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# One-pot two-steps synthesis of hydroxymethylated unsaturated VHOSO. Application to the synthesis of biobased polyurethanes

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**Running Title:** Partial hydrohydroxymethylation of oleochemicals

**Keywords:** hydroformylation, hydrogenation, vegetable oils, catalysis, polyurethanes.

**Abbreviations:** VHOSO, very high oleic sunflower oil; HHM, hydrohydroxymethylation.

## Abstract

In this study, we developed a one-pot two-step procedure to catalytically convert very high oleic sunflower oil (VHOSO) into hydroxymethylated unsaturated derivatives featuring both primary alcohols and carbon-carbon double bonds. The degree of functionalization in alcohols and C=C double bonds can be accurately controlled affording low and high substituted hydroxymethylated VHOSO. The key point to achieve such control is to partly hydroformylate the C=C bonds at 80 °C and subsequently reduce the reaction temperature to 20 °C to selectively reduced the aldehydes, while keeping a high CO/H<sub>2</sub> pressure. Step growth polymerization of highly substituted hydroxymethylated VHOSO with cyclohexyl isocyanate or 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) furnish biobased polyurethanes with improved thermal stability compared to similar polyurethanes synthesized from castor oil.

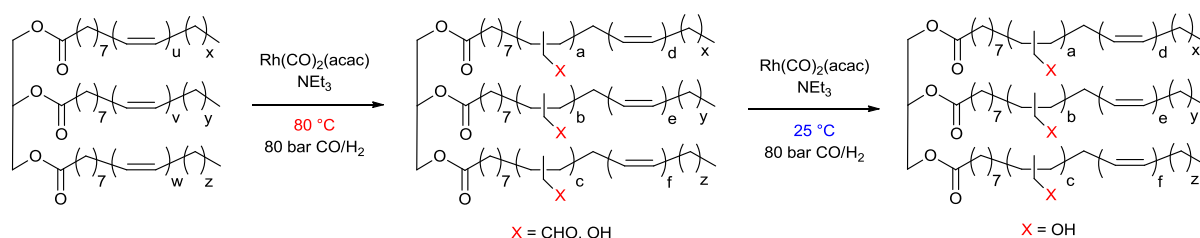
## Practical applications

This study highlights the implementation of triglycerides featuring both C=C double bonds and hydroxymethyl groups. The synthesis proceeds through a one-pot two-steps procedure which consists in a hydroformylation reaction at 80 °C followed by a hydrogenation reaction carried out at room temperature. This simple synthetic procedure is of major interest in a context of an industrial-environmental approach. The high reactivity of the obtained primary alcohols allows the synthesis of bio-PU's displaying untouched C=C double bonds, which could be further functionalized. This finding is of importance as the obtained bio-PU's can be used in many industrial areas such as foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants and fibers.

## Introduction

Preservation of fossil resources prompts chemists to develop eco-friendly alternatives for the production of organic materials. As such, bio-based polymers are continuously attracting attention<sup>1</sup> as they are easily accessible and behave similarly (or better) than their petro-sourced counterparts. Polyurethanes are one of the most produced polymer in the world with 18 Mt per year. The intensive research to reduce their impact on the environment led to bio-based polyurethanes (bio-PU's).<sup>2,3</sup> There has been a continuous rise in the demand for bio-PU's materials in the last 20 years, owing to their increasing use in end segment industries, with applications in foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibers, and so on.<sup>4,5</sup> Bio-PU's are now the first used bio-based polymer and the global production demand is expected to be more than 3 Mt by 2021.<sup>6</sup> To increase the renewable content, Bio-PU's are mainly obtained by reacting diisocyanates and polyols resulting from functionalization of vegetable oils extracted from various plants (rapeseed, soybean, palm...)<sup>7,8,9,10,11,12</sup> Natural vegetable oils contain saturated and unsaturated triglycerides but do not contain hydroxyl groups, with the exception of castor and lesquerella oils. However, functionalization of the carbon-carbon double bond through epoxidation followed by oxirane ring-opening,<sup>13,14,15</sup> hydroformylation followed by hydrogenation,<sup>16</sup> ozonolysis<sup>16</sup> or thiol-ene coupling<sup>17</sup> afford a wide range of bio-based polyols, enabling reactions with diisocyanates to get Bio-PU's.<sup>18</sup> Recently, some of us developed hydrohydroxymethylation (HHM) of triglyceride carbon-carbon double bonds.<sup>19</sup> The Rh-catalyzed reaction took place under homogeneous catalytic conditions and led to primary

alcohols. Herein, we showed how it was possible to implement a one-pot two-step procedure to afford triglycerides containing both carbon-carbon double bonds and hydroxyls in controlled proportions (Scheme 1). While the first step implies hydroformylation of triglycerides C=C bonds at 80 °C, the second step consists in the selective reduction of aldehydes at room temperature. To show the industrial interest of the obtained products, we carried out step growth polymerization of the derivative featuring the highest degree of alcohols for the synthesis of PUs in the presence of cyclohexyl isocyanate or 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI). The resulting Bio-PUUs were fully characterized using appropriate techniques including FTIR, TGA, DSC, DMA and NMR. Kinetics measurements clearly established the highest reactivity of primary alcohols *versus* secondary alcohols to get bio-PUUs.



**Scheme 1.** One-pot two-step procedure for controlled functionalization of VHOSO.

## Experimental Part

### Materials

Cyclohexyl isocyanate, cyclohexane and glycerol were purchased from Sigma Aldrich Merck (Darmstadt, Germany). 4,4'-Methylenebis(cyclohexyl isocyanate) (HMDI) was purchased from TCI Europe N. V. (Zwijndrecht, Belgique). Castor oil was purchased from Alberdingk Boley (Krefeld, Germany). Very High Oleic Sunflower Oil (VHOSO) was provided by Oleon (France). All materials were used as received. Deuterated solvent  $\text{CDCl}_3$  was obtained from Eurisotop for NMR study.

The hydroformylation/hydrogenation reactions were carried out at the laboratory scale in a 25 mL Hastelloy reactor from Parr Instrument Company (model 5500) fitted with a safety pad, a mechanical stirring (up to 1400 rpm) and a thermal probe immersed in the solution. Heating was provided by an electric oven connected to a regulator. Pilot-scale syntheses were carried out in a 5 L Hastelloy reactor (Büchiglasuster, Kiloclave) fitted with a safety pad, a stirring mechanical paddle (up to 2000 rpm) and a thermal probe immersed in the solution.

Heating was provided by a hot group (Huber, Unistat 430) circulating a heat transfer fluid (Jarytherm®) in the jacket of the reactor. The gas inlet system and the solenoid valves were managed by a system that can be controlled from a control screen (Instrumentation Serving).

### **Nuclear Magnetic Resonance analyses**

NMR analyses Proton Nuclear Magnetic Resonance ( $^1\text{H}$  NMR) analyses were performed in deuterated chloroform ( $\text{CDCl}_3$ , 99.50% isotopic purity) using Bruker DRX300 or Avance 400 MHz NMR spectrometers at a temperature of 25°C. NMR samples were prepared as follows: 10 mg of product for  $^1\text{H}$  experiment in approximately 0.4 mL of  $\text{CDCl}_3$ . The NMR peak assignment was obtained by comparison with previous works<sup>19</sup> and from data from the literature.<sup>20</sup>

### **Fourier Transform Infrared Spectroscopy**

Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared spectroscopy (FTIR) spectrometer. The characteristic IR absorptions mentioned in the text are reported in  $\text{cm}^{-1}$ . Materials analyses were recorded using an ATR accessory.

### **Thermogravimetric Analyses**

Thermogravimetric Analyses (TGA) were performed using TG 209F1 apparatus (Netzch). Approximately 10 mg of sample were placed in an aluminum crucible and heated from room temperature to 580 °C at a heating rate of 20 °C/min under nitrogen atmosphere (60 mL/min).

### **Differential Scanning Calorimetry**

Differential Scanning Calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, *n*-octadecane and *n*-octane standards. Nitrogen was used as purge gas. Approximately 10 mg of sample were placed in perforated aluminum pans and the thermal properties were recorded between -100 °C and 280 °C at 20 °C/min to observe the glass transition temperature. The  $T_g$  values were measured on the second heating ramp to erase the thermal history of the polymer. All the reported temperatures are average values.

## Dynamic mechanical analyses

Dynamic mechanical analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Samples were tested according to uniaxial tension mode while heating at a rate of 3 °C/min from  $\approx T_g - 80$  °C to  $T_g + 80$  °C, at a frequency of 1 Hz with a fixed strain of  $10^{-5}$  m. These conditions have been chosen to study the elastic behavior of the materials. All the thermosets were analyzed at least two times for repeatability.

## Titration of the alcohol equivalent weight by $^1\text{H}$ NMR

The Alcohol Equivalent Weight (AEW) is the amount of product needed for one equivalent of reactive alcohol function. It was determined by  $^1\text{H}$  NMR using an internal standard (benzophenone). A known weight of product and benzophenone were poured into an NMR tube and 500  $\mu\text{L}$  of  $\text{CDCl}_3$  were added. AEW was determined using Equation 1 by comparing the integral of the protons of the benzophenone (7.5-7.8 ppm) and the integral of the alcohol moiety (3.5 ppm for VHOSO-3 and 3.6 ppm for castor oil).

$$\text{Equation 1} \quad AEW = \frac{\int_{\text{PhCOPh}} * H_{\text{alcohol}}}{\int_{\text{alcohol}} * H_{\text{PhCOPh}}} * \frac{m_{\text{alcohol}}}{m_{\text{PhCOPh}}} * M_{\text{PhCOPh}}$$

$\int_{\text{PhCOPh}}$ : integration of the benzophenone protons;  $\int_{\text{alcohol}}$ : integration of the protons in  $\alpha$  of the alcohol function;  $H_{\text{alcohol}}$ : number of protons in  $\alpha$  of the alcohol function;  $H_{\text{PhCOPh}}$ : number of protons of the benzophenone;  $m_{\text{alcohol}}$ : weight of the product;  $m_{\text{PhCOPh}}$ : weight of the benzophenone;  $M_{\text{PhCOPh}}$ : molecular weight of the benzophenone.

## Cross-linking density

From rubber elasticity theory, the uniaxial stretching was studied on the rubbery plateau at  $T > T_\alpha + 50$ , and at very small deformations. Under these hypotheses, the cross-linking density ( $\nu'$ ), can be obtained from Equation 2, where  $E'$  is the storage modulus (Pa),  $R$  is gas constant ( $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ ) and  $T_\alpha$  is the temperature, in K, of transition from vitreous to rubber domain of material determined at the maximum of the  $\tan \delta$  curve. Calculated values are given for information purposes and can only be compared.

$$\text{Equation 2} \quad \nu' = \frac{E'_{\text{at } T_\alpha + 50}}{3RT_{\alpha + 50}}$$

## Swelling index

Three samples of around 20 mg each were separately put in THF for 24 h. The swelling index (SI) was calculated using the Equation 3 where  $m_2$  is the mass of the material after swelling in THF and  $m_1$  is the initial mass of the material.

$$\text{Equation 3} \quad SI = \frac{m_2 - m_1}{m_1} \times 100$$

## 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 drying and  $m_1$  is the initial mass of the material.

$$\text{Equation 4} \quad GC = \frac{m_3}{m_1} \times 100$$

## Kinetics measurements on model reactions

Castor oil (1 g, 1 eq.) and cyclohexyl isocyanate (0.340 g, 1 eq.) were mixed in a round bottom flask with 3 mL of cyclohexane with mechanical stirring at 80 °C. Sampling were performed at 0 min, 30 min, 1 h and 2 h and directly dissolved in  $\text{CDCl}_3$  for  $^1\text{H}$  NMR analyses. The same procedure was performed with the VHOSO-3. Conversion was calculated using the Equation 5 where  $\int_{\text{urethane}}$ : integration of the protons in  $\alpha$  of urethane (4.0 ppm for VHOSO-3 and 4.7 ppm for castor oil);  $\int_{\text{alcohol initial}}$ : integration of the protons in  $\alpha$  of alcohol before reaction (3.5 ppm for VHOSO-3 and 3.6 ppm for castor oil).

$$\text{Equation 5} \quad \text{Conversion} = \frac{\int_{\text{urethane}}}{\int_{\text{alcohol initial}}} \times 100$$

## Materials syntheses

Materials were synthesized with a molar ratio alcohol/isocyanate of 1/1. For PU1 and PU3 glycerol was used at 20 mol%. To prepare samples, the mass of glycerol was calculated with Equation 6, the mass of HMDI was calculated with Equation 7.

$$\text{Equation 6} \quad m_{\text{glycerol}} = \frac{n_{\text{glycerol}}}{n_{\text{triglyceride}}} \times \frac{m_{\text{triglycerol}}}{AEW} \times \frac{M_{\text{glycerol}}}{3}$$

$$\text{Equation 7} \quad m_{\text{HMDI}} = \frac{M_{\text{HMDI}}}{2} \times \left( \frac{m_{\text{triglyceride}}}{AEW} + \frac{3 \cdot m_{\text{glycerol}}}{M_{\text{glycerol}}} \right)$$

The triglyceride, glycerol and HMDI were stirred using a SpeedMixer™ under vacuum and then the homogeneous mixture obtained was put in a silicon mold and cured at 140 °C overnight.

PU0 was prepared with 2 g (1 eq.) of VHOSO-3 and 551 mg (1 eq.) of HMDI. PU1 was prepared with 2 g (0.8 eq.) of VHOSO-3, 31 mg (0.2 eq.) of glycerol and 688 (1 eq.) mg of HMDI. PU2 was prepared with 2 g (1 eq.) of castor oil and 712 mg (1 eq.) of HMDI. PU3 was prepared with 2 g (0.8 eq.) of castor oil, 42 mg (0.2 eq.) of glycerol and 890 mg (1 eq.) of HMDI.

### **Catalytic experiments**

At the laboratory scale: In a typical experiment to obtain a triglyceride containing 50% OH and 50% C=C, Rh(CO)<sub>2</sub>(acac) (3.9 mg, 0.015 mmol) was degassed three times by vacuum-N<sub>2</sub> cycles and dissolved in a degassed amine solution (typically NEt<sub>3</sub> (418 μL, 3 mmol) in 6 mL of toluene). The resulting solution was stirred at room temperature until all the rhodium complex was dissolved (2 h). VHOSO (1 mL, 1 mmol) was poured into the autoclave and N<sub>2</sub>-purged. The catalytic solution was then cannulated under nitrogen into the autoclave. Once the desired temperature was reached, the autoclave was pressurized under CO/H<sub>2</sub> (1/1) pressure (typically 80 bar) and the solution was vigorously stirred (1600 rpm) for 3 h at 80 °C. The apparatus was then allowed to cool down to room temperature. The solution was subsequently stirred for 24 h at 20 °C. Once the reaction was complete, the autoclave was depressurized, the solvent was removed under vacuum and the products were analyzed by <sup>1</sup>H and <sup>13</sup>C NMR experiments. All runs were performed at least twice in order to ensure reproducibility.

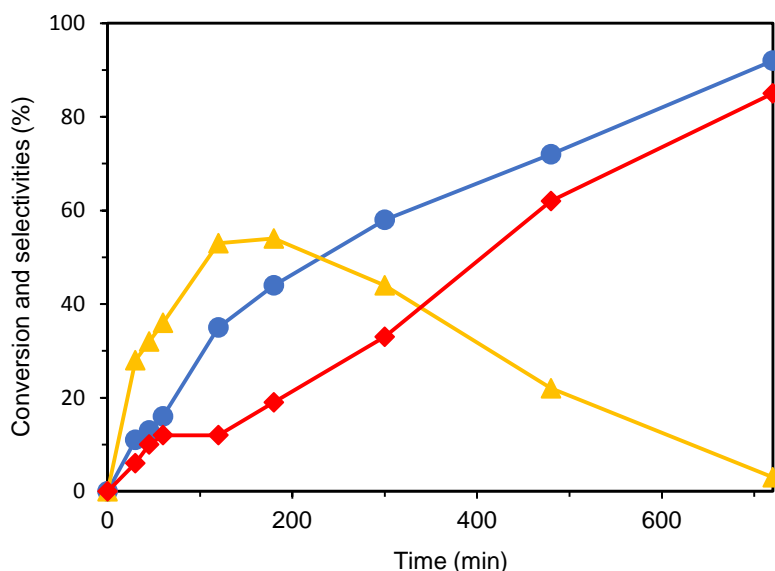
At the pilot scale: In a typical experiment to obtain a triglyceride containing 50% OH and 50% C=C, Rh(CO)<sub>2</sub>(acac) (1/200 equiv., 2 g), NEt<sub>3</sub> (3 equiv., 471 g), VHOSO (1 equiv., 1372 g) and 1428 g of toluene were introduced into the reactor and purged three times under 10 bar of nitrogen. Once the desired temperature was reached (typically 80 °C), the reactor was pressurized under CO/H<sub>2</sub> (1/1) pressure (typically 80 bar) and the solution was vigorously stirred (1600 rpm). Once the reaction was complete, the reactor was cooled down to room temperature and depressurized. The solvent was removed under vacuum and the products were analyzed by <sup>1</sup>H and <sup>13</sup>C NMR experiments. All runs were performed at least twice in order to ensure reproducibility.



## Results and discussion

### Controlled hydroxymethylation of VHOSO

Hydroformylation of VHOSO was first performed under catalytic homogeneous conditions at the lab scale. The reaction was carried out at 80 °C under 80 bar CO/H<sub>2</sub>. The results are gathered in Figure 1. In the first stage of the reaction, aldehydes and hydrogenated products were mainly formed. In the second stage of the reaction, the proportion of aldehydes regularly decreased upon reduction of the formyl groups to the benefit of alcohols. The Rh-catalyzed hydroformylation/reduction sequence is in line with the HHM reaction described in introduction. Interestingly, when the reaction temperature was reduced to room temperature after a defined period, we found by serendipity that the selective reduction of aldehydes into primary alcohols still took place at room temperature while the hydroformylation of carbon-carbon double bonds (which required higher activation energy) was totally suppressed (Scheme 1). To illustrate this one-pot two-steps process, the Rh-catalyzed hydroformylation of VHOSO was carried out at 80 °C under 80 bar of CO/H<sub>2</sub> for 3 h (first step of the process). Then, the reaction temperature was lowered to 20 °C and the solution was stirred under 80 bar of CO/H<sub>2</sub> over incremental reaction times until all the aldehydes were hydrogenated into alcohols (second step of the process, Table 1).



**Figure 1.** Conversions and selectivities with time in Rh-catalyzed hydroformylation of VHOSO at the lab-scale. Conditions: VHOSO (1 mL, 1 mmol), Rh(CO)<sub>2</sub>(acac) (3.9 mg, 0.015 mmol), NEt<sub>3</sub> (418 μL, 3 mmol), toluene (6 mL), 80 bar of CO/H<sub>2</sub> (1/1), 80 °C. ● Conversion of C=C, ▲ Aldehyde selectivity, ◆ Alcohol selectivity.

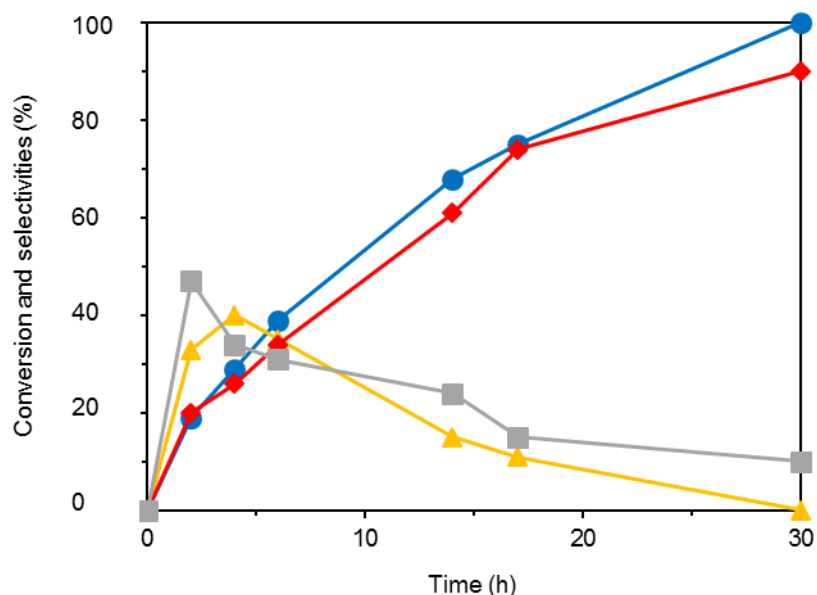
**Table 1.** Conversion and selectivities in the Rh-catalyzed hydrogenation of aldehydes into alcohols under CO/H<sub>2</sub> pressure at room temperature at the lab scale (25 mL reactor).

Entry	t hydrogenation (h)	Conv. (%)	S1 (%)	S2 (%)	S3 (%)
1	0	46	54	19	27
2	1	46	52	24	24
3	5	47	41	33	26
4	8	47	32	41	27
5	10	46	25	50	25
6	18	46	3	70	27
7	20	47	0	73	26
8	18 <sup>b</sup>	47	24	46	30
9	18 <sup>c</sup>	45	50	23	27

<sup>a</sup>Conditions: VHOSO (1 mL, 1 mmol), Rh(CO)<sub>2</sub>(acac) (3.9 mg, 0.015 mmol), NEt<sub>3</sub> (418 μL, 3 mmol), toluene (6 mL), 20 °C. 80 bar of CO/H<sub>2</sub> (1/1). <sup>b</sup>10 bar of CO/H<sub>2</sub> (1/1) after cooling down to 20 °C. <sup>c</sup>80 bar of H<sub>2</sub> after cooling down to 20 °C. t hydrogenation: reaction time for hydrogenation of C=O. Conv.: conversion of C=C. S1: selectivity in aldehydes. S2: selectivity in alcohols. S3: selectivity in hydrogenated products.

Neither the conversion of C=C bonds nor the proportion of hydrogenated products did evolve over time, while aldehydes were totally converted into alcohols within 20 h (Table 1, entries 1 to 7). Note that reduction of the CO/H<sub>2</sub> pressure to 10 bar significantly altered the reduction of aldehydes, as only half of them were hydrogenated into alcohols, even over 18 h (Table 1, entry 8). To get further information about the nature of the selective hydrogenation Rh-catalyst, the autoclave was depressurized after 3 h and refilled with only hydrogen (without carbon monoxide). In that case, very few aldehydes were converted into alcohols (Table 1, entry 9), thus highlighting the crucial role of CO over the catalytic activity of the Rh-catalyst in hydrogenation of aldehydes. This is in line with our previous works,<sup>Erreur ! Signet non défini.</sup> where such CO-coordinated species were already identified as catalytic species capable of hydrogenation of formyl groups. Unfortunately, we did not get additional clues to fully establish the structure of the Rh-catalyst because of its transient nature.

Once the one-pot two-step process was validated at the laboratory scale, we sought to develop the process at the kg-scale using a 5 L reactor. In this context, we first replicated the HHM conditions on larger quantities.



**Figure 2.** Conversions and selectivities with time in Rh-catalyzed hydroformylation of VHOSO at the pilot-scale. ● Conversion, ▲ Aldehyde selectivity, ◆ Alcohol selectivity, ■ Selectivity in hydrogenated products. Conditions: VHOSO (1 equiv., 1372 g), Rh(CO)<sub>2</sub>(acac) (1/200 equiv., 2 g), NEt<sub>3</sub> (3 equiv., 471 g), toluene (1428 g), 80 °C, 80 bar of CO/H<sub>2</sub> (1/1).

Under similar experimental conditions (80 °C, 80 bar of CO/H<sub>2</sub>), the reaction time required for completion of the reaction was increased to 30 h. Interestingly, the selectivities remained unchanged when compared to the lab scale.

We then tried to replicate the synthesis of VHOSO featuring both hydroxymethyl groups and C=C unsaturations. In view of Figure 2, we arbitrarily choose a reaction time of 8 h for the hydroformylation step carried out at 80 °C under 80 bar of CO/H<sub>2</sub>. Then, conversion variation and the relative proportions of products were quantified over time using the 5 L reactor (Table 2).

**Table 2.** Conversion and selectivities in the Rh-catalyzed hydrogenation of aldehydes into alcohols under CO/H<sub>2</sub> pressure at room temperature at the pilot-scale (5 L reactor).

Entry	Time (h)	Conv. (%)	S1 (%)	S2 (%)	S3 (%)
-------	----------	-----------	--------	--------	--------

<b>1</b>	0	39	35	34	31
<b>2</b>	16	43	17	59	24
<b>3</b>	19	44	15	63	22
<b>4</b>	21	45	13	65	22
<b>5</b>	26	45	3	75	22
<b>6</b>	28	46	0	78	22

Conditions: VHOSO (1 equiv., 1372 g), Rh(CO)<sub>2</sub>(acac) (1/200 equiv., 2 g), NEt<sub>3</sub> (3 equiv., 471 g), toluene (1428 g), 80 bar of CO/H<sub>2</sub> (1/1), RT. Conv.: conversion of C=C. S1: selectivity in aldehydes. S2: selectivity in alcohols. S3: selectivity in hydrogenated products.

The conversion only slightly increased from 39 to 46 over 28 h, confirming that the hydroformylation of the C=C bonds was significantly reduced. Note that the 4% increase from 39 to 43% observed over the first 16 h resulted from the inertness of the solution during cooling from 80 °C to room temperature. Rh-catalyzed hydrogenation of aldehydes led to 90% alcohols within 28 h. The percentage of hydrogenated products did not significantly change from 16 to 28 h. Hence, the one-pot two-step process was reproducible on a larger scale with little impact on the catalytic activity and no impact on the product's selectivities. 1393 g of products were isolated. The final composition of the mixture after 28 h was 54% of C=C bonds, 36% of alcohols and 10% of hydrogenated products.

In a third set of experiments, we sought to tune the percentage of C=C bonds and hydroxyl groups on the triglyceride's backbone at the pilot-scale. Three triglycerides were partly hydroformylated over 8 h, 14 h and 18 h and subsequently reduced by hydrogenation for 28 h (Table 3). Three functionalized triglycerides VHOSO-1, VHOSO-2 and VHOSO-3 featuring 37%, 60% and 69% hydroxyl groups, respectively, were formed. The percentages of C=C were 55%, 30% and 20%, respectively. Carbon-carbon double bonds were also hydrogenated in rather small proportions (<11%). Accordingly, it is possible to control the unsaturation and hydroxymethylation rates on the triglyceride's structure just by adjusting the reaction time of the hydroformylation period and by lowering the reaction temperature to room temperature in a second step.

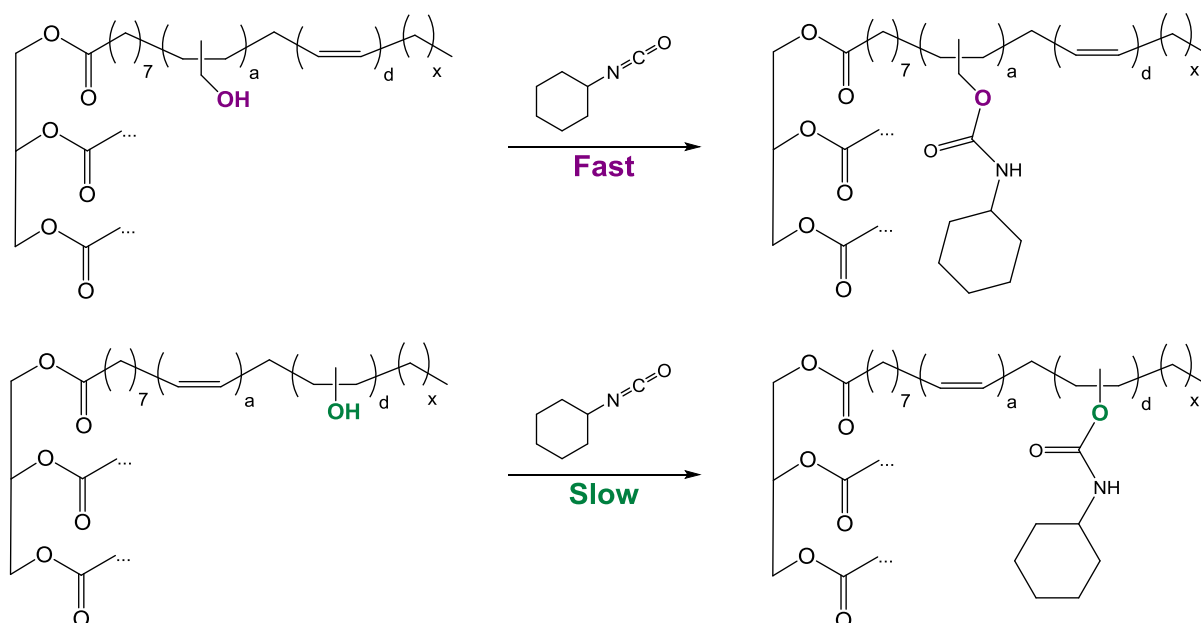
**Table 3:** Syntheses of VHOSO derivatives having various percentages of C=C bonds and hydroxymethyl groups.

Compound	t hydroformylation (h)	Conv. (%)	C=C (%)	Final composition		
				Aldehydes (%)	Alcohols (%)	Hydrogenated products (%)
VHOSO-1	8	45	55	0	37	8
VHOSO-2	14	70	30	0	60	10
VHOSO-3	18	80	20	0	69	11

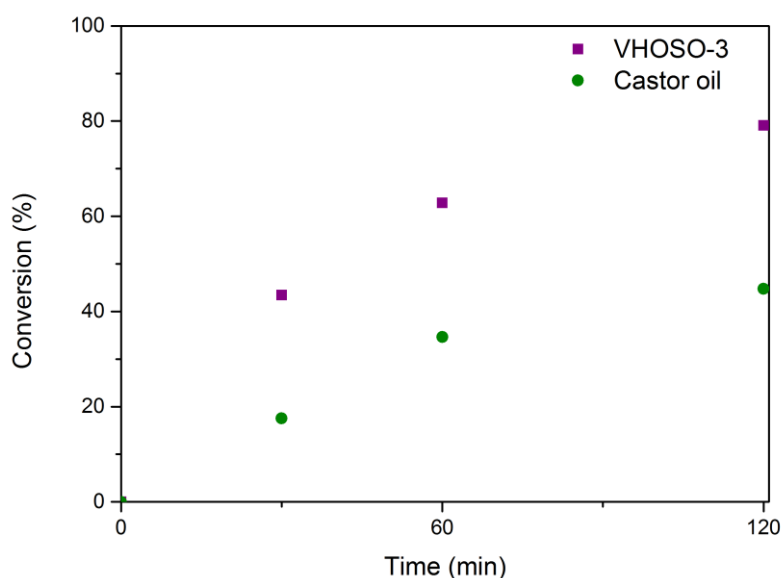
Conditions: reactor volume = 5 L. VHOSO (1 equiv., 1372 g), Rh(CO)<sub>2</sub>(acac) (1/200 equiv., 2 g), NEt<sub>3</sub> (3 equiv., 471 g), toluene (1428 g), 80 bar of CO/H<sub>2</sub> (1/1), T<sub>hydroformylation</sub>: 80 °C, T<sub>hydrogenation</sub>: 20 °C, reaction time for hydrogenation: 28 h. Conv.: conversion of C=C.

### Alcohol reactivity

In order to show the interest for obtaining triglycerides containing primary alcohols, Bio-PU s thermosets were synthesized from triglycerides featuring the highest rate of hydroxyl groups (VHOSO-3) to promote the synthesis of a three-dimensional PU network. Primary alcohols are more reactive toward isocyanates than secondary ones.<sup>21</sup> Therefore, such modified triglycerides are a good way to obtain more easily PU from vegetable oils at lower temperature, without catalyst or with less reactive isocyanates. In order to compare the reactivity of secondary alcohols of castor oil and the primary ones of VHOSO-3, we first studied a model reaction with a monofunctional isocyanate to avoid crosslinking and perform NMR. We selected cyclohexyl isocyanate since its structure is similar to the difunctional 4,4'-methylenebis(cyclohexyl isocyanate) (HMDI) further used to obtain PU materials. The reaction was performed at 80°C in cyclohexane at an alcohol concentration of 0.9 M. The progress of the reaction over 2 h was monitored by following the disappearance of the signal corresponding to the protons in  $\alpha$  of alcohols at 3.6 ppm <sup>1</sup>H NMR. At the same time, the appearance of the signals corresponding to the protons in  $\alpha$  of urethane functions was observed at 4.0 ppm and 4.7 ppm respectively to VHOSO-3 and castor oil. Overlays of the <sup>1</sup>H NMR spectra over time of the two reactions are shown in Supporting Information (Figure S1 and S2).



**Scheme 2.** Reactivity difference between primary and secondary alcohols at 0.9 M towards isocyanates in cyclohexane at 80°C for 2 hours.

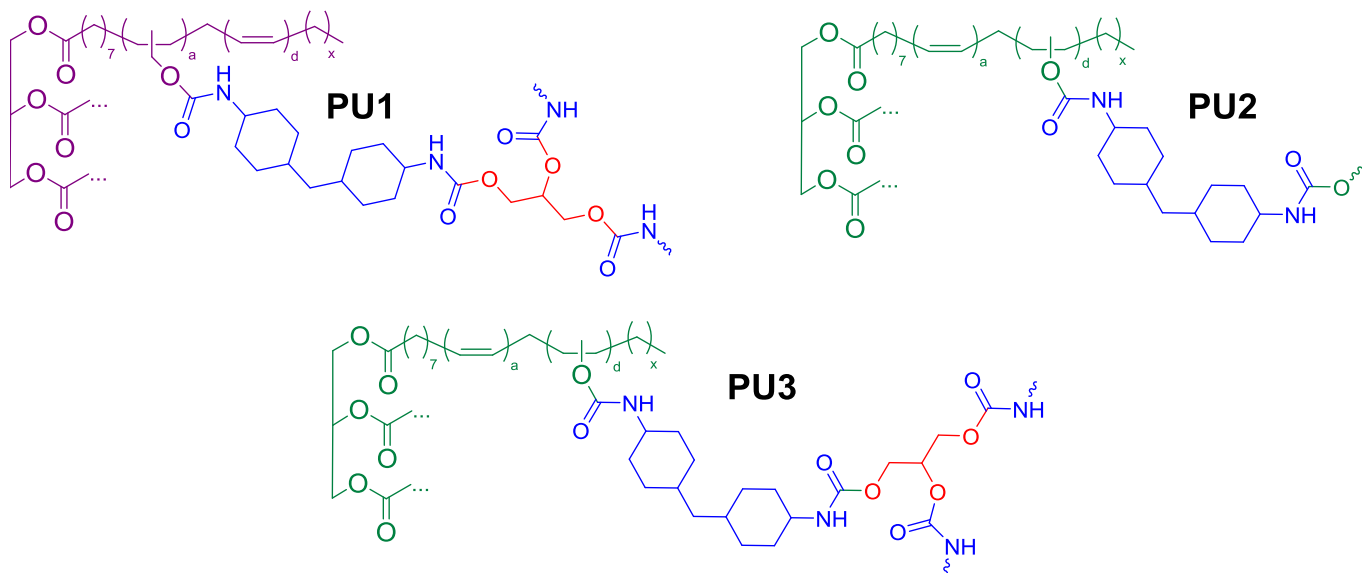


**Figure 3.** Conversion of VHOSO-3 hydroxyl and Castor oil hydroxyl with cyclohexyl isocyanate monitored by  $^1\text{H}$  NMR.

As expected and as it can be deduced from Figure 3, the alcohols from VHOSO-3 reacted much faster than the alcohols from castor oil. Indeed, conversion of alcohols to urethanes reached 79 % in 2 hours for primary ones, whereas only 45 % of secondary alcohols reacted over the same period. These results thus confirmed the higher reactivity of primary alcohols

of VHOSO-3 towards isocyanate functions. The use of highly reactive alcohols is very interesting to achieve high conversion, without using catalyst or high temperature.

### Thermosets syntheses



**Figure 4.** Chemical structures of synthesized polyurethanes

The hydroxyl functionality of VHOSO-3 (around two hydroxyl per triglyceride  $f \approx 2.0$ ) does not easily lead to crosslinking. Indeed the reaction of VHOSO-3 with HMDI (PU0) led to a linear polymer (viscous liquid), its swelling capacity and gel content could not be measured as it was soluble in THF. In order to increase the number of hydroxyl groups and to obtain crosslinked PUs, we added 20 mol% of glycerol in the formulations. Castor oil has a higher functionality ( $\approx 2.6$ ) that allows crosslinking, but in order to compare to VHOSO-3, 20 mol% of glycerol were added as well. We synthesized three thermosets (Figure 4). Formulations are given in Table 4. The triglyceride, glycerol and HMDI were stirred using a SpeedMixer<sup>TM</sup> under vacuum and the resulting homogeneous mixture was poured in a silicon mold and cured at 140 °C overnight. The conversion of isocyanates and alcohols to PU was confirmed by FTIR, the three materials presenting the characteristic peak of urethane at  $1688 \text{ cm}^{-1}$  (Figure 5 SI). The high gel content values of PU2 and PU3 (>94 %) confirmed cross-linking in agreement with DSC measurements (Figure 6 SI), which did not present any residual enthalpy of reaction after the curing process. Despite a slightly lower gel content (82%), PU1 did not exhibit any residual enthalpy of reaction in DSC, which also demonstrated a

complete curing of the material. This lower gel content can be explained by the nature of the starting VHOSO oil used. As it is mainly composed of oleic acid (86.1 %), which is mono unsaturated, and as all the unsaturations were not modified to hydroxyl, the probability of having non-functional triglycerides (triglycerides without any hydroxyl group) is not negligible. Concerning swelling ratio, due to its lower cross-link density, PU1 is able to have higher swelling ratio (458 %) than PU2 and PU3 which have been prepared with more functional monomers (castor oil and glycerol).

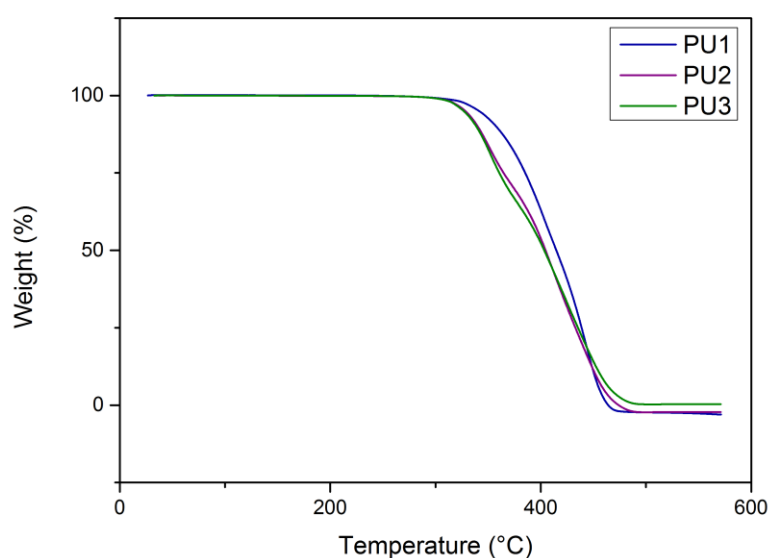
**Table 4.** Formulation of PU thermosets.

PU	VHOSO-3 (%mol)	Castor oil (%mol)	Glycerol (%mol)	Ratio OH/NCO	Swelling index (%)	Gel content (%)
0	100	-	-	1:1	-	-
1	80	-	20	1:1	458	82
2	-	100	-	1:1	288	94
3	-	80	20	1:1	229	96

### Thermal properties

The thermal stability of PU was explored by thermogravimetric analyses (TGA) from room temperature to 580 °C under inert atmosphere of N<sub>2</sub>. A two-step degradation was observed for the three thermosets (Figure 5). First, we observed breakage of urethane linkages, followed by the degradation of triglycerides.<sup>22</sup> This phenomenon was more visible for PU2 and even more for PU3. Indeed, as the first step corresponds to urethane linkages degradation, the higher was the cross-link density, the more numerous were the urethanes groups, thus the lower was the T<sub>d5%</sub>. Moreover, thermal stability of both castor oil, VHOSO-3 and PU0 was similar (T<sub>d5%</sub> = 352 °C). PU1 presented indeed the best thermal stability (T<sub>d5%</sub> = 341 °C), because of its lower cross-link density ( $\nu' = 124$ ), compared to PU2 and PU3 ( $\nu' = 306$  and  $\nu' = 382$  respectively) since they have more urethane linkages within their network (Table 5).





**Figure 5.** TGA curves of cured thermosets.

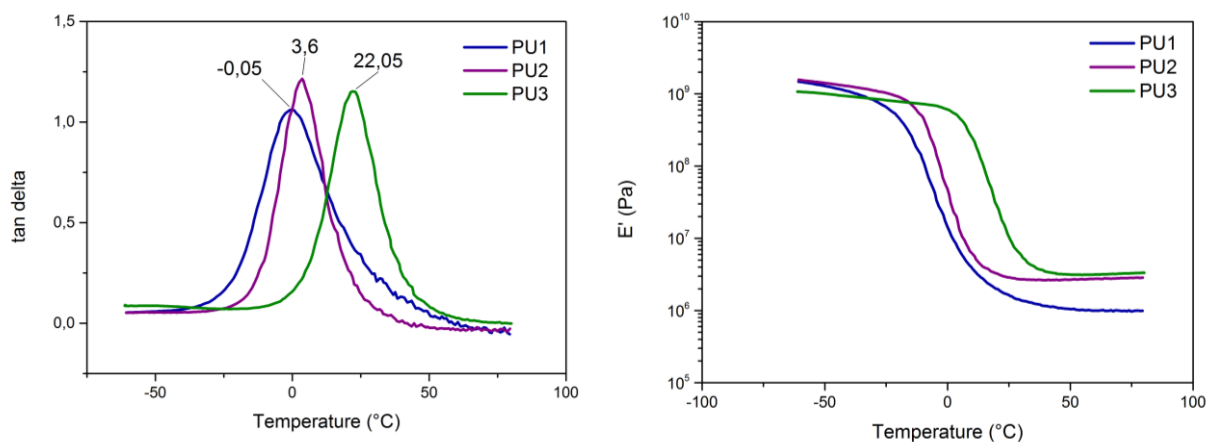
### Thermo-mechanical properties

Glass transition temperature values ( $T_g$ ) of thermosets were as well obtained by DSC analyses (Table 5).  $T_g$  is linked to chain mobility and network structure. PU0 presented the lowest  $T_g$  (-39 °C) as it is not cross-linked indeed, the chain mobility is high in comparison to the three thermosets. A high cross-link density leads to a low chain mobility thus a high  $T_g$ . As PU1 has the lowest cross-link density, even with the addition of glycerol, it exhibited the lowest  $T_g$  value (-20 °C) among the three synthesized thermosets. By adding glycerol to castor oil based formulation, the cross-link density was increased and therefore chain mobility was reduced leading to a PU3 with a slightly higher  $T_g$  (0 °C) than PU2 ( $T_g$  = -11 °C).

**Table 5.** Physico-chemical properties of cured materials.

PU	$T_{d5\%}$ (°C)	Char yield (%)	$T_g$ (°C)	$T_\alpha$ (°C)	$E'_{\text{glassy}}$ (GPa)	$E'_{\text{rubbery}}$ (MPa)	$\nu'$ (mol/m <sup>3</sup> )
0	352	0	-39	-	-	-	-
1	341	0	-20	0	1.2	1	124
2	328	0	-11	4	1.3	2.5	306
3	326	0	0	22	0.8	3.3	382

Thermo-dynamical properties of thermosets were studied with dynamic mechanical analyses (DMA), results are summarized in the Table 5. Storage modulus ( $E'$ ) and  $\tan \delta$  as function of temperature are shown in Figure 6. Alpha-transition temperature ( $T_\alpha$ ) was measured at the maximum of  $\tan \delta$  of each material. According to the theory of rubber elasticity, the molecular weight between the crosslinking-nodes of a cured network is proportional to its storage modulus in the rubbery region. Therefore, cross-linking density ( $\nu'$ ) was calculated on the rubbery domain at  $T_{\alpha+50^\circ\text{C}}$  for each PU. Compared to  $T_g$  values,  $T_\alpha$  values were higher but followed the same trend. In the same way than  $T_g$ , the higher was the cross-link density, the higher was  $T_\alpha$ , leading to the same following rank: PU3 > PU2 > PU1. In the glassy state, the three thermosets have close storage modulus values, whereas in the rubbery state the difference between PU based on VHOSO-3 and PU based on castor oil is clear. The large space between its cross-linked nodes ( $\nu' = 124$ ) makes PU1 the softer synthesized material ( $E'_{\text{rubbery}} = 1 \text{ MPa}$ ), whereas highly functional starting material (castor oil) and glycerol led to stiffer PU2 and PU3 (respectively 2.5 MPa and 3.3 MPa).



**Figure 6.** DMA measurements of thermosets (left:  $\tan \delta$ ; right: storage modulus ( $E'$ )).

## Conclusions

In this study, a two-step procedure was developed to control the degree of hydrohydroxymethylation of VHOSO under homogeneous conditions. Once the carbon-carbon double bonds of VHOSO were partly hydroformylated under 80 bar of  $\text{CO}/\text{H}_2$  at  $80^\circ\text{C}$  for 8 h, lowering the reaction temperature to  $20^\circ\text{C}$  led to the selective reduction of the resulting aldehydes without further hydroformylation of the remaining carbon-carbon

double bonds. The rate of hydrohydroxymethylation can be accurately tuned with the reaction time. Interestingly, the presence of CO was required even for the reduction of formyl groups to alcohols.

The hydrohydromethylated VHOSO featuring the highest rate of hydroxyl groups was used as a monomer in the formation of bio-PU. Moreover, remaining double bonds of triglycerides are still unreacted. This not only allows the presence of non-functionalized dangling chains that could reduce the Tg and help to obtain structured PUs with hard and soft segments, but also offer the possibility for functionalization of the bio-PU and bring specific properties.

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