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Reactive jojoba and castor oils-based cyclic carbonates for biobased polyhydroxyurethanes

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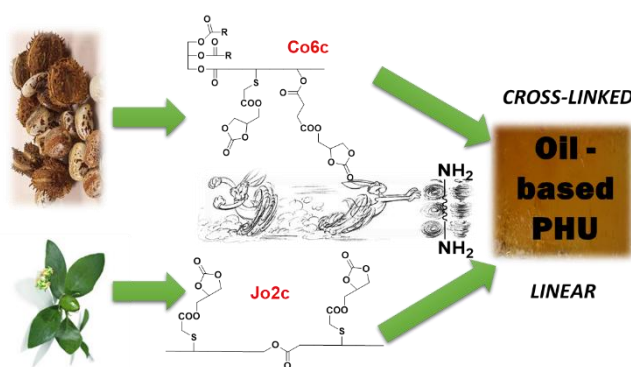
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Keywords: jojoba oil; castor oil; thiol-ene coupling; polyhydroxyurethane; cyclic carbonate.

Abstract

Syntheses of novel biobased PolyHydroxyUrethane (PHU) have been performed from Jojoba and castor oil. Cyclic carbonate monomers with various functionality were synthesized from both jojoba and castor oils. Pendant cyclic carbonate groups were obtained by a two-step reaction: thiol-ene coupling with thioglycolic acid followed by esterification with glycerin carbonate. These novel cyclic carbonate monomers exhibited higher reactivity than previous intra-chain plant oil-based cyclic carbonates. Di-functional jojoba oil-based cyclic carbonate was synthesized for the first time. PHUs were obtained by aminolysis of plant oil-based cyclic carbonates with various aliphatic and aromatic diamines. Structured linear and cross-linked PHUs were obtained with Tg ranging from -45 to 20°C. The different PHU materials were characterized by SEC, FTIR, DSC, ATG and DMA measurements. These results showed the potentiality of this environmentally friendly approach to prepare plant oils-based PHU materials with interesting performances.

Graphical Abstract



1 Introduction

Polyurethanes (PUs) represent one of the most versatile families of synthetic polymers. In 2016, with a global production of 18 Mt, PUs ranked 6th among all polymers based on annual worldwide production¹. PUs are largely used in various applications such as furnishing, automotive, clothing, shoes, elastomers, coatings, insulation due to the variety of their properties such as light weight, excellent mechanical and chemical resistance, steady compression behavior²... The global production of PUs is still increasing. Indeed, PUs market size was \$53.94 billion in 2015 and is projected to grow at an annual rate of 7% from 2016 to 2025³. One of the most common methods to obtain PUs is the reaction of polyols with a diisocyanate or polyisocyanate. Most of these isocyanates and polyols are coming from fossil resources.

Due to environment concerns, biobased polyols are becoming a very attractive alternative to petro-based polyols. Hence, among the large variety of natural resources that could be used to obtain biobased polyols, vegetable oils (VO), fatty acids (FA) and their derivatives were abundantly studied in the literature and led to several promising biobased polyols⁴⁻⁸. Indeed, long aliphatic chain of fatty-acid derived polyols confers interesting flexible properties to PUs.

Hence, castor oil, with its naturally occurring hydroxyl groups, is one of the most used VOs for the synthesis of PUs^{4,9}. Moreover, many studies have been performed to synthesize polyols from other VOs, such as soybean¹⁰, rapeseed¹¹ and palm oils¹². In literature, most of the reported routes for the synthesis of polyols from VOs are based either on the functionalization of double bonds of unsaturated fatty acids or on the coupling of FA with ester groups. Hence, most of these routes consist in the oxidation/reduction or in the epoxidation/ring-opening reaction of the double bonds into hydroxyl groups. Additionally, thiol-ene coupling reaction on VOs has been largely studied by Caillol et al.^{13,14}, Meier et al.^{15,16} and Cramail et al.¹⁷ and was reviewed by Lligadas¹⁸. Thiol-ene coupling interestingly leads to the grafting of more reactive primary alcohols, whereas other routes generally lead to less reactive secondary alcohols¹⁹.

However, the main health and environmental concerns of PUs remain the use of isocyanates. Indeed, these substances are harmful for human and environment and most of the time, they are classified CMR (Carcinogenic, Mutagenic and Reprotoxic). Therefore academic and industrial studies have been carried out to design non-isocyanate polyurethane (NIPU). One of the most promising routes consists in reaction between cyclic carbonates and amines which results in polyhydroxyurethanes (PHU).²⁰⁻²² Indeed, the ring opening aminolysis of cyclic carbonate leads to an additional hydroxyl function hanging off the main polymer chain. Hence, biobased PHUs were already reported as elastomers,²³ adhesives,²⁴ foams,²⁵ coatings,²⁶ hydrogels,²⁷ vitrimers²⁸ or latexes²⁹ with promising properties. However, one of the main

drawbacks of PHUs synthesis concerns the reactivity of 5-membered cyclic carbonates. Indeed, this reactivity strongly depends on direct atomic environment³⁰. Hence, first vegetable oil-based cyclic carbonate monomers were synthesized by epoxidation/carbonation of double bonds. The resulting internal cyclic carbonate exhibited a poor reactivity^{1,17}.

Furthermore, all VOs are not equivalent in terms of double bonds functionality or chemical structure. For example, linseed, soybean and canola oils contain respectively 6.6, 4.6 and 3.9 double bonds per triglyceride, while palm oil contains 1.7 double bonds per triglyceride. Jojoba is the only plant species known to use liquid wax esters as storage in seeds. It is a vegetable oil obtained from the crushed bean of the jojoba shrub (*Simmondsia chinensis*). The oil is half of the weight of the nut. Yet, jojoba oil (JO) is almost entirely (~97%) composed of two mono-unsaturated hydrocarbon chains linked by an ester moiety³¹. The molecular structure of the esters is depicted in Figure 1 where (n) varies between 5, 7 or 9 and (m) varies between 10, 12 or 14, depending on the growing environment of the plant⁶. The features of JO differ totally from other common VOs. Indeed, conventional oil seed crops produce triglycerides that consist of three fatty acids attached to a glycerol molecule; whereas JO is exempt of glycerol, and is composed of fatty acids directly connected to fatty alcohols³². If jojoba oil was already used for various applications, only a handful of studies are reported in literature. Hence, native jojoba oil has been used in the fields of cosmetics, pharmaceuticals³³, lubricants^{34, 35}, corrosion inhibitors³⁶ or to generate biofuels³⁷. However, only our previous study reported the use of JO for the synthesis of materials³⁸. In this pioneering study, the unique structure of JO allowed to obtain, in one step, a diol with primary hydroxyl groups, for the synthesis of biobased PUs.

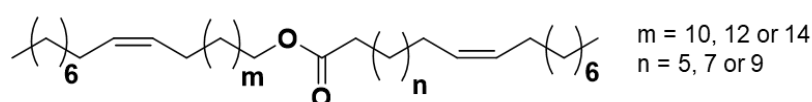


Figure 1: Structure of Jojoba Oil (JO)

In this context, the present paper reports the synthesis and characterization of new cyclic carbonate monomers from both jojoba and castor oils. Jojoba-based cyclic carbonate was synthesized in two steps. First, jojoba oil was functionalized by thiol-ene coupling with thioglycolic acid, and then esterified with glycerol carbonate by Steglich esterification. Two other cyclic carbonates were synthesized from castor oil with a different functionality. In a first step, castor oil was functionalized into two different polyacids. The first one was synthesized by ring opening of succinic anhydride with hydroxyl function of castor oil. The second one was obtained by thiol-ene coupling of the first one with thioglycolic acid. Then both polyacids were functionalized with glycerol carbonate by the Steglich esterification. These new cyclic carbonates present atomic environment that allows a good reactivity. They all were used for the synthesis of PHUs, by

ring opening aminolysis with diamines in bulk and without catalyst. Two diamines were used in this study: the aromatic m-xylylenediamine (MXDA) and the biobased aliphatic 1,4 diaminobutane. The obtained materials were characterized by FTIR and ^1H NMR and their thermal and mechanical properties were studied by TGA, DSC and DMA.

2 Materials and methods

2.1 Reagents

Jojoba oil, castor oil, thioglycolic acid $\geq 99\%$, AIBN, ethyl acetate, dichloromethane, dioxane, m-xylylenediamine (MXDA), glycerol-1,2-carbonate, 1,4-diaminobutane (DAB), 1,1'-carbonyldiimidazole (CDI) and succinic anhydride were purchased from Sigma or ABCR and used without purification. AIBN was recrystallized in methanol before use.

2.2 Analytical techniques

All nuclear magnetic resonance (^1H , ^{13}C NMR) measurements were recorded on a Bruker Avance 400 MHz spectrometer at room temperature in deuterated chloroform (CDCl_3). The chemical shifts were reported in part per million (ppm) relative to tetramethylsilane. Spin multiplicity is shown by s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. 10-15 mg of samples were placed on a platinum pan and heated from room temperature to $650\text{ }^\circ\text{C}$ under air flow ($60\text{ mL}\cdot\text{min}^{-1}$).

Differential scanning calorimetry (DSC) analyses were carried out on a NETZSCH Maia DSC200 calorimeter. Cell constant calibration was performed using tin, zinc, gold, indium, n-octadecane, and n-octane standards. Nitrogen was used as the purge gas. Approximately (10 mg) of samples were sealed in pierced aluminum pans or on a stainless steel high pressure capsules. The thermal properties were analyzed at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ between -120 and $120\text{ }^\circ\text{C}$ to observe reaction enthalpy, glass transition as well as crystallization/fusion processes. All the reported temperatures are onset values.

Dynamic Mechanical Analyses (DMA) was carried out with Dynatest 6.8 software on Metravib DMA 25. Two studies were performed, firstly linear region of polymer to determine the strain then a heating with a rate of $3\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from $-100\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$, with 1 Hz frequency.

Size exclusion chromatography (SEC) was performed on a Varian ProStar Model 210 equipped with an RI refractive index detector. Two PL gel $5\text{ }\mu\text{m}$ Resipore were used at $70\text{ }^\circ\text{C}$ with a $0.8\text{ mL}\cdot\text{min}^{-1}$ flow rate of

DMF with 0.1% of LiBr, calibrated using PMMA standards, sample injection amount was typically 20 µL at a concentration of 10 mg/mL.

IR spectra were recorded on a Nicolet 510P FTIR spectrometer with a band accuracy of 4 cm⁻¹ using the attenuated total reflection module (ATR) at room temperature.

A list of equations obtained with ¹H NMR and titration results was detailed below. They allowed to determine some important parameters : (X_{at}) is the number of acid thiol molecule (AT) grafted per JO, and I_a is acid number (Figure 2A), (% C_d) is the conversion ratio of double bond, (% Tf) is the conversion of thioester formation, (X_j) is the number of cyclic carbonate functions per JO2ac (Figure 2B), and (X_c) is the number of cyclic carbonate functions per triglyceride (Figure 3B), (X_{at2}) is the number of acid thiol molecule (AT) grafted per castor triglyceride (Figure 4A) and lastly, (X_{c2}) is the number of cyclic carbonate functions per triglyceride after the second modification of castor oil (Figure 4B).

$$X_{at} = \frac{I_{7'}}{I_{10}} \times 2 \quad (\text{Equation 1})$$

$$\% C_d = \left(1 - \frac{I_{7'}/4}{I_{10}/2}\right) \times 100 \quad (\text{Equation 2})$$

$$\text{Tf \%} = \% C_d - \frac{I_{11}}{I_{11} + (I_{11'} + I_{11''})/2} \quad (\text{Equation 3})$$

$$I_a = \frac{V_e \times N \times 56.1}{m_e} \quad (\text{Equation 4})$$

$$X_j = \frac{I_{17}}{I_{10}} \times 2 \quad (\text{Equation 5})$$

$$X_c = \frac{I_{11}}{I_{13}} \quad (\text{Equation 6})$$

$$X_{at2} = \frac{I_{7'}}{3.09 \times I_{13}} \times 3 \quad (\text{Equation 7})$$

$$X_{c2} = \frac{I_{12}}{I_{13}} \times 1 \quad (\text{Equation 8})$$

Where (I) is integration of the peak area in ¹H NMR spectrum, (V_e) is the added volume of KOH and (m_e) is the mass (g) of sample and (N) is the normality of KOH solution.

Swelling index: Three samples of around 30 mg each were separately put in THF for 24 h. The swelling index (SI) was calculated using the Equation 3 where m_1 is the mass of the material after swelling in THF and m_2 is the initial mass of the material.

$$SI = \frac{m_1 - m_2}{m_2} \times 100 \quad (\text{Equation 9})$$

Gel content: After SI measurements, the three samples were dried in a ventilated oven at 70 °C for 24 h. The gel content (GC) was calculated using the Equation 4, where m_3 is the mass of the material after the oven and m_2 is the initial mass of the material.

$$GC = \frac{m_3}{m_2} \times 100 \quad (\text{Equation 10})$$

2.3 Synthesis of jojoba diacid (Jo2ac)

The synthesis of jojoba diacid (Jo2ac) was achieved with a with a thiol/ene/AIBN ratio of 3/1/0.1. 50g (1 eq, 0.084 mol) of jojoba oil (JO) and 2.75g (0.2 eq, 16.8 mmol) of AIBN were mixed under inert atmosphere in a three-necked round-bottom flask equipped with a magnetic stirrer, a thermometer and a condenser tube. The mixture was heated at 80°C, then 46g (6 eq, 0.504 mol) of thioglycolic acid (TA) was dropped to the reaction flask during 20 min. After 6h the product was purified by a liquid-liquid extraction: the mixture was dissolved in ethyl acetate then washed by an aqueous solution of sodium chloride, the organic layer was dried with magnesium sulfate followed by filtration and concentration in rotary evaporator. A mixture of two diacids was obtained with the following ratios (calculated by NMR): 83 mol% of main acid product and 17 mol% of side product with a thioester function.

FTIR (λ , cm^{-1} , fig SI-1B): 3200 (O-H acid group), 2921-2851 (CH aliphatic); 1750 (C=O ester), 1706 (C=O acid).

^1H NMR (δ , 400 MHz, ppm, fig 2A): 0.80 (H_1 , CH_3 , t); 1.21 (H_2 , CH_2 , m); 1.33 (H_3 , CH_2 , m); 1.48 (H_4 , $\text{CH}_2\text{-CH}$, m); 1.60 (H_5 , CH_2 , m); 2.25 (H_6 , $\text{CH}_2\text{-C=O}$, t); 2.75 ($\text{H}_{7'}$, CH-S , m); 3.25 (H_{11} , $\text{CH}_2\text{-S}$, s); 4.0 (H_{10} , $\text{CH}_2\text{-O}$, t) for the main product and 3.36 ($\text{H}_{11'}$, $\text{SCO-CH}_2\text{-S}$, t); 3.65 ($\text{H}_{11''}$, $\text{HOOC-CH}_2\text{-S}$, t) for the minor product.

^{13}C NMR (δ , 100.6 MHz, ppm, fig SI-2A): 14.1 (C_1); 20 - 30 ($\text{C}_{2,3,5,8}$); 31.9 (C_6); 34.2 (C_4); 40.2 (C_{11}); 46.6 (C_7); 64.5 (C_{10}); 173.9 (C_{12}); 174.36 (C_{13}) for the main product and 39.4 ($\text{C}_{11''}$); 42.0 ($\text{C}_{11'}$); 176.96 ($\text{C}_{13''}$); 196.56 ($\text{C}_{13'}$) for the minor product.

2.4 Synthesis of jojoba dicyclic carbonate (Jo2c)

The synthesis of jojoba dicyclic carbonate (Jo2c) was performed by an esterification reaction at room temperature with the use of CDI as catalyst. 25g (1eq, 0.033 mol) of Jo2ac was mixed with 11.34g (2.1eq, 0.070 mol) of CDI in 15 ml of dichloromethane under inert atmosphere, then 8.26g (2.1eq, 0.070 mol) of glycerol carbonate (GC) was added dropwise over 30 min to the reaction mixture. Purification of the dicyclic carbonate was proceeded after 16h, by a liquid-liquid extraction, by washing three times the reaction mixture with an acid aqueous solution followed by basic washing. The organic layer was dried with magnesium sulfate, filtrated then concentrated in rotary evaporator. The ratio for the 2 dicyclic carbonate products was: 70 mol% of the main product and 30 mol% of the minor product calculated by NMR.

FTIR (λ , cm^{-1} , fig-SI-1C): 2922-2852 (CH aliphatic); 1797 (C=O cyclic carbonate), 1784 (C=O ester).

^1H NMR (δ , 400 MHz, ppm, fig 2B): 0.80 (H_1 , CH_3 , t); 1.21 (H_2 , CH_2 , m); 1.33 (H_3 , CH_2 , m); 1.48 (H_4 , $\text{CH}_2\text{-CH}$, m); 1.60 (H_5 , CH_2 , m); 2.25 (H_6 , $\text{CH}_2\text{-C=O}$, t); 2.75 (H_7 , CH-S , m); 3.25 (H_{11} , $\text{CH}_2\text{-S}$, s); 4.0 (H_{10} , $\text{CH}_2\text{-O}$, t); 4.3-4.50 ((H_{14} , $\text{CH}_2\text{-O,d}$) ($\text{H}_{18'}$, $\text{CH-CH}_2\text{-O,d}$)); 4.5 - 4.6 (H_{18} , $\text{CH-CH}_2\text{-O,d}$). 4.9 (H_{17} , $-\text{CH}_2\text{-CH-CH}_2\text{,m}$) for the main product and 3.40 ($\text{H}_{11'}$, $\text{SCO-CH}_2\text{-S}$, t); 3.66 ($\text{H}_{11''}$, $\text{HOOC-CH}_2\text{-S}$, t) for the minor product.

^{13}C NMR (δ , 100.6 MHz, ppm, fig SI-2B): 14.1 (C_1); 20 - 30 ($\text{C}_{2,3,5,8}$); 31.9 (C_6); 34.2 (C_4); 41.3 (C_{11}); 46.8 (C_7); 64.0 (C_{14}); 64.5 (C_{10}); 67.2 (C_{18}); 74.0 (C_{17}); 155.1 (C_{19}); 173.7 (C_{12}); 174 (C_{13}) for the main product and 39-44 ($\text{C}_{11',11''}$); 168.4 ($\text{C}_{13''}$); 196.3 ($\text{C}_{13'}$) for the minor product

2.5 Synthesis of castor oil triacid (Co3ac)

The functionalization of castor oil was carried out with succinic anhydride. In a 250 mL three-necked round bottom flask, 17.87g (3.2eq, 0.178 mol) of succinic anhydride was solubilized in 40 ml of 1,4-dioxane then added to 50g (1eq, 0.0558 mol) of castor oil. The solution was stirred at 70°C during 6h under inert atmosphere. The mixture was then solubilized in methylene chloride and washed with an acidic aqueous solution and dried before the evaporation of solvent.

FTIR (cm^{-1} , fig SI-3B): 3200 (OH acid); 3010 (C=CH); 2925-2854 (CH aliphatic); 1733 (C=O ester), 1711 (C=O acid)

^1H NMR (δ , 400 MHz, ppm, fig 3A): 0.80 (H_1 , CH_3 , t); 1.20 (H_2 , CH_2 , m); 1.40-1.60 (H_8, H_3 CH_2 , m); 1.92 (H_7 , CH_2 , t); 2.25 (H_5 , H_9 , $\text{CH}_2\text{,q}$); 2.5-2.6 ($\text{H}_{9'}$, CH_2 , t); 4.0-4.25 (H_{10} , CH_2 , d); 4.8 (H_4 , CH , m); 5.2 - 5.5 ($\text{H}_{13}, \text{H}_6$, CH-O , CH=CH , m).

^{13}C NMR (δ , 100.6 MHz, ppm, fig SI-4B): 14 (C_1); 20-25 ($\text{C}_{3,8,9'}$); 26-35 ($\text{C}_{2,5,7,9}$); 61 (C_{10}); 67 (C_{13}); 75 (C_4) 124 (C_6) ; 133 (C_6); 170-180 ($\text{C}_{11,11'}$).

2.6 Synthesis of castor oil tricyclic carbonate (Co3c)

The synthesis of castor oil based tricyclic carbonate (Co3c) was performed by an esterification reaction at room temperature with CDI as catalyst. 40 g (0.033 mol) of Co3ac was mixed with 16.2 g (0.1 mol) of CDI in 15ml of dichloromethane under inert atmosphere, and then 11.8 g (0.1 mol) of GC was added dropwise over 30 min to the reaction mixture. Purification of the tricyclic carbonate was proceeded after 16h by a liquid-liquid extraction. The organic layer was dried with magnesium sulfate, filtrated then concentrated in rotary evaporator.

FTIR (cm^{-1} , fig SI-3C): 3008 (C=CH); 2925-2854 (CH aliphatic); 1830 (C=O carbonate), 1730 (C=O ester).

^1H NMR (δ , 400 MHz, ppm, fig 3B): 0.8 (H_1 , CH_3 , t); 1.2 (H_2 , CH_2 , m); 1.4 (H_3 , CH_2 , m); 1.6 (H_8 , CH_2 , m); 1.9 (H_7 , CH_2 , t); 2.25 (H_5 , H_9 , CH_2 , q); 2.5-2.6 ($\text{H}_{9'}$, $\text{CH}_2\text{-CH}$, t); 4.0-4.25 ($\text{H}_{10,10',11}$, CH_2 , m); 4.5 (H_{11} , CH , t); 4.8 (H_4, CH , m); 4.9 (H_{12} , CH , m); 5.2 (H_{13} , CH-O , m); 5.25-5.5 (H_6 , CH=CH , m).

^{13}C NMR (δ , 100.6 MHz, ppm, fig SI-4C): 14 (C_1); 20-35 ($\text{C}_{2,3,5,7,8,9,9'}$); 63 (C_{16}); 64 (C_{10}); 67 ($\text{C}_{10'}$); 69 (C_{13}); 74 (C_{12}); 75 (C_4); 124 (C_6); 133 (C_6); 155 (C_{14}); 172-175 ($\text{C}_{11,11'}$).

2.7 Synthesis of castor oil hexacid (Co6ac)

Castor triacid was functionalized with thioglycolic acid by thiol-ene coupling at 80°C , with a thiol/ene/AIBN ratio of 3/1/0.1. 50 g (1 eq) of castor triacid with 0.3 eq of AIBN were placed at 80°C , then 9 eq of acid thioglycolic solution was added dropwise over 20 min to the reaction mixture. After purification, the hexacid castor oil Co6ac was characterized by FTIR, ^1H and ^{13}C NMR.

FTIR (cm^{-1} , fig SI-5B): 3200 (OH acid); 3010 (C=CH); 2926-2855 (CH aliphatic); 1733 (C=O ester), 1706 (C=O acid)

^1H NMR (δ , 400 MHz, ppm, fig 4A): 0.8 (H_1 , CH_3 , t); 1.2-1.6 (H_2 , H_2' , H_3 , H_5 , H_8 , CH_2 , m); 2.25 (H_9 , CH_2 , q); 2.5-2.75 (H_9' , H_7' , CH_2 , t); 3.2 (H_{14} , CH_2 , s); 4-4.25 (H_{10} , CH_2 , dd); 4.8 (H_4 , CH, m); 5.25 (H_{13} , CH, m). Presence of minor product with thioacid function around 3.4-3.65 ($\text{H}_{14'}$ and $\text{H}_{14''}$, CH_2 , s).

^{13}C NMR (δ , 100.6 MHz, ppm, fig SI-6A): 14 (C_1); 20-35 ($\text{C}_{2,2',3,5,7,8,9,9'}$); 39 (C_7); 43 (C_{14}); 61-75 ($\text{C}_{10,13,4}$); 170-180 ($\text{C}_{11,11',11'',15}$).

2.8 Synthesis of castor oil hexacyclic carbonate (Co6c)

The obtained Co6ac was used to synthesize a hexacyclic carbonate functional castor oil by Steglich esterification reaction with glycerol carbonate. 1 eq of Co6ac and 6.2 eq of CDI and 60 ml of CH_2Cl_2 were placed in a three-necked round bottom flask at room temperature, then 6.2 eq of glycerol carbonate was added dropwise over 30 min to the reaction mixture. Purification of product is done by a liquid-liquid extraction. After purification, the product Co6c was characterized by FTIR, ^1H and ^{13}C NMR.

FTIR (cm^{-1} , fig SI-5C): 2917-2849 (CH aliphatic); 1795 (C=O carbonate), 1730 (C=O ester).

^1H NMR (δ , 400 MHz, ppm, fig 4B): 0.80 (H_1 , CH_3 , t); 1.20 (H_2 , CH_2 , m); 1.40-1.6 (H_8, H_3 , CH_2 , m); 2.25 (H_5, CH_2 , q); 2.5-2.6 (H_9 , H_9' , $\text{CH}_2\text{-CH}$, t); 4-4.25 ($\text{H}_{10,10',11}$, CH_2 , m); 4.5 (H_{11} , CH, t); 4.8 (H_4, CH , m); 4.9 (H_{12} , CH, m); 5.2 - 5.50 ($\text{H}_{13}, \text{H}_6$, CH-O, CH=CH, m).

^{13}C NMR (δ , 100.6 MHz, ppm, fig SI-6B): 14 (C_1); 20-35 ($\text{C}_{2,2',3,5,7,8,9,9'}$); 39 (C_7); 43 (C_{14}); 61-75 ($\text{C}_{10,10',12,13,4}$); 154 (C_{17}); 170-180 ($\text{C}_{11,11',11'',15}$).

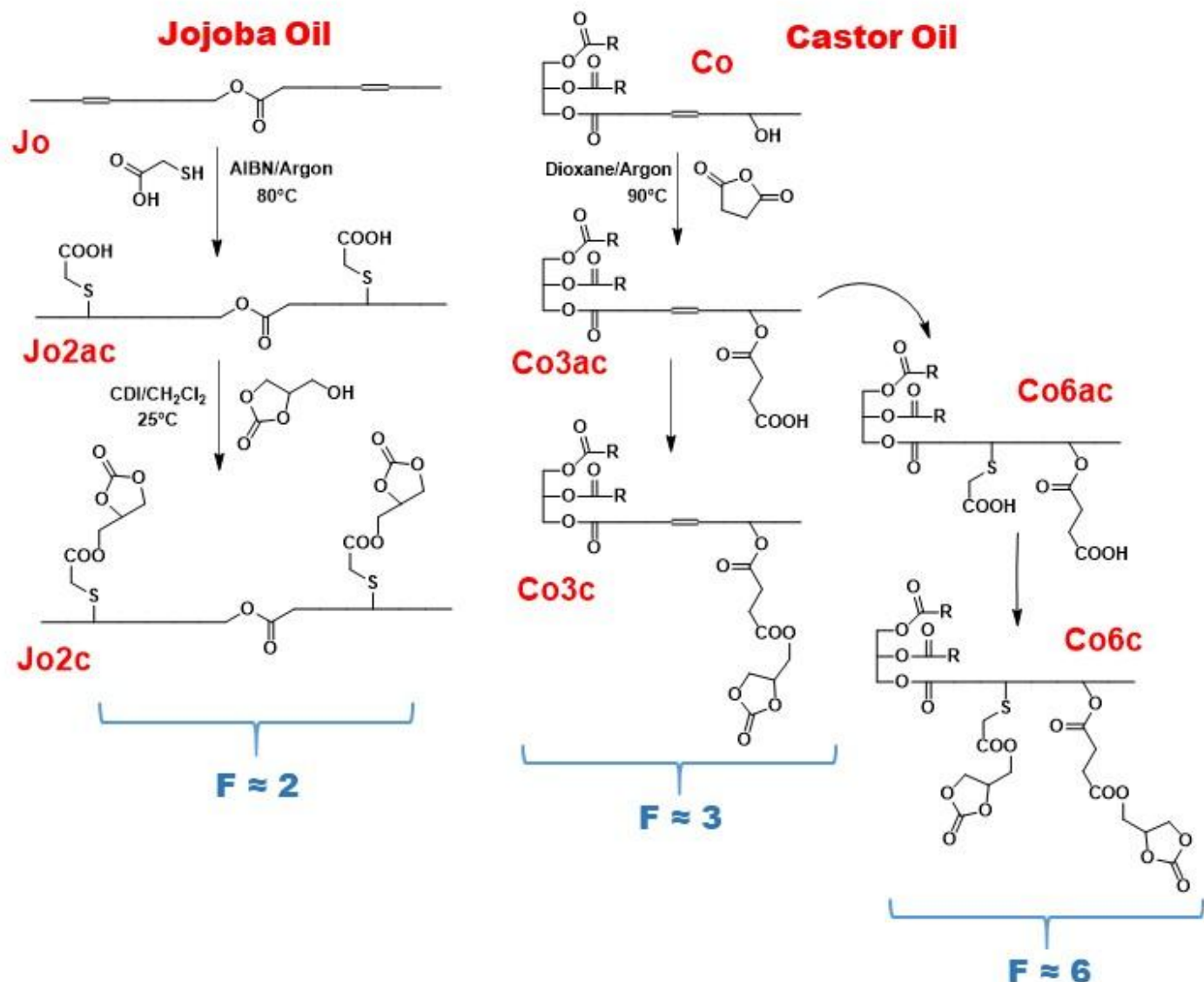
2.9 Synthesis of PHUs

Many formulations were carried out using Jo2c, Co3c, Co6c as cyclic carbonate monomers and 1,4-diaminobutane (DAB) and m-xylylenediamine (MXDA) as amine reagents. CEW and AHEW correspond respectively to cyclic carbonate equivalent weight and amine equivalent weight. Before the formulation of materials, AHEW and CEW were determined by titration with ^1H NMR. Table 1 summarizes the monomer properties. The materials were formulated with a molar ratio cyclic carbonate/amine of 1:1. The polyaddition reactions were performed at 40 °C and compositions of mixtures are shown in table 2.

To estimate the reactivity of pendant cyclic carbonate, 1g of a mixture of Jo2c and DAB with a molar ratio cyclic carbonate/amine of 1:1 was done and analyzed in FTIR. The conversion of the cyclocarbonate band (1797 cm^{-1}) in function of time was detailed in figure SI-8.

3 Results and Discussion

Vegetable oils represent ideal substrates for the synthesis of cyclic carbonate monomers, as their unsaturations can be easily epoxidized and carbonated. This direct route allows to obtain only weakly reactive carbonate within the aliphatic chain. Consequently high temperature and catalyst are needed in order to perform cyclic carbonate aminolysis. However, it has been reported that from 70°C, amidification reaction starts to occur between amines and fatty esters³⁹. This side reaction was reported by Lamarzelle et al.⁴⁰ and Besse et al.⁴¹, leading thus to the decreasing of molar masses of the final PHU. Indeed, amidification reactions could be avoided by decreasing the temperature below 70 °C. Our strategy is to design novel monomers with pendant cyclic carbonate ~~hanging off~~ on the main chain, with improved reactivity⁴². These monomers were synthesized with various functionalities, from both jojoba and castor oils (Scheme 1). Hence, jojoba oil with its well-defined chemical structure allows to obtain a difunctional cyclic carbonate monomer in order to achieve linear PHUs. Castor oil has two types of functionalization sites: the double bonds and the hydroxyl functions. Therefore 2 different types of functionalization were performed to obtain precursors with either 3 or 6 carbonate functions per triglyceride in order to yield various crosslinked polymers.



Scheme 1: General strategy for the functionalization of jojoba and castor oils

3.1 Synthesis of jojoba dicyclic carbonate (Jo2c)

Jojoba oil (JO) is a golden liquid, composed by two mono unsaturated hydrocarbon chains linked by an ester moiety (Figure 1). Its structure was determined in a previous work³⁸. The average number of double bonds per JO molecule is 2.06. The first step allowed to obtain a biobased diacid by thiol-ene coupling (TEC) at 80°C under inert atmosphere. Many studies have already used TEC to functionalize vegetable oils with various functions and have determined the optimum stoichiometric conditions to obtain a quantitative conversion of double bonds (thiol/ene/AIBN 3/1/0.1)^{43, 44}. Conversion of JO in jojoba diacid (Jo2ac) was confirmed by FTIR, ¹H and ¹³C NMR. As shown in Figure SI-1A, disappearance of double bonds C-H sp² stretching absorbance at 3004 cm⁻¹ and the appearance of characteristic OH vibration and C=O carbonyl

stretching of acid groups at 3200 and 1706 cm^{-1} , respectively, confirmed the total conversion of double bonds, and the successful synthesis of Jo2ac.

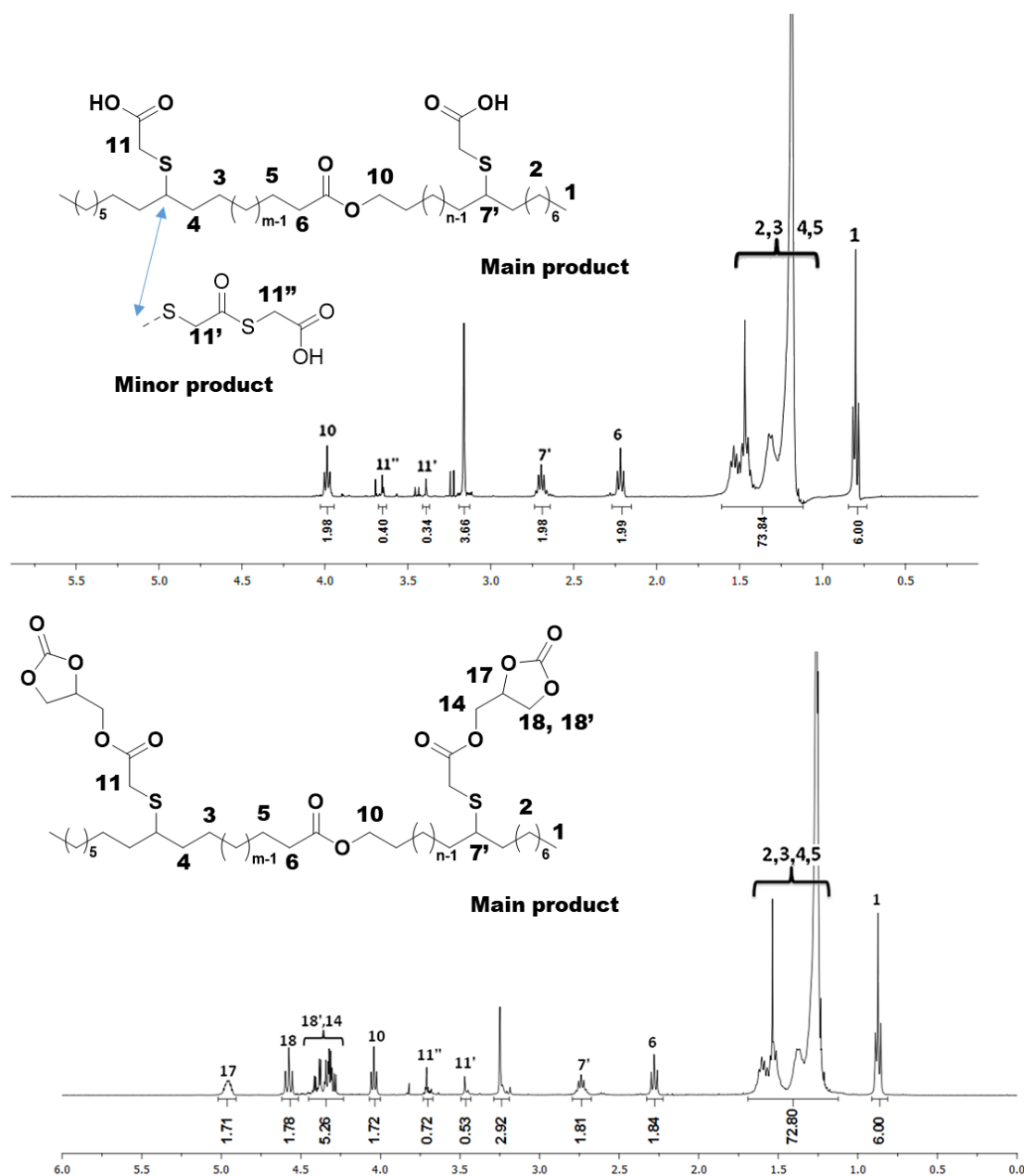


Figure 2: ^1H NMR spectra of A) Jojoba diacid (Jo2ac) and B) Jojoba dicyclic carbonate (Jo2c)

In the ^1H NMR spectrum shown in Figure 2A, the appearance of multiplet between 1.2-1.6 ppm was attributed to protons of methylene H_{2-5} of the aliphatic chain and particularly CH_2 in β position of S. The appearance of the signal at 2.75 ppm characteristic of protons $\text{H}_{7'}$ of CH-S corresponding to the thioether formation and the presence of singlet at 3.25 ppm belong to protons H_{11} of thioglycolic acid proved the successfully addition of thioglycolic acid on JO. The total conversion of reaction was proved by disappearance of vinyl protons and α protons of double bonds at 5.3 ppm and 2 ppm respectively. The appearance of singlets at 3.4 and 3.5 ppm, is due to thioesterification side-reaction, a minor product with

thioester function was estimated to 17 mol%. Previous works of our team showed that thioesterification may occur in the case of thioglycolic acid but does not modify the final acid functionality⁴⁴. Contrariwise, no disulfide formation was detected in our product, demonstrated by the absence of the signal of CH₂ protons of disulfide at 4.8 ppm. Owing to the Eq 1 and 2, the number of acid functions grafted per JO molecule and conversion of double bonds were determined equal to 1.98 and 96% respectively. Moreover ¹H NMR analysis (Figure 2A) and eq 3 allowed determining thioesterification ratio of 9%. Confirmation of acid amount was made by acid titration: Acid index I_a is calculated by eq 4 and 98.55 mg KOH/g (1.75 mmol KOH/g of product) was obtained. Jo2ac was also characterized by ¹³C NMR (Figure SI-2A). Indeed, disappearance of double bonds signal at 130 ppm and appearance of two signals at 174 and 42 ppm characteristic of carbonyl of thioglycolic acid C₁₃ and CH₂ (C₁₅) in α position relative to carbonyl respectively, confirmed the formation of Jo2ac.

The jojoba cyclic carbonate was synthesized by Steglich esterification of Jojoba diacid (Jo2ac) with glycerol carbonate. This reaction occurred at room temperature with carbonyl diimidazole (CDI), a less toxic reagent than dicyclohexyl carbodiimide, which allows easy purification. The obtained yellowish viscous liquid of jojoba cyclic carbonate (Jo2c) was characterized by ¹H, ¹³C NMR and FTIR. Regardless of their structure, complete conversion of the acid groups was achieved. In the FTIR spectrum (figure SI-1C), the disappearance of the absorbance of stretching of –OH groups of thioglycolic acid and C=O groups of acid at 3200 cm⁻¹ and 1706 cm⁻¹ respectively and the appearance of the characteristic bands C=O at 1797 cm⁻¹ attributed to carbonyl of cyclic carbonate were highlighted. ¹H NMR spectrum of Jo2c (figure 2B) showed signals at 4.9, 4.3 and 4.6 ppm attributed to CH (H₁₇ proton) and CH₂ (H₁₈, H_{18'} protons) respectively assigned to the cyclic carbonate group and the signal at 4.25 ppm for H₁₆ protons linked to the ester group. The number of cyclic carbonate function per jojoba oil was determined by eq 5 and was 1.98 cyclic carbonates per JO molecule. Lastly ¹³C NMR confirms the formation of Jo2c (figure SI-2B), where the apparition of carbon signals C₁₄, C₁₈, C₁₇ and C₁₉ at 63, 67, 74 and 155 ppm due to the addition of cyclic carbonate functions was highlighted. General characteristics of Jo2c are presented in Table 1, carbon equivalent weight (CEW) was determined equal to 606 by eq SI-3.

3.2 Synthesis of castor oil tricyclic carbonate (Co3c)

Castor oil based cyclic carbonate (Co3c) was obtained in two steps. First, succinic anhydride undergoes ring opening reaction with hydroxyl functions of castor oil, leading to acid functionalized castor oil (Co3ac). The formation of Co3ac is confirmed by FTIR, ¹H and ¹³C NMR (figure SI-3B, figure 4A, figure SI-4B).

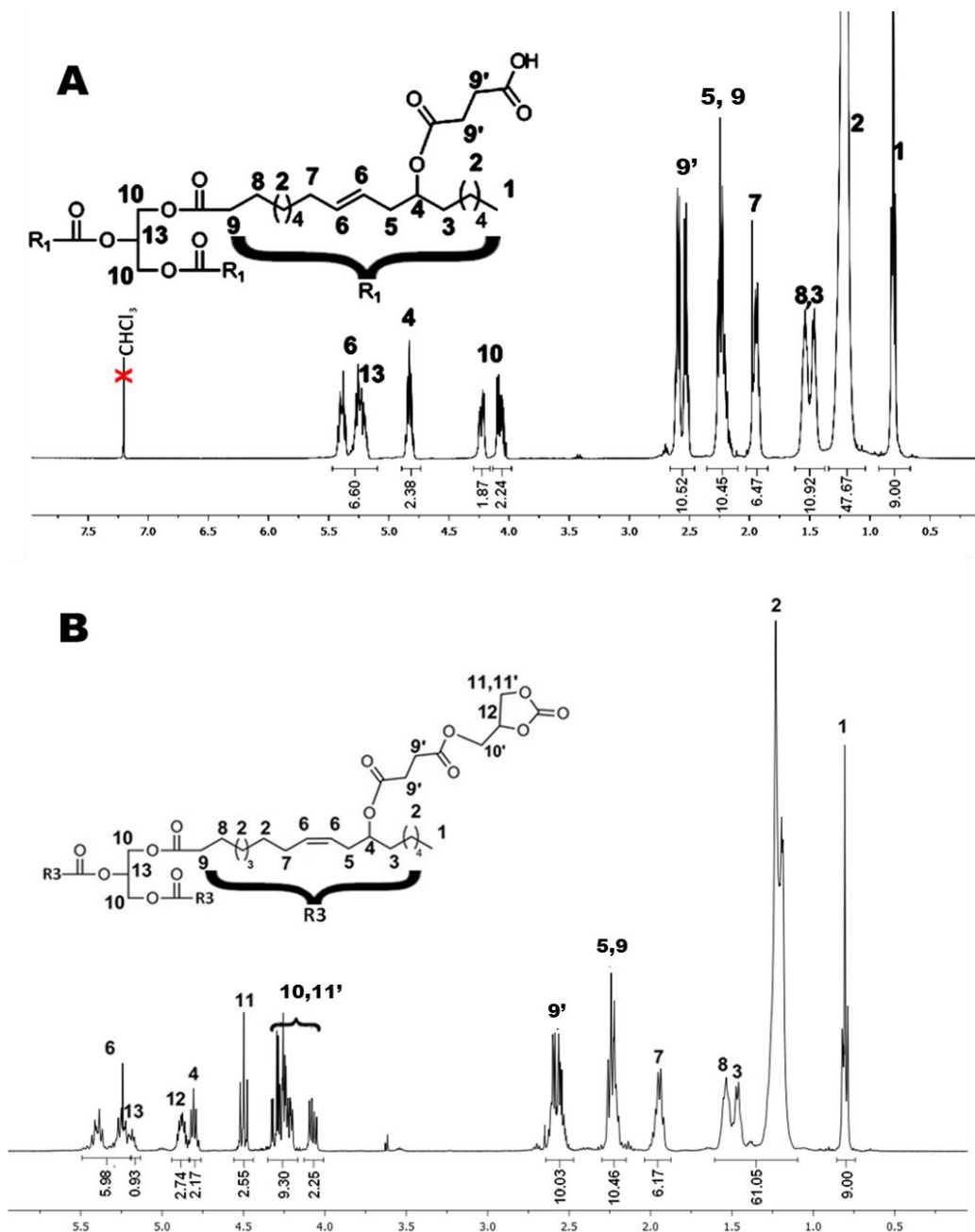


Figure 3: ^1H NMR spectra of A) Castor oil triacid (Co3ac) and B) Castor oil tricyclic carbonate (Co3c)

The second step consists in the Steglich esterification between Co3ac and GC in presence of CDI. FTIR analysis of Co3c (figure SI-3C) shows the disappearance of $-\text{OH}$ and $\text{C}=\text{O}$ acid signals at 3200 and 1711 respectively, and the appearance of $\text{C}=\text{O}$ signal at 1760 cm^{-1} attributed to cyclic carbonate. In the NMR spectrum (figure 4B) the appearance of H_{12} , H_{11} , $\text{H}_{11'}$ protons signals of carbonate at 4.9, 4.5 and 4.25 ppm respectively was highlighted. The number of cyclic carbonate by molecule was determined by eq 6, is 2.8 cyclic carbonates by triglyceride. The CEW determined by NMR titration is 545. ^{13}C NMR spectrum (figure SI-4C) shows the formation of cyclic carbonate confirmed by the appearance of C_{16} and C_{12} signals at 63 ppm and 74 ppm, also the carbonyl of cyclic carbonate C_{14} signal appears at 154 ppm.

3.3 Synthesis of hexacyclic carbonate castor oil (Co6c)

Co6c cyclic carbonate castor oil was synthesized from Co3ac in two steps. First, Co6ac castor oil was functionalized with acid groups by TEC with thioglycolic acid in the same conditions used for the synthesis of Jojoba diacid (Jo2ac). The obtained product was characterized by ^1H , ^{13}C NMR and FTIR. It should be noted that castor oil presents 3.09 double bonds per triglyceride. FTIR spectrum (figure SI-5B) shows the disappearance of C=C-H stretching vibration at 3010 cm^{-1} due to the conversion of double bonds and the appearance of the -OH stretching vibration signals at 3200 cm^{-1} and a new peak at 1706 cm^{-1} attributed to the C=O of acid groups. ^1H NMR analysis (figure 3A) shows the disappearance of double bonds H_6 proton signal at 5.3 ppm and the appearance of thioester signals ($\text{H}_{7'}$ proton) at 2.75 ppm. Number of grafted acid functions is determined by eq 7 owing to ^1H NMR and is equal to 3.02 acid functions per triglyceride. ^{13}C NMR spectrum presented in Figure SI-6A shows the disappearance of $\text{C}_{6,6'}$ of double bonds at $124 - 133\text{ cm}^{-1}$ and the appearance of thioether $\text{C}_{7'}$ at 39 ppm and C_{14} signal of carbon in α position of thioesters at 43 ppm.

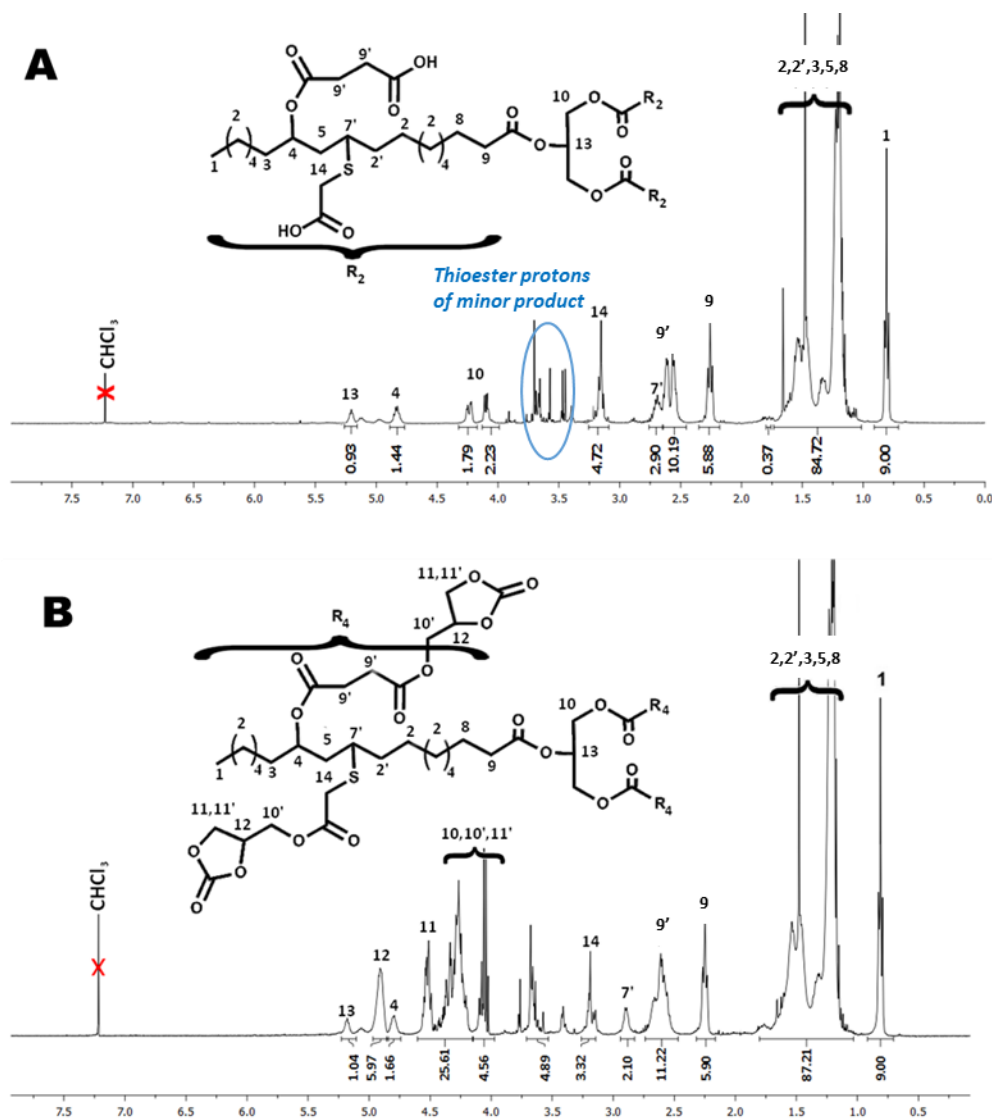


Figure 4: ^1H NMR spectra of A) Castor oil hexacid (Co6ac) and B) Castor oil hexacyclic carbonate (Co6c)

The Co6c cyclic carbonate was synthesized by esterification of castor oil triacid Co6ac with glycerol carbonate. In Figure SI-5C, by comparing the FTIR spectrum of Co6ac and Co6c, disappearance of OH stretching vibration at 3200 cm^{-1} was noted, while new peak at 1795 cm^{-1} has appeared due to the formation of the cyclic carbonate moieties. ^1H NMR spectrum (Figure 4B) demonstrates the grafting of cyclic carbonate groups with the appearance of cyclic carbonate signals H_{12} , H_{11} and $\text{H}_{10',11'}$ at 4.9, 4.55 and 4.25-4.5 respectively. The number of cyclic carbonate functions per triglyceride determined by eq 8 is equal to 5.7. ^{13}C NMR spectrum (Figure SI-6B) highlighted the appearance of carbonate with the signals C_{17} and C_{16} signals at 158 ppm and 74 ppm, also signals of new α carbons of esters appear between 60 and 75 ppm.

3.4 PHUs synthesis and characterizations

In this study, several linear or crosslinked PHUs were synthesized by reaction between Jo2c and castor oil based cyclic carbonate monomers (Co3c and Co6c) with two different primary diamines, namely aliphatic DAB and aromatic MXDA. Differential scanning calorimetry (DSC) was performed in order to determine the suitable temperature for carbonate/amine reaction. DSC shows an exothermic peak beginning at 30°C for all formulations (Figure SI-7). A FTIR kinetic study was performed at room temperature on a formulation with Jo2c:DAB 1:1. The decrease of the carbonyl band of the cyclic carbonate at 1797 cm^{-1} was completed in 30 min (Figure SI-8). To confirm this result, a reaction between Jo2c and DAB at 40°C in solution was monitored by ^1H NMR. After less than one hour reaction the cyclic carbonate proton signals (at 4.9, 4.5 and 4.3 ppm) disappeared completely. This fast reaction kinetic demonstrates the high reactivity of the synthesized jojoba cyclic carbonate Jo2c compare to internal cyclic carbonate in linseed⁴⁵ or soybean²⁶ oils. Indeed, in the literature, the reaction between internal cyclic carbonate and diamine was performed at higher temperature (from 70 to 120°C) and the kinetics of the aminolysis of cyclic carbonate ring was slower (180 min minimum). The higher reactivity of our novel cyclic carbonate is not only due to the presence of inductive effect of ester which decreases carbonyl electronegativity of cyclic carbonate carbonyl, or to the reduced steric hindrance. Indeed, the main effect is due to the creation of H bonds between amine protons and ester oxygen, which suitably orients amine to favor aminolysis⁴². Hence, step-growth polymerization to yield different PHUs was achieved during one night at 40°C , with a stoichiometric carbonate:amine ratio 1:1 in bulk, without catalyst. The consumption of the cyclic carbonate during the polymerization was confirmed by FTIR (Figures SI-9, SI-10 and SI-11) which shows a significant disappearance of the characteristic signal of the carbonyl group of the cyclic carbonate around 1800 cm^{-1} . Moreover, the appearance of three new bands at 3300 cm^{-1} , 1530 and 1650 cm^{-1} , respectively assigned to OH stretching and deformation and NH deformation vibrations highlighted the formation of hydroxyl

urethane groups for all the polymers. Jo2c led to linear PHUs whereas castor oil-based cyclic carbonate (Co3c and Co6c) led to cross-linked PHUs. ^1H NMR analyses were performed on the Jo2c-based linear PHUs. The ^1H NMR spectra of PHU 1 and PHU 2 are presented in figure SI-12, the disappearance of characteristic signals H_{17} of cyclic carbonate at 4.9 ppm with an appearance of H_{15} characteristic signal of α protons of urethane function for PHU 1 and the phenyl signals $\text{H}_{16,16'}$ around 7.1 ppm for PHU 2 are noticed.

3.5 Properties of PHU polymers

SEC analysis was performed on soluble Jo2c-based PHUs (1 and 2). No great difference was detected between the two materials. The molar masses are respectively $7,100 \text{ g.mol}^{-1}$ for PHU 1 and $6,100 \text{ g.mol}^{-1}$ for PHU 2 with dispersity (Đ) around 1.4. These values are quite similar to the molar masses of PHUs reported in literature. Low dispersity is due to non-complete advancement of polyaddition. Indeed, low temperature does not allow to break hydrogen bondings that block diffusion of growing oligomers.

As shown in figure 5, the glass transition temperature values of the PHU were determined by dynamic DSC analysis. T_g values of PHU materials ranged between -46°C and 20°C . Due to low amount of cyclic carbonate functions and presence of dangling chain of jojoba, the T_g of PHU 1 and 2 are low, respectively -46°C and -32°C . Aromatic MXDA-based PHUs exhibited a higher T_g compare to the aliphatic DAB-based PHUs. This is explained by the higher content of hard segments in the MXDA-based PHU which limits the chain mobility. The thermal stability of Co6c-based PHUs is higher than other PHUs, due to a higher crosslinking degree. The T_g value are 6°C and 20°C for PHU 5 and PHU 6 respectively. This suggests that the thermal resistance of our synthesized PHUs can be effectively influenced by the structure of the diamine and the number of cyclic carbonate groups in oil (between 2 and 6).

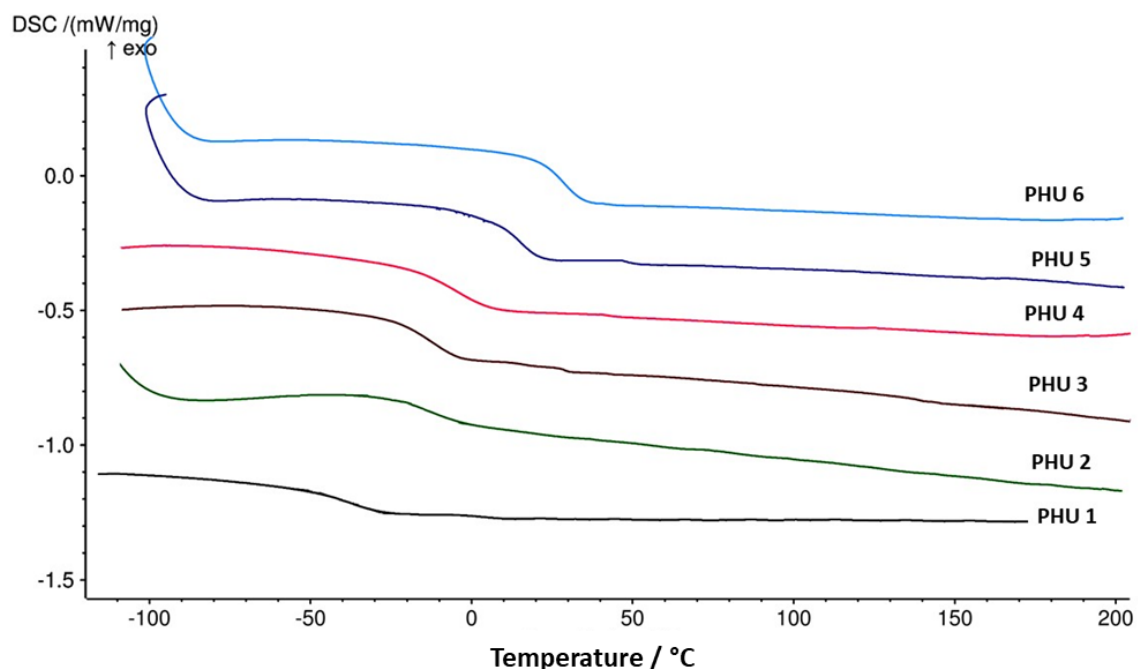


Figure 5: DSC curves of the different PHUs under N₂ atmosphere (15°C/min)

The thermal degradation behavior of the PHU materials was examined by TGA under air atmosphere, as shown in figure 6 and resumed in table 3. The data illustrated that all samples were stable up to ~200 °C. The T_d values of 6 samples were measured between 203 and 269 °C with an amount of residues between 0 and 3 %. The slope of the weight loss curves changed during three temperature ranges, indicating that the degradation of PHU materials processed in three stages. The first decomposition took place in the temperature range 220 - 320 °C, and was attributed to the decomposition of the urethane bonds. Then the weight of samples significantly decreased (300–420 °C) due to complete decomposition of the cross-linked network.

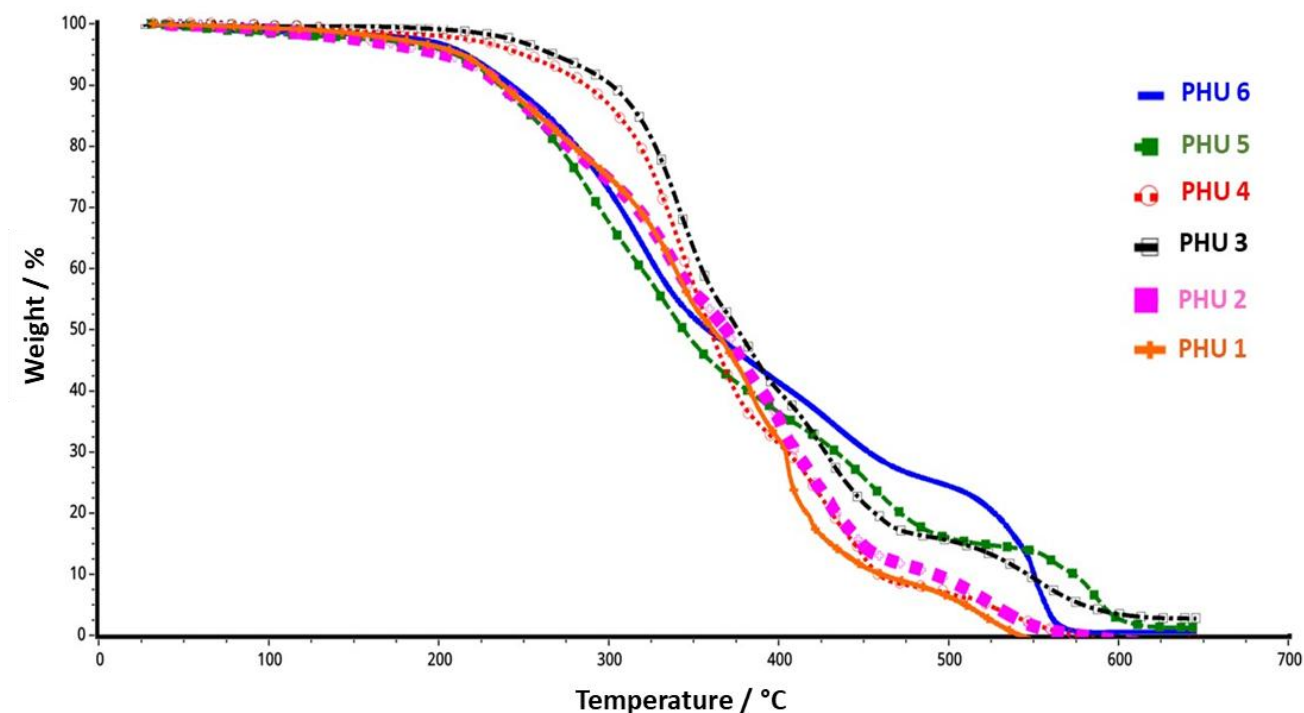


Figure 6: Thermogravimetric analysis (TGA) curves of different PHUs under air atmosphere (20°C/min)

Equation 9 and Equation 10 allowed determining the swelling index and the gel content of crosslinked materials (PHU 3 to 6). All gel contents are higher than 90%, which correspond to highly crosslinked networks and quantitative advancement of reaction. Moreover, the Co6c-based PHUs are more crosslinked than the Co3c-based PHUs. The swelling index of PHU 3 and 4 are respectively 398 and 300%, higher than those of PHU 5 and 6, respectively 106 and 95% (Table 3). These results were expected because Co3c, with lower cyclic carbonate functionality, would lead to lower a crosslinking density.

Thermomechanical performances of the studied PHUs were evaluated by DMTA experiments. Dynamic mechanical properties of Co3c-based materials are displayed in figure 7. Thermograms are expressed in terms of storage modulus E' , and damping factor $\tan \delta$ in function of temperature. The maximum of $\tan \delta$ curves allows determining the T_{α} temperature. The storage moduli of PHU 3 and 4 are respectively 994 MPa and 1460 MPa at the end of the glassy state -30°C, in accordance with their structures. Indeed, the leathery regions of both materials are quite the same between -30 and -15°C and then the rubbery plateau took place with the storage moduli of 0.714 and 0.461 MPa for PHU 3 and PHU 4 respectively. Concerning $\tan \delta$, the PHU 4 shows a T_{α} value of -7°C while the curve of aliphatic PHU 3 shows a plateau between -20 and 0°C. This result is due to the aliphatic chain of DAB which slows down the evolution of cooperative movements along the skeleton of the chain. For higher crosslinked PHUs 5 and 6, the study was performed

between -40 and 120°C. The end of the glassy state is at -20°C and about 0°C, and the rubbery plateau starts at 3°C and 22°C for PHUs 5 and 6 respectively. The $\tan \delta$ curve of PHU 5 also presents a plateau between -10 and 16°C. T_{α} of PHU 6 is 32°C. We observe clearly that the functionality, which allows to increase the number of hard segments, affects the thermomechanical properties of materials.

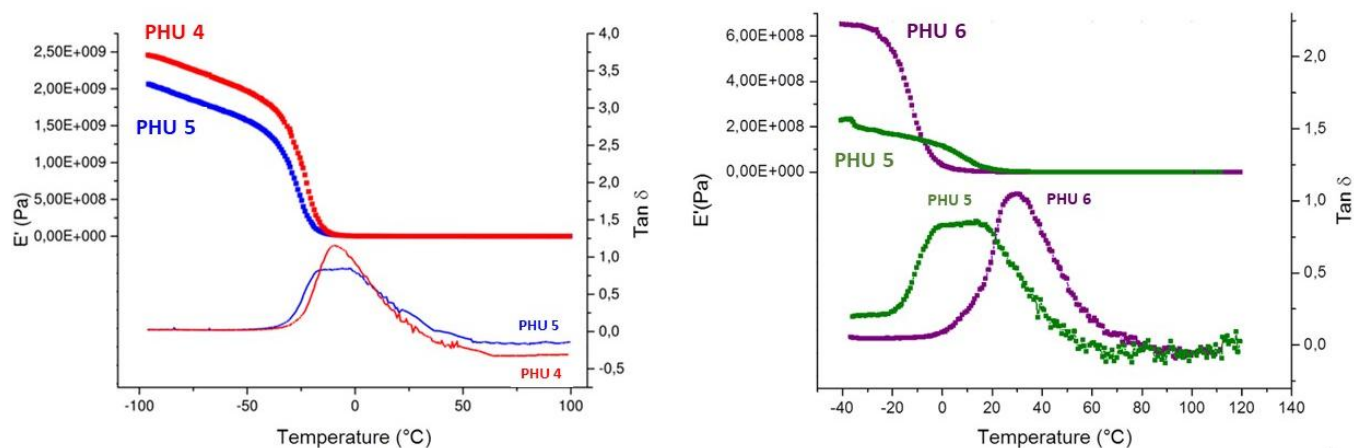


Figure 7: DMA thermograms with E' and $\tan \delta$ as function of temperature for PHU 3, 4, 5 and 6.

4 Conclusions

The use of vegetable oils-based cyclic carbonates represents a safe and eco-friendly way for the production of non-isocyanate polyurethanes. Most of the reported works in literature generally use catalysts or solvents and high temperature reactions. The goal of this study was to produce PHU polymers by reaction between plant oil-based cyclic carbonates and diamine in bulk, at low temperature and without catalyst. The innovative approach of this study was the use of jojoba oil for the synthesis of linear PHUs and the synthesis of highly reactive cyclic carbonate monomers from vegetable oils.

Hence, jojoba oil was functionalized by thiol-ene coupling with thioglycolic acid prior Steglich esterification reaction with glycerol carbonate. Jojoba dicyclic carbonate led to linear PHUs. Crosslinking cyclic carbonate monomers were synthesized from castor oil. Linear and crosslinked PHUs were synthesized, with various composition in jojoba and castor oil-based cyclic carbonates and with different diamines. One of the outcomes of this study lies in the interest of these novel pendant cyclic carbonates that exhibited more reactivity and led to low T_g with their dangling chains. Another outcome concerns the promising use of jojoba oil for the synthesis of new vegetable oil-based polymers that could be interestingly mixed to other oils to tune properties of polymers.

The authors have declared no conflict of interest.

Tables ((including table captions))

Table 1. General characteristic of PHUs monomer.

| Monomer | CEW | AHEW | f | M (g.mol^{-1}) |
|---------|-----|------|------|---------------------------|
| Jo2c | 606 | - | 1.98 | 1204 |
| Co3c | 545 | - | 2.77 | 1510 |
| Co6c | 376 | - | 5.74 | 2158 |
| MXDA | - | 34 | 2 | 136 |
| DAB | - | 22 | 2 | 88 |

Table 2. Formulation of the different PHU

| Polymers | Stoichiometry carbonate/amine | Jo2c (g) | Co3c (g) | Co6c (g) | DAB (g) | MXDA (g) |
|----------|----------------------------------|----------|----------|----------|---------|----------|
| PHU 1 | 1 | 2 | - | - | 0.146 | - |
| PHU 2 | 1 | 2 | - | - | - | 0.22 |
| PHU 3 | 1 | - | 2 | - | 0.16 | - |
| PHU 4 | 1 | - | 2 | - | - | 0.25 |
| PHU 5 | 1 | - | - | 2 | 0.23 | - |
| PHU 6 | 1 | - | - | 2 | - | 0.35 |

Table 3. Characteristic properties of PHUs from TGA, DSC, DMA and SEC.

| Sample | T _g (°C) | T _{d5%} (°C) | T _α (°C) | m _r (%) | M _n (g.mol^{-1}) | Đ | E' (MPa) (-30°C) | E' (MPa) (30°C) | SI | GC |
|--------|---------------------|--------------------------|---------------------|-----------------------|---|-----|---------------------|--------------------|------|-----|
| PHU 1 | -46 | 203 | - | 0% | 7100 | 1.3 | - | - | - | - |
| PHU 2 | -32 | 219 | - | 1% | 6100 | 1.4 | - | - | - | - |
| PHU 3 | -33 | 250 | (-20) - 0 | 0% | - | - | 994 | 0.714 | 398% | 90% |
| PHU 4 | -26 | 269 | -7 | 3% | - | - | 1460 | 0.461 | 300% | 92% |
| PHU 5 | 6 | 214 | (-10) - 16 | 1% | - | - | 628 | 0.634 | 106% | 98% |
| PHU 6 | 20 | 218 | 32 | 0.6% | - | - | 1970 | 1.59 | 95% | 99% |

m_r residual mass, T_{d5%} degradation temperature of 5% of product.

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