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## From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products

Myriam Desroches, Maxime Escouvois, Rémi Auvergne, Sylvain Caillol,  
Bernard Boutevin

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**From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products**

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5 **main industrial products**  
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9 Myriam Desroches, Maxime Escouvois, Remi Auvergne, Sylvain Caillol\*,  
10 Bernard Boutevin  
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12  
13 *Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, Equipe*  
14 *I.A.M., 8 Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France*  
15

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18 \*Corresponding author. Dr Sylvain CAILLOL. Address: ENSCM, 8 Rue de l'Ecole  
19 Normale, 34296 Montpellier Cedex 5, France - E-mail [sylvain.caillol@enscm.fr](mailto:sylvain.caillol@enscm.fr).  
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## From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products

Most of biobased polyols for polyurethanes are synthesized from vegetable oils. In a first part, the present review goes into details of these different synthetic routes to obtain polyols. Firstly, olefinic functionalities of triglycerides could easily be epoxidized, leading to reactive epoxide groups. Secondly, triglycerides double bonds could undergo a wide range of reaction to yield polyols. Finally, the carbonyl group could also be used as a reactive group to yield various polyols. In a second part, the present review is dedicated to the commercial biobased polyols, and, based on the patent literature; focus on the industrial synthetic routes.

Keywords: vegetable oils; biobased polyols; polyurethanes; epoxidized vegetable oils; commercial polyols; oxidation

### Introduction

Uncertainty in terms of price and availability of petroleum, in addition to global political and institutional tendencies toward the principles of sustainable development, urge chemical industry to a sustainable chemistry and particularly the use of renewable resources in order to synthesize biobased chemicals and products. A biobased product is a product synthesized from renewable resources (vegetal, animal or fungal) but doesn't mean that it is a biodegradable material. Biodegradability is a special functionality conferred to a material, biobased or not, and biobased sourcing does not entail biodegradability. Biobased sourcing could be measured by renewable carbon content owing to D6866ASTM standards. The use of renewable resources for chemical synthesis results in reduction of environmental impacts such as non-renewable resources consumptions and greenhouse gas emission. But hazards of chemicals should also be taken into account in order to reduce human toxicity and eco-toxicity impacts. Indeed, it is not sufficient to synthesize exactly the same chemicals from renewable

resources, even if they are harmful. Biobased chemicals could also be very dangerous. New processes have to be developed to replace hazardous reactives by harmless, biobased ones. Among this new developments, we report some polyamides, such as polyamide 11 synthesized from castor oil by Arkema Group under the brand name Rilsan<sup>1</sup>, biofuels and polyols. Polyols represent increasing industrial developments in various applications and particularly in polyurethanes.

Polyurethanes (PUs), having a relatively short history, of slightly more than 70 years, became one of the most dynamic groups of polymers, exhibiting versatile properties suitable for use in practically all the fields of polymer applications - foams, elastomers, thermoplastics, thermorigids, adhesives, coatings, sealants, fibers and so on. With a global production of 14Mt in 2006, PUs are the 6th most widely used polymer<sup>2</sup>. Additionally, they are used in some specialty applications such as biomedical surgery. PUs are obtained by the reaction of an oligomeric polyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate) (Scheme 1). All these raw materials come from petroleum but recently, chemical industry has paid intensive interest to the production of biobased polyols, mainly synthesized from vegetable oils<sup>3-5</sup>.

#### **Insert Scheme 1:** Polyurethane synthesis from diol and diisocyanate

Indeed, most of polyols currently used for polyurethanes synthesis are polyether polyols (75%), resulting from the reaction between a “starter” polyol and an alkylene oxide, both petrobased. Other polyols used for polyurethanes synthesis are polyesters polyols (25%), obtained by step growth polycondensation between dicarboxylic acid and polyol in excess<sup>6</sup>. A first approach to increase the renewable content of polyurethanes consists in replacing the “starter” polyol by a biobased polyol from saccharides (sorbitol, sucrose) for the synthesis of partially biobased polyether polyols

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3 (30% renewable carbon). However, it results in low renewable content polyurethanes  
4  
5 (around 8%). Therefore it is more interesting to work on prepolymers that account for  
6  
7 higher percentage of renewable content. Polyether polyol could also be obtained by  
8  
9 polycondensation of propane-1,3-diol coming from glycerin. Furthermore, biobased  
10  
11 polyester polyols generally result from condensation of biobased dicarboxylic acids  
12  
13 such as adipic or succinic acid with biobased polyols (propane-1,3-diol).  
14  
15

16 Finally, another approach to obtain biobased polyols consists in the use of  
17  
18 natural oils (vegetable or animal) i.e. the most abundant and cheapest renewable organic  
19  
20 resources<sup>7</sup>.  
21  
22

23  
24 **Insert Scheme 2:** Triglyceride formula with R0, R1 and R3 aliphatic chains of fatty  
25  
26 acids  
27

28 Vegetable oils are coming from various plants (soybean, palm, rapeseed...) and  
29  
30 contain mainly triglycerides molecules where the three hydroxyl functions of glycerin  
31  
32 are esterified with fatty acids (Scheme 2). These fatty acids could be saturated – with  
33  
34 non reactive aliphatic chains (stearic or palmitic acids...) or unsaturated – with aliphatic  
35  
36 chains bearing double bonds (oleic, linoleic, linolenic, ricinoleic acids...). These natural  
37  
38 oils, and particularly unsaturated ones, are very interesting since various reactions could  
39  
40 be performed from their different groups in order to obtain biobased polyols, enabling  
41  
42 reactions with diisocyanates to get polyurethanes.  
43  
44  
45

46 Fundamental research has investigated vegetable oils functionalization for  
47  
48 several years and several reviews were published<sup>7-19</sup>. However, none of these review  
49  
50 report so far current industrial applications of depicted methods, patented processes and  
51  
52 synthesized biobased polyols. Therefore general presentation of vegetable oil  
53  
54 functionalization reaction is reported in part A of this review, whereas the industrial  
55  
56 state of the art of industrial processes and products is reported in part B.  
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## Part A: synthetic routes from vegetable oils to polyols

Chemistry routes followed to functionalize vegetable oils are extremely various and are based on several reactions. In order to summarize these routes, we reported the main reactions discussed in this review (Table 1).

### Insert Table 1: Mains reactions used on vegetable oils

In order to facilitate reading reaction schemes reported in this review, triglycerides were presented owing to formula of Scheme 3, with aliphatic chain  $R_0$  corresponding to oleic acid (one double bond between carbons 9 and 10).  $R_1$  and  $R_2$  chains could correspond to a fatty acid mono- or poly- unsaturated or non saturated.

### Insert Scheme 3: Triglyceride formula with $R_0$ chain corresponding to oleic acid

#### *I. Routes from epoxidized vegetable oils*

Epoxidized soybean oil could be used in addition to other commercial polyols in polyurethanes formulation<sup>20</sup>. Epoxide group are particularly interesting since after nucleophilic attack, they lead to various molecules owing to the nature of nucleophiles. The first route reported to functionalize triglycerides processes in two steps: epoxidation of double bonds of unsaturated fatty acids (reaction A, Table 1) followed by nucleophilic ring opening of epoxide group (reaction B, Table 1). Thus one or more alcohol functions (owing to nucleophiles) can be added onto the fatty acid aliphatic chain.

##### *I.1. Double bonds epoxidation*

Vegetable oils can be epoxidized (reaction A, Table 1), leading to interesting building blocks for biobased chemistry<sup>21</sup>. The most currently used method to epoxidize vegetable oil is based on peracetic acid formed in situ from reaction between acetic acid

1  
2  
3 and hydrogen peroxide, with ion-exchange resin catalyst, at 60°C in toluene, during 12h  
4 (Scheme 4). Double bond conversion into epoxide functions can be quantitative <sup>22</sup>.  
5  
6  
7 Vegetable oils can also be epoxidized by micro-waves. This interesting process leads to  
8  
9 yields higher than 90% within 5mn <sup>23</sup>. Enzymatic epoxidation of vegetable oils were  
10  
11 also reported <sup>24-26</sup> but is not detailed in this review.  
12  
13

14  
15 **Insert Scheme 4:** Synthesis of epoxidized triglycerides  
16  
17

### 18 *I.2. Epoxide ring opening in situ*

19  
20 Epoxide ring opening can be performed *in situ*, by sulfuric acid and water at 65°C  
21 (Scheme 5). In a first step, double bonds are epoxidized (reaction A, Table 1), then  
22 epoxide groups are converted in vicinal secondary alcohol <sup>27-29</sup> (reaction B, Table 1  
23 where NuH is water). This simple method yields hydroxylated vegetable oil <sup>30-35</sup>. A  
24  
25 method wit organometallic catalyst was also reported <sup>36</sup>.  
26  
27  
28  
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31

32 **Insert Scheme 5:** *In situ* triglyceride epoxide ring opening  
33  
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35

### 36 *I.3. Conversion of epoxide groups by monofunctional reagents*

37  
38 Alcoholysis of epoxidized vegetable oils with mono-alcohol and an acid catalyst  
39 also leads to polyols with secondary alcohols (reaction B, Table 1 where NuH is a  
40 mono-alcohol). Methanol is often used (Scheme 6), at refluxing temperature, with  
41 concentrated sulfuric acid <sup>37-39</sup> or p-toluenesulfonic acid <sup>40</sup> as catalyst. Following the  
42  
43 same protocol, other alcohols, such as 2-Ethyl-1-hexanol, are used <sup>41, 42</sup>.  
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50 **Insert Scheme 6:** Triglycerides epoxide ring opening by methanol  
51  
52

53 For recent years, the most used epoxide ring opening reaction consists in a reaction with  
54 methanol (or other mono-alcohol), in water, with fluoroboric acid catalyst (Scheme 6).  
55  
56 After heating 30 min between 50 and 65°C (refluxing temperature for methanol)  
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3 reaction yield reaches around 80%<sup>4, 22, 43-48</sup>. The obtained polyester polyol could thus  
4  
5 react with diisocyanates to lead to polyurethanes, particularly in aqueous cationic  
6  
7 dispersion for polyurethane films casting with interesting stretching properties<sup>49</sup>.  
8

9  
10 The epoxidation of triolein after metathesis reaction (reaction M, Table 1) is an  
11  
12 interesting example. Epoxide groups are ring opened by methanol in presence of  
13  
14 fluoroboric acid. This three steps reaction leads to terminal hydroxyl groups that could  
15  
16 react with diisocyanates to yield polyurethanes with short dangling chains<sup>22</sup> (Scheme  
17  
18 7).  
19

20  
21 **Insert Scheme 7:** Synthesis of primary terminal alcohols from triolein for polyurethanes  
22  
23 formulation  
24

25  
26 The use of heterogeneous catalysts was reported for alcoholysis of epoxidized vegetable  
27  
28 oils, such as activated clay<sup>50</sup> or ion-exchange resins<sup>51</sup>.  
29

30  
31 Epoxide ring opening polymerization of epoxidized methyl oleate was also  
32  
33 reported in presence of HSbF<sub>6</sub>. Polymerization is followed by partial reduction of esters  
34  
35 (Scheme 8), yielding to alcohol functions<sup>52</sup>. This original method allows obtaining  
36  
37 polyether polyols with interesting functionality comprised between 2 and 5 for  
38  
39 polyurethane formulation.  
40  
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42  
43 **Insert Scheme 8:** Epoxide ring opening polymerization of epoxidized methyl oleate  
44  
45

46  
47 Another method used a thiol as nucleophile instead of alcohol<sup>53-55</sup> (reaction B,  
48  
49 Table 1). Thus reaction of triglycerides with butane-1-thiol was reported at 45°C, during  
50  
51 1h under nitrogen with perchloric acid catalyst (Scheme 9)<sup>54</sup>.  
52

53  
54 **Insert Scheme 9:** Triglyceride epoxide ring opening with butane-1-thiol

55  
56 A secondary amine could also be used as nucleophile (reaction B, Table 1).  
57  
58 Thus, diethylamine was used for epoxide ring opening of triglycerides with zinc  
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3 chloride, at 80°C, during 4h<sup>56</sup> (Scheme 10). In this study, choice of amine, catalyst and  
4  
5 synthesis parameters were optimized in order to favour epoxide ring opening reaction  
6  
7 instead of amide formation (reaction J, Table 1). Indeed, reaction of amines with  
8  
9 triglycerides esters may compete epoxide ring opening.  
10

11  
12 **Insert Scheme 10 :** Oxirane ring opening with diethylamine

13  
14 Reactions with halogen reagents such as HCl or HBr were also reported<sup>57-60</sup>.  
15  
16 Brominated and chlorinated polyols exhibit higher densities and viscosities than the  
17  
18 methoxylated or hydrogenated ones. Epoxide ring opening could also be performed by  
19  
20 reaction with carboxylic acid (reaction B, Table 1), such as fatty acid<sup>61</sup>, acetic acid<sup>62</sup>,  
21  
22 cinnamic acid<sup>63</sup>, acrylic acid<sup>64</sup> (Scheme 11), lactic acid<sup>5</sup>, levulinic acid<sup>65</sup> or  
23  
24 anhydrides<sup>33, 66</sup>. These reactions lead to saturated polyester polyols with improved  
25  
26 resistance towards oxidation and interesting antiwear properties for lubricating  
27  
28 applications. Similarly, epoxidized fatty ester react with carboxylic acid to yield stearates  
29  
30 with hydroxyl and ester functions on both 9<sup>th</sup> or 10<sup>th</sup> carbons of aliphatic chain<sup>67</sup>.  
31  
32 Propionic, levulinic, hexanoic or octanoic are the most currently used carboxylic acids  
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**Insert Scheme 11 :** Triglyceride epoxide ring opening with acrylic acid

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*1.4. Hydrogenation of epoxide groups*

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44 Epoxide groups can also be directly hydrogenated (reaction C, Table 1) from  
45  
46 dihydrogene addition with Raney nickel catalyst (Scheme 12). In that case, the obtained  
47  
48 triglycerides exhibit only secondary hydroxyl functions<sup>57, 58, 70</sup>.  
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**Insert Scheme 12:** Direct hydrogenation of triglyceride epoxides

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53 Triglycerides with secondary hydroxyl functions were used for polyurethane  
54  
55 synthesis<sup>3</sup>. However, considering the higher reactivity of primary alcohols towards  
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3 isocyanates, it is more interesting to functionalize triglycerides with polyfunctional  
4  
5 reactants in order to insert primary hydroxyl functions on triglycerides chains.  
6  
7

#### 8 9 *1.5. Conversion of epoxide groups by polyfunctional reagents*

10 Diol could be used as nucleophile for epoxide ring opening in order to insert at least  
11  
12 both primary and secondary hydroxyl functions on each epoxide group of triglyceride  
13  
14 (reaction B). Literature reports the reaction with ethan-1,2-diol (Scheme 13). This  
15  
16 reaction is performed with concentrated sulfuric acid at 100°C<sup>38, 71</sup>, with  
17  
18 tetrafluoroboric acid at 50°C to 95°C in 2h<sup>72-74</sup> or with a diethylether-trifluoride borate  
19  
20 complex between 60°C and 100°C<sup>75</sup>.  
21  
22

#### 23 24 **Insert Scheme 13:** Triglyceride epoxide ring opening by ethan-1,2-diol

25  
26 Various polyols were also described in order to insert three or more hydroxyl  
27  
28 functions per epoxide group with two or more primary hydroxyl functions<sup>76</sup>. Reactions  
29  
30 were reported with diethanolamine (2,2'-iminodiethanol), or triethanolamine (2,2',2"-  
31  
32 nitrilotriethanol), with sulfuric acid at 200°C during 2-4h, or with LiOH catalyst at  
33  
34 150°C<sup>77</sup>. However, several issues are raised when using polyfunctional molecules<sup>78</sup>:  
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36

- 37  
38 • A side-reaction of oligomerization occurs between triglycerides bearing primary  
39  
40 hydroxyl functions and epoxidized triglycerides. This oligomerization is favored  
41  
42 by high catalyst concentration and low alcohol concentration;
- 43  
44 • Side reactions involving ester groups of triglycerides (reaction I, J, Table 1) are  
45  
46 competitive to epoxide ring opening reactions.  
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50 The use of different temperatures (ranging from 110°C to 180°C) as well as  
51  
52 different reaction times (ranging from 5 to 7h) lead to various mixtures of fatty amide  
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54 polyols and glycerin, resulting from the amidification reaction, and amine diols,  
55  
56 obtained from oxirane ring opening reaction (Scheme 14). It was demonstrated that  
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3 epoxide ring opening by diethanolamine is favored by using both high temperature  
4  
5 (~180°C) and long reaction time (~7h) <sup>79</sup>.  
6

7 **Insert Scheme 14:** Competitive reactions occurring during triglyceride amidification by  
8 diethanolamine  
9

10  
11 A patent <sup>80</sup> reports a two steps process to synthesize polyols from vegetable oils.  
12 In a first step, vegetable oil is epoxidized by H<sub>2</sub>O<sub>2</sub> in acidic conditions. In a second step,  
13 epoxide ring opening occurs with polyols or alcoholamines. More than 80% of epoxide  
14 groups are converted into primary or secondary hydroxyl functions. The obtained  
15 product is a mix of polyesters and polyether polyols, resulting from partial  
16 transesterification of triglycerides (reaction I, Table 1) and epoxide ring opening  
17 (reaction B, Table 1), respectively.  
18  
19

20  
21 Alcanolamides were also synthesized directly from laurel oil (45% of saturated  
22 fatty acids) by reaction with ethanolamine (2-aminoethanol) at room temperature with  
23 sodium methoxide catalyst <sup>81</sup>. The same catalyst was used to synthesize  
24 diethanolamides from hydroxyl methyl oleate <sup>82</sup>. Polyols polyamines were also  
25 synthesized from epoxidized vegetable oils by reaction with a mixture of amines or  
26 alcoholamines at temperatures between 100°C and 200°C. Glycerin co-produced was  
27 distilled and epoxidized fatty amides were obtained <sup>79, 83, 84</sup>. These products were  
28 reacted with diisocyanates to yield crosslinked polyurethanes.  
29  
30

31  
32 A study reports the synthesis of polyols from tallow by reaction with  
33 trimethylolpropane (2-(hydroxymethyl)-2-ethylpropane-1,3-diol) in the presence of acid  
34 or basic catalyst <sup>85</sup>. Oxirane ring opening by polyol is favored by an acid catalyst such  
35 as p-toluenesulfonic acid (reaction B, Table 1), whereas a basic catalyst such as sodium  
36 methoxide favors transesterification of ester group (reaction I, Table 1).  
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3 Finally, an hydroxyl-acid such as lactic acid (Scheme 15) is also able to graft  
4 hydroxyl groups onto epoxidized vegetable oils. The reaction was performed at 90°C  
5 under nitrogen during 6h, leading to an epoxide conversion around 70%<sup>5</sup>.  
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12 **Insert Scheme 15:** Triglyceride epoxide ring opening with lactic acid

13  
14 Finally, epoxide ring opening by difunctional nucleophile yields polyols with  
15 higher functionality. Polyols systematically exhibit secondary hydroxyl groups and may  
16 also bear primary hydroxyl groups from extra function of nucleophile.  
17  
18  
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### 20 21 22 *I.6. Epoxide groups carbonatation*

23 Direct carbonatation of epoxidized soybean oil was also reported (reaction O, Table 1)  
24 <sup>86-88</sup>. In a second step, polyols are synthesized by ring opening with ethanolamine  
25 (Scheme 16).  
26  
27  
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30  
31 **Insert Scheme 16:** Polyols synthesis from carbonated oil

32 It is to be noted that this reaction leads to carbonated oils that are able to react  
33 with polyamines to give interesting nonisocyanate polyurethanes <sup>89, 90</sup>. The different  
34 methods to functionalize epoxidized vegetable oils are given in Scheme 17.  
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39  
40 **Insert Scheme 17:** Summary of most common functionalizations on epoxidized vegetable oils

## 41 42 *II. Double bonds oxidation to alcohols*

43  
44 The synthesis of polyols from vegetable oils could also be carried out directly by  
45 oxidation of double bonds. Various reactions of direct oxidation reaction are reported.  
46  
47  
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### 50 51 *II.1. Ozonolysis-hydrogenation process*

52 Oxidative cleavage of a double bond by ozone (reaction D, Table 1) leads to aldehyde  
53 group <sup>91</sup>. Therefore, the application of this reaction to an unsaturated vegetable oil  
54 yields a maximum of three aldehyde functions per triglyceride molecule (one terminal  
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3 aldehyde on each fatty acid chain). A following reaction of reduction of aldehyde  
4  
5 functions into primary alcohols leads to a polyol with a maximum of three hydroxyl  
6  
7 functions (reaction H, Table 1).  
8

9  
10 Ozonolysis was performed on soybean oil, rapeseed oil or synthetic triglycerides  
11  
12 yielded polyols with primary hydroxyl groups (Scheme 18). Oxidative cleavage of oleic  
13  
14 acid by ozone into azelaic (nonanedioic) and pelargonic (nonanoic) acids is the most  
15  
16 important industrial application of ozonolysis <sup>25</sup>.  
17

18 **Insert Scheme 18:** Ozonolysis of unsaturated triglycerides leading to terminal primary  
19  
20 hydroxyl functions  
21

22  
23 Several ozonolysis methods were reported. Ozonolysis could be performed in a  
24  
25 mixture of solvents such as methanol and dichloromethane, with sodium borohydride <sup>92</sup>.  
26  
27 <sup>93</sup>. Another method reports ozonolysis in water, followed by hydrogenation in  
28  
29 tetrahydrofuran with Raney nickel <sup>94</sup>. The reaction in ethyl acetate with zinc powder  
30  
31 yielded polyols with highest hydroxyl functionality <sup>95</sup>. The ozonolysis with CaCO<sub>3</sub> was  
32  
33 also reported on soybean oil in the presence of ethylene glycol. The diol was added to  
34  
35 terminal carbons through an ester covalent bond, leading to a mixture of polyester  
36  
37 polyols <sup>91</sup>.  
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## 41 *II.2. Double bonds oxidation into peroxides and reduction into alcohols*

42  
43 Air oxidation of unsaturated vegetable oils leads to triglycerides with hydroxyl  
44  
45 functions and double bonds <sup>96-98</sup>. Oxidation may also yield vegetable oil derivatives  
46  
47 with enone groups <sup>18</sup> (Scheme 19). Oxidative methods of vegetable oils are extensively  
48  
49 reported in the review of Köckritz and Martin <sup>99</sup>. Double bonds were also oxidized  
50  
51 (reaction G, Table 1) into allyl hydroperoxides, which were reduced in a second step  
52  
53 into secondary hydroxyl functions (reaction H, Table 1).  
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3 **Insert Scheme 19:** Allyl hydroperoxides synthesis then converted into enone groups or reduced  
4 into secondary alcohols  
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7 Reaction is performed into a photoreactor equipped with a sodium vapor lamp,  
8 under oxygen flow, with thiamine pyrophosphate (TPP) and dichloromethane.  
9 Hydroperoxide compound is formed after 4h of irradiation. Then reduction is performed  
10 with sodium borohydride in methanol at 0°C. Then, catalytic hydrogenation is  
11 performed on platin/carbon (Pt/C) in ethyl acetate solvent during 3h.  
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### 18 19 *II.3. Hydroformylation*

20 The hydroformylation of vegetable oils (reaction E, Table 1) leads to aldehyde functions  
21 that can be hydrogenated to yield primary alcohols <sup>8</sup> (Scheme 20). Hydroformylation  
22 step was performed with a rhodium catalyst <sup>100, 101</sup>, such as rhodium triphenylphosphine  
23 complex <sup>82, 102</sup> or rhodium dicarbonyl acetylacetonate <sup>103</sup>, at 110°C, under carbon  
24 monoxide and hydrogen flow. Hydroformylation was also catalyzed by cobalt complex  
25 <sup>100</sup>, but yielded lower conversion (67% instead of 95%), resulting in polyurethanes with  
26 lower mechanical properties. The hydrogenation step (reaction N, Table 1) is generally  
27 realized under hydrogen flow with Raney nickel <sup>101-103</sup>. The obtained polyols are  
28 directly used in polyurethane synthesis <sup>103</sup> or are functionalized by further reactions  
29 such as esterification <sup>104</sup>. Hydroformylation followed by hydrogenation was also  
30 performed on unsaturated fatty acids or esters <sup>105</sup>. Noteworthy, acetalization of the  
31 aldehyde function leads to polyacetals <sup>106</sup>.  
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48 **Insert Scheme 20:** Hydroformylation followed by reduction on unsaturated triglyceride  
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50 The hydroformylation route, adding a carbon atom on the chain, leads to  
51 primary hydroxyl functions compared to epoxide ring opening route that leads to a  
52 polyol with a mixture of primary and secondary hydroxyl functions.  
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3 Hydroaminomethylation of fatty esters with various amines was also reported,  
4 particularly with valinol, yielding the insertion of secondary amine and primary alcohol  
5 on the chain (Scheme 21)<sup>107</sup>.  
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7

8  
9  
10 **Insert Scheme 21:** Hydroaminomethylation of ethyl oleate by valinol (dioxane, 140°C, 20h,  
11 rhodium complex catalyst, yield 95%)  
12

13  
14 This reaction proceeds in three steps through hydroformylation (reaction E,  
15 Table 1) followed by condensation of aldehyde function with primary or secondary  
16 amine, and then hydrogenation (reaction N, Table 1) yielding secondary or tertiary  
17 amine.  
18  
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#### 22 23 24 *II.4. Fatty acids dimerization*

25  
26 Dimerization of fatty acids is a complex reaction realized at high temperature.  
27 The catalysts used are homogeneous such as ionic salts of alkali metals or  
28 heterogeneous (most currently used) such as clays (montmorillonite or bentonite) or  
29 aluminosilicates<sup>108</sup>. The synthesized dimers are reduced (reaction H, Table 1) to yield  
30 fatty diols dimers (Scheme 22). Several mechanisms of dimerization were reported,  
31 owing to used fatty acids.  
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39 **Insert Scheme 22:** Fatty acid dimer (left hand) and fatty diol dimer (right hand)

40  
41 Concerning linoleic acid, reaction proceeds as follows (Scheme 23): a  
42 conjugated linoleic acid molecule undergo a Diels-Alder reaction (reaction K, Table 1)  
43 with another linoleic acid molecule, yielding a cyclohexene adduct<sup>16</sup>. Conjugated  
44 linoleic acid is obtained from isomerization of linoleic acid<sup>109-113</sup> or by extraction and  
45 isolation from some natural oils.  
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52 **Insert Scheme 23 :** Dimerization reaction of conjugated linoleic acid

53  
54 Concerning oleic acid, dimerization is also possible but proceeds through a  
55 different mechanism. Reaction occurs with clay catalyst through protonation of double  
56  
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3 bond. This protonated molecule reacts with another molecule of oleic acid to dimerize  
4  
5 (Scheme 24).  
6

7 **Insert Scheme 24:** Dimerization reaction of oleic acid  
8

9 Fatty acid dimers can further be reduced into fatty diol dimers (reaction H) in order to  
10 confer high hydrophobic, stretching and chemical stability properties to polyurethane  
11 synthesized thereof. Diels-Alder reaction with unsaturated conjugated vegetable oils  
12 and dienophiles was extensively studied and is industrially performed with maleic  
13 anhydride (furan-2,5-dione). Indeed, with Lewis acid such as boron trichloride or  
14 stannous tetrachloride and with catalytic quantity of iodine, it is possible to obtain  
15 adducts even at low temperature <sup>25</sup>. Metal triflates are also interesting catalysts for the  
16 reaction of methyl conjugate with butanone, leading to cyclic product with yield  
17 higher than 80% <sup>114</sup>. Moreover, oligomerization and polymerization of soybean oil with  
18 diethyl diazenedicarboxylate at room temperature through Diels-Alder reaction was  
19 depicted <sup>115</sup>.  
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34 Furthermore, cyclic-trimerization of fatty acids was also reported, yielding an  
35 aromatic triol with terminal primary hydroxyl functions (Scheme 25) <sup>116</sup>. This synthetic  
36 pathway for fatty triols is one of the most interesting since it leads to aromatic  
37 molecules from renewable resources <sup>25</sup>.  
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43 **Insert Scheme 25:** Aromatic triols synthesis from (a) methyl-9-octadecenoate and (b) methyl-  
44 10-undecenoate  
45  
46  
47

#### 48 *II.5. Thiol-ene coupling*

49

50 The double bonds of vegetable oils are electron-rich, which allows radical addition of  
51 various molecules (Scheme 26) <sup>117</sup>. Thus, thiol-ene coupling (reaction F, Table 1) is an  
52 interesting functionalization method.  
53  
54  
55

56 **Insert Scheme 26:** Mechanism of thiol-ene coupling  
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3 The literature contains many references to reactions of fats with thiols<sup>118</sup>. Thiol  
4 addition is particularly interesting since it may proceed through a photoreaction<sup>117, 119-</sup>  
5  
6  
7<sup>122</sup>. Moreover, thiol-ene coupling is poorly sensitive to oxygen and it was evidenced that  
8  
9 photoinitiators are not required. This reaction was notably employed to improve anti-  
10 wear properties of vegetable oils, directly used after thiol-ene coupling<sup>53, 54, 123</sup> or after  
11 grafting onto metallic surfaces pre-treated with mercaptosilanes<sup>124, 125</sup>. Several works  
12 studied oligomerization<sup>119</sup> (Scheme 27) or cross-linking<sup>126</sup> reactions with  
13 polyfunctional thiols.

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21 **Insert Scheme 27:** Fatty ester trimerization by thiol-ene coupling

22  
23 Recently, a study reported the synthesis of telechelic alcohols from allyl 10-  
24 undecenoate by thiol-ene coupling with mercaptoethanol<sup>127</sup>. Another work used either  
25 mercaptoethanol or 1-thioglycerol to functionalize methyl undecenoate. The resulting  
26 monomers were polymerized to yield polyesters with molecular weights ranging from  
27 4.000 to 10.000 g/mol<sup>128</sup>. This technique was also applied to the synthesis of di/tri-  
28 carboxylic acids used as polyanhydride precursors<sup>129</sup>. The thiol-ene functionalization  
29 was also carried out onto polyoxazoline to yield polyols with controlled molecular  
30 weight and hydroxyl content<sup>130</sup> (Scheme 28).

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41 **Insert Scheme 28:** Synthesis of the poly-2-oxazoline polyols from 10-undecenoic and decanoic  
42 acid

43  
44 A study reported the thiol-ene coupling of 2-mercaptoethanol (2-sulfanylethan-  
45 1-ol) directly on unsaturated triglycerides to produce interestingly fatty polyols suitable  
46 for polyurethane synthesis. In that case, thiol-ene coupling leads in one step to polyols  
47 with primary alcohols. This study detailed side-reactions that occurred, leading to  
48 various by-products. The mixture of obtained products was directly used in  
49 polyurethane synthesis without any purification, since most of by-products are  
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3 hydroxyl-functionalized and react advantageously with diisocyanate molecules (Scheme  
4  
5 29)<sup>131</sup>.

6  
7 **Insert Scheme 29:** Products and by-products of thiol-ene coupling of 2-mercaptoethanol on  
8  
9 fatty acid

10  
11 The thiol-ene coupling was also applied to synthesize various polyfunctional  
12 precursors suitable for polycondensation polymerization <sup>132</sup>, for instance pseudo  
13 telechelic diols from fatty methyl esters and mercaptoethanol <sup>133, 134</sup>, and polyamines  
14 from grapeseed oil and cysteamine<sup>135</sup>.

## 21 II.6. Electrophilic additions

22  
23 Electrophilic additions are generated from a Lewis acid. Therefore,  
24 formaldehyde (methanal) addition onto unsaturated fatty acids yields hydroxyl-  
25 carboxylic acids (Scheme 30) <sup>25, 136</sup>. Friedel-Crafts acylation is also an interesting  
26 method to functionalize fatty acids. Indeed, a study reports Friedel-Crafts acylation of  
27 oleic acid by acyl chloride with EtAlCl<sub>2</sub> yielding  $\beta,\gamma$ -unsaturated oxocarboxylic acid.  
28  
29

30  
31 **Insert Scheme 30:** Formaldehyde addition onto fatty acid

32  
33 Moreover acylation of undecylenic acid by acyl chlorides or cyclic anhydrides  
34 yields unsaturated ketones with carboxylic or hydroxyl terminal group, respectively  
35 (Scheme 31) <sup>136</sup>.

36  
37 **Insert Scheme 31:** Undecylenic acid acylation

38  
39 Direct alkylation of vegetable oils with phenol in the presence of acid catalysts  
40 was also investigated <sup>137</sup>. According to a recent study, side reactions take place during  
41 this Friedel-Craft alkylation, such as esterification, oligomerization and Diels Alder  
42 reactions. The aromatic-aliphatic polyol mixture obtained was nevertheless used for  
43 polyurethane synthesis.  
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## II.7. Metathesis and alkoxy carbonylation

The olefin metathesis of natural vegetable oils is a selective catalytic reaction that can efficiently convert oleochemicals into valuable products<sup>138, 139</sup>. This reaction provides a convenient route to unsaturated diesters which can be reduced to diols.

A recent study presents the isomerizing alkoxy carbonylation of unsaturated fatty acid esters, yielding C19 and C23 diesters. The diesters have been reduced to diols (reaction H, Table 1) using ruthenium as the catalyst in high yield and purity (>99%)<sup>140</sup>. Polyesters and polyamides were synthesized from the obtained precursors (Scheme 32).

### **Insert Scheme 32:** Linear diols from unsaturated fatty esters alkoxy carbonylation

Several functionalization reactions of fatty acids or esters, some of them being advantageously solvent-free, are also reported in the reviewing papers of Schneider<sup>25</sup>,<sup>141</sup> or Metzger and al.<sup>142</sup>. They are summarized on Scheme 33.

### **Insert Scheme 33:** Double bond modifications for the synthesis of polyols from vegetable oils and derivatives

## **III. Reactions of carbonyl group**

The synthesis of polyols from vegetable oils could also be obtained by reaction on ester carbonyl group. Various reactions on carbonyl group of vegetable oils are reported.

### *III.1. Transesterification*

The choice of the catalyst is the major concern for the transesterification of fatty esters. Bondioli deeply investigated these catalytic reactions and sum up his results in an interesting review<sup>143</sup>. Firstly, transesterification could be catalyzed by homogeneous catalysts. Thus, transesterification reaction (reaction I, Table 1) is generally realized with alkali catalysts<sup>144</sup> such as sodium methoxyde, sodium or potassium hydroxyde.

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2  
3 The saponification side-reaction is the main drawback of these catalysts <sup>143</sup>. Hartman  
4 reported significant information on different alkali catalysts such as their activity, their  
5 solubility, and the saponification rate they entailed <sup>145</sup>. Even if acid catalysis leads to  
6 slower reaction time, it is very useful for vegetable oils having a too high acid index <sup>146</sup>.  
7  
8 The most currently used acid catalyst for fatty acid esterification is concentrated sulfuric  
9 acid <sup>147</sup>, due to a low price and high activity. Moreover, solid catalysts exhibit easier  
10 work up and present lower corrosion toward reactors. However both drastic temperature  
11 and higher pressure are generally required to reach high yields. These catalysts consist  
12 in zeolites, metal oxides, composite materials and polysulfonic acids based on organic  
13 materials such as glucose <sup>148</sup>. An interesting review compares these different  
14 heterogeneous catalysts owing to their activity, selectivity and thermal stability <sup>149</sup>. On  
15 account of these different parameters, zirconium sulfate was found to be one of the best  
16 catalysts for biodiesel production. Recent works suggested the use of stannous chloride  
17 for saturated and unsaturated fatty acids ethanolysis, reaching yields close to 90% at  
18 temperature around 80°C <sup>150</sup>. This cheap catalyst is less corrosive than sulfuric acid and  
19 could be re-used during several catalytic cycles. Another method <sup>151</sup> proposes cupric  
20 acetate monohydrate in ethanol with hydrochloric acid, at room temperature, allowing  
21 quantitative conversion in one hour.  
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42 Beyond ethanol and methanol <sup>152, 153</sup>, a lot of different alcohols were used as  
43 reagent for the transesterification of fatty esters, such as glycosylated starch <sup>154</sup>, 1,4-  
44 butanediol <sup>155</sup>, a mix of PET/PEG <sup>156</sup> (polyethyleneterephthalate/polyethyleneglycol), or  
45 trimethylolpropane <sup>157</sup>, with various catalysts. Homogeneous ones produce a lot of side-  
46 products with a low selectivity <sup>158</sup>, whereas heterogeneous ones give better results <sup>153,</sup>  
47 <sup>159, 160</sup>. The use of glycerin is widespread (Scheme 34), it yields interestingly a mixture  
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3 of mono and di-glycerides that could be directly formulated with diisocyanates with  
4  
5 chain extender and catalyst to lead to polyurethanes<sup>3, 158, 161, 162</sup>.

6  
7 **Insert Scheme 34:** Transesterification reaction of a triglyceride with glycerin

8  
9 Sodium methylate was reported<sup>163</sup> for transesterification reaction of fatty  
10  
11 methyl esters with trimethylolpropane, reaching 85% yield at 110°C under reduced  
12  
13 pressure. Enzymatic catalysts were also reported<sup>163-166</sup> but are not detailed in this  
14  
15 review.  
16  
17

### 18 19 20 *III.2. Esterification*

21  
22 In the case of high molecular weight alcohols, it is more interesting to perform a  
23  
24 direct esterification of fatty acids (Scheme 35), compared to transesterification, owing  
25  
26 to the relative volatility of water and alcohols.  
27

28 **Insert Scheme 35:** Esterification reaction on fatty acid

29  
30 Esterification reaction is generally performed at high temperature (above 200°C)  
31  
32 and under reduced pressure<sup>143</sup>. The synthesis of polyols from ricinoleic acid and  
33  
34 ethylene glycol was reported<sup>167</sup> owing a process called fusion without catalyst, at high  
35  
36 temperature (230°C), in order to synthesize polyurethane adhesives. Either acid or basic  
37  
38 catalysis are useful for esterification reaction, but they both show some main  
39  
40 drawbacks, such as products coloration and salts formation, respectively. Two catalysts  
41  
42 are mainly used for the industrial synthesis of polyesters: stannous oxide and zinc  
43  
44 powder. Despite their advantages, they also present a disadvantage, i.e. the formation of  
45  
46 soluble salts, difficult to remove in esters produced.  
47  
48

49  
50 Fatty acids of vegetable oils could also be polymerized in a two steps  
51  
52 esterification<sup>168</sup> (Scheme 36). In a first step, alcohol and carboxylic acids functions of  
53  
54 fatty acids are condensed through an esterification reaction. Then in a second step,  
55  
56 condensed fatty acids are esterified with polyglycerol. This reaction is initiated by a  
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3 polyol, a polyamine or an alcoholamine and is catalyzed by a titan complex or an  
4  
5 enzyme<sup>169</sup>.  
6

7 **Insert Scheme 36:** Self condensation of fatty acids  
8  
9

### 10 *III.3. Amidification*

11 Amidification is also an interesting functionalization reaction on vegetable oils (reaction  
12  
13 J, Table 1). Unlike transesterification between alcohols and esters, amidification is not  
14  
15 thermodynamically balanced.  
16  
17

18  
19 Thus, amidification could be performed on fatty acids or esters of vegetable oils  
20  
21 with various amines<sup>170-173</sup>. Unsaturated vegetable oils could also react with an  
22  
23 alcoholamine and sodium ethoxide at 100°C, leading to an amide bearing hydroxyl  
24  
25 functions<sup>82, 174, 175</sup>. Example is reported in scheme 37 with castor oil and diethanolamine  
26  
27 (2,2'-iminodiethanol). The use of alcoholamine with methyl esters was also reported<sup>171</sup>,  
28  
29 thus methyl-9-hydroxystearate and 2-aminoethanol were heated at 85°C for 22h with  
30  
31 potassium hydroxide to yield alcoholamines.  
32  
33

34  
35 **Insert Scheme 37:** Synthesis of unsaturated amides by amidification/esterification  
36  
37

### 38 *III.4. Thioesterification*

39 Esterification could also proceed with a thiol function through thioesterification  
40  
41 reaction. In this case, a difunctional thiol reagent, such as 2-mercaptoethanol, could  
42  
43 functionalize vegetable oils, leading to fatty hydroxyl thioesters. A study reported this  
44  
45 reaction with 2-mercaptoethanol in isopropanol with sodium or potassium hydroxide<sup>176</sup>  
46  
47 (Scheme 38) but did not mention neither esterification by alcohol, nor thiol-ene addition  
48  
49 onto double bonds, which is very surprising, considering the reaction conditions.  
50  
51  
52

53  
54 **Insert Scheme 38:** Thioesterification of triglyceride with 2-mercaptoethanol  
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### III.5. Various reactions

III.5.1. *Fatty alcohols from fatty acids or esters.* The reduction of the carboxylic group of a fatty acid or ester by  $\text{LiAlH}_4$  yields a fatty alcohol (reaction H, Table 1), without modifying the unsaturations of the aliphatic chain. These fatty alcohols can also be produced by hydrogenolysis of fatty acids, fatty methyl ester or triacylglycerols<sup>177</sup>. Long chain fatty alcohols generally undergo ethoxylation or propoxylation reactions, leading to interesting surfactant properties (reaction L, Table 1). In a last step, alcohols react with chlorosulfonic acid or phosphoric anhydride to yield sulfates or phosphates surfactants, respectively<sup>178</sup> (Scheme 39).

**Insert Scheme 39:** Surfactant synthesis from fatty alcohols

III.5.2. *Lactones synthesis.* Oleic acid could also be converted into  $\gamma$ -stearolactone by reaction with perchloric acid at  $110^\circ\text{C}$  during 3h with a yield higher than 90% (Scheme 40). Reaction mechanism goes through reversible protonation of fatty acid double bonds, shifting and rearrangement of carbocation on chain until the carbonyl group attack. Furthermore, cyclization of methylundecanoate with manganese acetate also yields also a  $\gamma$ -lactone<sup>179</sup>.

**Insert Scheme 40 :** Synthesis of  $\gamma$ -stearolactone

More reactive lactones such as  $\delta$ -lactones, could also be synthesized from fatty acids bearing double bonds in position 4 or 5, such as 5-eicosenoic acid (20:1). These synthesized lactones could easily react with alcohols or amines to yield respectively hydroxyl esters or hydroxyl amides<sup>178</sup> (Scheme 41).

**Insert Scheme 41:** Synthesis of hydroxylesters or hydroxylamides from  $\delta$ -lactones

Furthermore, polylactones could be synthesized in several steps. For example, methyl oleate, after ozonolysis, hydrogenation, saponification and hydrolysis leads to 9-hydroxynonanoic acid. This hydroxyl acid was finally converted into a lactone and then in polynanolactone<sup>180, 181</sup> (Scheme 42).



1  
2  
3 **Insert Scheme 42:** Synthesis of polynonanolactones

4  
5 *III.5.3. AB monomers synthesis.* Recently, ricinoleic and oleic acids were used as  
6  
7 precursors for AB monomers synthesis leading to polyurethanes synthesis by direct  
8  
9 polycondensation<sup>182, 183</sup> (Scheme 43). This multi-step process goes through an azidation  
10  
11 reaction with NaN<sub>3</sub> at 0°C for 1h. The next step consists of either a self condensation at  
12  
13 80°C for 24h, or by a transurethane reaction catalyzed by Ti(OBu)<sub>4</sub> at 130°C for 6h.

14  
15 **Insert Scheme 43:** Synthesis of AB monomer for polyurethanes synthesis by direct  
16  
17 polycondensation

18  
19  
20 The carboxylic group of fatty compounds offers several ways to insert hydroxyl  
21  
22 functions onto triglycerides and fatty acids, as showed in scheme 44.

23  
24 **Insert Scheme 44 :** Summary of various products obtained by functionalization of ester group  
25  
26 of vegetable oils and derivatives

27  
28 To conclude, we reported in this part several methods to functionalize natural  
29  
30 oils into polyols, through double bonds or carbonyl group of triglycerides. The type of  
31  
32 alcohol, the functionality and the route followed for functionalization are crucial  
33  
34 parameters for the final properties of synthesized polyurethanes thereof.

### 35 36 37 38 **Part B: commercial polyols and industrial state of the art**

39  
40 In this part, we focused on commercial polyols synthesized from renewable resources.  
41  
42 Therefore we have been interested in biobased polyols proposed by different industrial  
43  
44 companies.

#### 45 46 47 48 ***I. Polyols from saccharides***

49  
50 Several polyols are synthesized from various monosaccharides and derivatives, such as  
51  
52 glucose. Thus, DUPONT has proposed since 2006 CERENOL™, a polyol dedicated to  
53  
54 polyurethanes synthesis for elastomers and fibers. Dupont synthesized biobased 1,3-  
55  
56 propanediol (Scheme 45) from corn by glucose fermentation<sup>184</sup>. CERENOL™ polyol, a  
57  
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1  
2  
3 polytrimethylene ether glycol, is synthesized by step growth polymerization of 1,3-  
4  
5 propanediol with a homogeneous or heterogeneous catalyst, under reduced pressure and  
6  
7 at high temperature (around 200°C) <sup>185</sup>.  
8

9  
10 **Insert Scheme 45:** Summary of various products obtained from biomass

11 ROQUETTE proposes polyols for polyurethanes syntheses such as  
12  
13 NEOSORB® and POLYSORB®. NEOSORB® is a syrup solution of sorbitol. In the  
14  
15 POLYSORB® range, we find a syrup solution of maltitol and sorbitol and also an  
16  
17 isosorbide diol (Scheme 45). Sorbitol is coming from hydrogenation of glucose. The  
18  
19 sorbitol yields isosorbide with an acid catalyst. These polyols are bearing secondary  
20  
21 alcohol groups and they could react with isocyanates to yield polyurethanes. Generally,  
22  
23 these polyols are preferably used to synthesize polyols polyethers from alkylene oxide.  
24  
25  
26  
27

## 28 *II. Epoxidation of vegetable oils*

29  
30 Most biobased polyols are synthesized from vegetable oils. And most of them are  
31  
32 synthesized from epoxidized vegetable oils.  
33  
34

35 Thus, JEFFADD™ B650 is a biobased polyol, exhibiting 65% of renewable  
36  
37 carbon. This polyol, commercialized since March 2010 by HUNTSMAN Company, is  
38  
39 dedicated to polyurethane synthesis for rigid foams, sprays, coatings, adhesives, mastics  
40  
41 and elastomers. This polyol is synthesized by the reaction of epoxidized soybean oil  
42  
43 bearing 2 to 6 epoxide groups per molecule with an alcohol amine at 120°C during 4  
44  
45 hours (reaction B where NuH is ethanolamine for instance). Alcohol amines react with  
46  
47 epoxide groups and yield a mixture of primary and secondary hydroxyl groups<sup>186</sup>.  
48  
49 However, the amine could also react with ester functions of triglycerides by  
50  
51 amidification reaction, yielding shorter amide polyols (reaction J, Table 1).  
52  
53  
54

55 BIOBASED TECHNOLOGIES developed a range of products: AGROL®  
56  
57 which is a biobased polyol from soybean oil. AGROL® polyols content of 96% of  
58  
59  
60

1  
2  
3 renewable carbon, owing to ASTM 6866 standard. The number of hydroxyl group per  
4  
5 molecule varies from 2 to 7 owing to different products. AGROL® polyols are  
6  
7 synthesized from soybean oil in two steps. In the first step, double bonds of vegetable  
8  
9 oils are epoxidized with a peracid (reaction A, Table 1). Oxirane groups are then ring-  
10  
11 opened by the acid by-product of the first step<sup>187</sup> (reaction B, Table 1). AGROL®  
12  
13 DIAMOND polyol is prepared from AGROL® polyols by aminolysis of ester functions  
14  
15 of triglycerides by an alcohol amine (reaction J, Table 1)<sup>188</sup>. This explains the high  
16  
17 hydroxyl index of DIAMOND polyols compared to other AGROL polyols (Table 2).  
18  
19

20  
21 CARGILL has proposed since 2006 a biobased polyol from soybean oil,  
22  
23 BIOH®, with a content of renewable carbon higher than 95 % owing to ASTM 6866  
24  
25 standard. Polyurethane flexible foams elaborated with this polyol exhibit a content of  
26  
27 renewable carbon between 5% and 20%. This polyol is synthesized from vegetable oils  
28  
29 by epoxidation followed by epoxide ring opening by methanol in presence of  
30  
31 fluoroboric acid as catalyst (reaction B, Table 1 where NuH is CH<sub>3</sub>OH)<sup>189,190</sup>. Therefore  
32  
33 synthesized polyol bears only secondary alcohols functions on aliphatic chain of fatty  
34  
35 acid. Even if this structure is similar to castor oil, double bonds are absent from this  
36  
37 polyols which improve thermal stability. Two formulations of this polyol are proposed.  
38  
39

40  
41 COGNIS, and now BASF, proposes an abundant range of biobased polyols from  
42  
43 vegetable oils and derivatives under the brand name SOVERMOL® for various  
44  
45 applications such as adhesives, binders, floor coatings, castings, electro potting... The  
46  
47 chemical route to yield these polyols is also based on epoxidation of vegetable oils  
48  
49 followed by ring-opening of epoxides by nucleophilic attack of an alcohol (reaction B,  
50  
51 Table 1 where NuH is CH<sub>3</sub>OH for instance). Then, in a third step, hydroxylated oils  
52  
53 undergo transesterification with the same alcohol<sup>37</sup> (reaction I, Table 1).  
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2  
3 A large range of biobased products from vegetable oils is also proposed by  
4 HOBUM OLEOCHEMICALS. This Company functionalizes vegetable oils such as  
5 castor oil, linseed oil and soya bean oil, to synthesize polyols by epoxidation followed  
6 by nucleophilic attack (reaction B, Table 1). Nucleophilic reagent could be water,  
7 alcohol (mono or diol), alcoholamine or amine <sup>191</sup>. These polyols are commercialized  
8 under the brand name MERGINOL and are used for polyurethane synthesis for various  
9 applications: foams, coatings, dispersions... There are two kinds of polyols in this range,  
10 polyester polyols and polyether-polyester polyols.  
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20  
21 OLEON, owned by SOFIPROTEOL, commercialize three polyols under the  
22 brand name RADIA® (formerly NOVENOL® at NOVANCE): two polyesters polyols  
23 for soft polyurethane foams (RADIA® 7291 and 7292) and a polyether polyol for rigid  
24 polyurethane foam (RADIA® 7293). These polyols are based on different vegetable  
25 oils (sunflower, rapeseed, soya bean) and their renewable carbon content varies from  
26 96% to 100%. Several patents of NOVANCE<sup>192, 193</sup> describe the synthesis of polyols  
27 from fatty acids or vegetable oils : double bonds of fatty acids or vegetable oils are  
28 epoxidized by hydrogen peroxide with a metal catalyst (molybdenum or tungsten), then  
29 the epoxides undergo nucleophilic attack by water <sup>194</sup> (reaction B, Table 1 where NuH is  
30 H<sub>2</sub>O).  
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43 BAYER develops a biobased polyurethane, BAYDUR® PUL 2500, showing  
44 20% of renewable carbon and used in flexible and rigid polyurethane foams. It seems  
45 that these polyols are synthesized from vegetable oils (preferably soybean oil) by  
46 epoxidation followed by hydrogenation to lead secondary alcohols functions (reaction  
47 C, Table 1). These alcohol functions are then ethoxylated or propoxylated by alkylene  
48 oxide (reaction L, Table 1) with metal cyanide in order to lead to primary alcohol  
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3 functions <sup>195</sup>. Another patent of BAYER describes alkoxylation of hydroxylated  
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5 vegetable oils, whatever the hydroxylation method <sup>196</sup>.  
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7 **Insert Table 2:** Properties of commercial polyols from vegetable oils epoxidation  
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### 10 *III. Various functionalization reactions of vegetable oils*

11 DOW CHEMICAL started the production of biobased Renuva™ polyol, synthesized  
12 from soybean oil, used for flexible foams, coatings, adhesives, mastics and elastomers.  
13 This polyol is synthesized in several steps. Firstly, soybean oil undergoes  
14 transesterification with methanol (reaction I) to yield fatty acids methyl esters  
15 (FAMES). In a second step, by hydroformylation followed by hydrogenation (reaction  
16 E), double bonds of these FAMES are converted in hydroxyl groups. The hydroxyl  
17 content depends on the number of double bonds in starting oil. In a third step, these  
18 hydroxylated FAMES react with a polyols (such as propan-1,2,3-triol) or a polyamine  
19 (such as 1,2-diaminoethane) with a catalyst during about 5 hours under vacuum <sup>169, 197</sup>  
20 (reaction I or J, Table 1). Owing to recent information from Dow Europe, the  
21 production of this polyol has been stopped due to a too high variability of fatty acids  
22 double bonds composition. Therefore FAMES with different hydroxyl contents had to  
23 be separated before polyols synthesis which entails a too high price for this process.  
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42 Concerning BASF, this Company produces LUPRANOL® BALANCE 50, a  
43 polyether polyol for rigid foams and mattress that partly comes from castor oil. And  
44 now BASF develops Lupranol Balance 35, synthesized by hydroformylation (rhodium  
45 or cobalt catalyst) followed by hydrogenation (nickel based catalyst) on castor oil  
46 (reaction E, Table 1). This polyol is then etherified (reaction L, Table 1) with alkylene  
47 oxide (ethylene or de propylene oxide) with double metal cyanide catalyst (Scheme 46).  
48 Another polyol polyether is added for the elaboration of polyurethane foams <sup>198</sup>.  
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57 **Insert Scheme 46:** Structure of Lupranol® Balance 50 polyol  
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3 The functionality of Lupranol is surprisingly claimed lower than 3, whereas the  
4 process used by BASF could lead to around 6 hydroxyl groups per molecule. It seems  
5 that secondary hydroxyl groups are considered as non reactive, not only towards  
6 ethoxylation/propoxylation, but also towards polyurethanes synthesis.  
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11 COGNIS also proposes biobased polyols from fatty acid dimers, under the brand  
12 name SOVERMOL®. The chemical route to yield these polyols is based on  
13 dimerization fatty acids catalyzed by montmorillonite clay at 250°C (Scheme 24),  
14 followed by reduction of carboxylic acid groups into alcohol functions <sup>199</sup> (reaction H,  
15 Table 1).  
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23 The US Company URETHANE SOY SYSTEMS proposes biobased SOYOL  
24 polyols from soybean oil used in various polyurethane applications: foams, sealing,  
25 coatings... The process is based on transesterification of triglycerides with propan-  
26 1,2,3-triol previously modified with saccharide (reaction I, Table 1) <sup>200</sup>.  
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32 CRODA sells several biobased products such as PRIPOL™ fatty acids dimers  
33 and PRIPLAST™ polyether polyols, with a renewable carbon content between 36% and  
34 100% owing to the formulation. The chemical synthesis of fatty acids dimers was  
35 described previously (Scheme 24) CRODA uses acid catalyst at high temperature <sup>201</sup>.  
36 Diols dimers are obtained by reduction (H<sub>2</sub> with nickel) of carboxylic acid function of  
37 fatty acids dimers <sup>202</sup> (reaction H, Table 1). Noteworthy, no double bond remains in the  
38 final diols.  
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47 MITSUI patented the synthesis of biobased polyols for polyurethane by  
48 transesterification of fatty acids with short polyols (reaction I, Table 1) followed by  
49 ethoxylation or propoxylation of terminal hydroxyl groups <sup>203</sup> (reaction L, Table 1).  
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54 **Table 3** : properties of commercial polyols from various reactions on vegetable oils  
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## CONCLUSION

This review shows that biobased polyols have an important place in the Polyurethanes industry. Indeed, most of biggest chemical groups have developed their own brand of biobased polyols, offering to users new various reactive polyols in order to increase renewable carbon content of final materials. In a first part, the present review goes into details of the different synthetic routes to obtain polyols from vegetable oils. Indeed, Part A describes several methods to graft hydroxyl functions onto vegetable oils and derivatives, owing to their epoxy groups (Scheme 17), double bond sites (Scheme 33) and/or carboxyl functions (Scheme 44).

In a second part, the present review is dedicated to the commercial biobased polyols, and, based on the patent literature; focus on the industrial synthetic routes. Indeed Part B sheds lights on the importance of biobased polyols in polyurethanes industry. The number of patents in this domain is one of the proofs of the main role of biobased polyols in industrial polyurethanes.

Among all these methods, epoxidation followed by epoxide ring opening remains the most currently used and patented method, due to the variety of usable nucleophiles in this reaction. Conversely, thiol-ene chemistry is not yet used at the industrial level despite the advantages reported in the first part. The use of biobased polyols for the manufacture of polyurethanes is a real positive point for the environmental impact of polymers. **It is all the more interesting to use biobased polyols in PU synthesis since polyols represent the major part of PU, generally between 60 to 70% in weight of PU.**

**Vegetable oils and fats are very important resources for polyols. The vegetable oils with a worldwide production of around 150 million t/year (in 2009 – data from FAO), are used mainly in human food applications (75%). But the technical uses and particularly oleochemical industry are increasing. (13% is used in oleochemical**



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3 industry). Vegetable oils lead to polyester polyols. And polyester polyols are the second  
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5 most important group of oligopolyols for the production of polyurethanes. The  
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7 production of polyester polyols, with a total worldwide production of around  
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9 600kt/year, represents around 18% of the polyols used globally in polyurethanes.  
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11 Moreover, about 60% of polyester polyols are produced in Europe<sup>204</sup>. Polyester polyols  
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13 were the only polyols available to the polyurethanes industry at the beginning, but now,  
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15 in spite of the leading position of polyethers in the total polyols usage in the  
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17 polyurethane industry, polyester polyols have stable and specific practical applications  
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19 due to some superior characteristics of the resulting polyurethanes<sup>204</sup>. Indeed, the  
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21 superior characteristics of polyester polyol based polyurethanes are explained by a  
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23 better crystalline structure in the urethane segment, compared to the majority of  
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25 polyether polyols which are amorphous, due to the superior secondary forces between  
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27 the polyester chains and also due to a superior thermal and fire resistance, compared to  
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29 polyether polyol based polyurethanes. Polyesterbased polyurethanes (flexible foams,  
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31 coatings), have a superior solvent resistance compared to the polyether-based  
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33 polyurethanes<sup>205</sup>.

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38 Indeed, purity of triglycerides from vegetable oils could be discussed. But in a  
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40 near future, new production units will be installed, for producing high-purity fatty esters  
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42 and acids (such as Pivert in Compiègne, France), giving an easy industrial access to  
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44 diols for linear PU based on chemical pathways depicted in this manuscript. And even if  
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46 one of the limitations of polyester polyols consists of their sensitivity to hydrolysis, the  
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48 the use of fatty alcohols to build the polyester structure, creates an extremely high  
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50 hydrophobic environment alongside a low concentration of labile ester bonds and  
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52 improves hydrolysis resistance.  
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3 However, isocyanates are still used and are generally very harmful for human  
4 health, particularly for people exposed during polyurethanes synthesis, and could entail  
5 adverse health effects such as asthma, dermatitis, conjunctivitis and acute poisoning.  
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7 Moreover, REACH regulation prevents the use of major isocyanates such as methylene  
8 diphenyl diisocyanate MDI and toluene diisocyanate TDI<sup>206</sup>. Therefore the synthesis of  
9 Polyurethanes from step growth polyaddition of dicyclocarbonates and diamines should  
10 be favored. Thus, this old reaction is currently gaining a lot of attention as a substitution  
11 route for the synthesis of Polyurethanes and will be industrialized in a next future.  
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4 **Table 1:** Mains reactions used on vegetable oils

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6 **Table 2:** Properties of commercial polyols from vegetable oils epoxidation

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9 **Table 3:** properties of commercial polyols from various reactions on vegetable oils

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11 **Scheme 1:** Polyurethane synthesis from diol and diisocyanate

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13 **Scheme 2:** Triglyceride formula with R<sub>0</sub>, R<sub>1</sub> and R<sub>3</sub> aliphatic chains of fatty acids

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15 **Scheme 3:** Triglyceride formula with R<sub>0</sub> chain corresponding to oleic acid

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17 **Scheme 4:** Synthesis of epoxidized triglycerides

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19 **Scheme 5:** *In situ* triglyceride epoxide ring opening

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21 **Scheme 6:** Triglycerides epoxide ring opening by methanol

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23 **Scheme 7:** Synthesis of primary terminal alcohols from triolein for polyurethanes  
24 formulation

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26 **Scheme 8:** Epoxide ring opening polymerization of epoxidized methyl oleate

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28 **Scheme 9:** Triglyceride epoxide ring opening with butane-1-thiol

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30 **Scheme 10:** Oxirane ring opening with diethylamine

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32 **Scheme 11:** Triglyceride epoxide ring opening with acrylic acid

33  
34 **Scheme 12:** Direct hydrogenation of triglyceride epoxides

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36 **Scheme 13:** Triglyceride epoxide ring opening by ethan-1,2-diol

37  
38 **Scheme 14:** Competitive reactions occurring during triglyceride amidification by  
39 diethanolamine

40  
41 **Scheme 15:** Triglyceride epoxide ring opening with lactic acid

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43 **Scheme 16:** Polyols synthesis from carbonated oil

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45 **Scheme 17:** Summary of most common functionalizations on epoxidized vegetable oils



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3 **Scheme 18:** Ozonolysis of unsaturated triglycerides leading to terminal primary  
4 hydroxyl functions  
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7 **Scheme 19:** Allyl hydroperoxides synthesis then converted into enone groups or  
8 reduced into secondary alcohols  
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11 **Scheme 20:** Hydroformylation followed by reduction on unsaturated triglyceride  
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14 **Scheme 21:** Hydroaminomethylation of ethyl oleate by valinol (dioxane, 140°C, 20h,  
15 rhodium complex catalyst, yield 95%)  
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18 **Scheme 22:** Fatty acid dimer (left hand) and fatty diol dimer (right hand)  
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21 **Scheme 23:** Dimerization reaction of conjugated linoleic acid  
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24 **Scheme 24:** Dimerization reaction of oleic acid  
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27 **Scheme 25:** Aromatic triols synthesis from (a) methyl-9-octadecenoate and (b) methyl-  
28 10-undecenoate  
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31 **Scheme 26:** Mechanism of thiol-ene coupling  
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34 **Scheme 27:** Fatty ester trimerization by thiol-ene coupling  
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37 **Scheme 28:** Synthesis of the poly-2-oxazoline polyols from 10-undecenoic and  
38 decanoic acid  
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41 **Scheme 29:** Products and by-products of thiol-ene coupling of 2-mercaptoethanol on  
42 fatty acid  
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45 **Scheme 30:** Formaldehyde addition onto fatty acid  
46

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48 **Scheme 31:** Undecylenic acid acylation  
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51 **Scheme 32:** Linear diols from unsaturated fatty esters alkoxycarbonylation  
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54 **Scheme 33:** Double bond modifications for the synthesis of polyols from vegetable oils  
55 and derivatives  
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58 **Scheme 34:** Transesterification reaction of a triglyceride with glycerin  
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3 **Scheme 35:** Esterification reaction on fatty acid  
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5 **Scheme 36:** Self condensation of fatty acids  
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8 **Scheme 37:** Synthesis of unsaturated amides by amidification/esterification  
9

10 **Scheme 38:** Thioesterification of triglyceride with 2-mercaptoethanol  
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12 **Scheme 39:** Surfactant synthesis from fatty alcohols  
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14 **Scheme 40:** Synthesis of  $\gamma$ -stearolactone  
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17 **Scheme 41:** Synthesis of hydroxyesters or hydroxylamides from  $\delta$ -lactones  
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20 **Scheme 42:** Synthesis of polynonanolactones  
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23 **Scheme 43:** Synthesis of AB monomer for polyurethanes synthesis by direct  
24 polycondensation  
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27 **Scheme 44:** Summary of various products obtained by functionalization of ester group  
28 of vegetable oils and derivatives  
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31 **Scheme 45:** Summary of various products obtained from biomass  
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34 **Scheme 46:** Structure of Lupranol® Balance 50 polyol  
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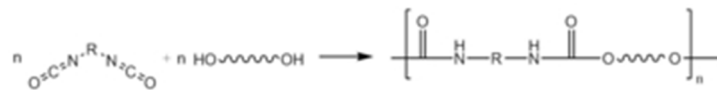
L	Ethoxylation / propoxylation	$R_1OH \xrightarrow{\text{R-epoxide}} R_1\left(\text{O}-\text{CH}_2-\text{CH}(\text{OH})\right)_n \text{OH} \quad R=\text{H}, \text{CH}_3$
M	Metathesis	$\begin{array}{c} R_1 & R_3 \\ & \backslash / \\ & \text{C} = \text{C} \\ & / \backslash \\ R_2 & R_4 \end{array} \xrightarrow{\text{ethylene, cat.}} \begin{array}{c} R_1 \\   \\ \text{C} = \\   \\ R_2 \end{array} + \begin{array}{c} R_3 \\   \\ \text{C} = \\   \\ R_4 \end{array}$
N	Hydrogenation	$\begin{array}{c} R_1 & R_3 \\ & \backslash / \\ & \text{C} = \text{C} \\ & / \backslash \\ R_2 & R_4 \end{array} \xrightarrow{\text{H}_2, \text{cat}} \begin{array}{c} R_1 & R_3 \\   &   \\ \text{C} - & \text{C} \\   &   \\ R_2 & R_4 \end{array}$
O	Carbonatation	$\begin{array}{c} \text{O} \\ \backslash / \\ \text{C} \\ / \backslash \\ R_1 & R_3 \\   &   \\ R_2 & R_4 \end{array} \xrightarrow{\text{CO}_2} \begin{array}{c} \text{O} \\    \\ \text{O} - \text{C} - \text{O} \\ / \quad \backslash \\ R_1 & R_3 \\   &   \\ R_2 & R_4 \end{array}$

Company	Commercial product	I <sub>OH</sub> (mg KOH/g)	I <sub>a</sub> (mg KOH/g)	Density (g/cm <sup>3</sup> )	Viscosity (cP)	f
HUNTSMAN	Jeffadd B650	650	0	1.080	30000	-
	Agrol 2.0	65-75	<1	0.955	230	2.0
	Agrol 3.6	107-117	<1	0.975	720	3.6
BIOBASED	Agrol 4.3	125-137	<1	0.976	1320	4.3
TECH	Agrol 5.6	151-170	<1	0.994	4770	5.6
	Agrol 7.0	175-195	<1	1.023	21500	7.0
	Agrol Diamond	320-350	<1	1.017	3400	3.0
CARGILL	BiOH X-0500	56	0.3	1.000	4500	2.0
	BiOH X-0210	235	1.7	1.010	8900	4.4
BASF	Sovermol 320	300-320	<6	-	800-1200	2.8
(COGNIS)	Sovermol 650	186-206	0-1	0.91-0.92	3700-4600	2.2
	Sovermol 750	300-330	<2	0.98-1.02	700-1400	3.0
	Sovermol 760	370-410	<2	1-1.04	1500-3000	3.5
	Sovermol 805	160-185	<3	0.98-1.02	2800-4000	3.5
	Sovermol 810	220-240	<3	-	700-1100	3.3
	Sovermol 815	200-230	<3	0.98-1.02	1300-1900	3.3
	Sovermol 818	223-248	<3	0.975-1.02	650-850	2.6
	Sovermol 819	230-250	>3	0.96-1.02	750-950	2.6
	Sovermol 860	190-220	<1.5	0.98-1.02	200-650	2.5
	Sovermol 908	200-212	<0.2	-	1800-2800	2.0
	Sovermol 1005	117-130	<3	0.94-0.96	600-900	2.2
	Sovermol 1014	155-168	<4	-	600-800	2.5
	Sovermol 1055	180-190	<1	0.90-0.91	10-20	-
	Sovermol 1058	180-200	<1	0.87-0.89	0-15	-
	Sovermol 1083	160-180	<3	0.98-1.02	1800-2500	3.3

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3		Sovermol 1092	268-298	<2	0.97-1.02	650-950 2.8
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5		Sovermol 1095	225-245	<2	1-1.01	1700-2300 3.3
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7		Sovermol 1102	210-245	<3	0.98-1.02	150-650 2.1
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9		Sovermol 1111	150-170	<3	0.96-0.97	300-700 3.0
10						
11		Sovermol 1140	190-230	<3	-	600-1400 2.7
12						
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14		Merginol 207	80	<1	-	3000 3.1
15						
16		Merginol 208	50	<1	-	1000 1.2
17						
18		Merginol 900	310	<3	-	800 2.8
19						
20		Merginol 901	300	<2	-	900 3.0
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22		Merginol 903	230	<3	-	150 2.1
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24		Merginol 904	240	<3	-	2500 3.4
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26		Merginol 905	170	<2	-	3000 3.2
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28		Merginol 908	210	<3	-	1400 3.4
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30	HOBUM	Merginol 909	230	<3	-	800 3.3
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32		Merginol 910	400	<2	-	2800 3.5
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34		Merginol 980	210	<3	-	150 1.8
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36		Merginol 1012	200	<2	-	500 2.8
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38		Merginol 1021	220	<2	-	500 2.9
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40		Merginol 8364	43	<1	-	3000 3.1
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42		Merginol 8570	65	<2	-	1800 2.7
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44		Merginol 8580	60	<2	-	1600 2.7
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49		Radia 7291	55-70	<2.5	-	<14000 2.5
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51	OLEON	Radia 7292	40-55	<2.5	-	<150 2.5
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53		Radia 7293	300-350	<1	-	600-800 4.0
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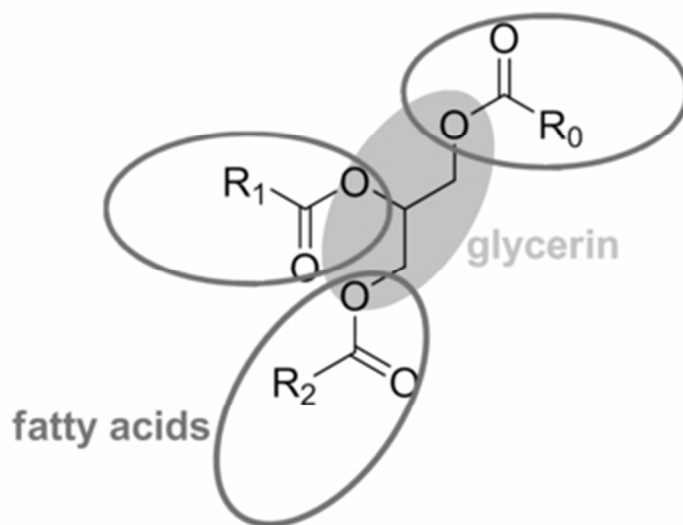
Company	Commercial product	I <sub>OH</sub> (mg KOH/g)	I <sub>a</sub> (mg KOH/g)	Viscosity (cP)
BASF	Lupranol balance 50	50	<0.06	725
Urethane Sos System	Soyol 1001	53-60	3-5	800-1500
	Soyol 2001	60-80	<5	1200-2500
	Soyol 2101	55-70	<3	1500-3000
	Soyol 2102	55-70	<3	1500-3000
	Soyol 2999	55-70	<1.5	1500-3000
Croda	Priplast 1838	60	0.3	-
	Priplast 3196	39	0.3	40020
Cognis	Sovermol 110	625-645	-	Solid at 25°C
	Sovermol 909/910	90-112/50-60	-	Solid at 25°C
	Sovermol 908	180-210	-	1800-2800

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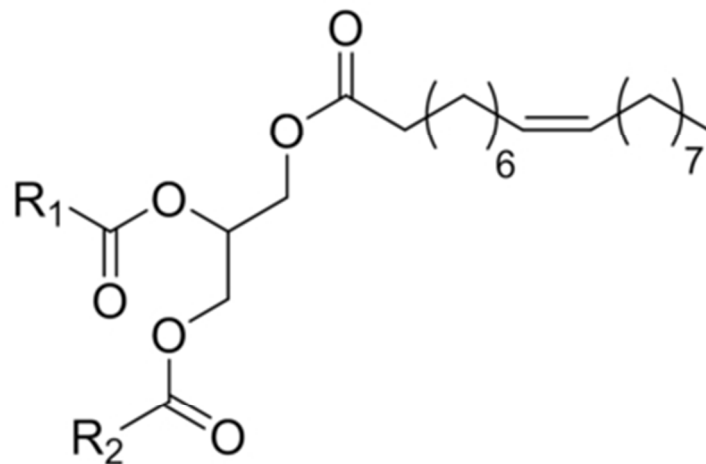
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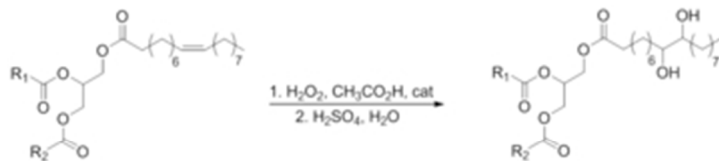




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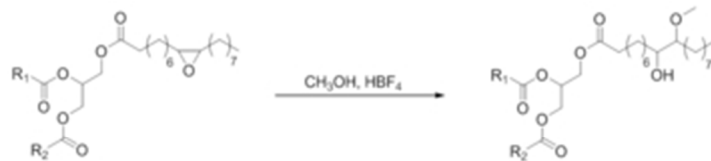
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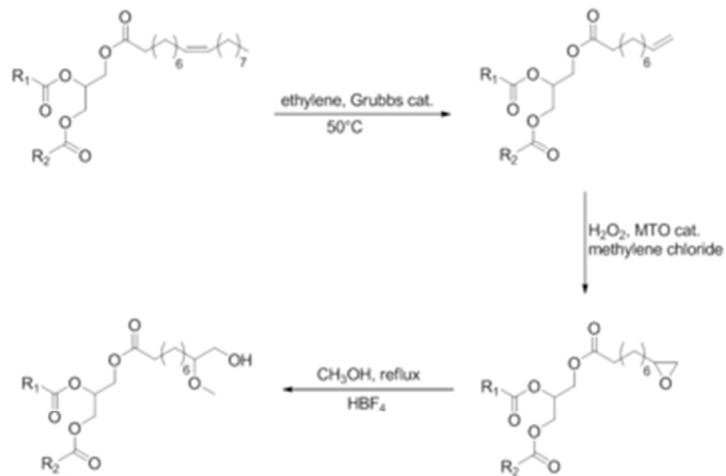




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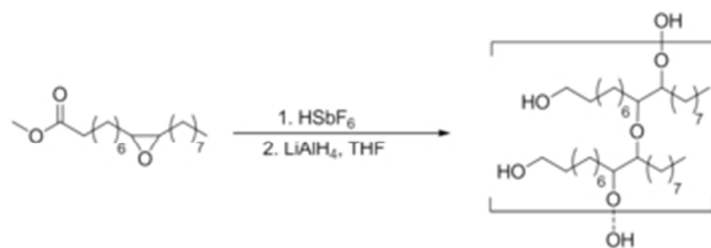
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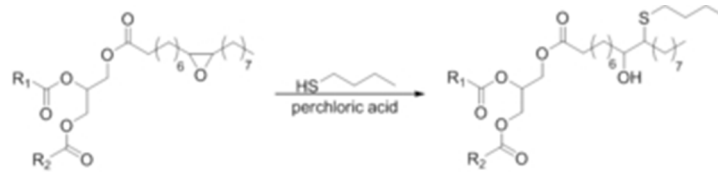
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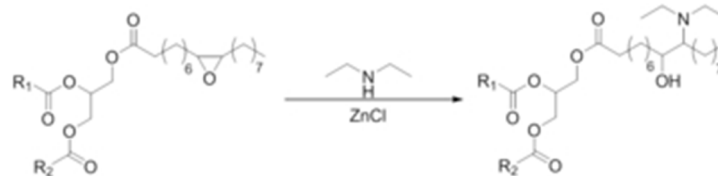
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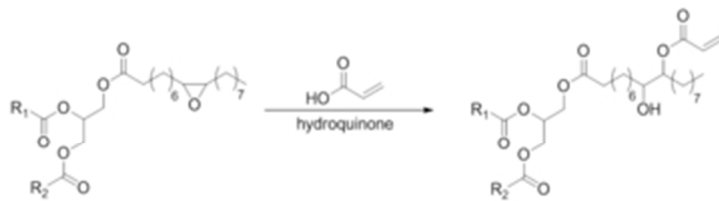




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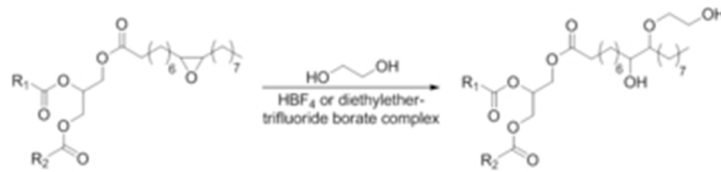


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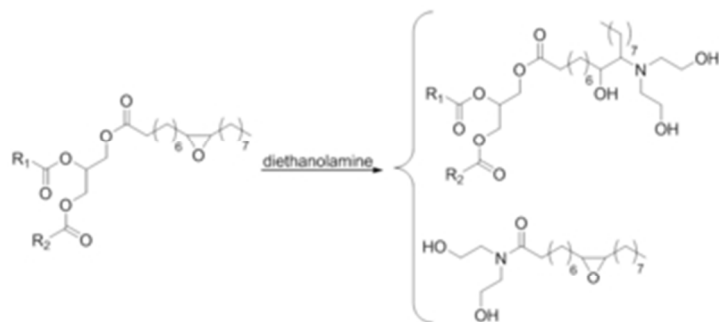


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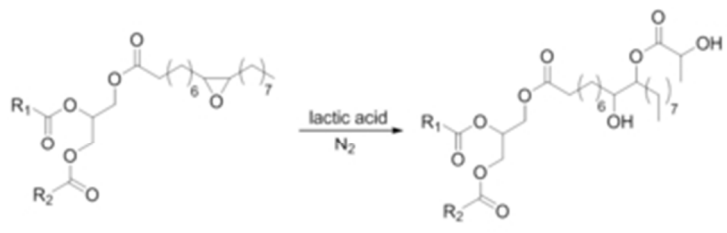
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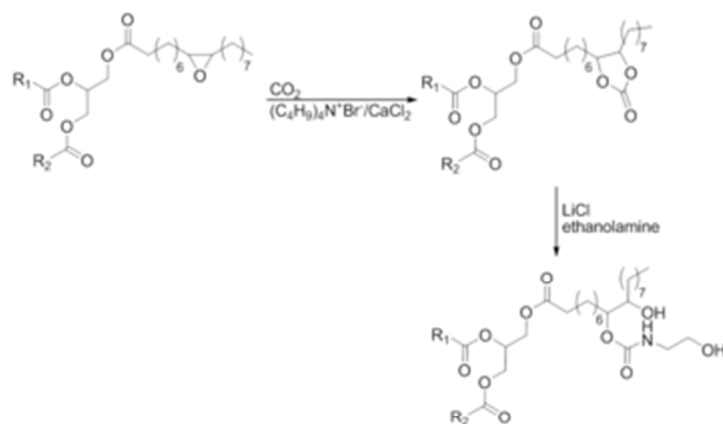
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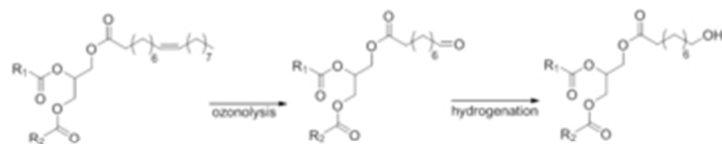


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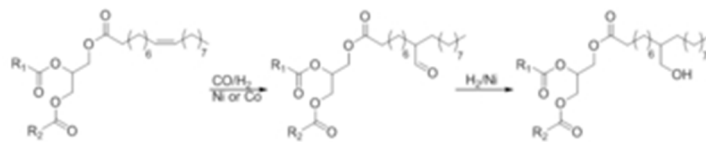




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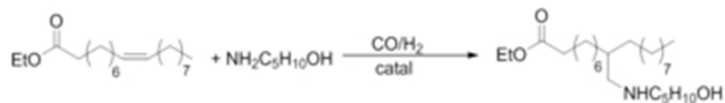
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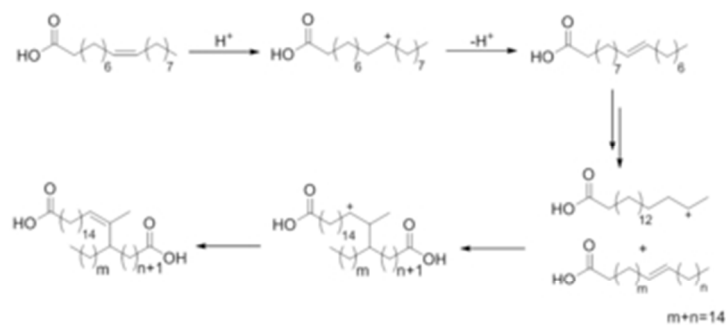
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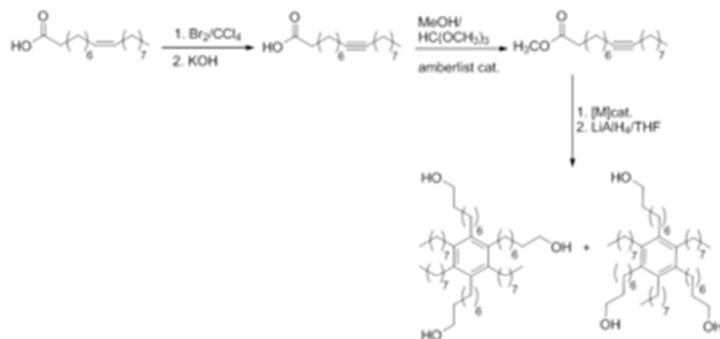
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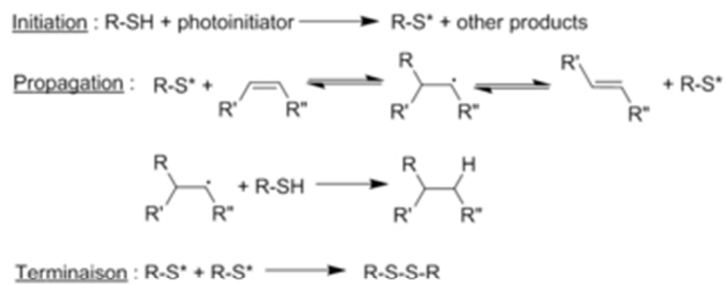
Review Only





30x22mm (300 x 300 DPI)

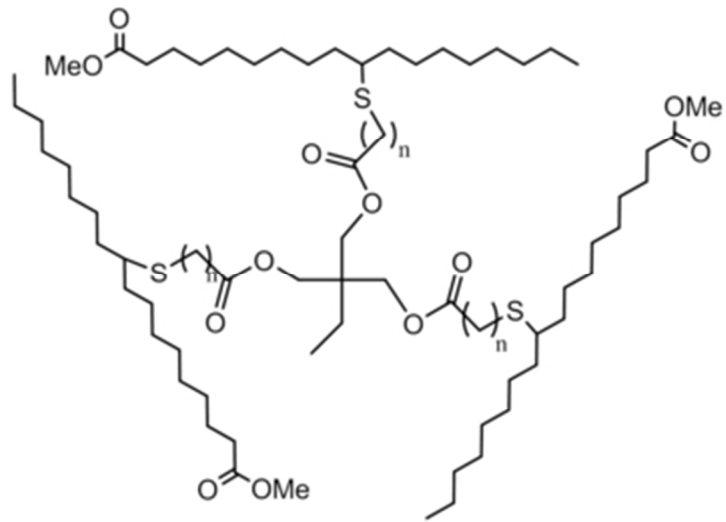
Review Only



30x22mm (300 x 300 DPI)

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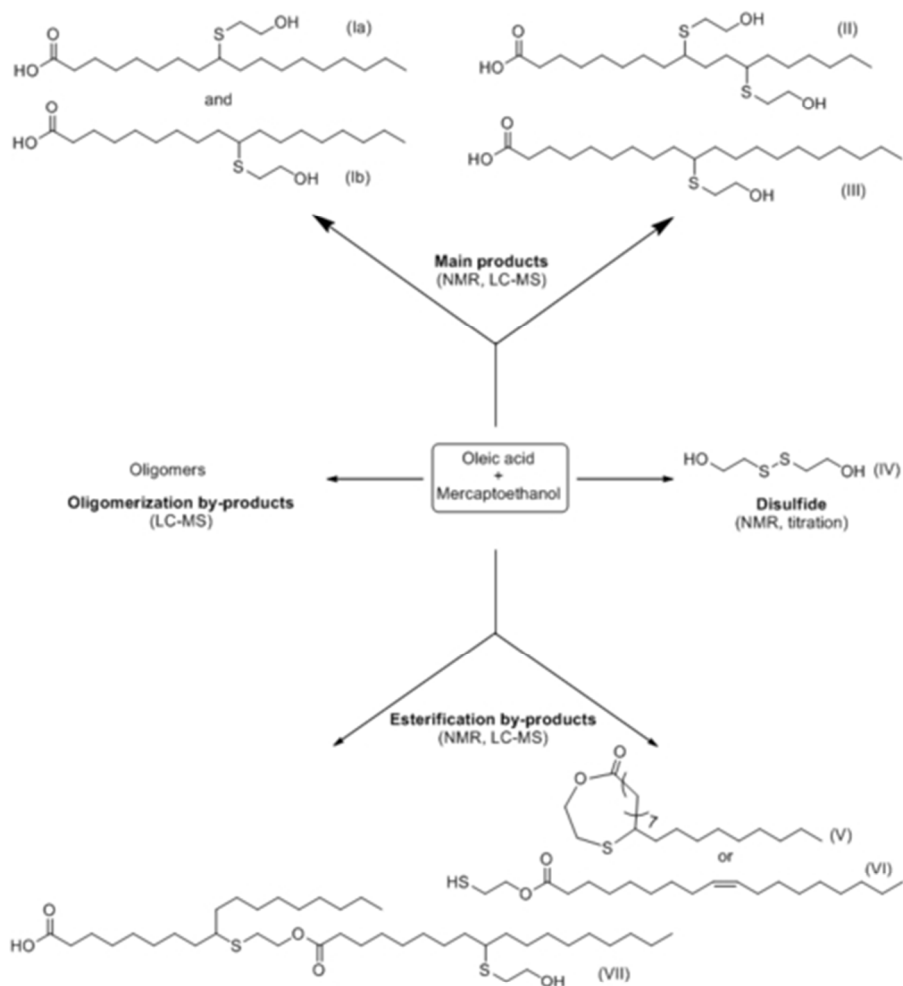
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30x22mm (300 x 300 DPI)

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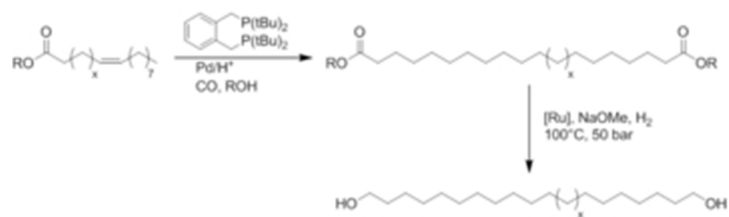
40x54mm (300 x 300 DPI)



30x22mm (300 x 300 DPI)

Review Only

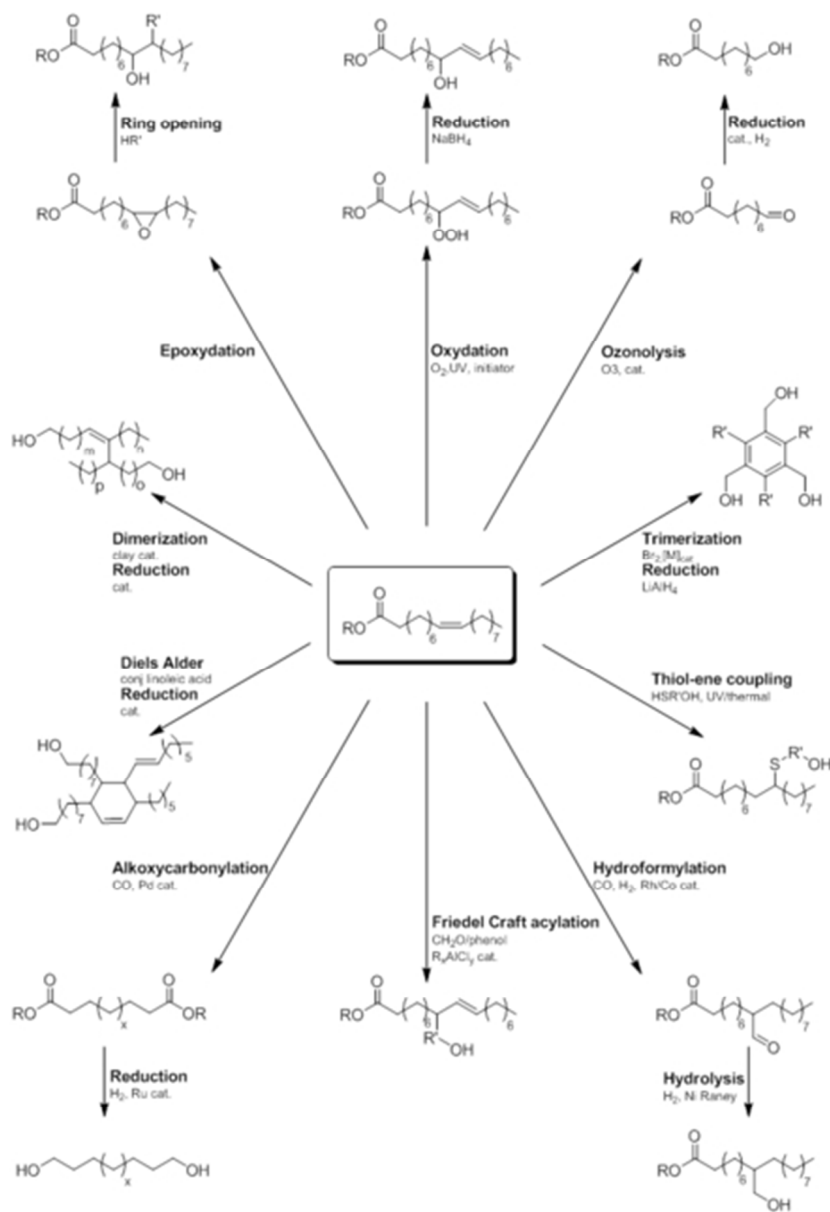




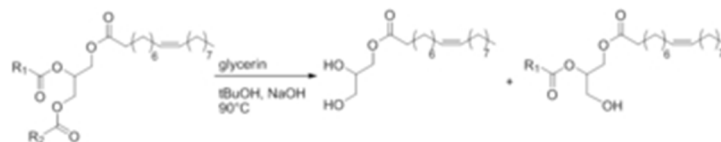
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40x54mm (300 x 300 DPI)



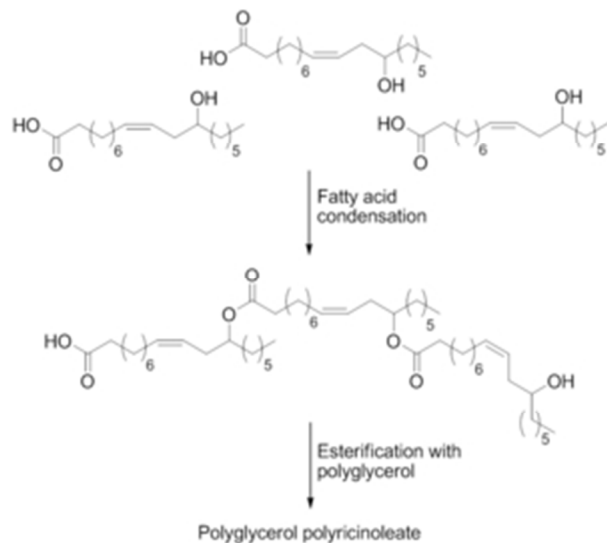
30x22mm (300 x 300 DPI)

Review Only



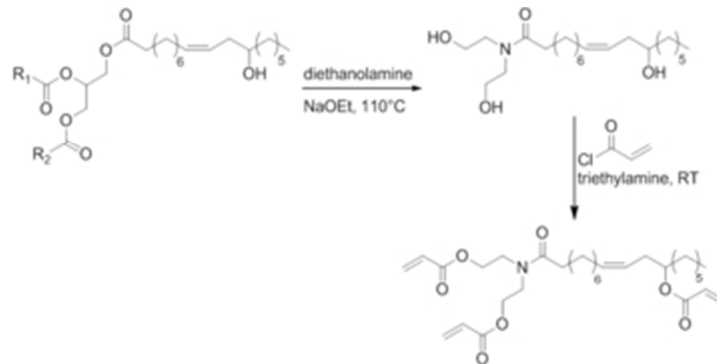
30x22mm (300 x 300 DPI)

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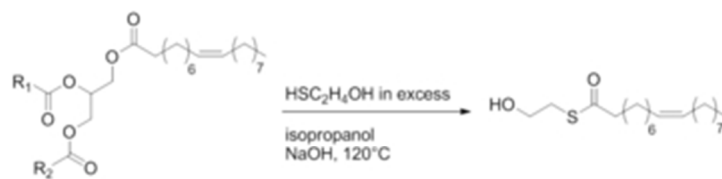
30x22mm (300 x 300 DPI)

Review Only



30x22mm (300 x 300 DPI)

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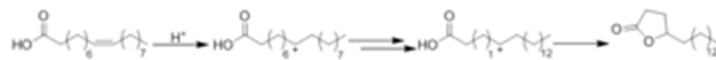


30x22mm (300 x 300 DPI)

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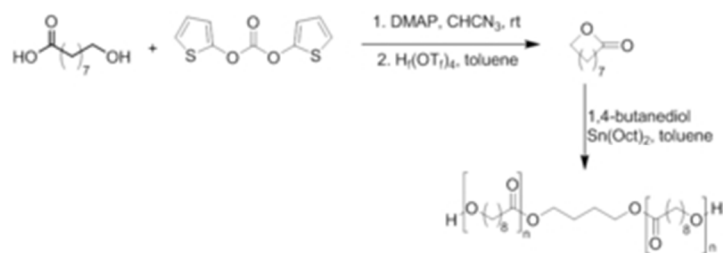


30x22mm (300 x 300 DPI)

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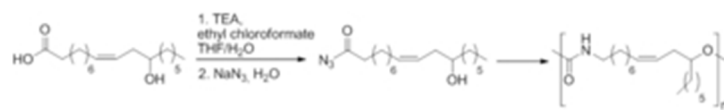






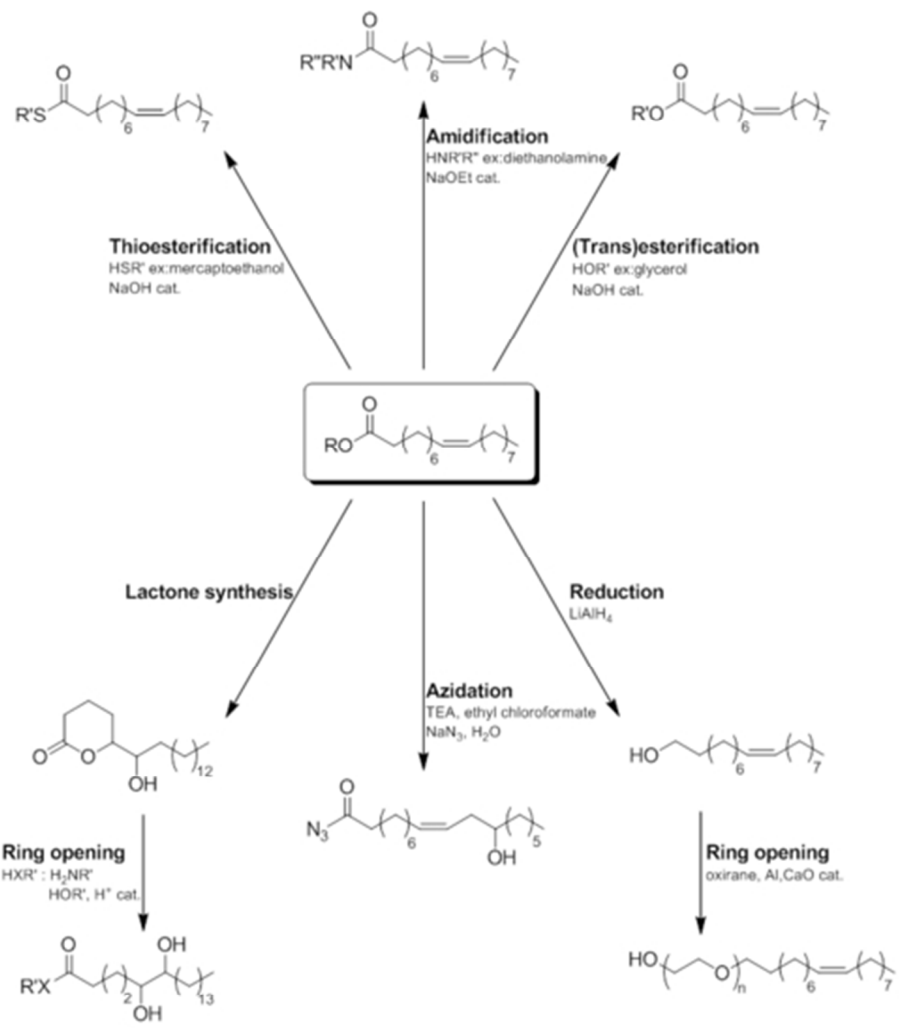
30x22mm (300 x 300 DPI)

Review Only



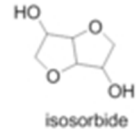
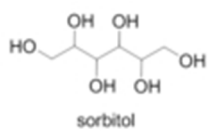
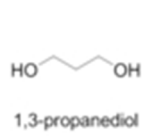
30x22mm (300 x 300 DPI)

Review Only



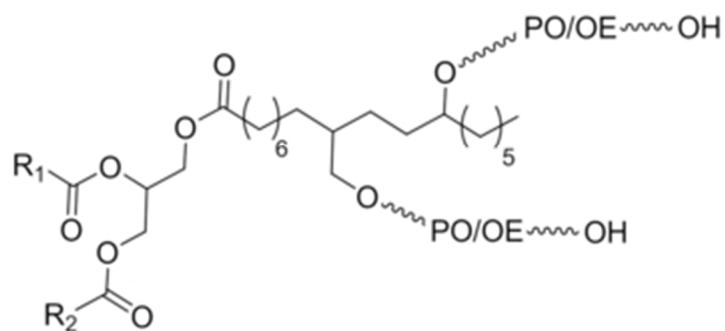
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