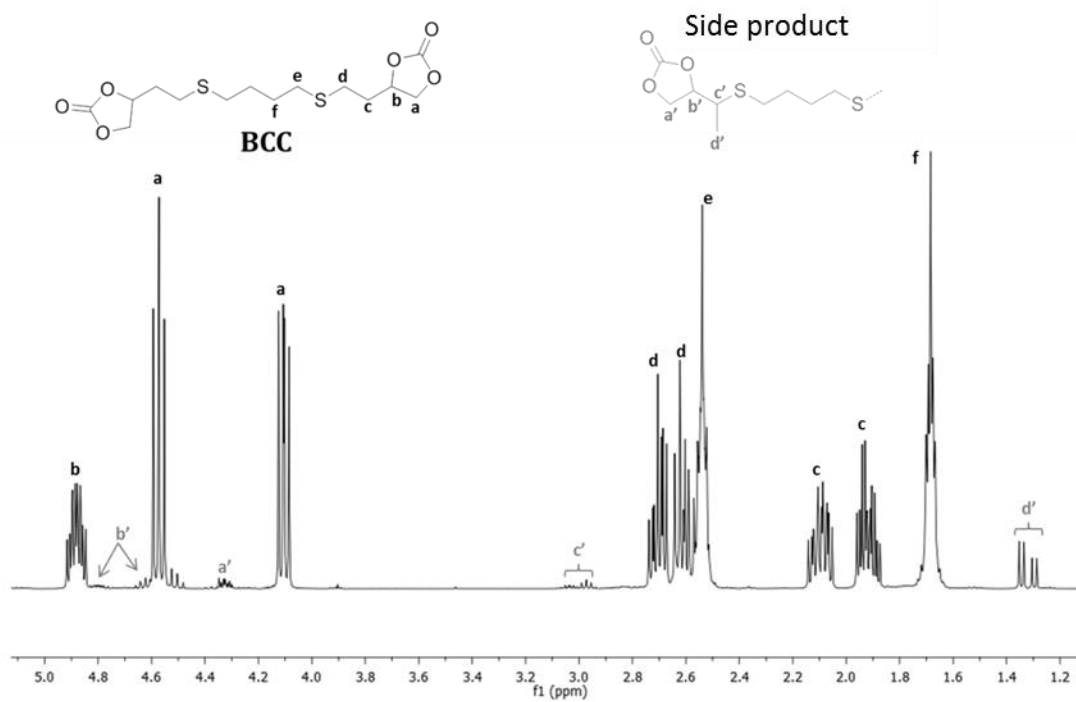


Figure S3: ^1H NMR spectrum in CDCl_3 of BCC

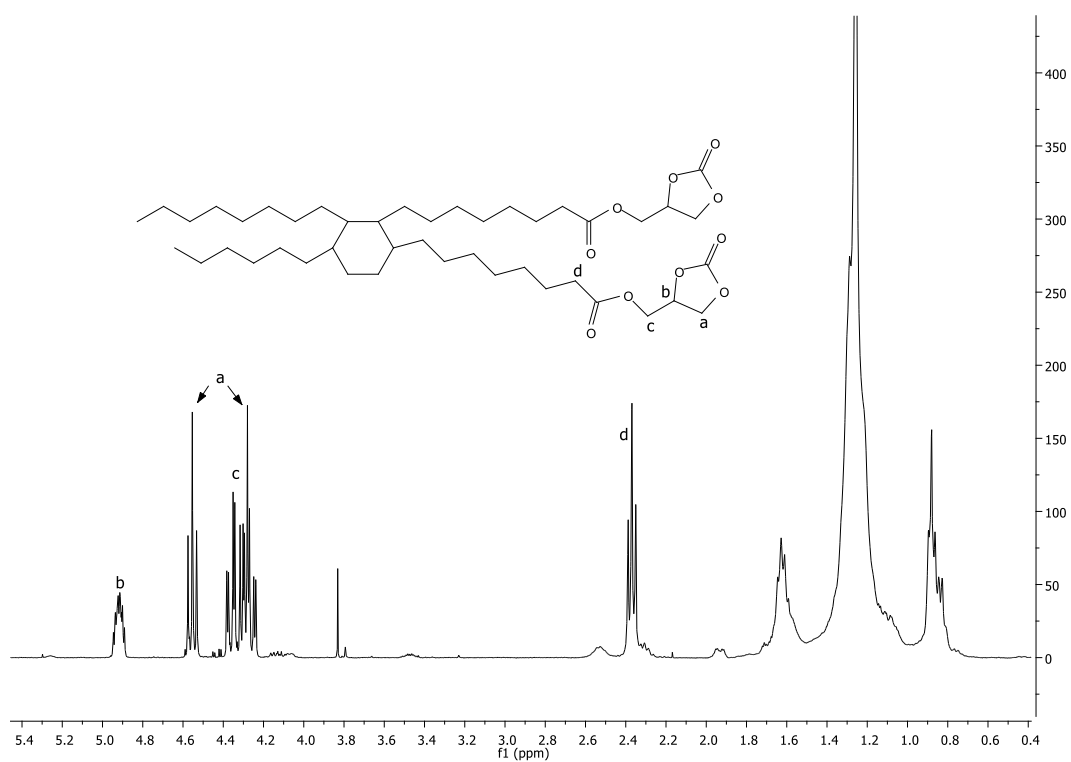


Figure S4: ^1H NMR spectrum in CDCl_3 of BGC-C₃₆

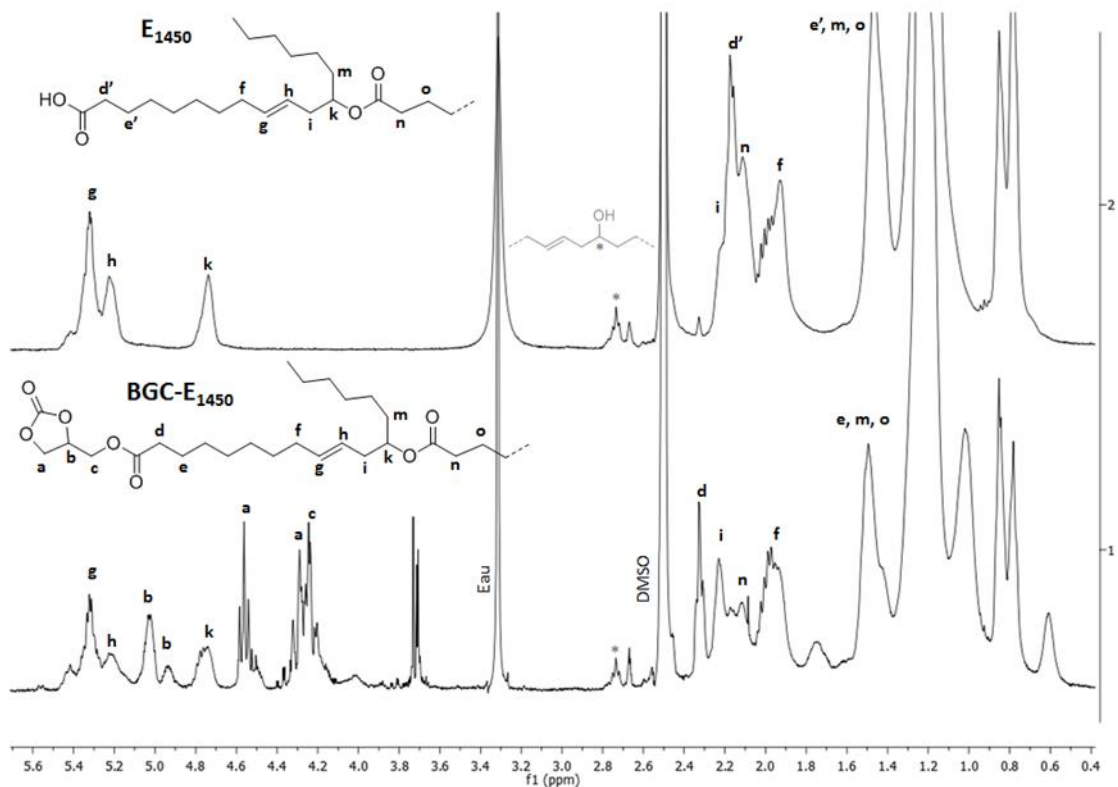


Figure S5: ^1H NMR spectrum in DMSO- d_6 of E_{1450} and BGC-E_{1450}

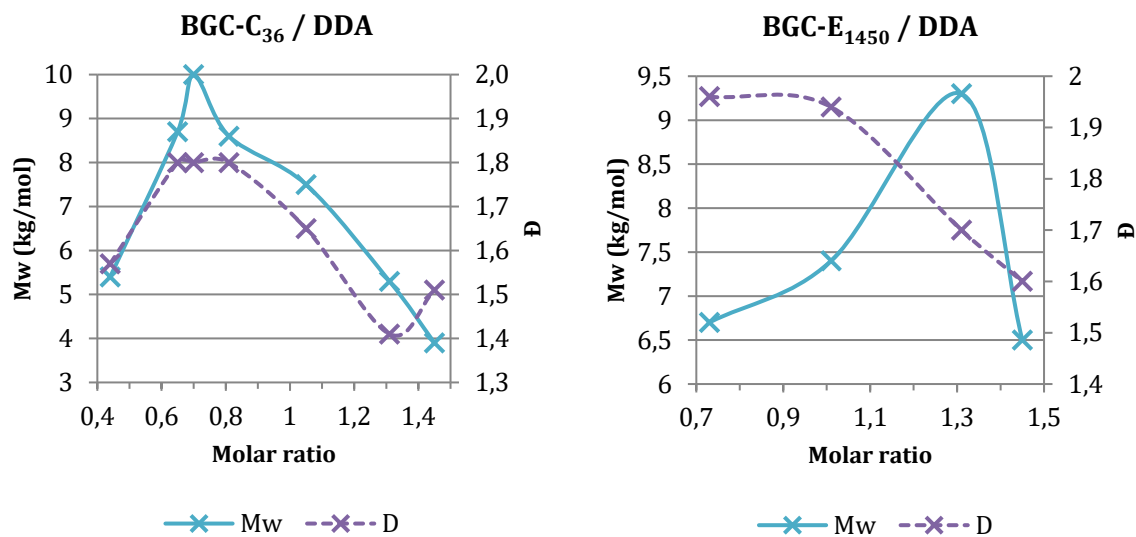


Figure S6: Mw and dispersity of PHUs obtained from polymerization of BGC-C_{36} or BGC-E_{1450} with DDA, after 24h at 60°C

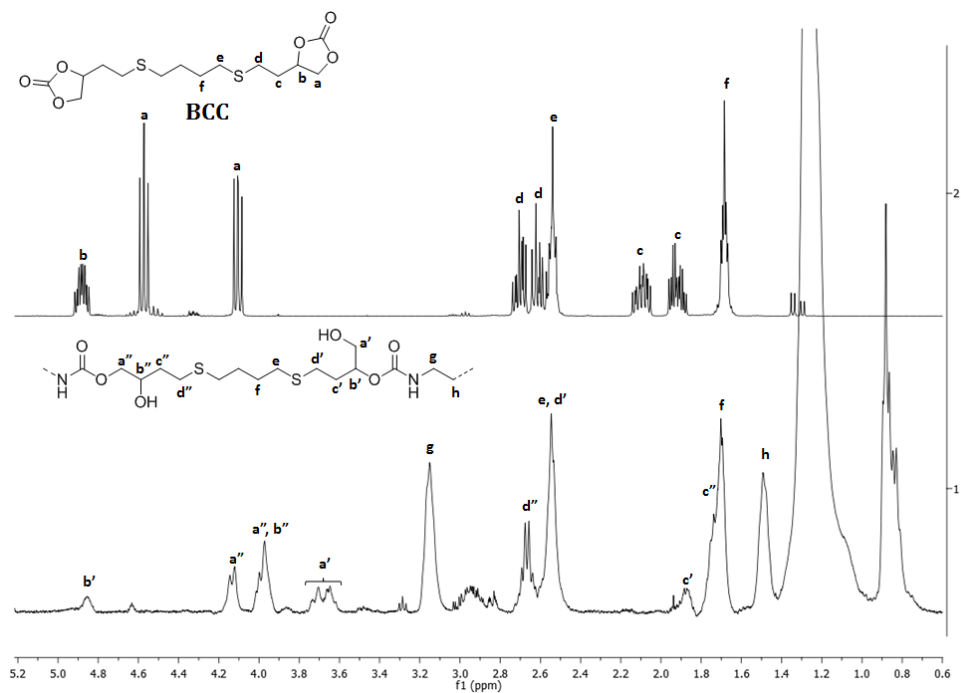


Figure S7: ^1H NMR spectrum in CDCl_3 of BCC and PHU obtained at 60°C after polymerization with Priamine® 1075 (DDA) after 14 days

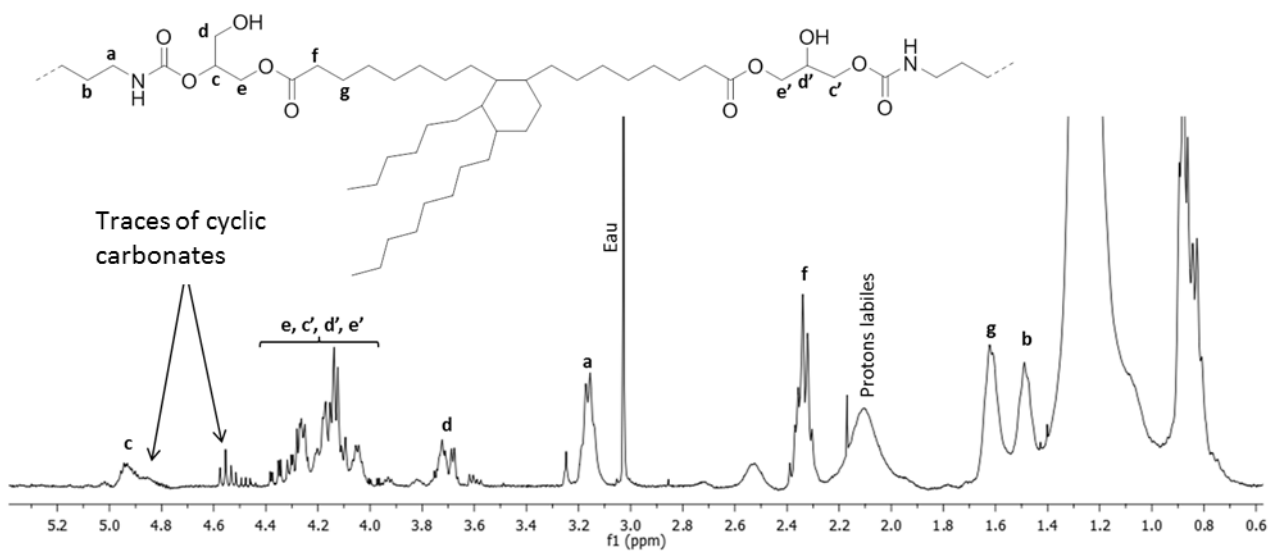


Figure S8: ^1H NMR spectrum in CDCl_3 of PHU obtained at 20°C in the case of BGC-C₃₆ / DDA polymerization

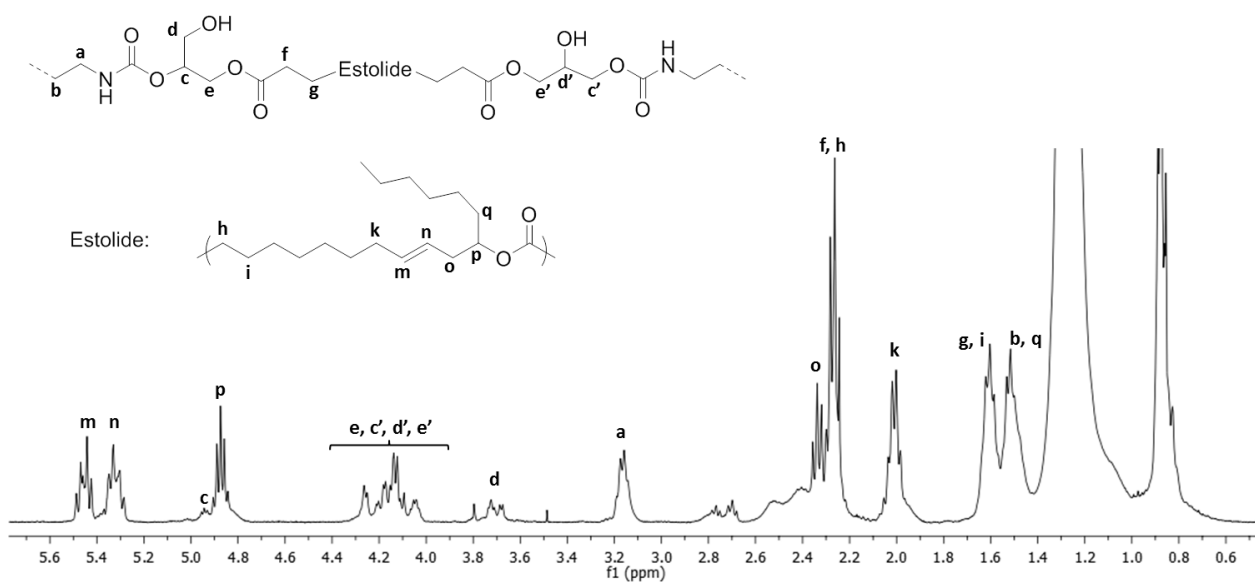


Figure S9: ^1H NMR spectrum in CDCl_3 of PHU obtained at 20°C in the case of BGC-E₁₄₅₀ / DDA polymerization

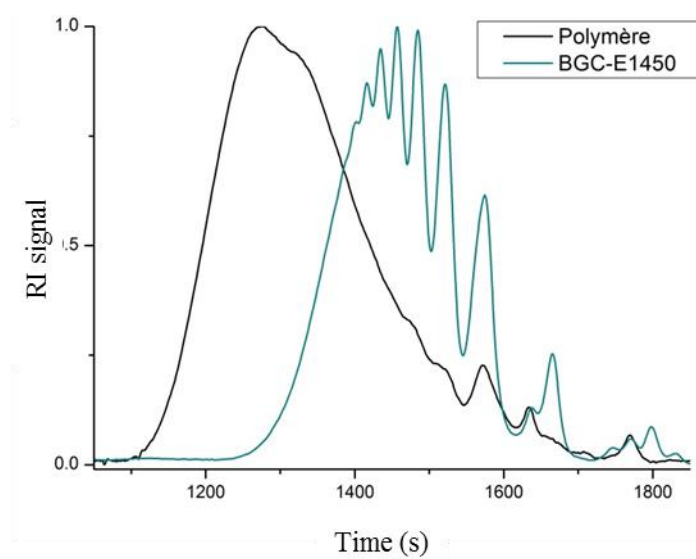


Figure S10: SEC traces of BGC-E₁₄₅₀ (greenish) and of PHU obtained after polymerization of BGC-E₁₄₅₀/DDA at 90°C in bulk

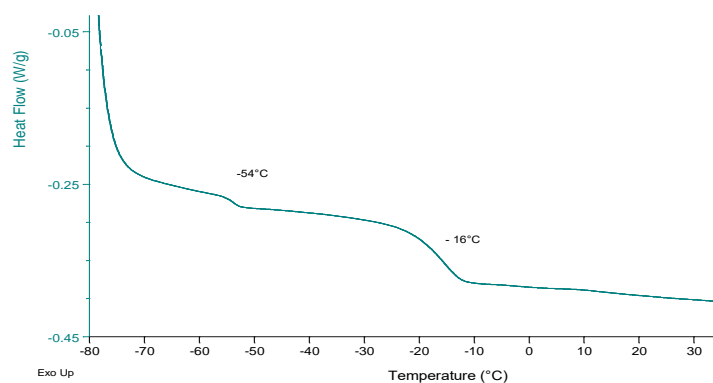


Figure S11: Typical DSC trace of PHU obtained by polyaddition of BCC with DDA after 14 days

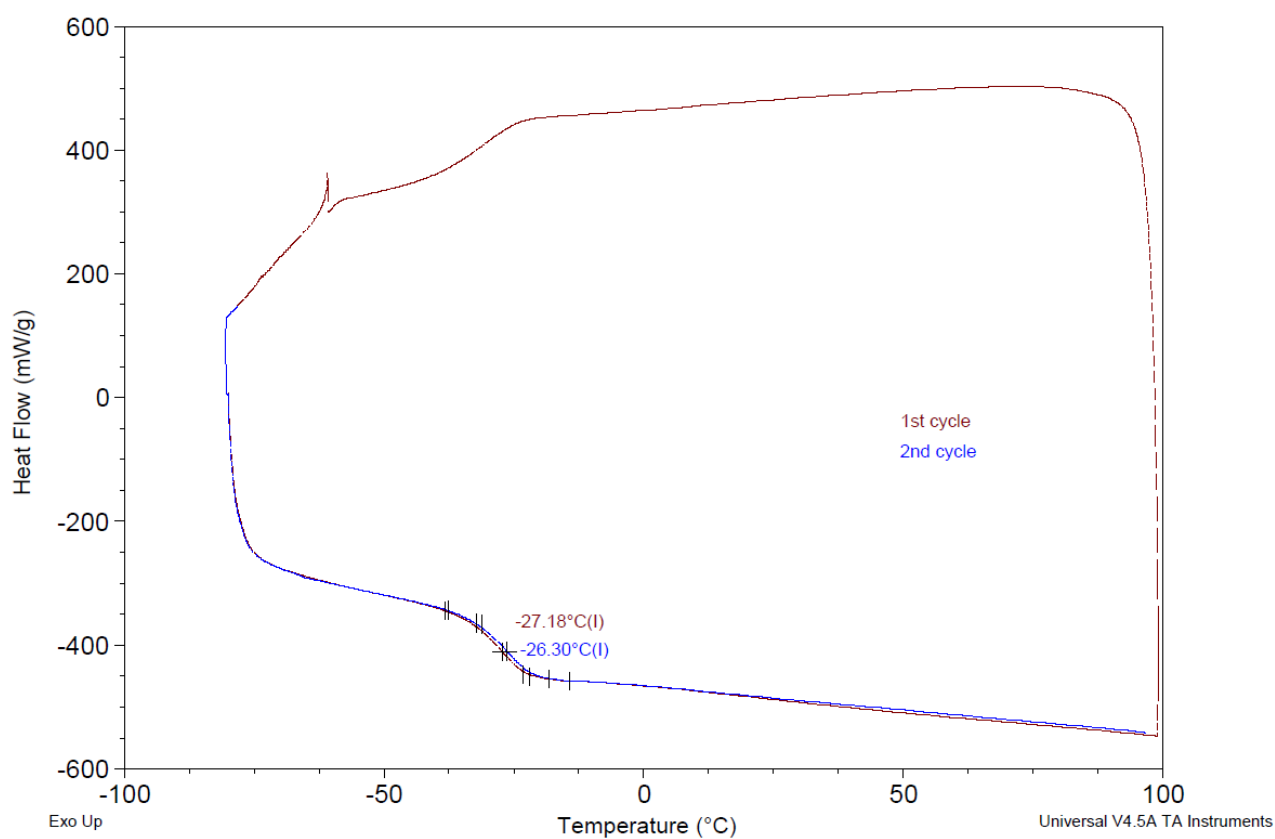


Figure S12: Typical DSC trace of PHU obtained by polyaddition of BGC-C₃₆ with DDA

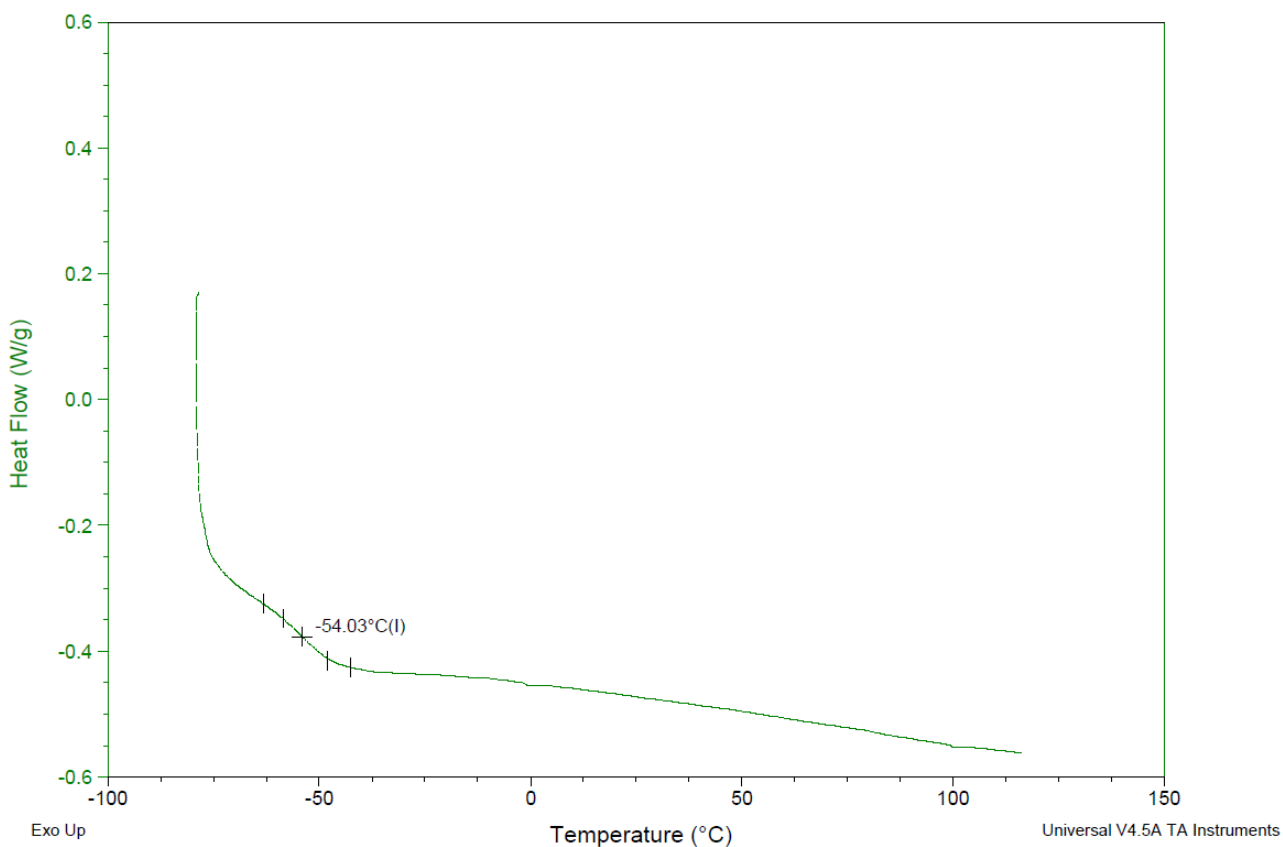


Figure S13: Typical DSC trace of PHU obtained by polyaddition of E₁₄₅₀-C₃₆ with DDA

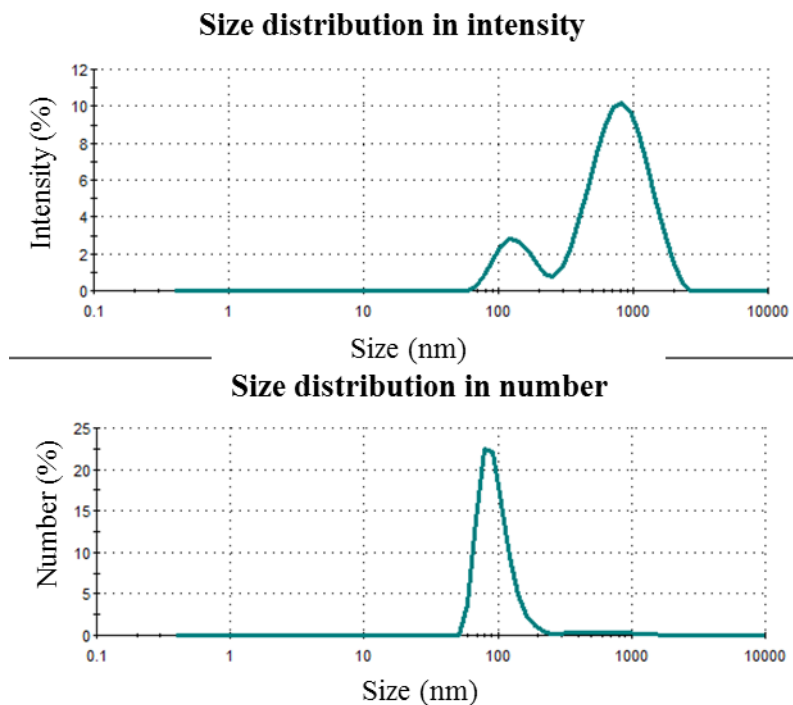


Figure S14: Size distribution of the mini-emulsion of BCC and DDA (20wt.%) in presence of 10wt.% of Tween®80 water solution (PDI=0,267)

Sample: ER63 - précipité
Size: 9.4000 mg
Method: ER

DSC

File: C:\DSC\Estelle\ER63-précipité.001
Operator: ER
Run Date: 02-Apr-2013 13:24
Instrument: DSC Q100 V9.9 Build 303

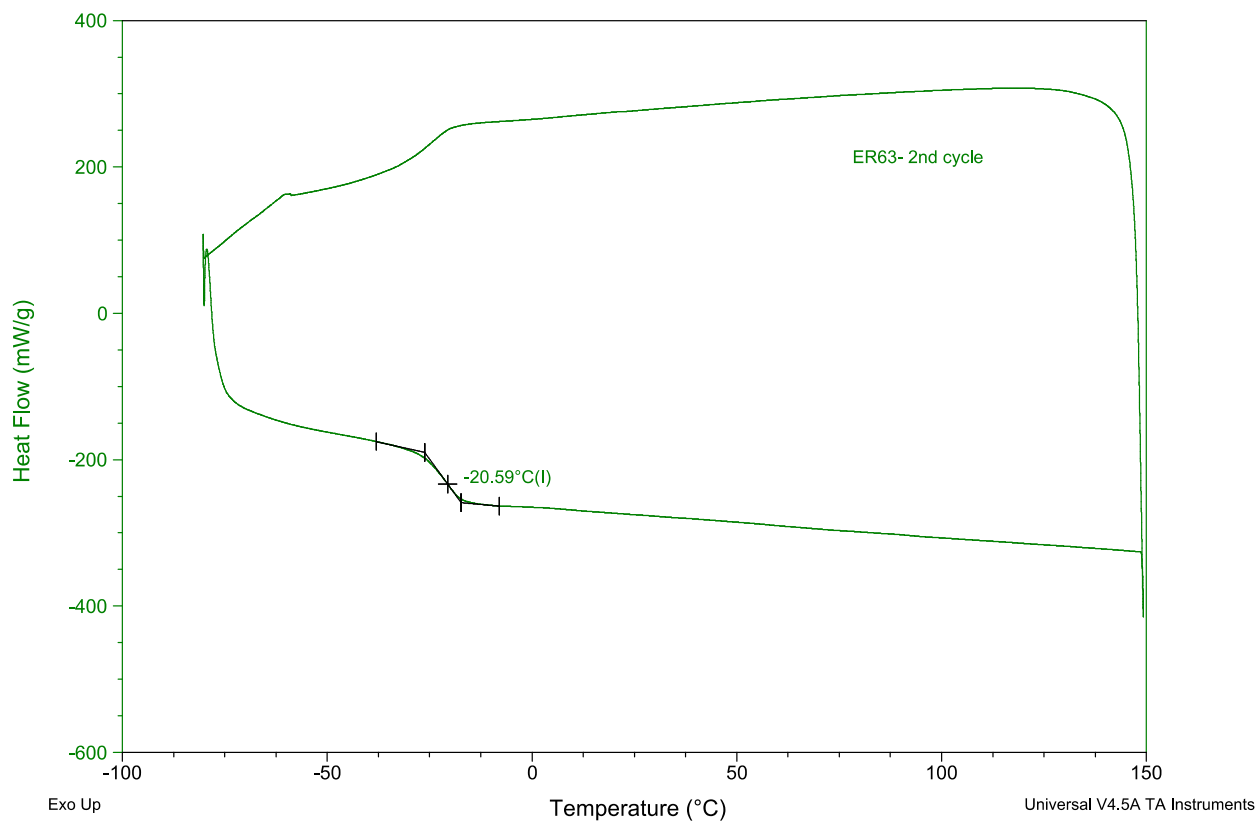


Figure S15: Typical DSC trace of PHU obtained by polyaddition in miniemulsion of BCC with DDA after 24 hours