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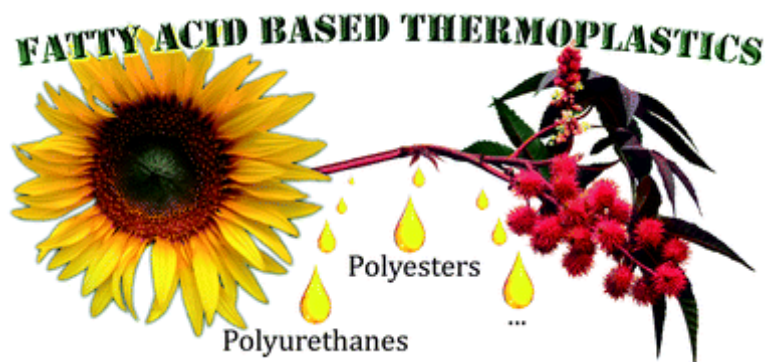
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Structure–properties relationship of fatty acid-based thermoplastics as synthetic polymer mimics

[Lise Maisonneuve](#), [Thomas Lebarbé](#), [Etienne Grau](#) and [Henri Cramail](#)*

Abstract

Nowadays the use of vegetable oils as polymer precursors is the subject of growing interest in the academic and industrial communities. Many synthetic pathways can be pursued from natural vegetable oils to yield different functionalized derivatives – also called synthons – and polymers, such as polyesters, polyurethanes, polyamides, *etc.* Herein, we widely overview recent progress in the preparation of vegetable oil-based thermoplastic polymers and, more precisely, thermoplastic polyesters and polyurethanes. Extra focus is also placed on the synthesis sustainability of these polymeric materials *via* atom efficient techniques, “green” catalyses and processes. The achievable bio-sourced polymers cover a wide range of thermo-mechanical properties that can respond to most of the current applications of synthetic polymers.





From left to right: Etienne Grau, Thomas Lebarbé, Lise Maisonneuve and Henri Cramail

Lise Maisonneuve received her Masters degree from the Polytechnic Institute of Bordeaux (ENSCBP) in 2010. She performed her masters thesis in the team of Dr P. Navard and Dr T. Budtova at the Centre for Material Forming (CEMEF, CNRS-MINES ParisTech), working on the functionalization of cellulose films. She is currently completing her PhD, funded by the ANR 'Polygreen', in the team of Prof. H. Cramail at the Laboratory of Chemistry of Organic Polymers (LCPO, CNRS-University of Bordeaux). Her PhD work mainly focuses on the synthesis of sustainable non-isocyanate thermoplastic polyurethanes from vegetable oils.

Thomas Lebarbé

Thomas Lebarbé received his Masters degree from the Polytechnic Institute of Bordeaux (ENSCBP) in 2010. His masters thesis was conducted in the group of Dr V. Héroguez at the Laboratory of Chemistry of Organic Polymers (LCPO) in Bordeaux, working on the synthesis of bio-functionalized nanoparticles by Ring Opening Metathesis Polymerization (ROMP). Since then, he has been a PhD student at the University of Bordeaux (LCPO) in the team of Prof. H. Cramail. His current PhD work, funded by ADEME and ITERG, is focused on the design of aliphatic polyesters from vegetable oils, as poly(L-lactide) toughening agents.

Etienne Grau

Etienne Grau obtained his Masters degree in chemistry from the Ecole Normale Supérieure of Cachan (ENS Cachan). He moved to the University of Lyon, where he received in 2010 his PhD degree studying ethylene polymerization under the guidance of V. Monteil, C. Boisson and R. Spitz. After a post-doc on Ziegler–Natta catalysis in the groups of P. Sautet, C. Copéret and V. Monteil, he joined the group of S. Mecking at the University of Konstanz. Since January 2013, he has been an Assistant Professor at the University of Bordeaux, in the team of Prof. H. Cramail, working on catalysis for bio-based polymers.

Henri Cramail

Henri Cramail received his engineering degree from ENSCPB in 1987 and obtained his PhD from the University of Bordeaux 1, in 1990. After a post-doctoral stay at the University of Durham, U.K., he became an Assistant Professor of Polymer Chemistry at the University of Bordeaux 1. In 1999, he was appointed Professor at the same University. Director of the Laboratory of Chemistry of Organic Polymers (LCPO) since 2007, he is currently leading the team 'Biopolymers and Bio-based Polymers' within LCPO. His research concerns the development of green pathways to bio-based polymers from renewable resources (vegetable oils, carbohydrates, terpenes, CO₂).

I Introduction

Both the limited and uncertain supply and the cost of fossil resources, as well as the environmental impacts of the consumption of non-renewable resources and greenhouse gas emissions have led to a growing interest in the use of renewable resources as potential fossil substitutes in the polymer and material fields. This strategy opens new opportunities to obtain innovative properties, but the range of known properties in current polymers is also required.

Vegetable oils, which are annually renewable, are the most important sustainable raw materials for the chemical industry. Indeed, vegetable oils are already widely used as raw materials for the manufacture of surfactants, cosmetic products, lubricants, paint formulations, coatings and 'resins'. The annual global production of the major vegetable oils in 2011/2012 amounted to 156 million tons.¹ About 20% is devoted to industrial applications mainly as sources of energy (fuels), compared with around 75% and 5% for food and feed utilizations respectively.² Vegetable oils are composed of different triglycerides which are the esterification products of glycerol with three various fatty acids. From these commercial vegetable oils, fatty acids (for instance C18 oleic acid from sunflower, C22 erucic acid from rapeseed and C18(OH) ricinoleic acid from castor oil) are also available in such purity that they can be used for chemical conversions as well as for the direct synthesis of polymers. Other very useful shorter fatty acids are commercialized such as azelaic, sebacic, undecenoic and brassylic acids. C9 azelaic dicarboxylic acid can be obtained by ozonolysis of oleic acid. Alkali pyrolysis of ricinoleic acid produces the C10 sebacic dicarboxylic acid and pyrolysis of ricinoleic acid gives the C11 undecenoic acid. Oxidation of erucic acid yields the C13 brassylic dicarboxylic acid.

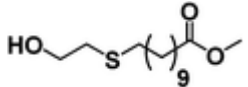
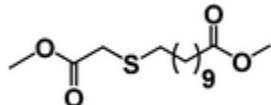
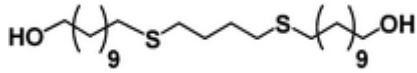
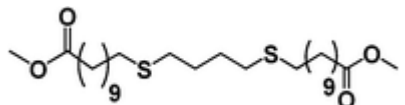
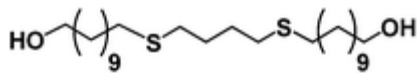
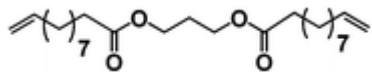
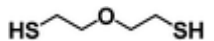
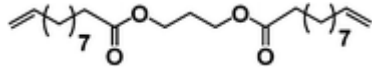
In addition, fatty acids are good candidates for biocompatible and biodegradable polymers, as they are natural body components containing hydrolyzable bonds.³

A remarkably large series of papers and reviews investigated the functionalization of triglycerides to obtain interesting monomers for the synthesis of polymer thermosets. One main problem encountered in this chemistry is the heterogeneity and variability of the triglycerides used, due to the statistical distribution of fatty acids per triglyceride, which does not allow a fine correlation between the material properties and the monomer structures. In light of this, the purpose of this review is to widely overview recent progress in the preparation of fatty acid-based thermoplastic polymers and more precisely thermoplastic polyesters and polyurethanes. Vegetable oil derivatives have chemical structures different from conventional petrochemical stocks that can offer polymers with specific properties. Therefore, it is interesting to highlight the conventional polymer properties that are now available from fatty acid resources and to assess the main challenges and opportunities of such thermoplastic polymers. The use of difunctional fatty acid-based monomers with a well-defined molecular structure that can lead to bio-based polymers with precise properties will be discussed. Moreover, the significant use of more sustainable synthetic methodologies such as the thiol-ene reaction, click chemistry, metathesis, non-isocyanate chemistries, and enzymatic catalysis will also be underlined in this review. Various classes of thermoplastic polymers will be described with a special focus on two important families, *i.e.* thermoplastic polyesters and polyurethanes.

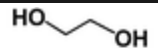


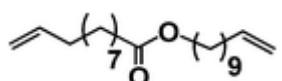
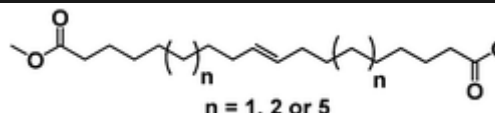
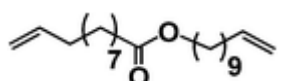
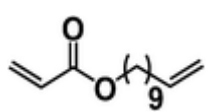
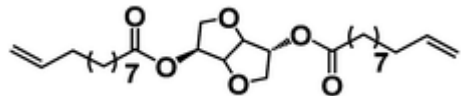
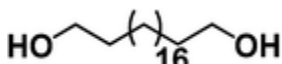
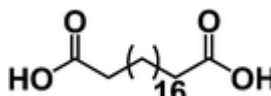
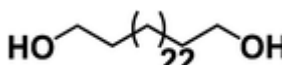
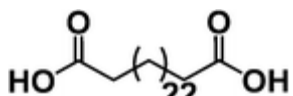
II Polyesters

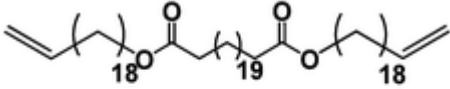
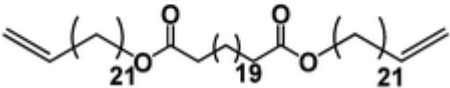
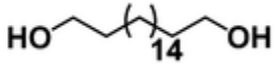
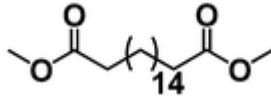
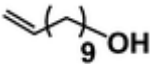

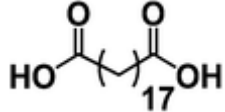

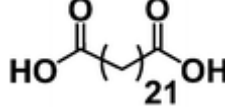
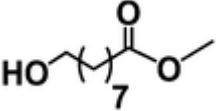
Aliphatic polyesters constitute a polymer family that has been extensively studied since the pioneering work of Carothers. This class of materials has gained widespread interest in the past years due to the growing demand for environmentally friendly and biodegradable polymers. Indeed the ester linkage is known to be hydrolysable and degradable, thus polyesters are prone to degradability under specific conditions. Biodegradability is often mentioned for aliphatic polyesters as these materials can degrade because of the action of naturally occurring microorganisms such as bacteria, fungi and algae. Due to their lower impact on the environment, aliphatic polyesters are no longer restricted to biomedical applications, but have great potential in packaging applications, elastomers, *etc.* Hydroxylic and carboxylic derivatives are easily obtained from biomass, which enables an easy chemical or biochemical synthesis of strategic building blocks. Indeed poly(lactic acid) and poly(hydroxyalkanoate)s represent the two main examples of commercialized bio-based polymers.⁴⁻⁶ These polymers are usually obtained from carbohydrate fermentation. However, plant oils and more particularly fatty acids represent promising feedstock for aliphatic polyester formation as the substrate already provides aliphatic acidic or ester functions. Depending on the chemistry used, a huge range of different polyesters has been obtained (see [Table 1](#)). In this section, we summarize recent developments in the synthesis of aliphatic polyesters starting from fatty acid derivatives.

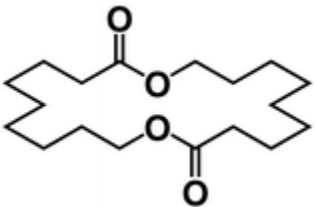
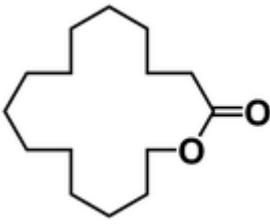
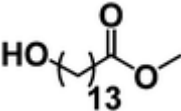
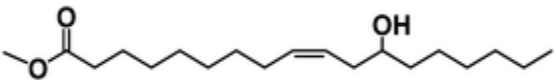
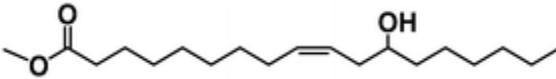


Table 1 Summarized literature concerning fatty acid based precursors for thermoplastic polyesters

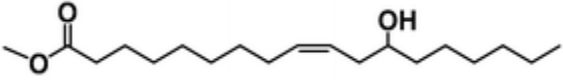
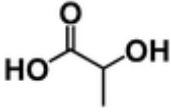
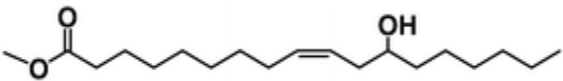
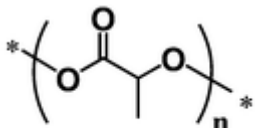
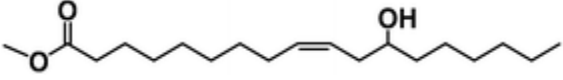
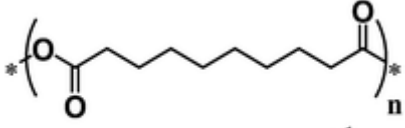
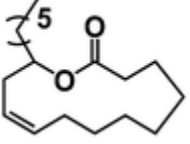
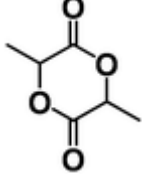
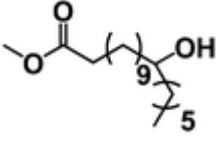
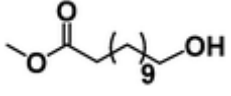
Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
	—	5850	—	66	Thiol-ene, $T_{5\%} = 344$ °C	8
		8900	—	62	Thiol-ene, $T_{5\%} = 353$ °C	8
		9400	—	71	Thiol-ene, $T_{5\%} = 350$ °C	8
		11 850	—	44	Thiol-ene	9
	—	8300	—	45	ADMET, addition of chain stopper (6.5 mol%)	9

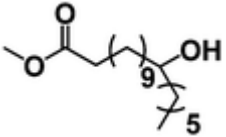
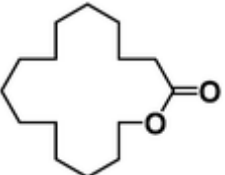
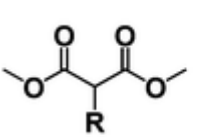
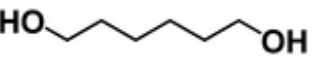
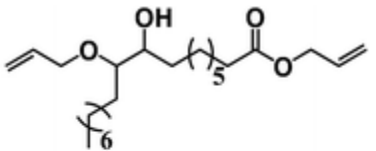
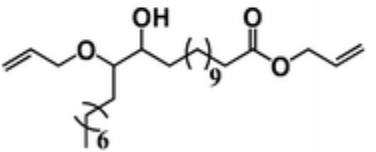
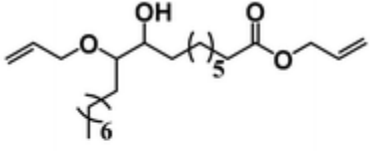
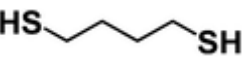
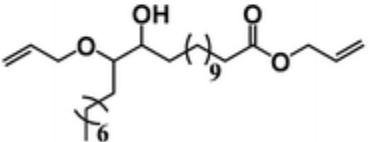
Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
		6100 19300	to -31 to -8	17 126	to Increase of the Young's modulus with the amount of amide functions (83 to 363 MPa)	10
		20800 22600	to -15 to 18	48 to 87	Young's modulus from 234 to 586 MPa	11
<p>n = 1, 2 or 5</p>	—	69100 99800	to —	—	ADMET	15

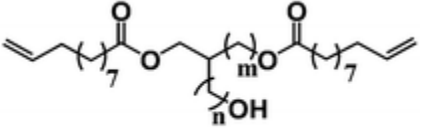
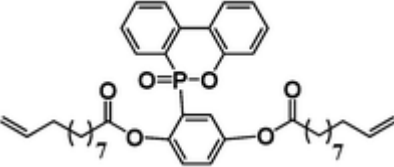
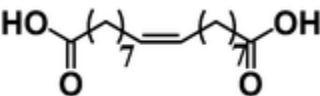
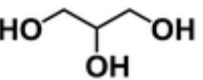
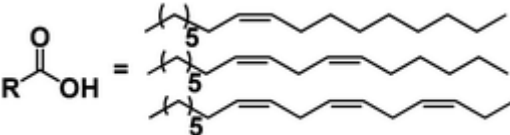
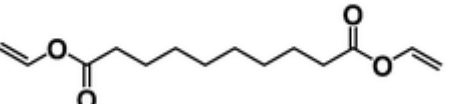
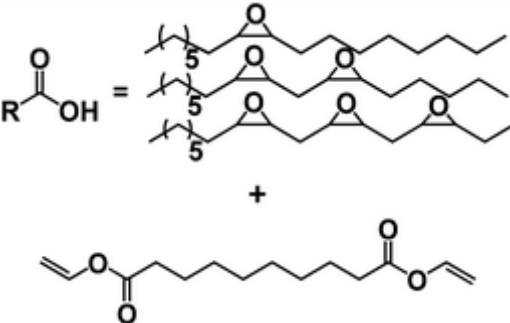
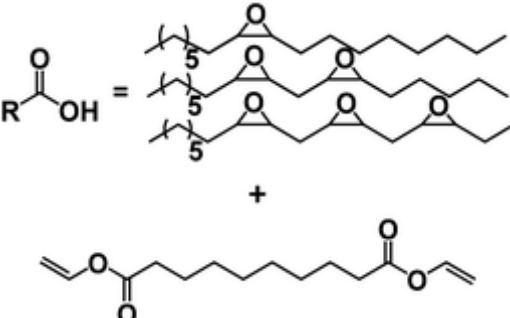
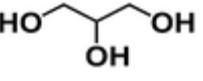
Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
   	 $n = 1, 2 \text{ or } 5$	21 400 to 109 200	—	53 to 92	ΔH_m from 55 to 117 J g ⁻¹ , $T_d > 320$ °C	15
	—	8700 to 26 500	—	—	ADMET, use of a PEG chain stopper led to block copolymer formation	16
	—	2300 to 8900	—	—	ADMET, formation of star-shaped polyesters when a triacrylate core was used	18
	—	4400 to 8400	—	17 to 56	ADMET, melting point highly dependent on the degree of isomerization	23
		10 000	—	108	$\Delta H_m = 151$ J g ⁻¹ , $T_c = 83$ °C	26
		14 100 to 24 000	—	104	$T_c = 92$ °C (ref. 27), 114 (ref. 28), $\Delta H_m = 160$ J g ⁻¹ (ref. 28)	27 , 28



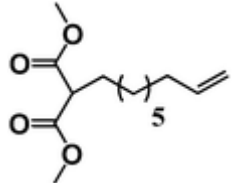

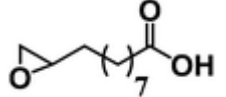
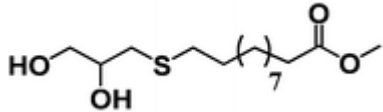
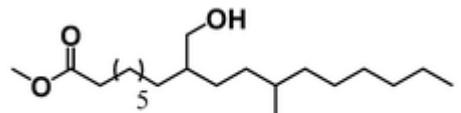
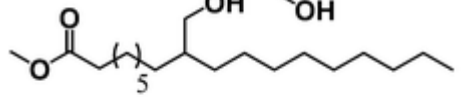
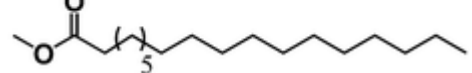
Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
   Mixture with C21 diol (C18:C21 = 73:27)	<p>—</p>  Mixture with C21 diester (C18:C21 = 73:27)	10 000, 10 000	—	109, 111	ADMET, $T_c = 90$ °C, $T_c = 93$ °C, $\Delta H_m = 182$ J g ⁻¹ , $\Delta H_m = 176$ J g ⁻¹	28
	Carbon monoxide	2000 to 23 000	—	55 to 70	About 20 to 30% of the repeat units are branched	30
		$M_w \sim$ 20 000	—	103	$\Delta H_m = 140$ J g ⁻¹	31 an d 32
		$M_w \sim$ 20 000	—	99	$\Delta H_m = 180$ J g ⁻¹	31 an d 32
	—	$M_w \sim$ 62 000	-38	70	$T_c = 57$ °C, $\Delta H_m =$ 94 J g ⁻¹ , Young's modulus = 200 MPa	35

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
	—	5000 to 7000	—	69	Ring-opening polymerisation, $\Delta H_m = 33\text{--}39$ J g ⁻¹	36
	—	25 000 to 480 000	-27	~100	Ring-opening polymerization, crystallinity ~60%, Young's modulus = 370 MPa, elongation at break ~100–600%	40 42 an d 47
	—	M_w from 53 000 to 140 000	-30	94	$\Delta H_m = 120$ J g ⁻¹ , Young's modulus ~420 MPa, elongation at break ~700%	54
	—	$M_w \sim 98\,000$	-75	—	Lipase catalysis, the resulting polymer was then cross-linked using dicumyl peroxide	58
	<p>Dimer diol</p>  	M_w from 724 to 4850	—	-19 to -7 °C	Lipase catalysis, potential use as biolubricants	57

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
		M_w from 2700 to 7800	—	From 55 to 98 °C	Direct polycondensation, various ricinoleic acid to lactic acid ratios	60
	 $M_n = 41\ 000\ \text{g}\cdot\text{mol}^{-1}$	M_w from 5600 to 14 000	—	From 93 to 147 °C	Transesterification of PLA by ricinoleic acid followed by repolymerization	60
	 $M_w = 37\ 000\ \text{g}\cdot\text{mol}^{-1}$	From 2000 to 60 000	—	From 24 to 77 °C		61
		M_w from 5700 to 16 200	—	From 105 to 189 °C	Polymerization by ROP, low reactivity of the ricinoleic acid lactone	66
		M_w around 100 000	—	From -56 to 85 °C	Lipase catalysis, decrease of the Young's modulus with the amount of 12-hydroxystearic acid	37

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
		M_w around d 250 000			From 43 to 96 °C Lipase catalysis, Young's modulus from 3 to 367 MPa	68
 <div style="border: 1px solid black; padding: 5px; display: inline-block; margin-top: 10px;"> <p>R = C₆H₁₃ C₈H₁₇ C₁₀H₂₁ C₁₂H₂₅ C₁₄H₂₉ C₁₆H₃₃</p> </div>		From 9000 to 17 000	-65 and -68 °C for R = C ₆ H ₁₃ and R = C ₈ H ₁₇ respective ly	From -35 to 27 °C	Increase of crystallinity and T_m with an increase of the dangling chain length	69
	—	From 4450 to 18 200	-55 °C, —	—, -25 °C	ADMET	73
						
		8600, 13 750	-63 °C, -48 °C	—, -18 °C	Thiol-ene addition polymerization	73
						

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
 <p>$n=0, m=1$ and $n=1, m=0$</p>		From 3700 to 7300	From -25 to 6 °C	From 22 to 41 °C	ADMET, use as flame-retardant materials, increase of the T_g and T_m with the content of phosphorus moiety	74
		From 1700 to 6000	—	From -33 to 14 °C	Lipase catalysis, formation of hyperbranched structures	76
 <p>+</p> 		From 3900 to 8500	—	—	Lipase catalysis	78
		From 4200 to 6500	—	—	Lipase catalysis	77

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g (°C)	T_m (°C)	Comments	Ref
		$M_w = 39\,000$	—	33 °C	Lipase catalysis	79
		10 200	-74 °C	—	Modification of the dangling terminal double bond by thiol-ene or cross-metathesis	80
	—	32 900	-8 °C	97 °C	Young's modulus = 198 MPa, elongation at break = 450%	81
	—	From 11 400 to 60 400	Around -10 °C	Around 45 °C	Hyperbranched polyester, degree of branching between 0.38 and 0.54	8 an d 87
	—	From 2130 to 41 990	—	—	Hyperbranched polyester	88
	—					
	—					

II.1 Semi-crystalline aliphatic polyesters: toward polyethylene mimics

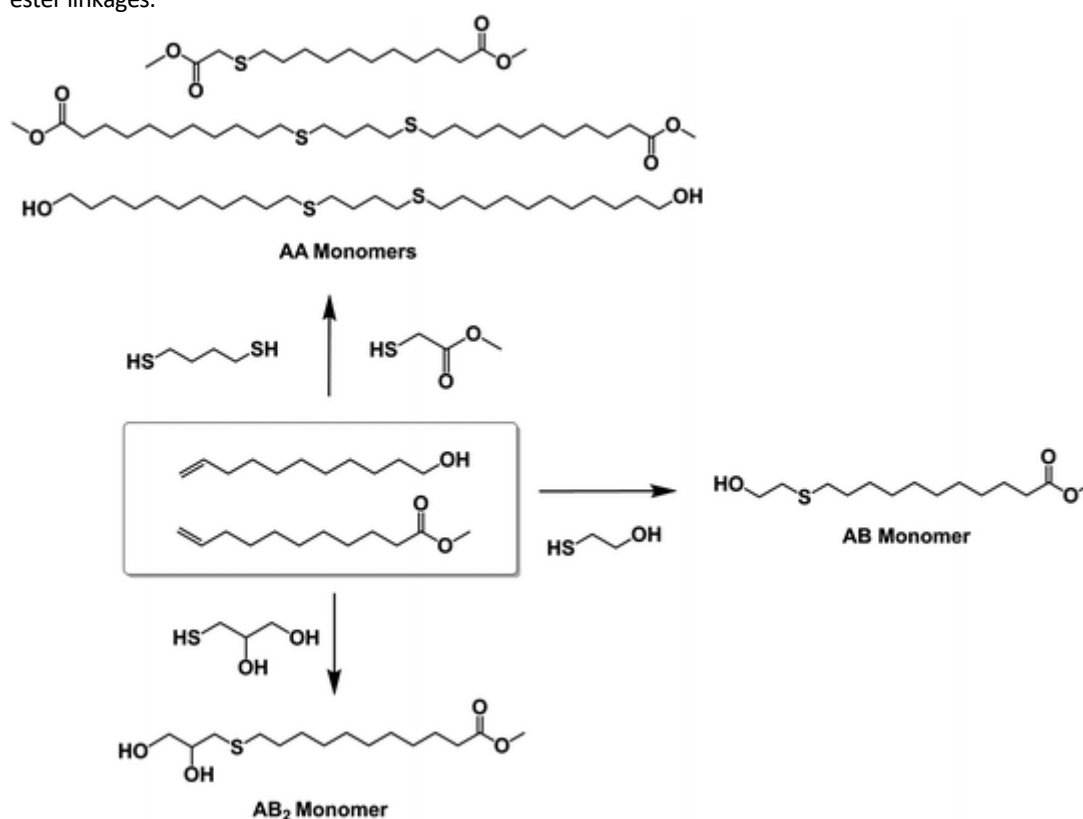
It is of high interest to find “greener” alternatives to polyolefins (polyethylene, polypropylene) in order to lower the carbon footprint of this huge class of materials. Recent efforts to find new pathways to biopolyolefin production have led to the development of biopolyethylene (bioPE) from ethanol.⁷

Another approach is to design a new class of bio-based building blocks that can lead to polymers with similar properties to polyethylene while presenting original features such as biodegradability and polarity. Ester linkage can solve these issues, thus it is important to develop polyesters that could mimic polyethylene or other polyolefins.

Polyethylene mimics can be obtained by a significant increase of the number of methylene units between two ester functions while keeping a purely linear structure in order to dilute the ester functions and thus to tend to the polyethylene crystal structure. To this aim, fatty acids from plant oils represent the perfect feedstock, as fatty acids already contain long alkyl chain linear segments. A number of investigations have been done to introduce bifunctionality to these fatty acids as they usually contain one carboxylic acid function and one double bond that need to be activated for step growth polymerization.

II.1.1 Thiol–ene click reaction

One type of double bond modification is based on the thiol–ene click reaction that can bring either an alcohol or a carboxylic function to a fatty acid backbone. In a first example, Meier's group described an efficient route to the development of a set of renewable monomers for polyester synthesis.⁸ Starting from castor oil derivatives, *i.e.* methyl 10-undecenoate and 10-undecenol, they synthesized various monomers ranging from hydroxyl methyl ester, diol and methyl diesters by using several thiols such as mercaptoethanol, butanedithiol, methylthioglycolate and thioglycerol in solvent-free conditions (Scheme 1). The obtained monomers were then polymerized, using TBD as a transesterification catalyst, leading to purely linear aliphatic polyesters bearing thio-ether linkages. The thermal properties of the resulting polymers revealed melting points ranging from 50 °C to 71 °C and thermal stabilities up to 300 °C. The structure–property relationship revealed higher crystallization ratio and higher melting points for longer chain lengths between ester linkages.



Scheme 1 Synthesis of condensable monomers by the thiol–ene click reaction.⁸

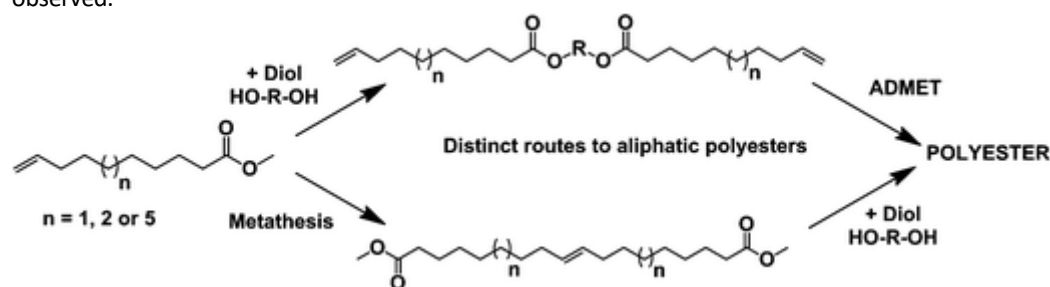
The same group used a bis-unsaturated diester, obtained by transesterification of methyl 10-undecenoate with bio-based 1,3-propanediol, as the starting material for polyester synthesis by thiol–ene addition with bis(2-mercaptoethyl) ether or ADMET polymerization using Zhan catalyst.⁹ Higher molecular weights were obtained for polyesters obtained from thiol–ene polyaddition. Nevertheless, the melting points of the so-formed materials, 44–45 °C, were similar regardless of the polymerization techniques. It should be noted that degradation of such polyesters under enzymatic or acidic conditions was demonstrated in order to target biomedical applications.

Recently, our group also employed thiol–ene addition to introduce hydroxyl functionalities on unsaturated diester or diamide compounds obtained from methyl 10-undecenoate.¹⁰ The resulting diols were condensed with a methyl diester obtained by self-metathesis of methyl 10-undecenoate yielding various polyesters and poly(ester-amide)s. Melting points of these polyesters and poly(ester-amide)s ranged from 17 °C to 126 °C while low T_g values were obtained (from –31 °C to –8 °C) due to the purely aliphatic nature of these polymers. Higher melting points were obtained thanks to the incorporation of cohesive functions such as amide functions in the polymer backbone. This strategy to obtain more robust fatty-acid based materials was previously used by Narine and coll.¹¹ The authors prepared three novel α,ω -amine precursors from methyl oleate. These precursors having different ratios of amine and ester functions were then polymerized using azelaoyl chloride as the comonomer. The structure–property relationship of these poly(ester-amide)s was clearly identified by studying the evolution of the thermo-mechanical properties with the hydrogen bond density resulting from the presence of amide functions in the polymer backbone. As expected, the T_g and the melting point of the poly(ester-amide)s increased with an increase of the hydrogen bond density. Mechanical properties were also highly affected by the presence of the amide functions as seen from the reduction of the Young's modulus (from 586 MPa to 234 MPa) and ultimate tensile strength (from 19.6 MPa to 8.5 MPa) values with the decrease of the amide to ester ratio.

II.1.2 Metathesis and ADMET

Functional monomers from unsaturated fatty acids can be obtained from the metathesis reaction. Thanks to the presence of double bonds in the chemical structure of fatty acids, olefin metathesis with oleochemicals has been extensively investigated since the development of function tolerant catalysts.^{12–14}

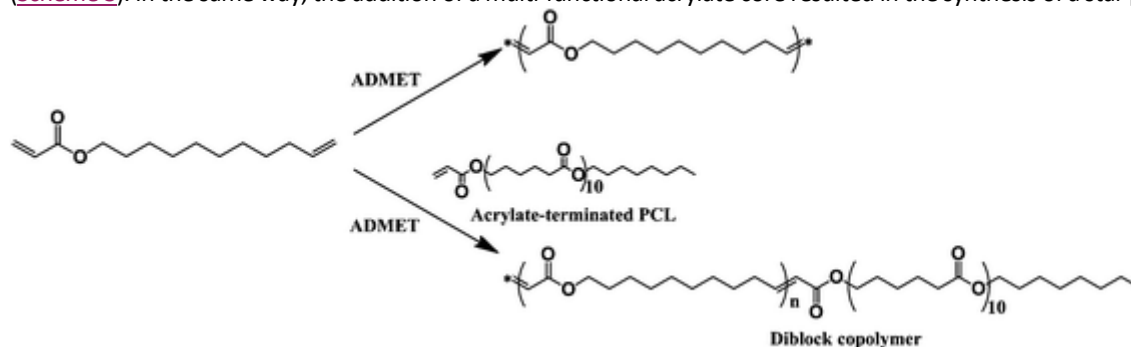
To illustrate these recent pathways to functional monomers, Warwel and coll. used ω -unsaturated fatty acids in self-metathesis reactions to obtain diesters that were polycondensed with diols.¹⁵ First the ω -unsaturated fatty acids were obtained by ethenolysis using various oils. These unsaturated compounds were then dimerized using homogeneous ruthenium or tungsten alkylidene complexes leading to C26, C20 and C18 symmetrical unsaturated diesters. These uncommon long unsaturated diesters were then polymerized with ethylene glycol, 1,4-butanediol or 1,4-bis(hydroxymethyl)cyclohexane by using $\text{Ca}(\text{ac})_2/\text{Sb}_2\text{O}_3$ or $\text{Ti}(\text{O}i\text{Bu})_4$ as the catalytic system. High molecular weights in the range of 21–109 kg mol⁻¹ were obtained. These polyesters showed melting points ranging from 53 °C to 92 °C depending on the monomers used. The authors also investigated a different pathway to obtain the same polymers using ADMET polymerization of a bis-unsaturated diester (Scheme 2). Similar melting points but lower molar masses were observed.



Scheme 2 Distinct pathways to unsaturated polyesters starting from ω -unsaturated fatty acid derivatives.¹⁵

Several studies based on this concept were done in the past years to always incorporate a higher number of methylene units between the ester functions and achieve purely saturated aliphatic features. For instance Meier and Rybak reported the synthesis of an α,ω -diene by using the transesterification of 10-undecenoic acid with the corresponding alcohol (10-undecenol).¹⁶ ADMET of this 100% sustainable monomer resulted in an unsaturated polyester bearing 20 carbons between the ester functions. The possibility to control the polyester molecular weights was demonstrated using a monofunctional chain stopper such as methyl 10-undecenoate. Based on the same principle, ABA triblock copolymers were prepared by adding an oligo(ethylene glycol) methyl ether acrylate as the end-capping agent.

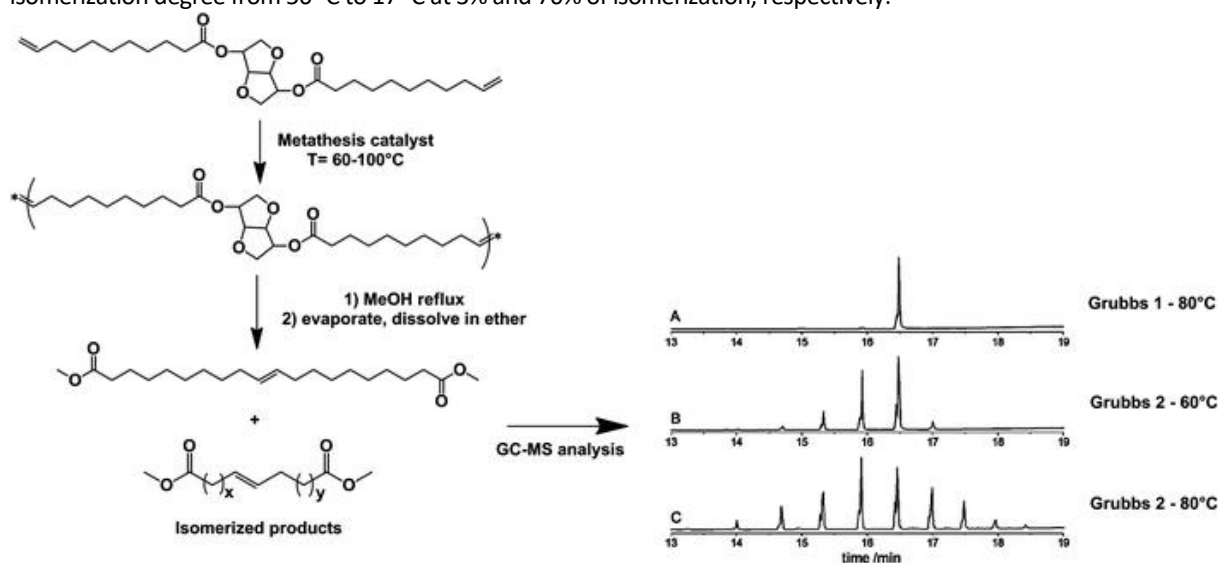
To further control the molecular architecture, the same group took advantage of the high selectivity of the cross-metathesis reaction between acrylates and terminal alkenes.^{17,18} Using 10-undecenyl acrylate, a head-to-tail polymer was obtained by ADMET polymerization. Moreover, by adding a polymeric chain containing a terminal acrylate function as the end-capper, such as acrylate-terminating poly(ϵ -caprolactone), the formation of a diblock copolymer was observed (Scheme 3). In the same way, the addition of a multi-functional acrylate core resulted in the synthesis of a star polymer.



Scheme 3 Head-to-tail ADMET polymerization of 10-undecenyl acrylate.¹⁸

Such metathesis reactions, especially with 2nd generation catalysts,¹⁹ exhibit side reactions such as isomerization of the unsaturation. This creates a flaw in the polyester structure decreasing its thermo-mechanical properties. Different parameters, such as the temperature or catalyst nature, can suppress or limit double bond isomerization.²⁰⁻²²

Fokou and Meier evaluated the influence of the reaction temperature and catalyst nature on the degree of isomerization during the ADMET reaction of a 100% renewable bis-unsaturated diester formed by transesterification of methyl 10-undecenoate with isosorbide.²³ To this aim, the synthesized polyesters were degraded and analyzed by GC-MS to determine the degree of isomerization (Scheme 4). With Grubbs' 2nd generation catalyst, high degrees of isomerization were observed: from 48% at 60 °C to 69% at 80 °C. For Grubbs' 1st generation catalyst, isomerization remains extremely low even at 80 °C (4%). As expected, the thermo-mechanical properties of the resulting polyesters were highly dependent on the degree of isomerization. Indeed the melting temperature decreases with the isomerization degree from 56 °C to 17 °C at 3% and 76% of isomerization, respectively.

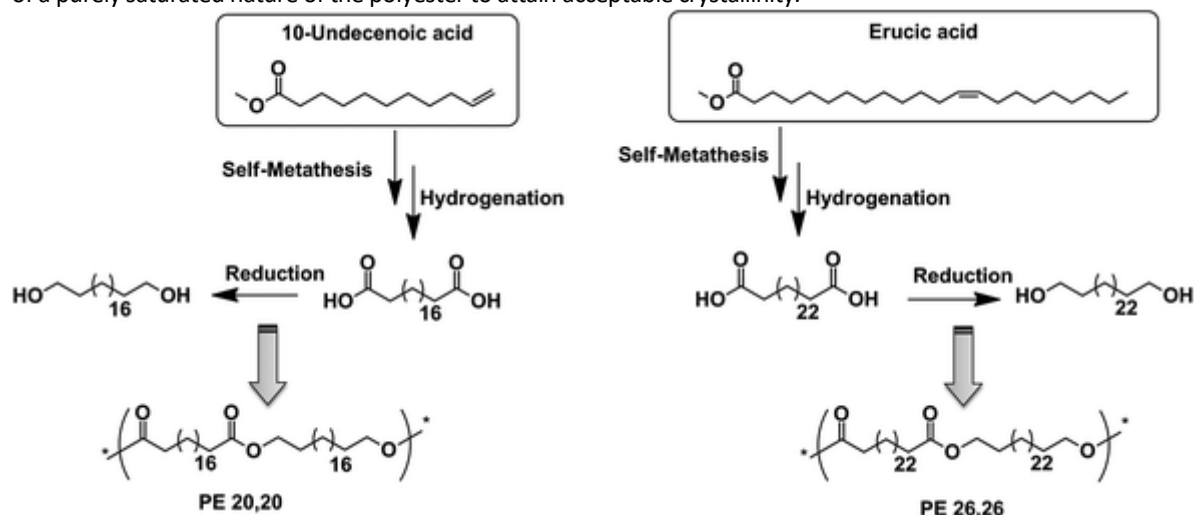


Scheme 4 Investigation of the dependence of isomerization reactions on temperature and nature of catalyst during ADMET of a 100% biobased monomer.²³

The limitation of isomerization, when 2nd generation catalysts are used, can be overcome by adding 1,4-benzoquinone, known to be a very efficient additive that prevents isomerization. The isomerization decreased from 91% at 80 °C using the Hoveyda–Grubbs 2nd generation catalyst to 18% when 2 mol% benzoquinone was added.^{24,25} This study shows that a good control of the polymer microstructure is possible even with 2nd generation metathesis catalysts.

All the described examples of aliphatic polyesters obtained by metathesis showed promising thermo-mechanical properties; however melting points are too low to expect similar thermal properties to polyethylene. This is partially due to the remaining internal double bonds in the final polymer structure that limit the crystallization. To overcome this limitation, Mecking and coll. used a metathesis reaction to synthesize an unsaturated α,ω -dicarboxylic acid by coupling

two undecenoic acid fragments.²⁶ This compound was hydrogenated to yield a purely saturated long chain C20 diacid. The reduction of this diacid using LiAlH₄ afforded the corresponding C20 diol. Polycondensation of these two monomers catalyzed by titanium alkoxides in bulk yielded a polyester 20,20 with a molecular weight of 10 kg mol⁻¹ and a melting point of 108 °C (Scheme 5). Similar thermal properties (*T_m* = 103 °C) were observed for the hydrogenated polymer resulting from the ADMET polymerization of undecenyl undecenoate. The large difference in terms of thermo-mechanical properties (+40 °C in melting points) of the saturated and unsaturated polyesters highlights the importance of a purely saturated nature of the polyester to attain acceptable crystallinity.



Scheme 5 Long chain aliphatic polyesters prepared by polycondensation of monomers obtained from 10-undecenoic acid and erucic acid.^{26,27}

By following the same strategy, erucic acid [(*Z*)-docos-13-enoic acid], a monounsaturated fatty acid readily available from rapeseed or cramble oils, was converted into a 1,26-diacid and diol.²⁷ These two monomers were polycondensed yielding a polyester 26,26 with a molecular weight of 14 kg mol⁻¹ (Scheme 5). This polyester showed a melting transition at 104 °C with a temperature corresponding to 5 wt% degradation equal to 386 °C. The crystal structure corresponds to the one of polyethylene since similar wide-angle X-ray diffractionspectra were observed.

Very recently, Mecking and coll. extended the library of long-chain aliphatic polyesters obtained from plant oils by describing new polyesters 38,23 and 44,23 by ADMET.²⁸ After hydrogenation of these polyesters, the measured melting points were 109 °C and 111 °C showing no increase compared to PE 26,26. This feature underlines that a much higher dilution of the ester functions in the polymer backbone is necessary to achieve, as an asymptote, polyethylene thermo-mechanical properties.

All the above studies using metathesis of fatty acid derivatives were performed on relatively pure compounds thus increasing the number of steps necessary to obtain polyesters from the crude plant oil. Recently, Meier and coll. demonstrated that a mixture of fatty acid methyl esters with a high ratio of polyunsaturated ones can constitute a very efficient material to obtain α,ω -difunctional monomers by self-metathesis.²⁹ Indeed, volatile products such as 1,4-cyclohexadiene, hex-3-ene, non-3-ene, dodec-3-ene and dodec-6-ene can be easily removed from the equilibrium reaction mixture thus shifting the equilibrium toward the desired α,ω -diester. From this approach, the authors isolated a mixture of C18 and C21 α,ω -diesters (C18 being predominant) that were subsequently hydrogenated and reduced to form the saturated mixture of diols. Both diesters and diols were then polycondensed to produce an aliphatic long-chain polyester with a melting point of 95 °C.

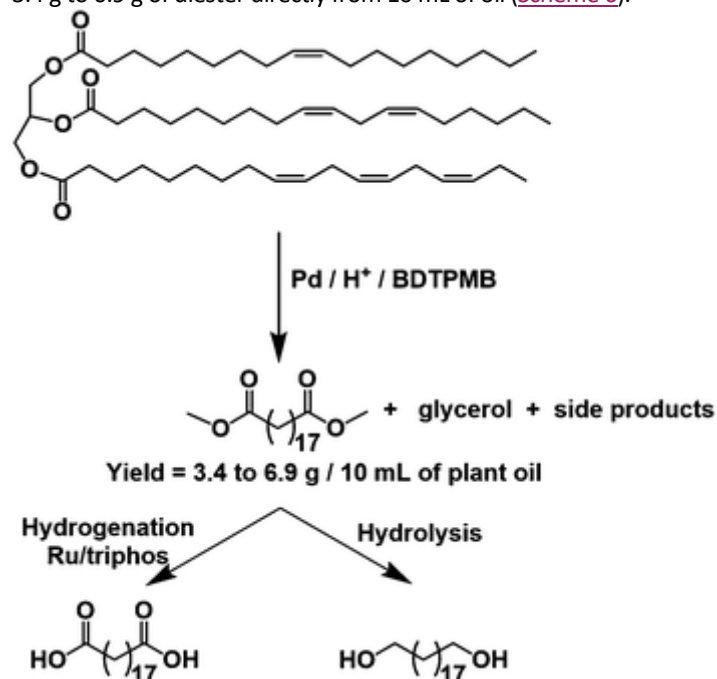
This section clearly demonstrates that metathesis reaction represents a powerful tool for the design of polyethylene-like materials. Moreover the easy hydrogenation of the resulting monomers or polymers allows the synthesis of highly crystalline materials.

II.1.3 Carbonylation/isomerizing alkoxy-carbonylation

Another route to obtain semi-crystalline linear polyesters from fatty acids is based on the alkoxy-carbonylation methodology. Quinzler and Mecking used the $[\text{Co}_2(\text{CO})_8]$ /pyridine catalytic system for the copolymerization of undec-1-en-10-ol with carbon monoxide (CO).³⁰ Molecular weights up to 23 kg mol^{-1} were achieved at high temperature ($160 \text{ }^\circ\text{C}$) and high pressure of CO ($>100 \text{ bar}$). ^1H and ^{13}C NMR studies revealed the presence of some alkyl branches as a result of 2,1-insertion of terminal double bonds or reaction of internal double bonds caused by isomerization thus leading to a complex melt behavior around $65 \text{ }^\circ\text{C}$.

The same group reported the efficient carbonylation of methyl oleate and methyl erucate by exposure to carbon monoxide in methanol or ethanol respectively in the presence of catalytic amounts of $\text{Pd}(\text{OAc})_2$, 1,2-bis[(di-*tert*-butylphosphino)methyl]benzene and methanesulfonic acid³¹ or bis(trifluoromethanesulfonato){1,2-bis(di-*tert*-butylphosphinomethyl)benzene}palladium(II)^{32,33} which exhibit enhanced activity and selectivity toward linear esters. By this way, C19 and C23 diesters were obtained when using methyl oleate and methyl erucate, respectively. Reduction of these diesters afforded the corresponding C19 and C23 diols that were subsequently polycondensed with their respective diacids. The resulting polyester 19,19 showed a melting transition at $103 \text{ }^\circ\text{C}$ while polyester 23,23 melts at $99 \text{ }^\circ\text{C}$. Wide-angle X-ray scattering revealed a degree of crystallinity of 70% for polyester 19,19 and 75% for polyester 23,23, values close to the one of polyethylene. Polyamides were also synthesized starting from the C19 and C23 diesters. The resulting properties will be discussed in the polyamide part.

To further target industrial applications of this synthetic method to α,ω -diesters, Cole-Hamilton and coll. reported an elegant route concerning the methoxycarbonylation of various commercial plant oils such as olive, rapeseed or sunflower oil.³⁴ To this aim, a palladium-based catalyst modified by the ligand bis(di-*tert*-butylphosphinomethyl)benzene (BDTPMB) was used and afforded the diesters in good yield ranging from 3.4 g to 6.9 g of diester directly from 10 mL of oil (Scheme 6).

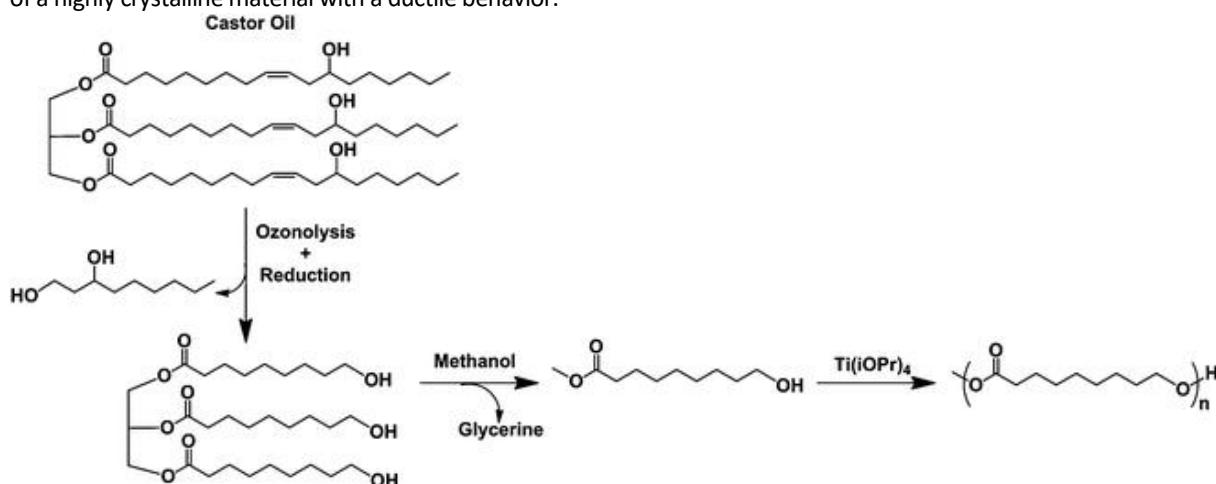


Scheme 6 Synthesis of α,ω -diesters and diols by methoxycarbonylation of commercial plant oils.³⁴

II.1.4 Other methodologies

Using a totally different approach, Petrović and coll. synthesized an oil-based polyester using 9-hydroxynonanoic acid methyl ester as an AB monomer.³⁵ To obtain this hydroxyl fatty acid methyl ester, ozonolysis of castor oil was first carried out followed by reduction and subsequent methanolysis of the triglyceride polyol. The resulting methyl 9-hydroxynonanoate was then polymerized using $\text{Ti}(\text{IV})$ isopropoxide as the transesterification catalyst (Scheme 7). A high molecular weight, 62 kg mol^{-1} , polyester was obtained. This polyester was revealed to be close to poly(ϵ -caprolactone)

with a higher melting point (70 °C), higher T_g and better thermal stability. Tensile properties of this polyester were typical of a highly crystalline material with a ductile behavior.

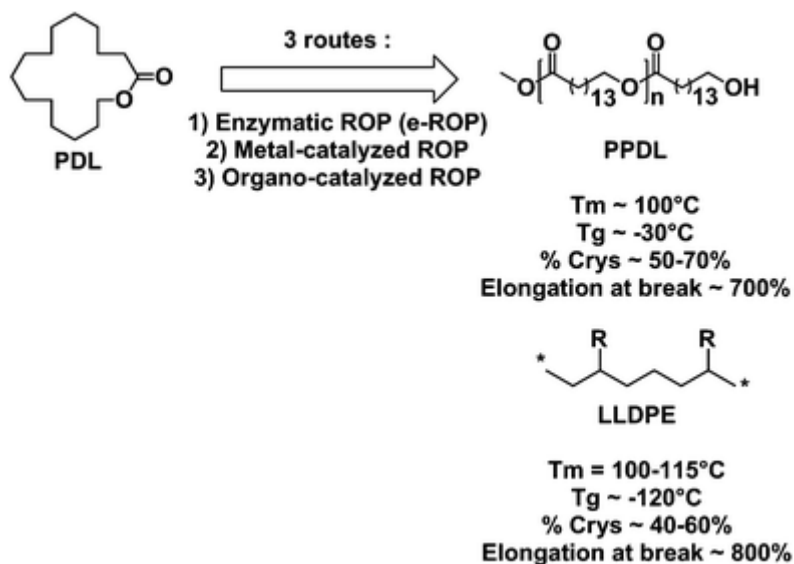


Scheme 7 Preparation of poly(9-hydroxynonanoic acid) from castor oil.³⁵

Narine and coll. used the same hydroxyl fatty acid but the ring opening polymerization method was retained after 9-hydroxynonanoic acid was converted to the dilactone with the help of two different catalysts (lanthanum chloride and aluminium isopropoxide).³⁶ The dilactone (1,11-dioxacycloicosane-2,12-dione), obtained in high yield (98%) and high purity (98%), was then subjected to ring-opening polymerization. Molecular weights in the range of 5–7 kg mol⁻¹ were obtained with dispersities of 1.4 and 1.5 depending on the catalyst used. The thermo-mechanical properties of these poly(nonanolactone)s were investigated by means of DSC analyses and revealed a melting point of 69 °C similar to the poly(9-hydroxynonanoic acid).

In order to increase the ratio of the number of methylene units to the ester function in the structure of the polyester, Matsumura and coll. used 12-hydroxydodecanoic acid as the starting material.³⁷ This linear C12 ω -hydroxyacid can be obtained from vernonia oil by oxidative cleavage. This monomer was subjected to polycondensation and the obtained polyester ($M_w = 105 \text{ kg mol}^{-1}$, $D = 2.9$) revealed a melting point of 88 °C.

Another promising monomer that can be obtained from fatty acids is ω -pentadecalactone (PDL). However the low ring strain of this lactone makes its ring opening polymerization difficult using traditional chemical methods. Contrarily, lipases have been reported to be highly active initiators for ROP of large ring size lactones.³⁸ Indeed, the rate determining step which is the formation of the lipase–lactone complex in enzymatic ROP (e-ROP), is promoted by the hydrophobicity of the lactone monomer.³⁹ Thus larger lactone rings induce higher e-ROP rates. Therefore, polypentadecalactone (PPDL) synthesis by e-ROP was reported to be highly efficient using Novozyme 435 and produced high molecular weights (M_n up to 480 kg mol⁻¹).^{40–42} Copolymerizations of ω -pentadecalactone with other lactone monomers such as *p*-dioxanone and ϵ -caprolactone as well as block copolymerization using hydroxyl-terminated polybutadiene as the macroinitiator for the eROP of PDL were also reported.^{43–46} Physical characterizations of PPDL revealed a T_g of –27 °C and a melting point of 97 °C. High values of crystallinity were observed in the range of 54–64%. The mechanical behavior, evaluated by tensile tests, revealed a hard tough feature as seen from the stress at yield of 14.5 MPa, Young's modulus value of 370 MPa and the high elongation at break of around 100–200%. These parameters are comparable to those of low-density polyethylene indicating the great potential of this biodegradable polyester in a wide range of applications (Scheme 8).⁴⁷



Scheme 8 Various catalytic routes to PPDL.^{40-42,47,50-52}

In order to highlight the similarities between PPDL and polyethylene, Gross and coll. investigated the effects of the molecular weight of PPDL on its mechanical and thermal properties.⁴² A series of PPDL of M_w ranging from 25 to 480 kg mol⁻¹ were prepared by lipase catalysis. Tensile tests revealed a brittle-to-ductile transition for samples with M_w values between 45 and 81 kg mol⁻¹ while samples with M_w over 189 kg mol⁻¹ showed a tough behavior with elongation at break around 600%. This strain hardening can be explained by enhanced entanglement strength in the amorphous regions. Young's modulus and stress at yield decreased with the molecular weight and presented similar trends to crystallinity. Thus, in comparison with high density polyethylene (HDPE), PPDL presented similar features in terms of Young's modulus and stress at yield with molecular weight but differing trends with respect to elongation at break. These differences can be explained by the presence of C–O bonds in ester linkages of PPDL.

Heise and coll. took advantage of the high molecular weight achievable by e-ROP of ω -pentadecalactone for melt processing of PPDL into fibers.⁴⁰ The authors first investigated the tensile properties of compression-molded films. They reported excellent mechanical properties: a Young's modulus value of 420 MPa, yield strength of 17.5 MPa and elongation at break of 1200%.⁴⁷ The high molecular weight PPDL was then melt-processed into fibers, which were further elongated. By playing on the processing conditions, different degrees of crystal orientation were obtained impacting the mechanical properties.

Some attempts of metal-catalyzed ROP of PDL were carried out with initiators such as Y(OiPr)₃ and Ln(BH₄)₃(THF)₃; however lower molecular weight (30–40 kg mol⁻¹) PPDL was obtained.^{48,49} Recently, Duchateau and coll. described the synthesis of high molecular weight ($M_n > 155$ kg mol⁻¹) PPDL by using an aluminium–salen complex as the initiator.^{50,51} Thus, this study revealed the feasibility of ROP of PDL by using cheap and robust metal-based catalysts.

More recently the same group published a complementary route to PDL ROP by using TBD as the organocatalyst in combination with an alcohol initiator.⁵² Various other N-heterocyclic organic molecules such as guanidines, amidines and N-heterocyclic carbenes (NHCs) were investigated as catalysts for PDL ROP, however the combination of TBD with an alcohol initiator was the only efficient system.

A linear long aliphatic polyester bearing 14 methylene units between two ester functions was also synthesized by Gross and coll. To this aim, they first described the biosynthesis of ω -hydroxytetradecanoic acid (ω -OHC14) and other long chain hydroxyacids from fatty acids (C12 and C16) by using engineered *C. tropicalis*.⁵³ The resulting ω -OHC14 methyl ester was then polymerized by an AB-type self-condensation using Ti(OiPr)₄ as a catalyst.⁵⁴ By varying the polymerization conditions such as the catalyst concentration or the reaction time, a series of poly(ω -hydroxytetradecanoate)s (P(ω -OHC14)) were prepared with various molecular weights (from 53 kg mol⁻¹ to 140 kg mol⁻¹). Thermal analysis showed a melting point of around 94 °C which is in accordance with the PPDL result (polyester with one additional methylene unit between two ester functions). Similar to PPDL, P(ω -OHC14) showed a dependence of its mechanical properties on molecular weight. A brittle-to-ductile transition was observed with M_w values between 78 kg mol⁻¹ and 140 kg mol⁻¹. The tough behavior of high M_w P(ω -OHC14) is underlined as seen from high values of elongation at break (around 700%) coupled with a high tensile strength (around 50 MPa). These values are comparable to the ones of HDPE. Copolymerization of ω -OHC14 with 1,4-butanediol and dimethyl terephthalate was carried out, by the same group, in order to target similar properties to the commercial product Ecoflex®. By varying the ratio between

the comonomers, a large range of thermo-mechanical properties was obtained. Particularly, the copolymer comprising 60 mol% of bio-based ω -OHC14 repeating units showed similar tensile properties to Ecoflex.⁵⁵

To conclude, many routes have been investigated to mimic polyethylene starting from plant oil feedstock. Indeed, fatty acids already contain long chain linear segments that make them suitable for the design of long methylene chain building blocks. The thiol–ene reaction was proposed as a powerful tool to induce bifunctionality in fatty acid derivatives. However, the presence of sulfur atoms in the resulting polymer backbone leads to more flexible materials and thus to lower melting points. Metathesis was revealed to be highly efficient for the design of polyethylene mimics. This reaction can be applied to many substrates and can be used for the design of step-growth polymerization building blocks or directly as a polymerization method (ADMET). By this way, several long methylene chain polyesters were synthesized. It is however necessary to perform a hydrogenation step of the building blocks or the unsaturated polymer in order to achieve maximum crystallinity. To date, one drawback of this pathway has been the high price of the metathesis catalysts. Other strategies were reported such as the carbonylation polymerization or the isomerizing alkoxycarbonylation of fatty acids. The latter strategy was highly efficient due to complete feedstock molecule utilization. Various other chemical syntheses or biosyntheses of monomers which allowed the polymerization of C9 to C15 ω -hydroxyacids (or lactones) were reported. To conclude, thermo-mechanical properties of linear polyethylene were approached with long chain fatty acid-based polyesters (Fig. 1). However, further dilution of the ester functions in the polymer backbone remains necessary to completely mimic polyethylene and to obtain similar crystalline lamellar thickness. Concerning low-density polyethylene, similar thermal and mechanical properties were obtained by using fatty acids as feedstock with the additional particularity of being hydrolytically degradable. This statement shows the great potential of plant oils as a reliable feedstock for the polymer industry even if biodegradability or biocompostability studies still need to be investigated.

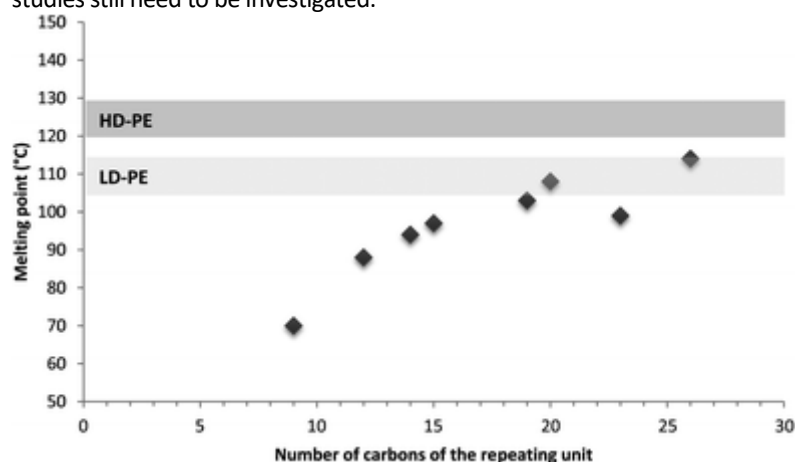


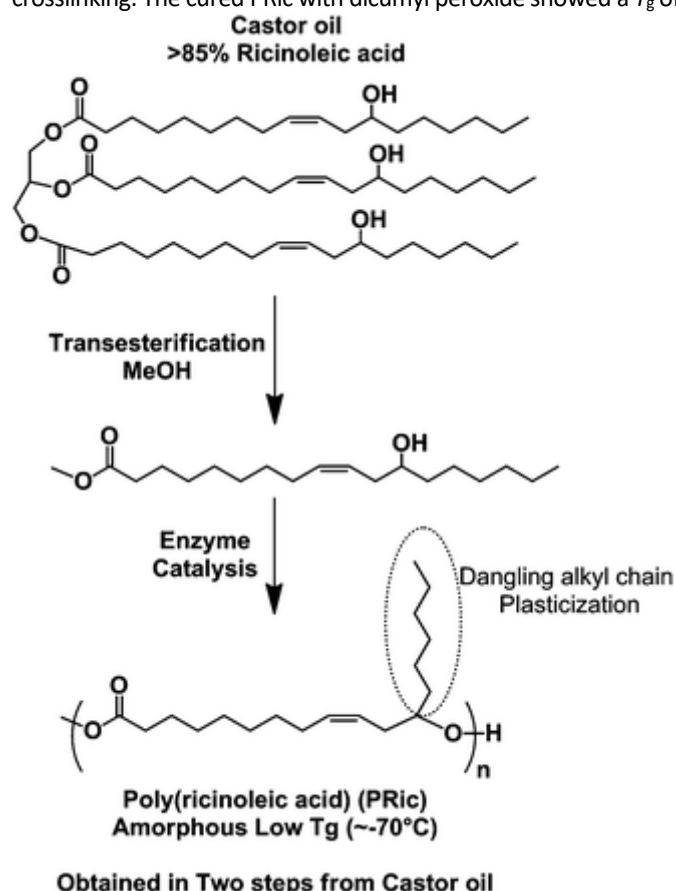
Fig. 1 Melting points of various polyethylene “like” aliphatic polyesters synthesized from fatty acids.

II.2 Soft and elastomeric polyesters

In the first part, we reviewed the different solutions that were found to develop new long chain aliphatic and linear polyesters. Modifications of the chemical structure of fatty acids were necessary as they usually present functionalization sites, such as double bonds or hydroxyl functions, in internal positions of the molecules. However the inherent internal position of the functionalization site can be of great interest when soft materials are targeted. Indeed, after reaction of the internal function, an alkyl dangling chain remains in the structure of the so-formed molecule. In the particular case of polymers, the alkyl dangling chains will serve as internal plasticizers leading to low T_g materials. When copolymerized with linear monomers or cross-linked, thermoplastic elastomers or thermosetting elastomers with interesting properties are achievable. Regarding the wide use of elastomers in industrial applications, it is thus of high interest to develop such a type of materials with an additional bio-based character. Moreover, in the case of polyesters, hydrolytic degradability endowed by the ester functions could be exploited for environmental concerns.

Among the triglyceride oils, castor oil has attracted much attention as it contains approximately 85–90% of ricinoleic acid, a naturally hydroxylated fatty acid which can be readily polymerized.^{13,56} In this line, Hayes and Kelly used the bifunctionality of ricinoleic acid to synthesize low molecular weight star-shaped poly(ricinoleic acid) (PRic).⁵⁷ Lipase-catalysed transesterification of ricinoleic acid with a polyol such as trimethylolpropane, pentaerythritol or dimer diol was used in this study. The resulting polymers showed melting points below -7 °C and a high viscosity index suggesting their potential use as lubricants. The same fatty acid was used for the synthesis of a cross-linked elastomer.⁵⁸ The authors first

synthesized high molecular weight PRic by lipase-catalyzed polycondensation (Scheme 9). The effect of several reaction parameters on the molecular weight of the polymer was investigated and revealed that high lipase loadings (up to 50 wt%) together with the use of molecular sieves were required to yield significant molecular weights. A PRic with a M_w of 98 kg mol^{-1} showed a fully amorphous feature with a low T_g of $-75 \text{ }^\circ\text{C}$. This value is close to the one of natural rubber and of synthetic polyisoprene (T_g in the range of -62 to $-67 \text{ }^\circ\text{C}$) suggesting the potential use of PRic as an elastomer after crosslinking. The cured PRic with dicumyl peroxide showed a T_g of $-65 \text{ }^\circ\text{C}$.



Scheme 9 Two-step synthesis of amorphous poly(ricinoleic acid) (PRic) from castor oil.⁵⁸

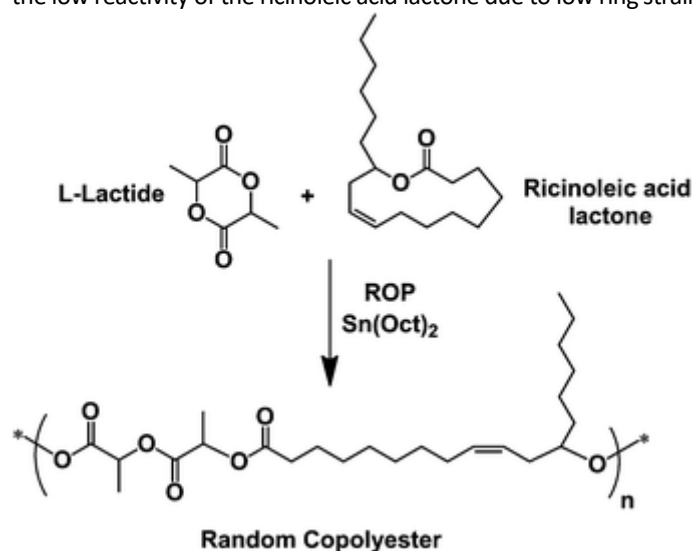
The same authors carried out the vulcanization of PRic of different molecular weights with sulfur curatives in the presence of carbon black as the filler.⁵⁹ The thermosetting elastomers obtained formed a rubber-like sheet with a smooth and non-sticky surface. Mechanical properties of the elastomers were highly dependent on the molecular weight of the PRic (M_w of 52 and 108 kg mol^{-1} were used in the study) as well as on the amount of the sulfur curatives introduced in the formulation. Optimal formulation revealed a tensile strength at break of 6.9 MPa with a corresponding elongation of 350%. Thus high molecular weight PRic may become a promising bio-based thermosetting elastomer that could substitute some of petroleum based synthetic rubbers.

The copolymerization of ricinoleic acid with lactic acid was also reported.⁶⁰ In a first method, ricinoleic acid and L-lactic acid were directly copolymerized by thermal polycondensation leading to random copolyesters of low molecular weights between 2 and 8 kg mol^{-1} . The random copolymers showed melting points below $100 \text{ }^\circ\text{C}$; over 20% of the ricinoleic acid unit, the copolymers were viscous liquids at room temperature. A second method was based on the transesterification of high molecular weight PLA with ricinoleic acid and post-polyesterification. In comparison to the previous methodology, this second route leads to semi-crystalline multiblock copolyesters of molecular weights ranging from 6 to 14 kg mol^{-1} .

Following a similar methodology, the same group investigated the synthesis of poly(ester-anhydride)s prepared by the melt polycondensation of diacid oligomers of poly(sebacic acid) transesterified with ricinoleic acid.⁶¹ Molecular weights in the range of $2\text{--}60 \text{ kg mol}^{-1}$ and melting temperatures of $24\text{--}77 \text{ }^\circ\text{C}$ were reported depending on the amount of ricinoleic acid that reacted. Stability to sterilization by γ -irradiation was confirmed allowing the use of these copolymers for biomedical applications.^{62–64}

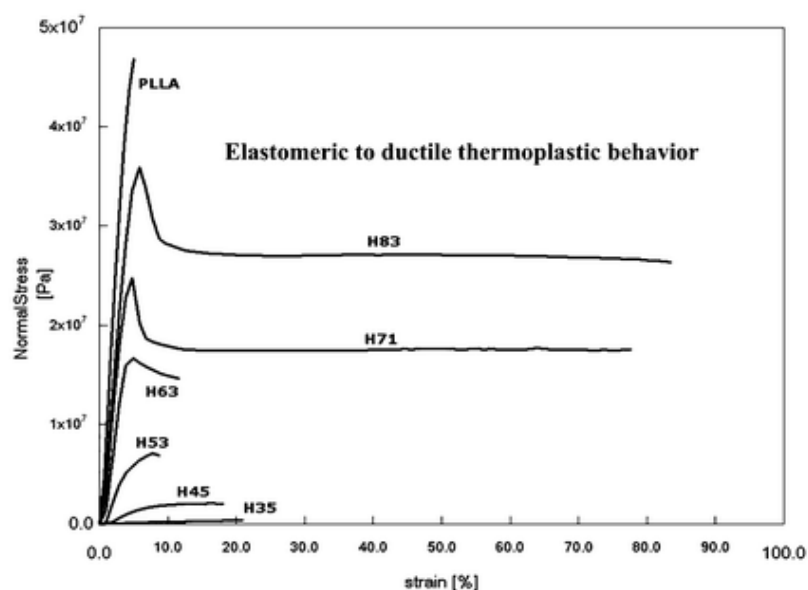
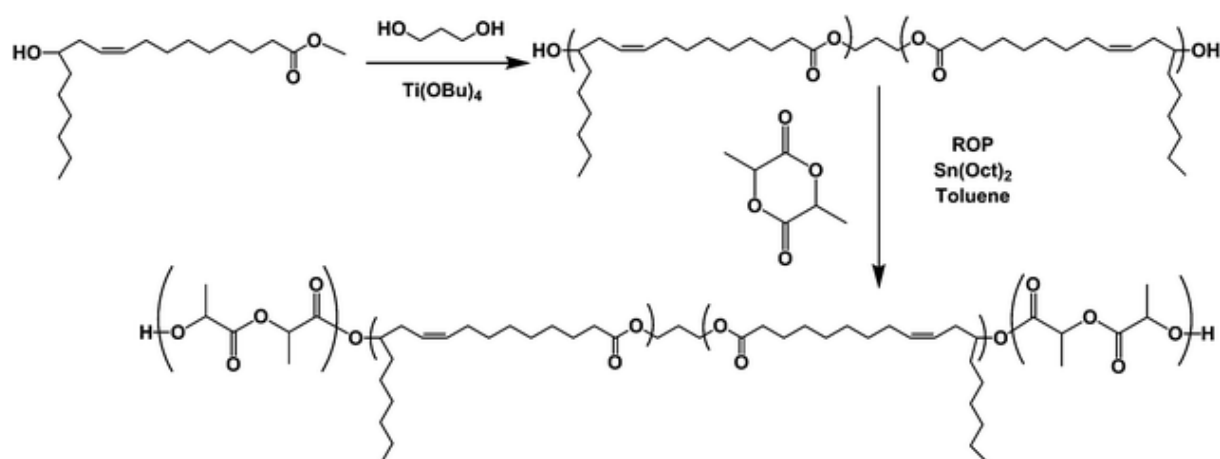
In another study, the same authors reported the stereocomplexation of poly(L-lactic acid-ricinoleic acid) multiblock copolyesters with PDLA.⁶⁵ The copolyesters were synthesized by polycondensation of ricinoleic acid with PLLA oligomers

of various molecular weights. Stereocomplexation by solventmixing was observed only for copolyesters with PLLA blocks of more than 10 repeating units as seen from the characteristic melting point of the stereocomplex. Ricinoleic lactone formation was also investigated by using intramolecular esterification of ricinoleic acid with DCC, DMPA and hydrochloric acid.⁶⁶ This procedure resulted in a mixture of lactones containing up to 6 ricinoleic units. Ring-opening polymerization of the isolated C12 and C24 or the C12–C72 mixture of lactones was carried out using two different initiators ($\text{Y}(\text{O}^i\text{Pr})_3$ and $\text{Sn}(\text{octate})_2$). For the ROP of the C24 lactone, only tin catalyst gave low molecular weight PRic ($M_n = 4.4 \text{ kg mol}^{-1}$). Copolymerization of the lactone mixture with lactide by ROP using $\text{Sn}(\text{Oct})_2$ as a catalyst yielded copolyesters of M_n in the range of 5–16 kg mol^{-1} (Scheme 10). The limitation of the molecular weight was explained by the low reactivity of the ricinoleic acid lactone due to low ring strain and steric hindrance of the lactone ester function.



Scheme 10 Copolymerization of L-lactide with ricinoleic acid lactone.⁶⁶

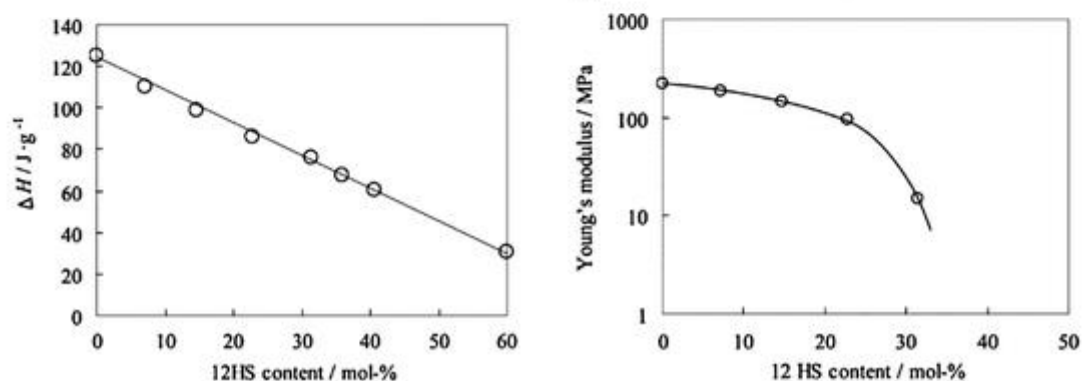
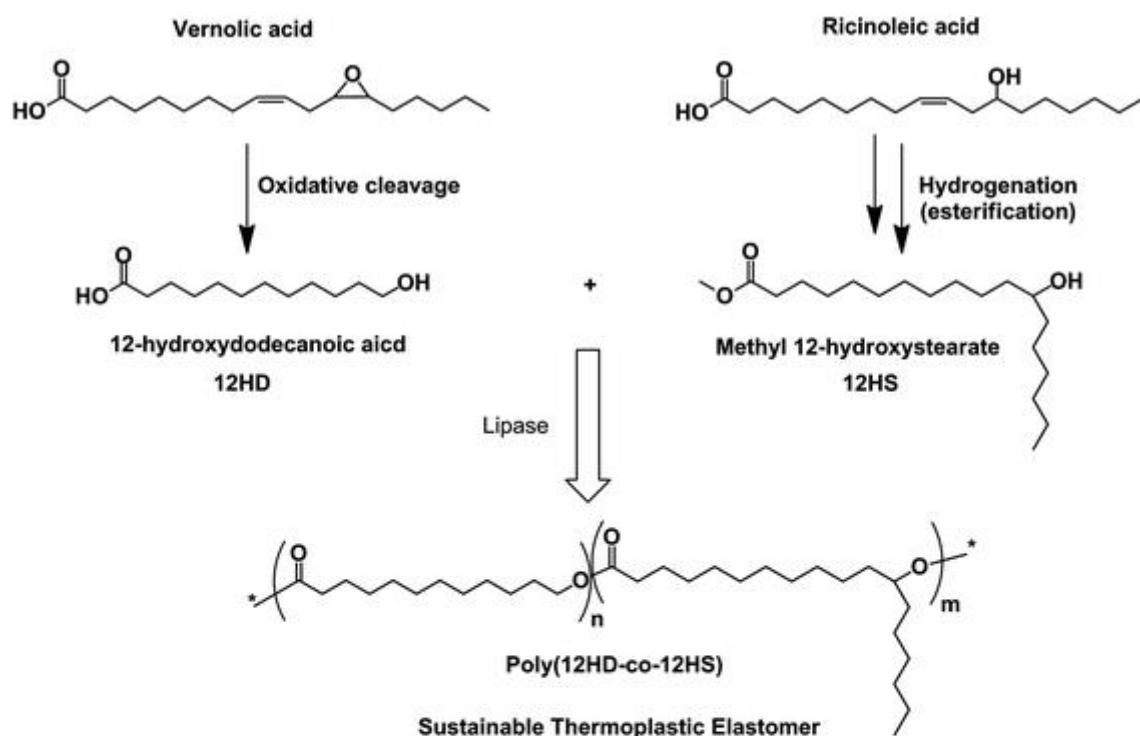
Very recently, our group described the synthesis and use of an α,ω -hydroxy-terminated PRic as a macro-initiator for the ROP of L-lactide.⁶⁷ In this manner, a series of ABA triblock copolymers with a composition ranging from 35 to 83 wt% of PLLA was developed (Scheme 11). The block structure of the copolymers provided good thermal properties with relatively high melting points (in the range of 140–180 °C). The mechanical properties range from thermoplastic to elastomeric depending on the block copolymer composition. Indeed, Young's modulus varied from 3 to 1062 MPa showing the high versatility of these copolymers.



H83 : 83 wt% of Hard block (PLLA)

Scheme 11 Poly(L-lactide)-*b*-poly(ricinoleic acid)-*b*-poly(L-lactide) formation by the combination of AB type self-condensation and ring opening polymerization. Stress-strain curves showing elastomeric to ductile thermoplastic behavior depending on the amount of soft segment in the copolymer.⁵⁷

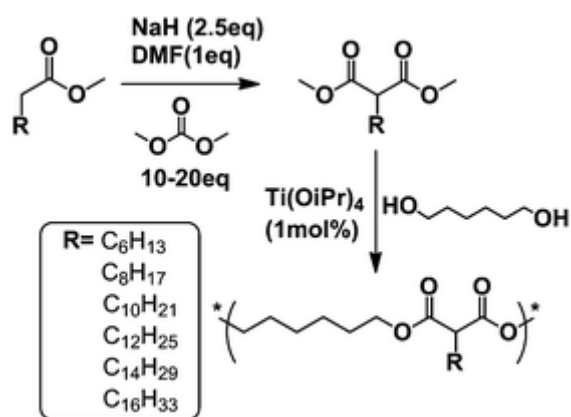
Since the remaining double bond of the ricinoleic acid repeating unit can be subjected to oxidation and to a loss of thermal stability, Matsumura and coll. used hydrogenated methyl ricinoleate (methyl 12-hydroxystearate) (12HS) as an AB-type monomer for polyester synthesis.³⁷ They have synthesized copolyesters by using 12-hydroxydodecanoic acid (12HD), which is obtained from vernolic acid, as a comonomer. By varying the amount of the two AB monomers, a series of high molecular weight copolyesters (M_w around 100 kg mol^{-1}) were synthesized by polycondensation in the presence of lipase (Scheme 12). The thermo-mechanical properties of the copolyesters varied with the amount of 12HS in the copolymer. Indeed, while poly(12HD) showed a melting temperature of $88 \text{ }^\circ\text{C}$, the copolyester's melting point (as well as the corresponding enthalpy) greatly decreased with an increase of 12HS units (T_m around $20 \text{ }^\circ\text{C}$ for 60 mol% 12HS). A similar trend was observed for the Young's modulus. Moreover these copolyesters were proved to be biodegradable allowing their use as green and sustainable soft materials. In terms of physico-chemical and mechanical properties, these bio-based thermoplastic elastomers present close similarities to the well-known petroleum-based ethylene-octene and ethylene-hexenecopolymers.



Scheme 12 AB type self-condensation route to biobased and biodegradable thermoplastic elastomers. Both melting enthalpy and Young's modulus decrease with an increase of 12HS content.³⁷

Copolymerization of methyl 12-hydroxystearate with pentadecalactone (PDL) was also reported with the same goal to develop bio-based thermoplastic elastomers.⁶⁸ Copolymers of various compositions were prepared by lipase-catalyzed copolymerization. By this way, a wide range of thermo-mechanical properties was obtained with respect to the amount of hard (PDL units) and soft (12HS units) segments in the copolymer structure. Indeed, while neat PPDL shows a Young's modulus of 367 MPa and an elongation at break of 500%, the copolymer with 60 wt% hydroxystearate presents a Young's modulus of 3 MPa and breaks at 2400% elongation. Biodegradation investigation was carried out on these copolymers and they showed an improvement of the biodegradability with the 12HS content in the copolymer.

Recently, Meier and Kolb proposed an interesting route to soft materials by using saturated fatty acid methyl esters as substrates.⁶⁹ The strategy employed in this study was the conversion of various saturated fatty acids to their malonate derivatives bearing an aliphatic chain of 6 to 16 methylene units depending on the saturated fatty-acid used. These malonate derivatives were then polymerized with 1,6-hexanediol using different catalysts (TBD, *p*-TsOH, Ti(OiPr)₄) yielding polyesters with aliphatic dangling chains differing in length (Scheme 13).



Scheme 13 Malonate synthesis from saturated fatty acids followed by subsequent polycondensation with 1,6-hexanediol.⁶⁹

Thermo-mechanical analysis of the resulting polyesters showed different behaviors depending on the length of the side chain. The polyesters with a dangling chain composed of 6 to 8 methylene units were fully amorphous with T_g below -65 °C. The polyesters synthesized from malonates with longer side chains were semi-crystalline with very low melting points. The latter increased with the length of the side chain to reach 27 °C for the longer side chain polyesters studied. The non-polar interactions of the long alkyl dangling chains were found to be responsible for the crystallinity of these polyesters.

Regarding the reported studies concerning the synthesis of soft polyesters, it is obvious that the choice and the modification of the substrate play a crucial role in defining the properties of the resulting materials. Indeed, a large palette of polyesters with a broad range of thermo-mechanical properties is accessible depending on the nature (linear or branched) and the ratio of comonomer incorporated. These soft polyesters can be applied as lubricants, cosmetics, pharmaceuticals or specialty polymers such as cross-linked elastomers and thermoplastic elastomers.

II.3 Functional polyesters

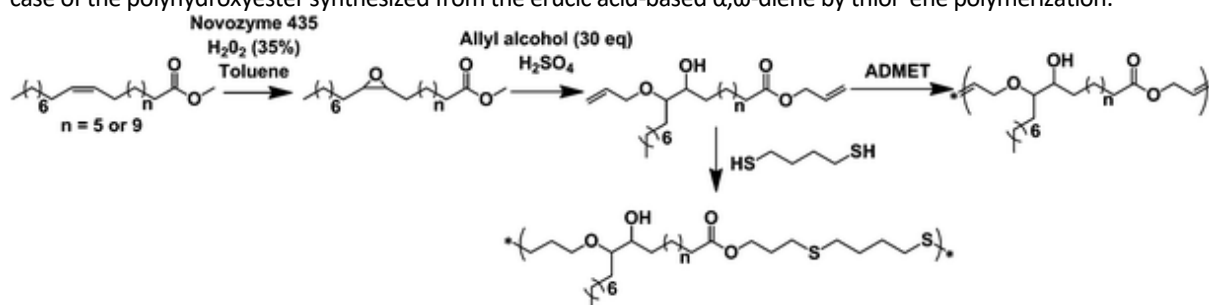
As demonstrated in the previous parts, many examples of aliphatic polyesters obtained from fatty acids have been reported. Most of them are potentially biodegradable and/or biocompatible suggesting their potential use for biomedical devices or for environmental applications. However these materials are hydrophobic and free of functional groups for further modification.^{70,71} Indeed, further reactions to induce branching, grafting or cross-linking as well as functionalization with biomolecules could be important pathways to improve the thermo-mechanical, chemical and biological properties of the resulting polyesters. The functionalization of polyesters has been extensively studied.^{71,72}

Poly(hydroxyester)s and poly(epoxyester)s represent the most studied functionalized polyesters. Indeed hydroxyl functions are very versatile due to a large number of functionalization possibilities in mild conditions. Regarding the epoxide function, it is noteworthy that epoxidation of double bonds is a well-established reaction notably in oleochemistry. In fact epoxidized vegetable oils such as soybean and linseed oils are mature industrial products and are widely used as acid and mercaptan scavengers, plasticizers, toughening agents, etc. This large range of applications is especially due to the variety of nucleophiles that are susceptible to ring-open epoxide functions. Therefore the incorporation of epoxide functions into polyesters is a convenient route to further modify the so-formed functionalized polyesters. Some relevant examples of functionalized polyesters that have been synthesized from fatty acid feedstock are described in the following part.

II.3.1 Polyesters with functional groups in the side-chains

A first study involves the use of ADMET and thiol-ene methodologies to synthesize functionalized polyesters from hydroxyl-bearing unsaturated compounds.⁷³ First, methyl erucate and methyl oleate were epoxidized and subsequently reacted with allyl alcohol in acidic conditions yielding the corresponding α,ω -dienes. These monomers were then polymerized by ADMET or thiol-ene addition with 1,4-butanedithiol to give poly(hydroxyester)s with molecular weights in the range of $3\text{--}18$ kg mol⁻¹ depending on the monomer and polymerization method used (Scheme 14). Thermo-

mechanical analysis of these polyesters has revealed a low T_g of around $-60\text{ }^\circ\text{C}$ and a melting transition at $-18\text{ }^\circ\text{C}$ in the case of the polyhydroxyester synthesized from the erucic acid-based α,ω -diene by thiol-ene polymerization.



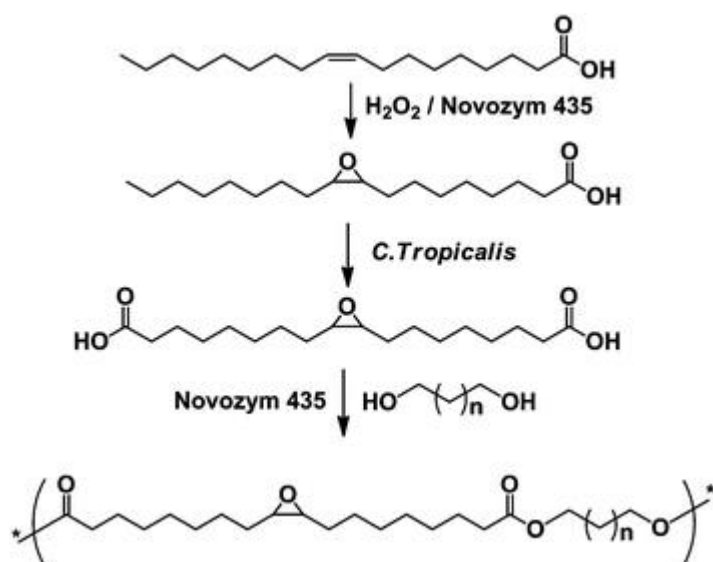
Scheme 14 ADMET and thiol-ene approaches to poly(hydroxyester).⁷³

In a similar work, another hydroxyl-bearing α,ω -diene was synthesized by the reaction of two equivalents of 10-undecenoic acid with one equivalent of 1,3-dichloro-2-propanol yielding through ADMET a semi-crystalline polyester of 5 kg mol^{-1} molecular weight with a T_g of $-25\text{ }^\circ\text{C}$ and a melting point of $41\text{ }^\circ\text{C}$.⁷⁴ Copolymerizations of this hydroxyl-bearing monomer with a phosphorus-bearing α,ω -diene synthesized from 10-undecenoic acid were carried out to target flame-retardant applications of the resulting materials.⁷⁵ Thermal properties of the copolymers varied with the amount of phosphorus-bearing monomer introduced in the copolymer structure. T_g increased from $-25\text{ }^\circ\text{C}$ to $6\text{ }^\circ\text{C}$ when 75 mol% of phosphorus-bearing monomer was reacted. Post-functionalization of the hydroxyl functions was then carried out by acrylation. The acrylated polyesters were then cross-linked using dicumyl peroxide. The resulting thermosets showed T_g in the range of $35\text{ }^\circ\text{C}$ to $52\text{ }^\circ\text{C}$, good thermal stabilities, and good flame retardancy.

The synthesis of poly(hydroxyester)s by reaction of a diacid with a triol is possible but is generally limited by the numerous branching reactions that occur prior to cross-linking of the system. Thus, it is necessary to control the stoichiometry as well as the reaction conditions in order to avoid undesirable side reactions. Gross and coll. demonstrated that immobilized *Candida antarctica* lipase B efficiently catalyzed the polycondensation of a diacid with a triol with very low degrees of branching and no cross-linking, which enables the synthesis of linear poly(hydroxyester)s.⁷⁶ For that purpose, the authors used an oleic diacid (1,18-*cis*-9-octadecenedioic acid) synthesized using *Candida tropicalis* ATCC20962. This diacid was then reacted with glycerol yielding polyol polyesters by enzyme catalysis.

Also by using lipase as a catalyst, Kobayashi and coll. synthesized epoxide-bearing polyesters using two functionalization routes.⁷⁷ The first one was the synthesis of aliphatic polyesters containing an unsaturated group in the side chain by reaction of divinyl sebacate, glycerol and unsaturated fatty acids⁷⁸ followed by the epoxidation of unsaturated fatty acid side chains using hydrogen peroxide and *Candida antarctica* lipase. In the second route, fatty acids were epoxidized and polymerized with divinyl sebacate and glycerol to give the epoxy-bearing polyesters. In all cases, high epoxidized ratios were achieved. The resulting functionalized polyesters were then thermally cured to yield biodegradable films.

A pre-functionalization pathway to functional polyesters was also reported by using an epoxy-bearing diacid.⁷⁹ This diacid was synthesized by a two-step procedure from oleic acid. Epoxidation of the internal double bond was first carried out using hydrogen peroxide and Novozyme 435. The resulting epoxy fatty acid was then converted to the epoxy-bearing α,ω -dicarboxylic acid by using *Candida tropicalis* ATCC20962. The lipase catalyzed copolymerization of this diacid with various diols yielded the corresponding copolyesters with molecular weight values in the range of $25\text{--}57\text{ kg mol}^{-1}$ (Scheme 15).

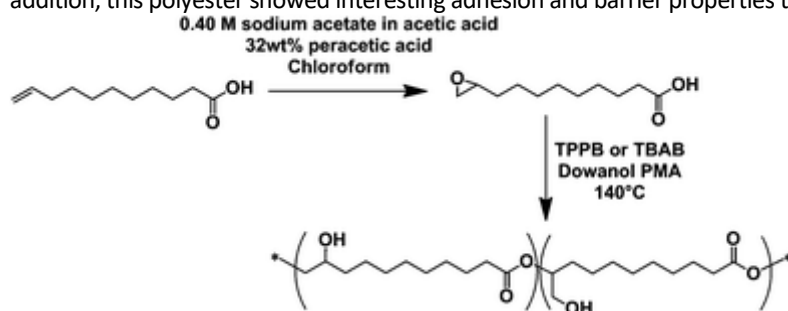


Scheme 15 Lipase catalyzed polymerization of an epoxide-bearing diacid with various diols.⁷⁹

Thiol-ene chemistry was also used for grafting functional groups onto polyesters bearing terminal double bonds that are more reactive. In order to synthesize a monomer with a terminal double bond, malonization of methyl 10-undecenoate was carried out.⁸⁰ The resulting malonate was then subjected to polycondensation with 1,6-hexanediol to afford an unsaturated aliphatic polyester. Thiol derivatives were reacted with the polyester in quantitative yields. In a second approach, the authors investigated cross-metathesis as a functionalization tool and observed very good conversions of the unsaturated polyesters into their functionalized counterparts.

II.3.2 Generation of functional groups during the polymerization

An elegant and simple route to polyhydroxyesters was proposed by Dettloff and coll. with the use of 10,11-epoxyundecanoic acid as a monomer.⁸¹ This epoxy fatty acid was polymerized *via* nucleophilic ring-opening of the epoxide group with the carboxylic acid moiety (Scheme 16). Initiation of the polymerization was carried out using quaternary ammonium or phosphonium salts. The polyester was fully characterized and exhibited similar thermomechanical properties to LLDPE as seen from the values of yield stress, elongation and Young's modulus. In addition, this polyester showed interesting adhesion and barrier properties to oxygen.



Scheme 16 Synthesis of poly(hydroxyester) by nucleophilic ring-opening polymerization.⁸¹

Similarly, Wang and coll. used epoxidized oleic acid for the preparation of poly(hydroxyester)s by simple heating of the monomer.⁸² Characterization of the obtained polymers showed mainly the presence of ester linkages that confirm the ring-opening of the epoxide by the carboxylic acid function of the monomer. Only a small amount of ether linkages, resulting from the nucleophilic ring-opening of the epoxide by alcohol moieties, was observed. These functionalized polyesters were subsequently cross-linked using various diisocyanates.

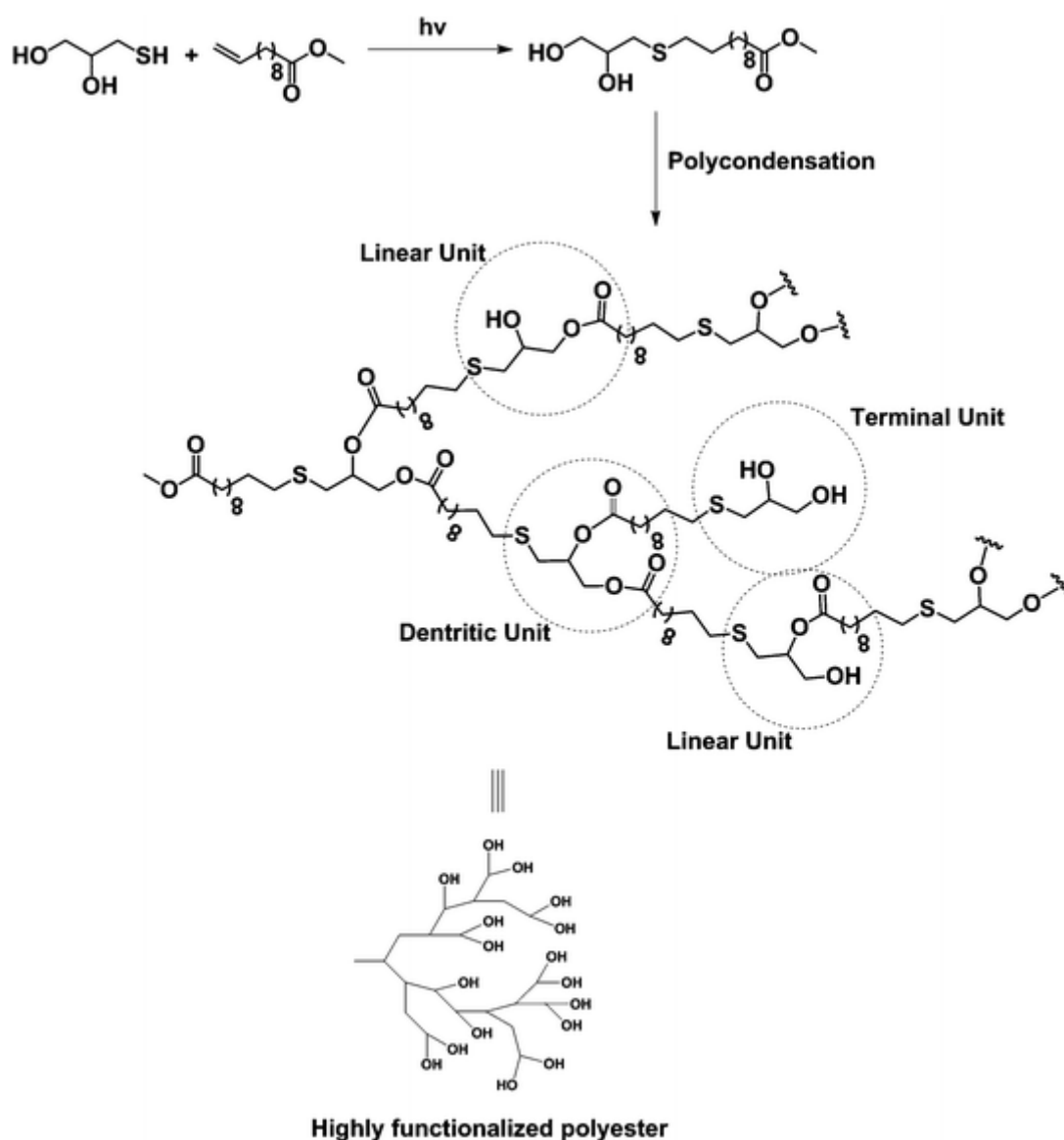
The same strategy was adapted to diglycidyl sebacate, a bisepoxy derived from sebacic acid.⁸³ This bisepoxy compound was reacted by nucleophilic ring-opening polymerization with sebacic acid to yield a polyester bearing free hydroxyl groups. Structural characterization of the so-formed polyester revealed a very low degree of branching of

around 10%. This value is much lower than the one observed for the corresponding polyester synthesized by polycondensation of sebacic acid with glycerol. Free hydroxyl functions of this polyester were then functionalized by esterification in mild conditions with Boc-protected glycine. Functionalization by reaction with maleic anhydride was also investigated. In both cases, high degrees of functionalization were achieved (80 to 90%).

II.3.3 Functional groups at the chain ends

Another functionalization approach is to introduce a specific functionality at the chain ends of the polyester for macromolecular engineering purposes. In a first example, the enzymatic ring-opening polymerization (e-ROP) of pentadecalactone (PDL) was performed by using Novozyme 435 in the presence of glycidol and a divinyl ester of adipic acid.⁸⁴ By this way, bisepoxy functionalised PPDL was synthesized. By playing on the stoichiometry of the building blocks, polyesters of various molecular weights were achieved (from 1.4 to 2.7 kg mol⁻¹). Curing of these macromonomers by photopolymerization with a cycloaliphatic bisepoxide resulted in polyester networks. Along the same line, PPDL was reacted with equimolar amounts of a functional initiator and terminator yielding α,ω -PPDL with thiol–thiol, acrylate–acrylate or thiol–acrylate end groups.⁸⁵

Functionalization at the chain ends generally leads to mono- or bi-functional chains considering the linear structure of most of the polyesters. When a higher functionalization degree is needed, the use of hyperbranched structures may prove appropriate. Meier and Türünc reported the thiol–ene addition between methyl 10-undecenoate and 1-thioglycerol as an efficient route for the synthesis of an AB₂ monomer (Scheme 17).⁸⁶ Polycondensation with or without a core-molecule (glycerol) was then carried out using TBD as a catalyst. The degree of branching, calculated using a reported equation,⁸⁶ was in the range of 0.40–0.47 which is in agreement with the values generally reported for similar systems. Interestingly, such hyperbranched (HB) polyesters exhibited a semi-crystalline character with a melting point of 50 °C. The unusually long aliphatic chain between two branching points allowed the crystallization of this polyester while amorphous polymers are generally obtained in HB structures. The same polyester was investigated after the polycondensation of this AB₂ monomer was carried out by using various catalysts such as titanium butoxide (Ti(OBu)₄), antimony trioxide (Sb₂O₃) and zinc acetate (Zn(Ac)₂).⁸⁷ Polyesters with high molecular weights were obtained when these catalysts were used instead of TBD.



Scheme 17 Hyperbranched polyester synthesis from an AB₂ monomer obtained from methyl 10-undecenoate.^{8,87}

Hydroformylation/hydrogenation is a well-known procedure in oleochemistry to introduce hydroxyl functions in the structure of plant oils and fatty acids, which can be used to produce HB polymers. Applied to methyl soyate, which consists of a mixture of saturated and unsaturated fatty acid methyl esters, hydroformylation followed by hydrogenation yielded a mixture of fatty acid methyl esters bearing zero, one, two and three hydroxyl groups.⁸⁸ As the bis-hydroxyl compound is the major compound, it is then possible to synthesize HB polyesters by simple polycondensation. Molecular weights up to 42 kg mol⁻¹ were obtained. By this way, very high values of weight average functionality can be obtained despite the presence of nonfunctional compounds.

We can conclude from this section that a large variety of functionalized polyesters are accessible from plant oils thanks to the various routes investigated to modify fatty acids. It is also possible to alter the macromolecular architectures to fit any application. Indeed hyper-branched polyesters will not have the same potential and properties as linear ones. Also modification strategies will not be the same if chain end-functionalized or side chain-functionalized polyesters are used showing the huge versatility of fatty oil-based polyesters.

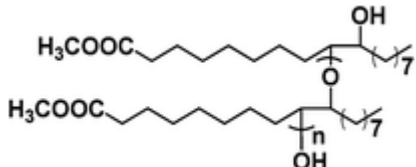
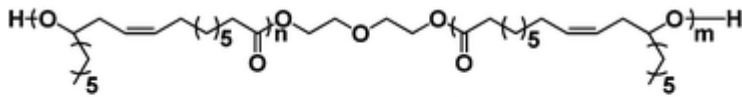
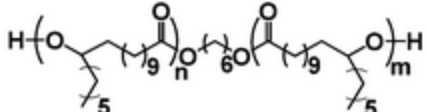
III Polyurethanes

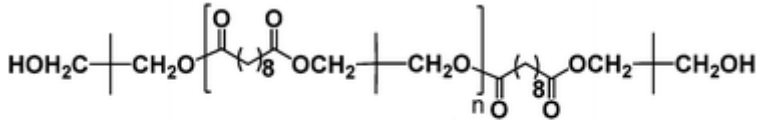
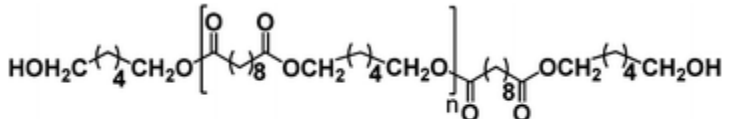
Polyurethanes (PUs) are likely the most versatile polymers and one of the most important classes of specialty polymers. The large range of monomers, mainly diols and polyols, that can be used for their synthesis make them suitable for many applications. PUs are mostly used in the form of flexible and rigid foams for mattresses, automotive and insulation applications, but are also utilized in coatings, adhesives, sealants and elastomers. Thermoplastic polyurethanes (TPUs) are widely applied because of their flexibility, elasticity, strength, and good abrasion resistance. Besides, TPUs present the advantage of processing by standard methods for thermoplastics such as injection molding, extrusion and thermoforming.⁸⁹ The urethane linkage can be synthesized by various methods, however the most widely used route is the classical reaction between hydroxyl and isocyanate functions. Due to hazard concerns, phosgene-free routes are also achievable and, among them, the reaction between cyclic carbonates and amine functions is the most used that yields poly(hydroxyurethane)s.

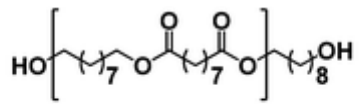
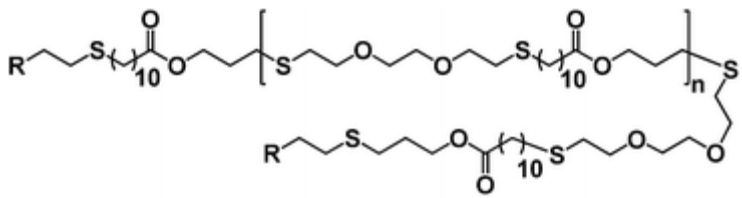
By taking advantage of the wide possibilities for chemical modification onto their active sites, vegetable oils can be converted into new tailored bio-based PU precursors. Indeed, a broad palette of strategies has been developed to functionalize vegetable oils with hydroxyl groups and in a much smaller contribution with isocyanate and cyclic carbonate functions. However, the large majority of the research on vegetable oil based PUs focuses on the synthesis of networks, and less attention has been paid to thermoplastic fatty acid based PUs.⁹⁰⁻⁹⁸

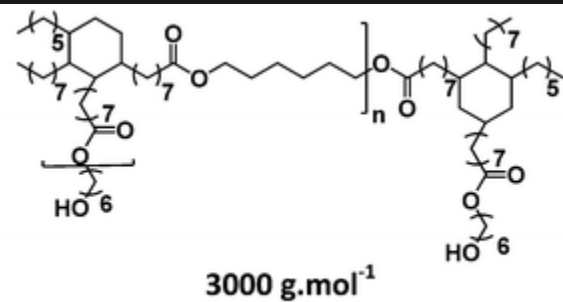
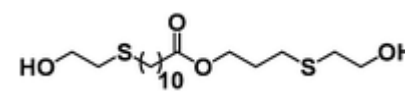
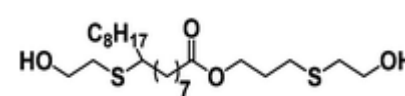
The following part covers the advances made in the synthesis of vegetable oil based difunctional PU precursors, collecting the literature data of the different synthetic routes used. [Table 2](#) summarizes all the literature concerning fatty acid based precursors for thermoplastic polyurethanes.

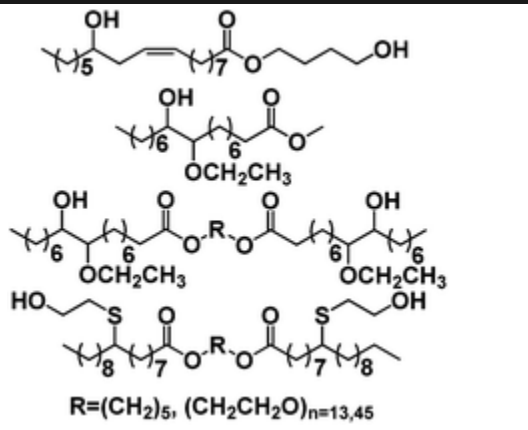
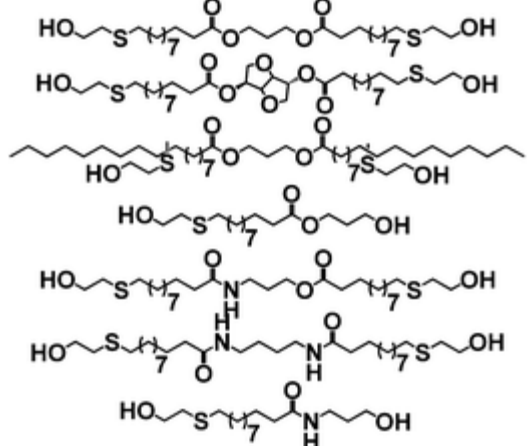
Table 2 Summarized literature concerning fatty acid based precursors for thermoplastic polyurethanes^a

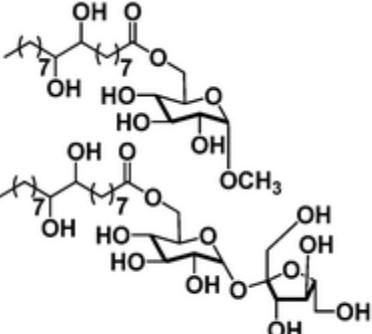

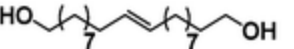
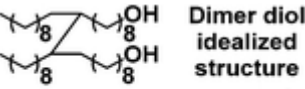
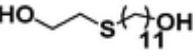
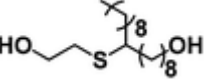
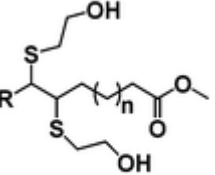
Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References
	MDI	—	-15 °C	—	$T_{5\%} = 307$ °C	100
 <p>2580 g.mol⁻¹ and 1,4-butanediol with SSC form 40% to 70%</p>	MDI	ns (40% SSC) ⁽¹⁾ 23 400 (50% SSC) ⁽¹⁾ 21 500 (60% SSC) ⁽¹⁾ 14 850 (70% SSC) ⁽¹⁾	From -71 °C to -56 °C (SS) and from 65 °C to 115 °C (HS)	From 170 °C to 220 °C (HS)	- TPE-U - Presence of “spherulitic-like” superstructures - Faster degradation rates than the corresponding petrochemical poly(ester urethane)s	101–103
 <p>1552 g.mol⁻¹ and 1,4-butanediol with SSC of 50% and 70%</p>	MDI	27 000 (50% SSC) ⁽¹⁾ 19 700 (70% SSC) ⁽¹⁾	-40 °C/-39 °C (SS) and 100 °C (HS)	-18 °C/-14 °C (SS) and 175 °C/180 °C (HS)		104
	HMDI	71 100 (83% SSC) ^(nr)	Below 0 °C (SS) and between 40 °C	Between 40 °C and 60 °C (SS)	- TPE-U	106

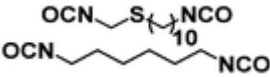
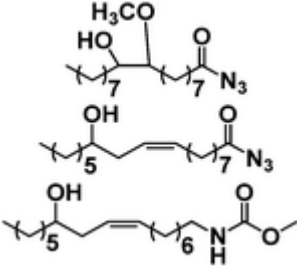
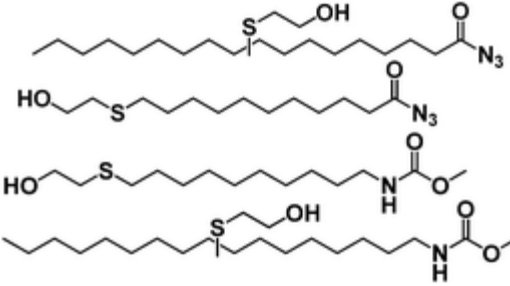
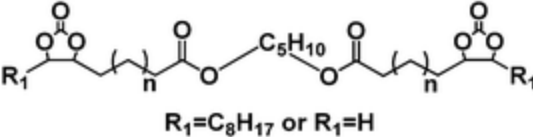
Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References
		73 100 (75% SSC) ^(nr)	°C and (HS)	60 °C and around 150 °C (HS)		
 <p style="text-align: center;">1320 g.mol⁻¹ and 1,3-propanediol with SSC from 54% to 83%</p>		56 300 (68% SSC) ^(nr)				
		48 500 (61% SSC) ^(nr)				
		39 200 (54% SSC) ^(nr)				
 <p style="text-align: center;">1900 g.mol⁻¹ and 3500 g.mol⁻¹ and 1,3-propanediol</p>	HMDI	74 500 and 63 400 (83% SSC) ^(nr)	Below 0 °C (SS)	Between 40 °C and 60 °C (SS)		106
		76 200 and 63 400 (75% SSC) ^(nr)		between 40 °C and 60 °C (HS)		
		35 700 and 64 100 (68% SSC) ^(nr)				
		31 700 and 59 700				

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References	
		(61% SSC) ^(nr) 34 350 and 42 100 (54% SSC) ^(nr)					
 <p>azealic acid + 1,9-nonanediol polyesters from 534 g.mol⁻¹ to 1488 g.mol⁻¹</p>	HPMDI	From 17 000 to 27 000 ⁽²⁾	-28 °C or not visible in DSC	From 54 °C to 71 °C	HPMDI: fatty acid based diisocyanate	107	
 <p>R=OH, COOH, CH₂-Si(OCH₃)₃ 3100 g.mol⁻¹ and 1,4-butanediol</p>	MDI	—	-45 °C (SS) and 55 °C (HS)	-9 °C (SS) and 190 °C (HS)		108	
	MDI	38 000 (90% SSC) ⁽²⁾ 28 300 (80% SSC) ⁽²⁾			From -51.3 °C to -47.8 °C (SS) and from 118.1 °C to 122.8 °C (HS)	Not clearly observable in DSC curves but around 200 °C	110

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References
 <p>3000 g.mol⁻¹ and 1,4-butanediol with SSC from 60% to 90%</p>		25 400 (70% SSC) ⁽²⁾ 14 700 (60% SSC) ⁽²⁾				
	MDI	50 900 and 71 200 ⁽¹⁾	20 °C	124 °C	Promising materials for 111 to good thermal and mechanical properties as well as no cytotoxic response to MTT tests	
	MDI	61 900 ⁽¹⁾	8 °C	—	Promising materials for 111 to good thermal and mechanical properties as well as no cytotoxic response to MTT tests	

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References
 <p>R=(CH₂)₅, (CH₂CH₂O)_{n=13,45}</p>	IPDI	From 2400 to 18 700 ⁽¹⁾	-49 °C to -11.5 °C	—		113–115
	IPDI, MDI	30 000 to 70 000 ⁽³⁾	-27 °C to 63 °C	116 °C to 183 °C	- Melt crystallization transitions from 83 °C to 158 °C upon heating - E(diester diol) = 287 MPa whereas E(diamide diol) = 775 MPa so 2.7 times higher	116

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References
 <p>Lipid based fatty acid polyols</p> <p>HO--OH</p> <p>HO--OH</p> <p>and 1,9-nonanediol</p> <p> Dimer diol idealized structure</p> <p>1000 to 2000 g.mol⁻¹</p> <p>HO--OH</p> <p>HO--OH</p> <p></p> <p>R=H or R=(CH₂)₇-CH₃</p>	IPDI	5700 to 32 000 ⁽³⁾	35 °C to 149 °C	—		117
	HMDI and HPMDI	38 000 and 41 000 ⁽⁴⁾	-5.6 °C and 0.3 °C	101.9 °C and 126.7 °C	and 1,7-Heptamethylene diisocyanate: fatty acid based diisocyanate	118 and 126
					Commercially available	121
	MDI	83 300 ⁽¹⁾	56 °C	115 °C and 141 °C		111
	MDI	36 300 ⁽¹⁾	28 °C	104 °C		111
	MDI	18 200 and 48 200 ⁽¹⁾	15 °C and 20 °C	—	The triol monomer can also be obtained after reduction of the ester function	122

Monomer 1	Monomer 2	M_n (g mol ⁻¹)	T_g	T_m	Comments	References
	Aliphatic, cyclo-aliphatic, fatty acid based diols	From 7900 to 26 000 ⁽³⁾	From -42.2 °C to 162.5 °C	From 45.1 to 171.4 °C	Fatty acid based diisocyanates using Curtius rearrangement without the use of sodium azide	128
		Up to 8900 ⁽¹⁾	From -22 °C to -53 °C (SS) and around 26 °C (HS)	—	Macrocycles formation	129
		Up to 11 800 ⁽¹⁾	From -44.5 °C to -7.7 °C (SS) and from 25.3 °C to 78.6 °C (HS)	Amorphous or Tm from 93.4 to 116.2 °C	- Preparation of copolymers - Macrocycles formation	130 and 131
 <p>$R_1 = C_8H_{17}$ or $R_1 = H$</p>	EDA, IPDA	From 3900 to 9000 ⁽¹⁾	From -25 °C to -13 °C	—	Side reaction of amide formation with EDA only	134 and 135

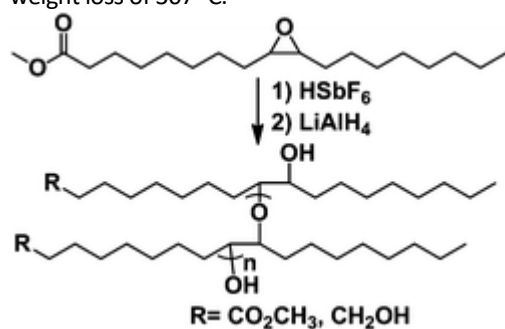
a SEC in THF⁽¹⁾, chloroform⁽²⁾, DMF⁽³⁾, chloroform–DMSO (1 : 1)⁽⁴⁾ or not referenced^(nr) with PS standards; T_g determined by DSC or DMA; SSC and HSC are the acronyms for soft and hard segment content; SS and HS are the acronyms for soft and hard segments; MDI = 4,4'-methylene diphenyl diisocyanate; IPDI = isophorone diisocyanate; HDI = 1,6-hexamethylene diisocyanate, HPMDI = 1,7-heptamethylene diisocyanate; IPDA = isophorone diamine; EDA = ethylene diamine.

III.1 Classical route from diols and diisocyanates

In line with the synthesis of fatty acid based thermoplastic PUs following the classical route, both diols and diisocyanates based on bio-resources are used.

III.1.1 Diols containing ether and ester functions

TPE-Us are commonly used because of their excellent properties, such as good transparency, tunable stiffness, good wear resistance, excellent biocompatibility, *etc.* These properties are obtained thanks to the alternating soft and hard segments in the structure of the polymer. Soft segments are usually flexible low glass transition polyether or polyester chains with molecular weight between 1000 and 4000 g mol⁻¹, and can be easily obtained from fatty acid derivatives. Hard domains are usually crystalline with high melting points. Polyetherpolyols represent 75% of the petrochemical polyols used for PUs.⁹⁹ However, only one example of TPUs from polyether diols was reported from vegetable oil derivatives.¹⁰⁰ This polyether diol containing ester pendant groups was obtained by the acid-catalyzed ring-opening polymerization of epoxidized methyl oleate and partial reduction with lithium aluminum hydride (LiAlH₄) (Scheme 18). These reactions were not well controlled and polyols with various hydroxyl functionality degrees were obtained depending on the conversion of the reduction step. PUs were synthesized with MDI. The TPU obtained with the polyether diol presented a low glass transition temperature of -15 °C and an interesting degradation temperature at 5% weight loss of 307 °C.

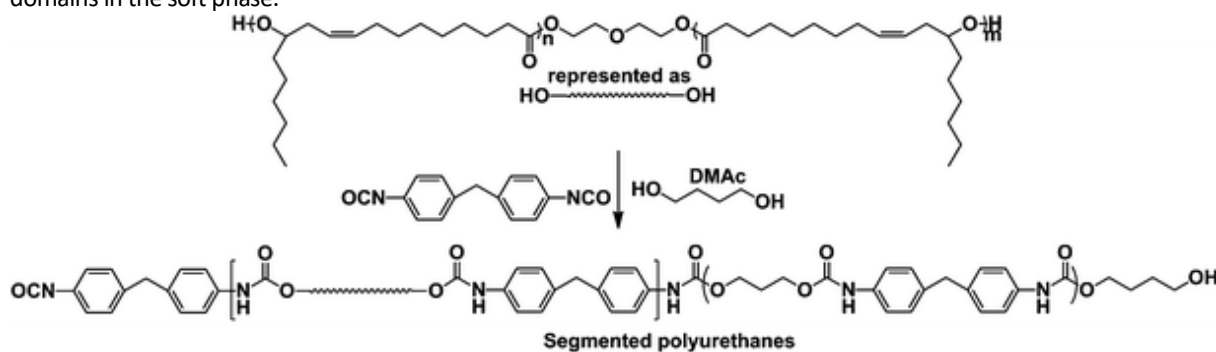


Scheme 18 Polyether diol containing ester pendant groups obtained by the acid-catalyzed ring-opening polymerization of epoxidized methyl oleate and a partial reduction with lithium aluminum hydride.¹⁰⁰

Polyester diols, diols containing ester and/or amide linkages, dimer diols, linear saturated or unsaturated diols and diols containing thioether linkages are reported using fatty acids or fatty acid methyl esters as starting materials. The synthesis of diols containing ester groups has been much more widely explored due to the initial presence of an ester or acid function in vegetable oil derivatives. Few research groups have prepared low T_g polyester diols from vegetable oil derivatives to use them in segmented thermoplastic elastomer polyurethanes (TPE-Us). The fatty acid based polyester diols were synthesized either by transesterification of methyl ricinoleate with diethylene glycol as an initiator, or by transesterification of diesters with diols in excess.

Petrović and coll. have used a poly(ricinoleic acid) diol of 2580 g mol⁻¹ as a soft segment to prepare a series of TPE-Us by reacting MDI and 1,4-butanediol with various soft segment weight concentrations ranging from 40% to 70% (ref. 101) (Scheme 19). The TPE-Us obtained display microphase separation and two glass transition temperatures at around -50 °C and 100 °C. Interestingly, "spherulitic-like" superstructures that are believed to arise from the nucleation and crystallization of the hard segments were noticed in these polymers. Melting points in the range of 170 °C to 220 °C were observed depending on the soft segment content. The mechanical and thermal features of these bio-based PUs suggest that they could be used in conventional TPE-U applications. Very recently, the same group has studied the phase structure of such segmented polyurethanes using DMA, AFM and SAXS.¹⁰² A co-continuous morphology with domains around 15 nm was obtained in the case of the TPE-Us with 50% of soft segment weight concentrations. However in the sample of TPE-Us with 70% of soft segment weight concentrations, dispersed hard domains were observed in the soft matrix. The biodegradation of these TPUs has been investigated by respirometry.¹⁰³ These TPE-Us with poly(ricinoleic acid) (PRic) as soft segments have been found to exhibit faster degradation rates than the corresponding petrochemical poly(ester urethane)s, even if this rate is relatively slow (about 11% carbon after 30 days). The authors observed that

TPE-Us with a co-continuous morphology demonstrated a slightly slower biodegradation than that with dispersed hard domains in the soft phase.



Scheme 19 Thermoplastic elastomer polyurethane prepared from poly(ricinoleic acid).¹⁰¹

Using the same methodology, a polyesterpolyol was prepared by transesterification of methyl 12-hydroxy stearate with 1,6-hexanediol catalyzed by titanium isopropoxide.¹⁰⁴ This precursor of molecular weight 1552 g mol^{-1} was used in segmented polyurethanes with MDI and 1,4-butanediol with 50% and 70% of soft segment content. Glass transition temperatures of $-40 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$ were obtained for the soft segments and hard segments respectively. Besides, melting points of $-18 \text{ }^\circ\text{C}$ to $-14 \text{ }^\circ\text{C}$ and $175 \text{ }^\circ\text{C}$ to $180 \text{ }^\circ\text{C}$ were observed for the soft segments and hard segments respectively.

More recently, polyester diols have been synthesized by transesterification of diesters with diols in excess. Using this strategy, Koning and coll. have prepared partially fatty acid based aliphatic polyester diols from dimethyl sebacate using TBD as a catalyst.¹⁰⁵ Moreover, Corcuera and coll. have used similar polyester diols from dimethyl sebacate with molecular weight from 1320 g mol^{-1} to 3500 g mol^{-1} to prepare TPE-Us with HMDI and 1,3-propanediol as the chain extender. The TPE-Us obtained by a two-step bulk polymerization without a catalyst exhibited a molecular weight in the range of 52.1 kg mol^{-1} to $138.9 \text{ kg mol}^{-1}$. The authors have studied the effect of the soft segment molecular weight on the morphology and the final properties.¹⁰⁶ A decrease in the polyester diol molecular weight leads to a better phase mixing between hard and soft domains, endowing higher glass transition temperature to the soft segments than the one for the pre-polyester diol. The same approach has also been used to synthesize polyester diols from azelaic acid and 1,9-nonanediol using titanium(IV) butoxide, with molecular weight in the range of 500 to 1500 g mol^{-1} . The effect of the polyester diol has then been studied in aliphatic thermoplastic poly(ester urethane)s with HPMDI.¹⁰⁷ Incorporation of various lengths of polyester diols into the TPUs enabled control of the crystalline morphology, chain dynamics, and eventually the strength of the polymer. The crystal structure and the physical properties are directly linked to the polyester chain length and can be explained by the interplay between polyester dipole–dipole intermolecular forces, as well as by the van der Waals and hydrogen bonding attractive interactions.

Another effective strategy developed by Cádiz and coll. has been used to prepare polyester diols.¹⁰⁸ These telechelic macrodiols with a molecular weight of 3.1 kg mol^{-1} have been synthesized through two one-pot thiol–ene reactions: first a step growth polymerization using 3,6-dioxa-1,8-octanedithiol and then an end-group postpolymerization modification with 2-mercaptoethanol. Then TPE-Us have been prepared with MDI and 1,4-butanediol. A low glass transition temperature and melting point at respectively $-45 \text{ }^\circ\text{C}$ and $-9 \text{ }^\circ\text{C}$ were observed, which correlate well with the thermal properties of the polyester diol precursor. The phase separated morphology has been confirmed by the hard segment transitions: a second glass transition at $55 \text{ }^\circ\text{C}$ and a broad melting endotherm at $190 \text{ }^\circ\text{C}$.

An alternative route to synthesize TPE-Us with a fatty acid based diol as the soft segment is to use the CRODA polyester diol synthesized by transesterification between dimerized fatty acids (obtained by Diels–Alder reaction) and an excess of linear diol. Averous and coll. have synthesized bio-based TPE-Us from this diol with dangling chains having a weight average molecular weight of 3 kg mol^{-1} , MDI and 1,4-butanediol with several hard segment contents from 10% to 40%.^{109,110} Molar masses of 14.7 kg mol^{-1} to 38.0 kg mol^{-1} with dispersity from 2.17 to 5.52 have been attained. Only one glass transition temperature at $-47.0 \text{ }^\circ\text{C}$ was noticed for the PU with 10% of hard segments. Otherwise two glass transition temperatures were obtained, one for the soft segments ($-51.3 \text{ }^\circ\text{C}$ to $-47.8 \text{ }^\circ\text{C}$) and one for the hard segments ($118.1 \text{ }^\circ\text{C}$ to $122.8 \text{ }^\circ\text{C}$). Melting points around $200 \text{ }^\circ\text{C}$ are observed for PU with a hard segment content of 30% and 40%. By selecting the appropriate hard segment concentration, different thermo-mechanical properties were achieved which could fulfill some industrial requirements in diverse fields.^{109,110}

In line with obtaining well defined monomers, several research groups have synthesized accurate bis-unsaturated compounds with one or two ester functions from methyl oleate and methyl undecenoate or from the corresponding acid derivatives.¹¹¹ Afterwards, the hydroxyl moieties were introduced on the double bonds by the thiol–ene reaction or ring opening of epoxy. By using the thiol–ene reaction method, asymmetric ester diols have been prepared from oleic

and undecylenic acids by esterification with allyl alcohol and thiol–ene reaction with 2-mercaptoethanol. Polymerizations with MDI and using tin(II) 2-ethylhexanoate as the catalyst have led to TPUs with molar masses from 50 to 70 kg mol⁻¹ and dispersity in the range of 1.6–1.9. Amorphous ($T_g = 8\text{ °C}$ to 20 °C) to semi-crystalline PUs ($T_m = 124\text{ °C}$) were obtained depending on the fatty derivative used. These TPUs revealed both good thermal and mechanical properties as well as no cytotoxic response thanks to the MTT test, which make them possible candidates for biomedical purposes.

Boutevin and coll. have used a similar strategy to prepare symmetrical diester diols by transesterification of methyl oleate with ethylene glycol followed by grafting of 2-mercaptoethanol onto the double bonds using thiol–ene click chemistry.¹¹² The diester diols appeared not pure enough to synthesize TPUs. Finally, PU networks with interesting thermal properties were obtained by step growth polyaddition with MDI.

To further explore the potential of such diester diols, Cramail and coll. have synthesized a plethora of diester diols by transesterification of methyl oleate or methyl undecenoate with various central diol blocks followed by either the thiol–ene reaction with 2-mercaptoethanol, or ring opening of epoxidized double bonds, as illustrated in Fig. 2.^{113–115} Diols containing ether linkages were also synthesized in this work. These diester diols have been polymerized with IPDI in the presence of dibutyl tin dilaurate (DBTDL) as a catalyst. The behavior of the PUs was correlated with the purity and chemical structure of the starting ester containing diols. As expected, the reactivity of primary diols obtained by the thiol–ene reaction was found to be higher than the one of secondary diols synthesized by ring opening of the epoxide, yielding higher molecular weight TPU up to 35 kg mol⁻¹. The rheological properties were also impacted by the monomer structure and purity. Glass transitions below room temperature were observed due to the pendant alkyl chains along the polyurethane backbone.

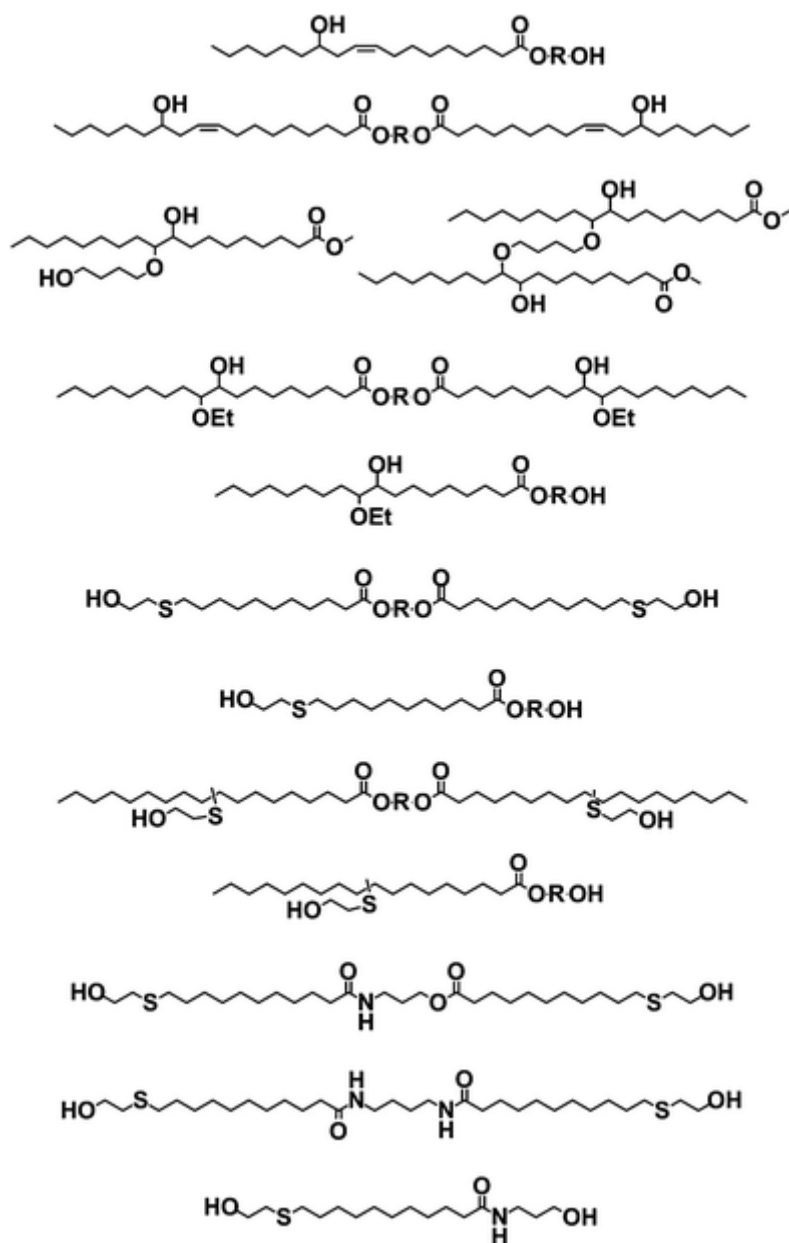
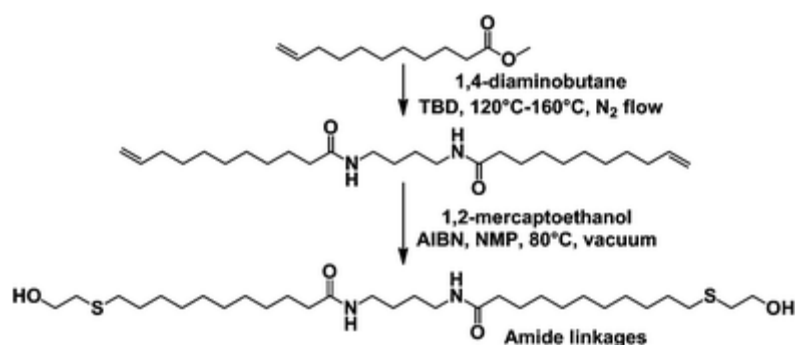


Fig. 2 The large range of diols that can be obtained from methyl undecenoate, methyl oleate and methyl ricinoleate by transesterification, amidation, thiol-ene reaction and epoxidation/ring opening of the epoxide.¹¹³⁻¹¹⁵

Very recently, we reported higher glass transition temperature amorphous and semi-crystalline fatty acid based TPUs.¹¹⁶ For that purpose methyl undecenoate was used, and stronger amide linkages were incorporated in the diols to end up with diols containing ester and/or amide linkages (Scheme 20). These diols were polymerized with IPDI and MDI as comonomers. Amorphous TPUs with glass transition temperature up to 51 °C were observed in the case of monomers with a linear structure with isosorbide as a central block, as well as in the presence of amide functions and/or high urethane function densities. The semi-crystalline TPUs exhibited melt crystallization transitions from 83 °C to 158 °C upon heating and melting point values from 116 °C to 183 °C. Amide moieties, due to strong hydrogen bonds, have been clearly proven to lead to TPUs with higher glass transition temperatures, melting points and Young's modulus and ultimate tensile strengths. As an example, the Young's modulus for diester diol TPU was 287 MPa, whereas the one for diamide diol TPU was 2.7 times higher (775 MPa). The ultimate strength was also higher for diamide diol TPU (48.3 MPa) than for diester diol TPU (17.4 MPa). However the maximum strain was lower for diamide diol TPU (44%) than for diester diol TPU (266%).



Scheme 20 Fatty acid based diol containing amide functions.¹¹⁶

Cramail and coll. also prepared sugar-based fatty ester polyols by selective transesterification of epoxidized methyl or ethyl oleate with unprotected methyl α -D-glucopyranoside and sucrose respectively, followed by hydrolysis of the epoxide moiety.¹¹⁷ The polyols were then used in polyurethanes with IPDI in the presence of dibutyl tin dilaurate (DBTDL) as a catalyst. The authors noticed that the reactivity of the hydroxyl functions attached to the sugar and to the fatty ester chain moieties respectively could be discriminated with respect to the solvent used, enabling the synthesis of either linear or cross-linked PUs.

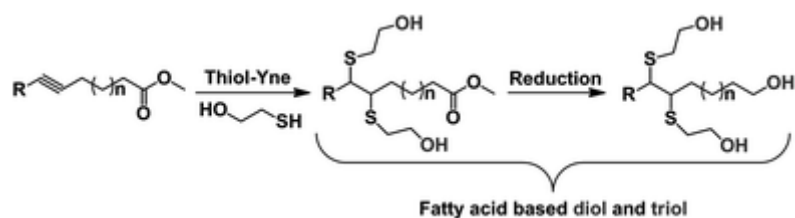
III.1.2 Saturated and unsaturated diols

By taking advantage of the prominent tool, which is the metathesis reaction, Narine and coll. have synthesized 1,18-octadec-9-enediol, a long chain diol from oleic acid, by self-metathesis followed by reduction to the diol with an overall yield of 58%.¹¹⁸ Alternatively, a saturated shorter terminal diol, 1,9-nonanediol, has been synthesized from oleic acid with a purity of 99% and an overall yield of 72%. These diols were reacted with different diisocyanates namely HMDI and the fatty acid based HPMDI to give TPUs. The properties of such aliphatic TPUs will be described in the section on fatty acid based diisocyanates.

Dimerization of oleic and linoleic acids could also be done to synthesize saturated diols with pendant chains. This complex reaction is realized at high temperatures with homogeneous catalysts such as ionic salts of alkali metals, or heterogeneous catalysts such as clays (montmorillonite or bentonite) or aluminosilicates. The synthesized diacids are reduced to yield fatty acid based diols. This methodology was initially introduced, in the 1950s, by General Mills Chemicals and Emery (became Cognis Corp. acquired by BASF).^{119,120} These fatty acid dimer diols are commercially available and used in TPUs providing biocompatibility, high hydrophobicity, stretching and chemical stability properties.¹²¹

III.1.3 Diols containing thioether linkages

In line with using efficient functionalization techniques such as thiol-ene and thiol-yne reactions, fatty acid based diols containing thioether linkages have been synthesized. Diols from the thiol-ene reaction of methyl oleate and methyl undecenoate with 2-mercaptoethanol followed by reduction of the ester group using LiAlH_4 have been reported.¹¹¹ Afterwards TPUs having molar masses from 40 to 80 kg mol^{-1} and dispersities in the range of 2.1–2.2 were obtained with MDI. Only semi-crystalline PUs were obtained with glass transition temperature from 28 °C to 56 °C and melting temperatures around 110 °C. No cytotoxic response was observed for these TPUs and hence they are suitable in the medical field. In a significant contribution, the same group demonstrated the use of the thiol-yne reaction for the synthesis of polyols and in particular diols for PUs.¹²² These diols were synthesized in two steps, the first being an alkyne derivatization of fatty acids by bromination and dehydrobromination of the double bond, and the second being a thiol-yne addition with 2-mercaptoethanol (Scheme 21). The TPUs obtained with MDI as a comonomer were amorphous ($T_g = 15\text{--}20$ °C). Based on the analyses of biocompatibility in terms of cell attachment of an osteoblastic cell line, the authors have suggested using these PUs as polymeric scaffolds for tissue engineering.



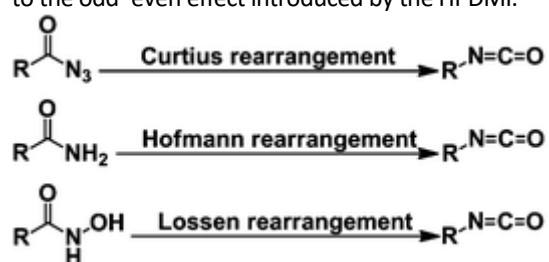
Scheme 21 Use of the thiol-yne reaction to prepare diols and triols.¹²²

Although the literature above proved the contribution of research groups to the synthesis of TPUs from fatty acid based diols, a lack of papers on fatty acid based diisocyanates is unfortunately observed. Besides, to avoid isocyanates due to their high toxicity, only very few papers present the use of isocyanate-free routes toward vegetable oil based TPUs.

III.1.4 Diisocyanates

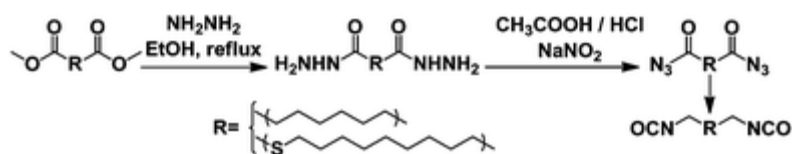
Vegetable oil based poly- or di-isocyanates have effectively been studied to a much lesser extent perhaps as a consequence of the inherent aliphatic structure of the isocyanate that could be prepared. Indeed the most commonly used diisocyanates industrially are aromatic namely MDI and TDI due to a higher reactivity required to produce foams. Thus, the uses of aliphatic diisocyanates are limited to coatings in which the absence of unsaturation is profitable. In industry, isocyanates are synthesized from primary amines by phosgenation. As primary amines are not easily introduced into vegetable oils, other strategies have been developed on vegetable oils and their derivatives. Two distinct methods have been employed to incorporate isocyanate functions on triglycerides involving either the use of expensive silver isocyanate,¹²³ or the use of iodo isocyanate reagent.¹²⁴

Isocyanates can be synthesized in other ways by taking the advantage of Curtius, Hoffman and Lossen rearrangements, which involve nitrene intermediates (see [Scheme 22](#)). In an effort to access fatty acid based diisocyanates, Narine and coll. used the Curtius rearrangement to prepare oleic acid based linear diisocyanates, both saturated and unsaturated.^{125,126} Two linear diacids were first synthesized by methods reported earlier in this review, then converted to acyl azides by the reaction with sodium azide, which upon heating decomposed to isocyanates. The fatty acid based HPMDI was used to prepare TPUs and compared with HMDI.¹¹⁸ The odd number of methylene groups in HPMDI based TPUs affected the thermo-mechanical properties, because the crystal structure was less ordered and the strength of the hydrogen bonding was weaker. Indeed lower glass transition and melting temperatures were obtained for HPMDI based TPUs than for HMDI based TPUs. Still the authors claim that HPMDI based TPUs exhibit comparable properties to HMDI based TPUs within acceptable limits considering the impacts on physical properties due to the odd-even effect introduced by the HPMDI.



Scheme 22 Rearrangements to isocyanates.

A very recent paper from our group reports the synthesis of fatty acid based diisocyanates using the Curtius rearrangement through acyl hydrazide fatty acid based derivatives without the use of harmful sodium azide ([Scheme 23](#)).¹²⁸ Diesters were first synthesized and then reacted with hydrazine hydrate to form diacyl hydrazides in quantitative yields. Afterwards, these diacyl hydrazides were converted into diacyl azides and then into diisocyanates via the Curtius rearrangement. A series of partially and fully vegetable oil based TPUs were synthesized and a large range of thermo-mechanical properties were achieved. Relatively good thermal behaviors were observed with decomposition temperatures at 5% weight loss from 230 °C to 280 °C. For some polyurethanes, a close resemblance to HDPE was obtained in terms of solubility and thermal transitions with melting points close to 145 °C.



Scheme 23 Fatty acid based diisocyanates using hydrazine hydrate.¹²⁸

III.2 Isocyanate-free and phosgene-free routes to polyurethanes

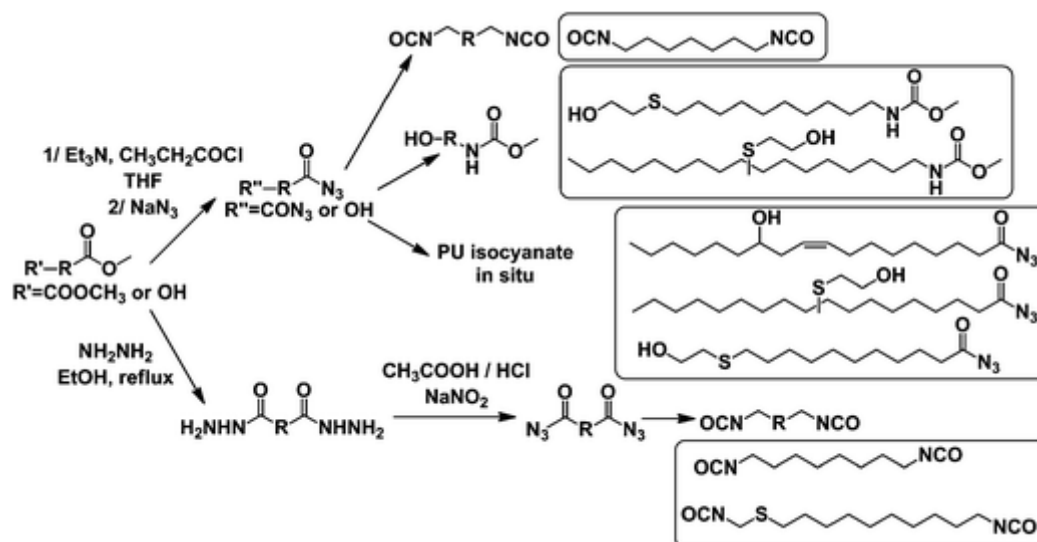
The development of isocyanate-free and phosgene-free chemistries is one of the major challenges in the field of PU thermosets and TPUs, and thus for vegetable oil based PUs and TPUs, due to their toxicity.

III.2.1 *In situ* generation of diisocyanates

Self-polycondensation and transurethane approaches have been used to prepare TPUs using novel vegetable oil-based AB-type monomers with *in situ* generation of isocyanates.

Two different kinds of monomers have been prepared from methyl oleate and ricinoleic acid. In both routes, the hydroxyl groups have been obtained either from the naturally occurring OH in ricinoleic acid, or by epoxidation of the double bond of methyl oleate and ring opening of the epoxide with methanol. In the first approach, AB-type monomers with hydroxyl and acyl azide functionalities, namely a mixture of 10-hydroxy-9-methoxyoctadecanoyl azide/9-hydroxy-10-methoxyoctadecanoyl azide (HMODAz) and 12-hydroxy-9-*cis*-octadecenoyl azide (HODEAz) were prepared as described previously using sodium azide.¹²⁹ The polymerizations of HMODAz and HODEAz monomers were carried out by the acyl-azido and hydroxyl AB-type self-condensation upon heating, with and without a catalyst. It was demonstrated that the polymerization of the acyl azide occurred through its thermal decomposition in the first minutes of the reaction to isocyanate, known as the Curtius rearrangement, which further condensed with the hydroxyl group to form the TPUs. In the second approach, AB-type monomers with hydroxyl and methyl carbamate functionalities, that is methyl-*N*-11-hydroxy-9-*cis*-heptadecen carbamate (MHHDC), were obtained by reacting the above acyl azide with methanol. Transurethanization can then be conducted using a titanium catalyst to give TPUs. Self-polycondensation of an AB-type monomer has the advantage of controlling the stoichiometry to achieve high molar mass TPUs. However, due to the formation of macrocycles, comparatively low molecular weights in the range of 740 to 8890 g mol⁻¹ with dispersity in the range of 1.5 to 2.3 were observed for all TPUs formed by both processes. Two different glass transition temperatures for soft segments (-53 °C to -22 °C) and hard segments (around 26 °C) were observed in these TPUs, which indicates a phase-separated morphology. Only a very small difference, in terms of thermo-mechanical properties, was noticed between the PUs obtained by the two methods.

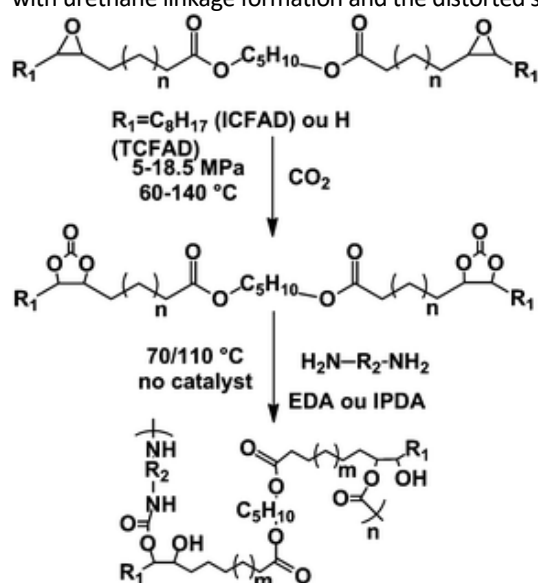
In line with obtaining higher glass transition TPUs and limiting macrocycle formation, we used methyl undecenoate as the starting material and introduced hydroxyl functions *via* the thiol-ene reaction. Therefore, four new AB type monomers from methyl oleate (HETOAz and MHETHC) and from methyl undecenoate (HETUAz and MHETDC) were synthesized following the same strategy. Both amorphous and semi-crystalline TPUs with reasonably high molar masses were achieved. By taking advantage of the different thermo-mechanical properties of poly(HETOAz) and poly(HETUAz), random copolymers were also prepared to adjust the final nature of the TPUs.^{130,131} In Scheme 24, the different routes to isocyanates or their equivalents are summarized.



Scheme 24 Summary of the different routes to isocyanates or their equivalents.^{125,129,130}

III.2.2 Poly(hydroxyurethane)s

In addition to the *in situ* generation of diisocyanates, a phosgene-free route has been studied to synthesize TPUs from vegetable oil based bis-cyclic carbonates and diamines. Reviews on the synthesis of poly(hydroxyurethane)s are available in the literature.^{95,96,127,132} The solubility of the fatty acid based bis-epoxides in supercritical CO₂ as well as the carbonation conditions has been studied.¹³³ The two bis-cyclic carbonates, internal carbonated fatty acid diester (ICFAD) and terminal carbonated fatty acid diester (TCFAD), were prepared from the corresponding methyl oleate and methyl undecenoate based bis-epoxides and carbon dioxide in the presence of tetrabutylammonium bromide (TBABr) as a catalyst. Further, these monomers were polymerized with ethylene diamine and isophorone diamine to form TPUs containing hydroxyl moieties (Scheme 25).^{134,135} The TPUs presented molecular weights up to 13500 g mol⁻¹ and exhibited relatively low glass transition temperatures ranging from -25 °C to -13 °C. As expected, TCFAD displayed a higher reactivity than ICFAD and poly(TCFAD) had slightly enhanced molecular weights and *T_g* values compared to poly(ICFAD). Nevertheless, an amidation side reaction occurs between amine functions and the ester linkages of the diester bis-cyclic carbonates giving amide groups. Thus the final polymer structure is affected due to the competition with urethane linkage formation and the distorted stoichiometry conditions.^{134,135}



Scheme 25 Poly(hydroxyurethane)s from fatty acid or fatty acid methyl ester.¹³⁴

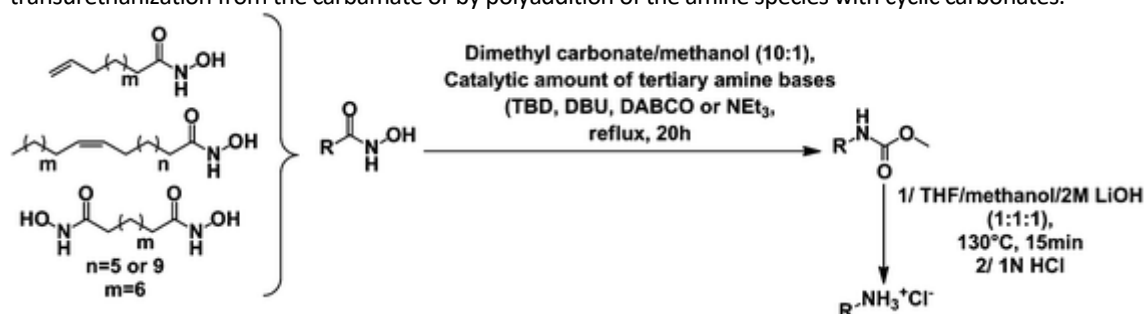
Besides, being at the end of a long alkyl chain in vegetable oil derivatives, the reactivity of the cyclic carbonates was lower than that of petrochemical systems due to +I inductive effects. Remarkably long polymerization times have been reported in vegetable oil based polyhydroxyurethane networks.¹³⁶⁻¹³⁸

Another possibility to synthesize bis-cyclic carbonates is to use glycerol carbonate¹³⁹⁻¹⁴² or unsaturated cyclic carbonates,¹⁴³⁻¹⁴⁵ but those strategies are out of the scope of this review.

Despite that amine groups have been introduced in vegetable oil derivatives to prepare bio-based polyamides, to the best of our knowledge, no reports refer to the use, in PUs and TPUs, of vegetable oil-based diamines.

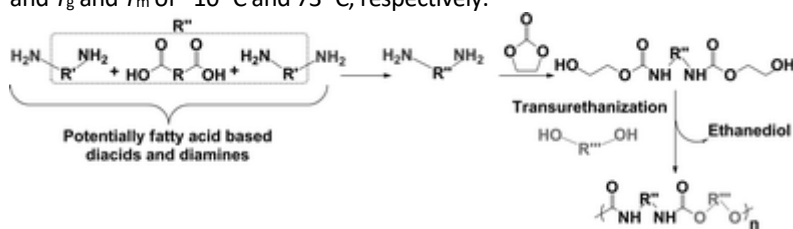
III.2.3 Transurethanization procedure

A promising route to fatty acid based carbamates and amines is described here. Recently, Meier and coll. used a variant of the Lossen rearrangement on fatty acid based hydroxamic acids to prepare methyl carbamates using dimethyl carbonate in methanol with a catalytic amount of tertiary amine bases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-biazabicyclo 5.4.0 undec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]octane (DABCO), and tri-ethylamine (Scheme 26).¹⁴⁶ This process could be used for polyurethane synthesis without the use of phosgene and isocyanate, either by transurethanization from the carbamate or by polyaddition of the amine species with cyclic carbonates.



Scheme 26 Promising route to fatty acid based carbamates and amines.¹⁴⁶

Transurethanization is effectively an interesting route to non-isocyanate and non-phosgene polyurethane. This approach, already described by Dyer and Scott,¹⁴⁷ Rokicki and Piotrowska¹⁴⁸ and Blank,¹⁴⁹ has been used on vegetable oil derivatives and was presented in the 2013 AOCs meeting by Narayan and coll.¹⁵⁰ Following this route, illustrated in Scheme 27, they have synthesized poly(amide urethane)s with a number average molecular weight of 8000 g mol⁻¹, and T_g and T_m of -10 °C and 73 °C, respectively.



Scheme 27 Polyurethanes from ethylene carbonate by transurethanization.¹⁵⁰

III.3 Conclusion (PU)

Vegetable oils provide a great opportunity to tailor TPUs *via* the synthesis of fatty acid based diols, diisocyanates, self-condensable monomers and bis-cyclic carbonates depending on the method used. TPUs for current applications have been developed. Numerous studies have been performed on the preparation of TPE-Us with phase separation induced by fatty acid based polyester diols. Click chemistry and precisely thiol-ene reactions have been widely used to functionalize vegetable oil derivatives in order to prepare TPU precursors. However, very few papers are available in the literature on the preparation of fatty acid based diisocyanates and phosgene-free thermoplastic poly(hydroxyurethane)s. Table 2 reports all the literature available on fatty acid based thermoplastic polyurethanes.

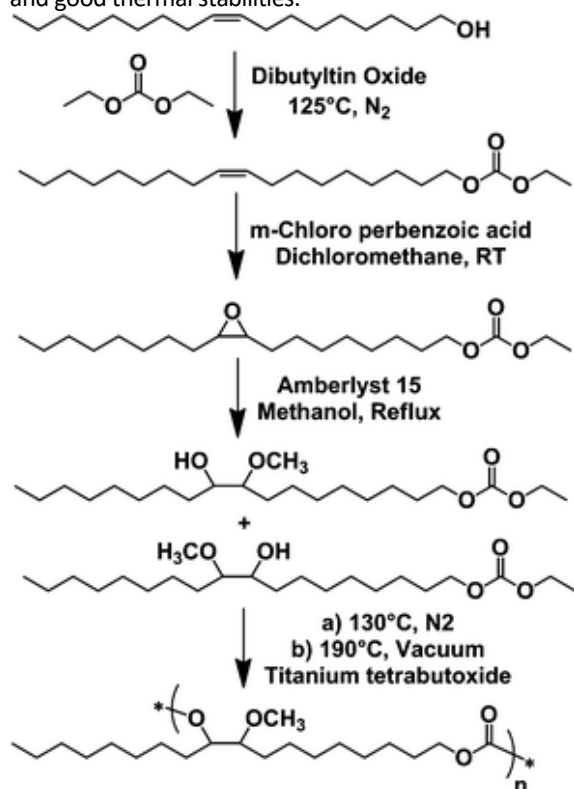
IV Miscellaneous

Other thermoplastic polymers such as polycarbonates, polyamides, polyethers, polyanhydrides, polyacetals, poly(alkylacrylate)s, poly(alkylmethacrylate)s and polyoxazolines have also been synthesized from vegetable oil derivatives.

IV.1 Polycarbonates

Polycarbonates are important engineering plastics that are generally divided into two classes: aromatic and aliphatic polycarbonates. Aliphatic polycarbonates are very useful in a wide range of applications thanks to their biocompatibility, biodegradability and low toxicity.

Enlarging the scope of monomers from fatty acids polymerizable by ADMET, Meier and coll. developed a methodology based on the use of dimethyl carbonate and TBD as a catalyst for the synthesis of various carbonate molecules.¹⁵¹ Among these carbonates, one was obtained by the reaction of 10-undecenol with dimethyl carbonate. The bis-unsaturated compounds were then polymerized by ADMET. High molecular weights were obtained whatever the catalyst used (from 9.5 to 27.5 kg mol⁻¹); however no thermal characterizations were done in this study. Soft aliphatic polycarbonates have also been described by Cramail and coll. using ricinoleic acid and oleic acid as a feedstock.¹⁵² A novel AB type monomer comprising a carbonate function and a hydroxyl function was first synthesized from oleyl alcohol (Scheme 28). This monomer was polymerized by alcohol-carbonate exchange self-polycondensation and revealed molecular weights in the range of 5 to 14 kg mol⁻¹ depending on the reaction time. These polycarbonates were fully amorphous due to plasticization with the alkyl dangling chain, and showed a low T_g of -60 °C. Using a different approach, a bis-carbonate monomer presenting an internal ester function was synthesized from ricinoleic acid. It was then polymerized with various diols yielding poly(ester-carbonate)s with molecular weights in the range of 6 to 15 kg mol⁻¹. ¹³C NMR analysis of these poly(ester-carbonate)s revealed the formation of random sequences due to the carbonate interchange reactions. The ricinoleic acid diol used for the synthesis of the bis-carbonate was also subjected to direct polycondensation with diethyl carbonate in stoichiometric amounts; however NMR analyses as well as MALDI-TOF spectroscopy revealed the formation of PRic mainly. All these polycarbonates revealed very low T_g (-60 to -70 °C) and good thermal stabilities.



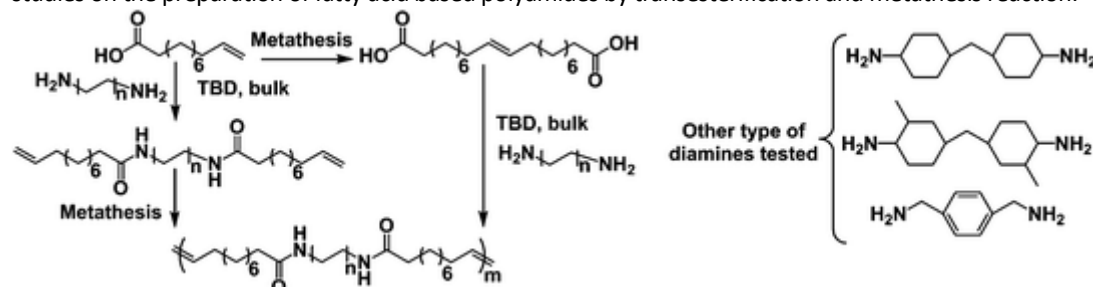
Scheme 28 Synthesis of a polycarbonate by AB-type self-condensation of a hydroxyl carbonate obtained from oleyl alcohol.¹⁵²

Starting from 1,10-decanediol, a molecule readily available from sebacic acid by simple reduction, Miller and Vanderhenst described two distinct routes to aliphatic polycarbonates.¹⁵³ In a first approach, an α,ω -bis-carbonate was synthesized from the reaction of the diol with either methylchloroformate or dimethyl carbonate. This monomer was then polymerized by carbonate interchange reactions in the melt in the presence of various catalysts yielding polycarbonates with molecular weight in the range of 8–50 kg mol⁻¹. In a second approach, the direct one-pot synthesis of the polycarbonate by reaction of the diol with dimethyl carbonate was realized and also afforded good molecular weight polymers (in the range of 8–30 kg mol⁻¹). The polycarbonate formed bearing 10 methylene spacers was semi-crystalline with a melting point of 58 °C.

IV.2 Polyamides

Thermoplastic polyamides (PA) are remarkable high performance engineering thermoplastics. Their demand increased by 28% from 2009 to 2011 in Europe.¹ Hydrogen bonds between amide linkages give rise to excellent properties, such as a high modulus, good toughness, relatively high melting points, and heat resistance, abrasion resistance, as well as chemical inertness.¹⁵⁴ Among the different types of polyamides, approximately 85–90% are PA-6 and PA-6,6. Concerning industrial fatty acid based polyamides, the most prominent example is the fully fatty acid based AB-type PA-11 which has been produced from ricinoleic acid present in castor oil for nearly fifty years by Arkema under the trade name Rilsan®.^{155,156} Various other chemical companies produced fatty acid-based polyamides such as Rhodia (Technyl® eXten, a PA-6,10), BASF (Ultramid® Balance, a PA-6,10), and Evonik (VESTAMID® Terra, PA-6,10 and fully bio-based or potentially fully bio-based PA-10,10 and PA-10,12).

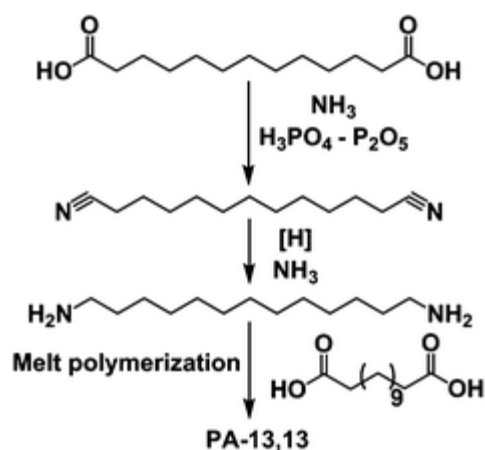
With regard to polyamides, vegetable oils represent an excellent source for obtaining aliphatic diacids or diesters and diamines. A lot of researchers have synthesized partially fatty acid based polyamides from azelaic acid (PA-6,9 and PA-6,6,9), sebacic acid (PA-6,10 (ref. 157)), dimer fatty acids^{158,159} and brassylic acid.¹⁶⁰ The polycondensation between diacids and diamines has also been reported by Meier and Mutlu.¹⁶¹ Unsaturated PA-X,20 has been synthesized by polycondensation of the self-metathesis product of 10-undecenoic acid and various diamines. Simultaneously, the preparation of PA-X,20 by ADMET of a bis-unsaturated diamide from methyl 10-undecenoate has been investigated. PA-X,20 with melting points from 180 °C to 226 °C were obtained. Fradet and coll. studied various diamines such as aliphatic-, cycloaliphatic-, or benzylic ones and used the same methodology.¹⁶² Scheme 29 illustrates those two latter studies on the preparation of fatty acid based polyamides by transesterification and metathesis reaction.



Scheme 29 Preparation of fatty acid based polyamides by polycondensation or metathesis.^{161,162}

In an effort to produce fully bio-based polyamides, Koning and coll. have synthesized a fully renewable polyamide from sebacic acid and diaminoisoidide as well as 1,4-diaminobutane.¹⁶³ Homopolymers and copolymers with various ratios of diaminoisoidide and 1,4-diaminobutane have been prepared. The polyamides presented melting point values in the range of 152 °C to 246 °C and temperature at 5% mass loss between 300 °C and 424 °C. The incorporation of diaminoisoidide resulted in the decrease of the melting temperature due to the structure of the monomer that induced more complex packing of the polymer chains, and thus led to a decrease of the temperature at 5% mass loss. However, very few literature data are available on fully fatty acid based thermoplastic polyamides. This observation is correlated with the few methods developed to introduce amine groups on vegetable oil derivatives.

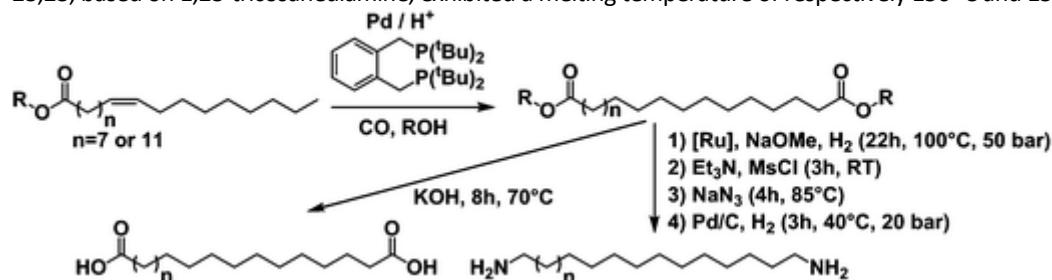
In the 1960s–1970s, the production of 1,13-tridecane diamine, from brassylic acid, and PA thereof was investigated. The diamine synthesis was performed *via* a dinitrile intermediate by reaction of brassylic acid with ammonia under specific conditions^{164,165} (Scheme 30). PA derived from brassylic acid presented lower water absorption than PA-11 and PA-6,10.



Scheme 30 Synthesis of PA-13,13 from brassylic acid.^{164,165}

Fu and coll. have fully characterized PA-13,13 in terms of thermal properties, crystal structure and mechanical properties.¹⁶⁶ The glass transition temperature (T_g) and melting temperature (T_m) were determined to be 56 °C and 174 °C respectively. Muñoz-Guerra and coll. also carried out structural analyses of PA-13,13.¹⁶⁷ Very recently, PA-13,6 was prepared from 1,13-tridecane diamine and adipic diacid.¹⁶⁸ PA-13,6 presented a similar glass transition temperature (60 °C) to PA-13,13 but a higher melting temperature (206 °C). A crystallite reorganization process has been underlined in this PA-13,6.¹⁶⁹

Mecking and coll. have reported on the isomerising alkoxy-carbonylation of either methyl oleate and ethyl erucate followed by hydrolysis yielding C19 (dimethyl 1,19-nonadecanedioate) and C23 (diethyl 1,23-tricosanedioate) long-chain α,ω -diacid compounds in good purity.³² C19 and C23 diamines were obtained *via* a four-step reaction through diol then dimesylate and finally diazide compounds (Scheme 31). The polycondensation of the diester compounds with their respective diamine derivatives resulted in polyamides with molecular weight around 10 kg mol⁻¹. PA-23,19 and PA-23,23, based on 1,23-tricosanediamine, exhibited a melting temperature of respectively 156 °C and 152 °C.

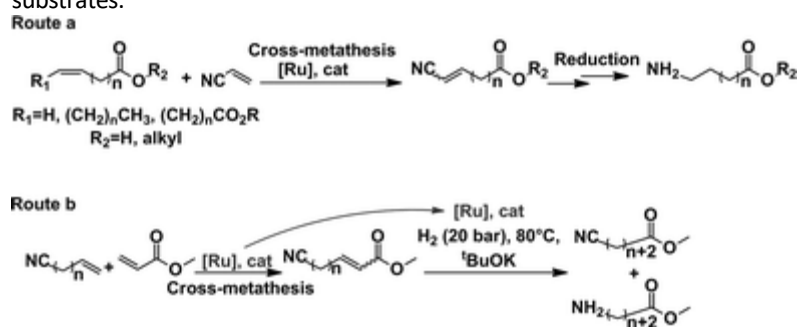


Scheme 31 Synthesis of diacids and diamines from methyl oleate and erucate.³²

Walther *et al.* have also prepared nonadecane 1,19-diamine by direct amination of the corresponding diol with excess ammonia at 140 °C for 48 h in the presence of a ruthenium phosphine catalyst.¹⁷⁰ The diol was obtained from the dimethyl ester, directly obtained from the high-oleic sunflower oil *via* a parallel and/or subsequent sequence of transesterification/isomerization, and methoxycarbonylation. The corresponding polyamides were not prepared.

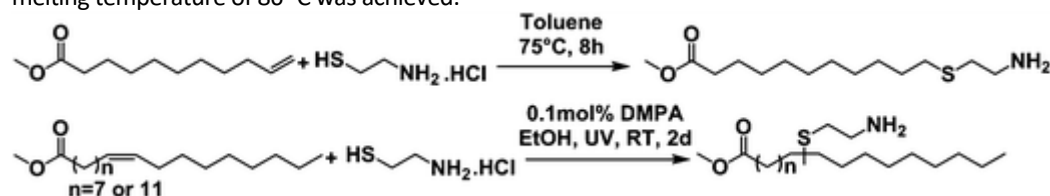
Another efficient way to produce PA is the polycondensation of aminocarboxylic acids. Greene *et al.* have synthesized 13-aminotridecanoic acid from erucic acid using various methods but PA-13 was not prepared.¹⁷¹ Dixneuf and coll. synthesized amino esters from methyl 10-undecenoate, dimethyl octadec-9-ene-1,18-dioate and methyl ricinoleate using a two-step reaction involving a metathesis reaction between the unsaturated fatty acid derivatives and acrylonitrile followed by amine formation by reduction (route a in Scheme 32).¹⁷² The best protocol was based on the slow addition of the catalyst, which allowed turnover numbers as high as 1900 (92% yield). In a second study, the same group analyzed a route involving the cross-metathesis of 10-undecenitrile arising from castor oil with methyl acrylate (route b in Scheme 32).¹⁷³ Under optimal conditions a turnover number of 17 200 (86% yield) of the fatty acid based nitrile is obtained. Hydrogenation of the C=C double bond and the nitrile moieties finally gives access to the amino ester. This procedure was preferred to the cross-metathesis between the fatty acid esters and the acrylonitrile due to higher turnover numbers. This amino ester, prepared by this sustainable way, could be useful for polyamide synthesis. Indeed, a single catalyst is introduced to perform three catalytic transformations (cross-metathesis, C=C double bond

hydrogenation and nitrile reduction) from methyl acrylate and undecenitrile, which are potential bio-based substrates.



Scheme 32 Synthetic routes to amino esters by sequential metathesis and hydrogenation reactions.^{172,173}

Meier and coll. prepared fatty acid based polyamides by AB polycondensation. The amine groups have been incorporated into methyl 10-undecenoate, methyl oleate and methyl erucate by the thiol–ene reaction with cysteamine hydrochloride, followed by subsequent neutralization (Scheme 33).¹⁷⁴ Polyamides and copolyamides, with dimethyl adipate and 1,6-hexamethylene diamine, were obtained with molar masses ranging from 4 kg mol⁻¹ to 20 kg mol⁻¹. A melting temperature of 138 °C was observed for PA obtained from methyl 10-undecenoate based aminocarboxylic acids, against 43 °C for PA from methyl erucate based aminocarboxylic acids, due to the dangling chains along the polymer backbone. A copolyamide (50:50) between those two AB monomers was also synthesized and a medium melting temperature of 86 °C was achieved.



Scheme 33 Thiol–ene reaction with cysteamine hydrochloride followed by neutralization of methyl undecenoate, oleate and erucate to obtain AB self-condensable monomers for polyamide synthesis.¹⁷⁴

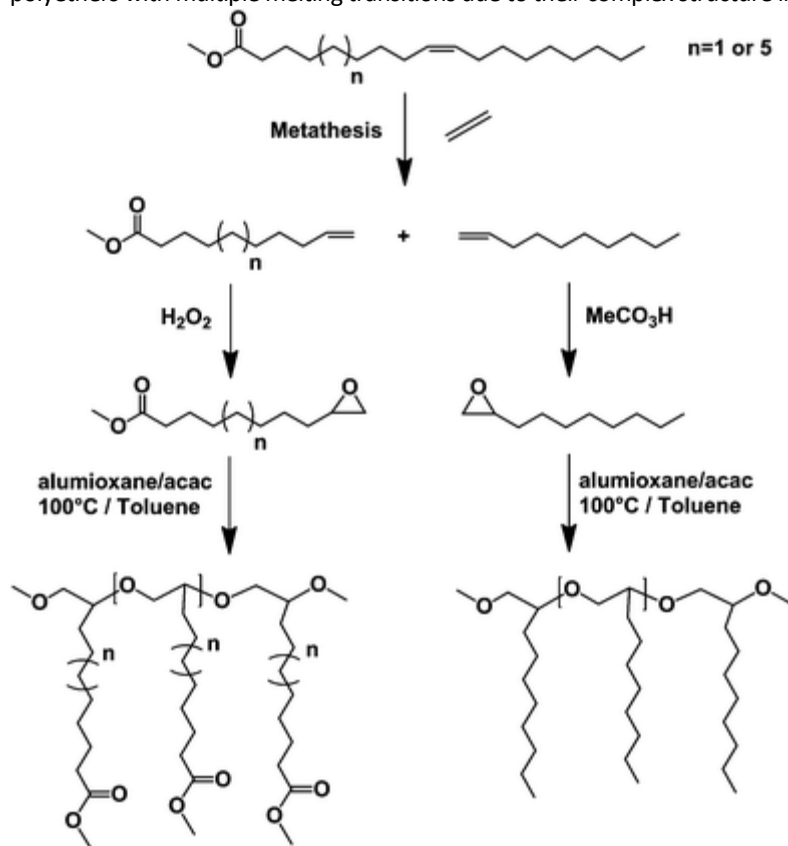
In another approach, Meier and coll. have synthesized thermoplastic polyamides from α -arylated fatty acid derivatives which were synthesized taking advantage of the α -CH-acidity of fatty acid esters.¹⁷⁵ The authors have performed the palladium catalyzed α -arylation reaction between 1,4-dibromobenzene and fatty acid *tert*-butyl esters in good yields (60–80%). After cleavage of the ester functions in acidic conditions to free carboxylic acids, the latter were polymerized with 1,6-hexanediamine but only low molecular weight oligomers ($M_n = 5.1 \text{ kg mol}^{-1}$) were obtained. The authors have concluded that the diesters synthesized were not suitable for polymer synthesis maybe due to steric hindrance.

Very recently, Meier and coll. used the Wohl–Ziegler bromination to prepare brominated fatty acid derivatives, which were transformed into amines after reaction with NaN_3 and the subsequent reduction with H_2 .¹⁷⁶ The AB monomers from methyl oleate and methyl erucate were then polymerized to obtain polyamides with molecular weights of 6500 and 7900 g mol⁻¹ and dispersities of 1.4 and 1.49. Melting points of 40 °C (from methyl oleate) and 89 °C (from methyl erucate) were observed.

IV.3 Polyethers and polythioethers

Polyethers constitute a broad family of polymers used in commercial or high performance applications. Poly(ethylene oxide), poly(propylene oxide) and poly(tetrahydrofuran) represent the most produced examples of this versatile polymer family. The main applications of these polyethers are as precursors for polyurethanes, surfactants, lubricants, or additives in biomedical or cosmetic domains. Polyethers are mainly synthesized by ring-opening polymerization of epoxide species by an ionic or coordination mechanism.¹⁷⁷ Despite the fact that epoxidation of fatty derivatives is a well-known process, very few studies report on the ring-opening polymerization of such types of monomers for the synthesis of thermoplastic polyethers. The most significant example was reported by Kunz and coll.¹⁷⁸ The authors synthesized ω -C10, C11 and C14 epoxy fatty acid methyl esters, 1,2-decene oxide and silylated 10,11-epoxyundecanols that were obtained from commercial sources (10-undecenol and methyl 10-undecenoate) or by cross-metathesis of the fatty acid

methyl esters with ethylene followed by epoxidation. The resulting terminal epoxides were then homo- and copolymerized to high molecular weight polyethers (up to 240 kg mol^{-1}) thanks to catalytic systems based on aluminoxanes and acetyl acetone (Scheme 34). Thermal analysis showed semi-crystalline behavior for most of the polyethers with multiple melting transitions due to their complex structure induced by tactic and atactic regions.



Scheme 34 Polyethers formation starting from methyl oleate and methyl erucate.¹⁷⁸

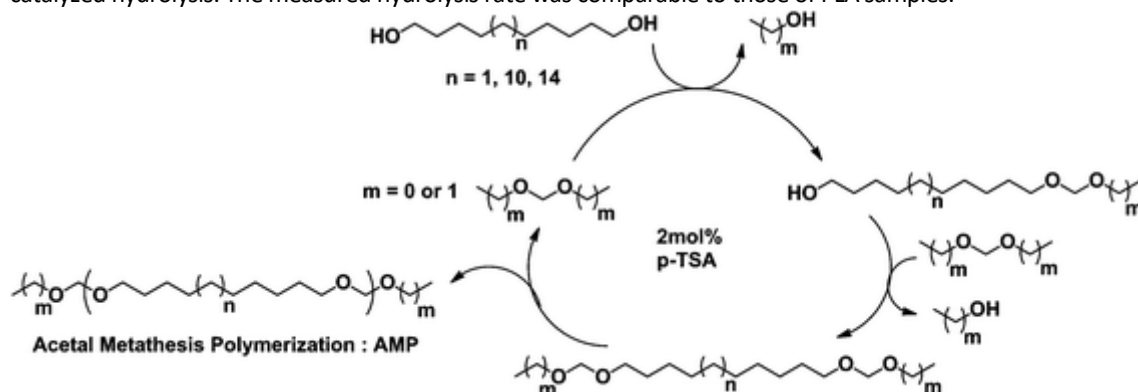
Polyethers and polythioethers can also be obtained by non-conventional routes such as ADMET and thiol-ene reaction.¹⁷⁹ Indeed thiol-ene addition provides the thioether linkage in very mild conditions. On the basis of this statement, Meier and coll. synthesized two bis-unsaturated monomers obtained from the 10-undecenoic acid platform. Dehydrohalogenation of 11-bromo-1-undecene provided a C11 bis-unsaturated monomer while Williamson ether synthesis using 11-bromo-1-undecene and 10-undecenol was carried out to yield a long bis-unsaturated ether compound. The resulting monomers were polymerized by ADMET or thiol-ene addition. The obtained polyether, polythioether and polythio/oxo-ethers showed melting points in the range of $40\text{--}80 \text{ }^\circ\text{C}$ with high values of corresponding enthalpies (up to 144 J g^{-1}).

Along the same line of using the castor oil platform for polythioether synthesis, a very recent study describes the synthesis of 10-undecene-1-thiol from 10-undecenoic acid.^{180,181} This AB monomer was then self-polymerized by varying the reaction conditions such as the type of initiation (photochemical or thermal) and the reaction time. Polythioethers with molecular weights up to 40 kg mol^{-1} were obtained. The molecular weight was dependent on the initiator concentration. The polythioethers were further subjected to oxidation successively into the sulfoxide and the sulfone polymers. A large increase of the melting point was observed by converting the polythioether into the corresponding polysulfone. The melting enthalpy, Young's modulus and thermal stability were also significantly improved by the polysulfone formation.

Polythioether synthesis was also described by Meier and Türünç taking advantage of the thiol-yne reaction.¹⁸² The methyl ester of 10-undecynoic acid was used as a monomer with either 1,4-butanedithiol or 3,6-dioxa-1,8-octane-dithiol as comonomers. Self-, thermal-, and UV-initiation were investigated with the latter being the most efficient. Polythioethers bearing an alkyl methyl ester dangling chain were obtained with molecular weights in the range of $11\text{--}15 \text{ kg mol}^{-1}$.

IV.4 Polyacetal

When looking at polymers that degrade easily by hydrolytical cleavage, polyesters, polycarbonates and polyanhydrides are the most cited. Thus, these polymer families are widely used for environmental or biomedical applications. However, inspiration by nature indicates that the use of acetal linkages could lead to promising opportunities for such applications. Indeed, nature's most abundant biopolymer, cellulose, is made of glucose repeating units connected by acetal functional groups. Cellulose is known to readily hydrolyze under acidic aqueous conditions by acetal cleavage. Thus other thermoplastics bearing acetal functional groups could be susceptible to hydrolytical cleavage in similar conditions. Miller and coll. described an elegant route to access such materials by acetal metathesis polymerization (AMP).¹⁸³ The methodology followed in this study involved the use of 1,10-decanediol (a castor oil derivative) as the starting molecule for the conversion into a bis-acetal derivative. This compound was then subjected to step growth polymerization driven by the release of the low boiling point diethoxymethane. The obtained polyacetal had a molecular weight of 22 kg mol⁻¹ and a melting point of 59 °C. The direct polymerization of a diol and diethoxymethane was also investigated leading to similar materials (Scheme 35). The abiotic degradation of polydecylene acetal was then investigated *via* acid-catalyzed hydrolysis. The measured hydrolysis rate was comparable to those of PLA samples.



Scheme 35 Direct conversion of a diol to a polyalkylene acetal *via* acetal metathesis polymerization.^{183,184}

Longer chain aliphatic α,ω -diols obtained by catalytic isomerizing alkoxy carbonylation of erucic and oleic esters were also converted to the corresponding bis-acetals by Mecking and coll.¹⁸⁴ More precisely, C19 and C23 diols were converted to the bis-acetals by reaction of the diols with dimethoxymethane under acidic conditions (Scheme 35). For comparison purpose, the C12 α,ω -diol was also used as the starting molecule. As expected, melting points increased with the number of methylene units in agreement with the previous study (from 68 °C to 88 °C). Melting enthalpy followed the same trend. Hydrolytical degradation of the resulting polymers in acidic media showed a decrease of the degradation rate with the increase of the methylene sequence length. This behavior was explained by the higher hydrophobicity and crystallinity of longer methylene chain polyacetals. The similarity to polyethylene in terms of the chemical structure promises great potential for environmental friendly packaging solutions.

IV.5 Polyanhydrides

Polyanhydrides are a class of materials that have been mainly used in biomedical applications as drug carriers.^{185–187} In fact, polyanhydrides readily hydrolyze to dicarboxylic acid monomers when placed in aqueous media. The degradation rate of the material has been proved to be highly dependent on the hydrophobicity of the monomers. Due to the high hydrophobicity of fatty acid-based derivatives, these compounds can then be used to optimize the degradation rate of polyanhydride materials.

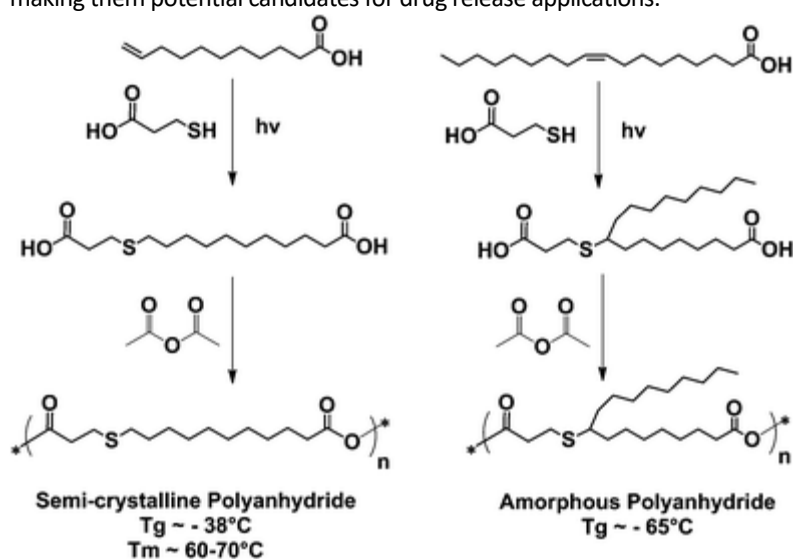
Using castor oil as a starting material, new diacids have been developed by esterification of ricinoleic acid with succinic or maleic anhydride.¹⁸⁸ Prepolymers of these ricinoleic acid-based monomers were then prepared by refluxing in acetic anhydride. Vacuum was then applied to perform polycondensation of the prepolymers with prepolymers of sebacic acid. All the polymers presented a semi-crystalline character with melting points in the range of 59 °C to 70 °C despite the presence of alkyl dangling chains in the structure. Drug release experiments were carried out and revealed good correlation of the degradation time of the material with the release of the drug. By using the same diacid monomer, Kumar and coll. have described the one pot polycondensation of ricinoleic acid maleate and sebacic acid with acetic anhydride.¹⁸⁹

In the same manner, Domb and Teomim synthesized fatty-acid terminated poly(sebacic anhydride) by condensation of sebacic anhydride polymers with acetate anhydrides of linear¹⁹⁰ and non-linear fatty-acids.¹⁹¹ Melting points and melting enthalpies were quite high compared to the previous study with values in the range of 70–82 °C and 60–103 J g⁻¹ respectively. The authors noticed a decrease of the degradation rate of the polyanhydride with an increase of the

fatty-acid chain length suggesting a strong influence of the hydrophobicity on the degradation rate of the material. Thus drug release could be affected and modulated by the incorporation of fatty-acid segments at the chain ends.

Also by targeting drug release applications, Huang and Guo reported the synthesis of copolyanhydrides from the dimers of C18 unsaturated fatty acids with dodecanedioic acid and tetradecanedioic acid.¹⁹² The copolymers, prepared by polycondensation, showed various amounts of dimer diacid in their chemical structure. Thermal analysis of these copolymers showed a decrease of both the melting point and crystallinity with an increase of the dimer diacid amount. This trend can be logically explained by the presence of dangling alkyl chains in the chemical structure that plasticize the polymer. As previously described, both the hydrophobicity and degree of crystallinity governed the release rate of the drug.

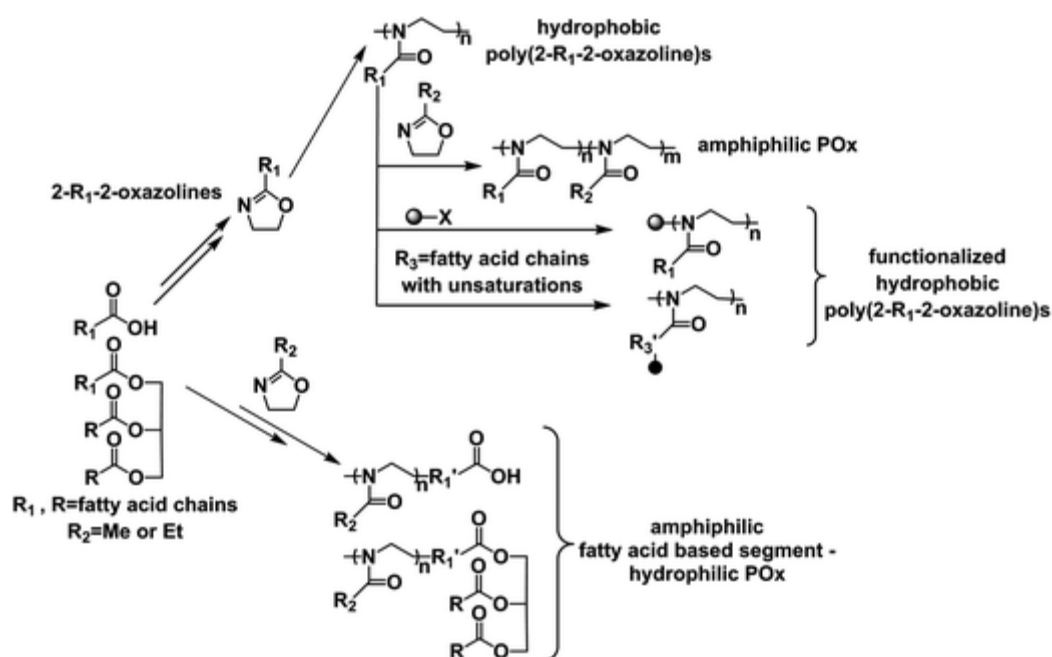
More recently, thiol–ene “click” reaction was employed for the synthesis of polycarboxylic precursors.¹⁹³ Indeed, oleic acid, undecenoic acid and 10-undecenoyl triglyceride were efficiently converted into polycarboxylic acid compounds by photoinduced addition of 3-mercaptopropionic acid on the double bonds of the starting materials (Scheme 36). Linear, branched and cross-linked polyanhydrides were prepared by activation of the carboxylic acid functions with acetic anhydride followed by melt condensation under vacuum. Soft materials were obtained as seen from the low glass transition and the low melting point values. Fast degradation and release rates were measured making them potential candidates for drug release applications.



Scheme 36 Preparation of polyanhydride precursors by thiol–ene addition.¹⁹³

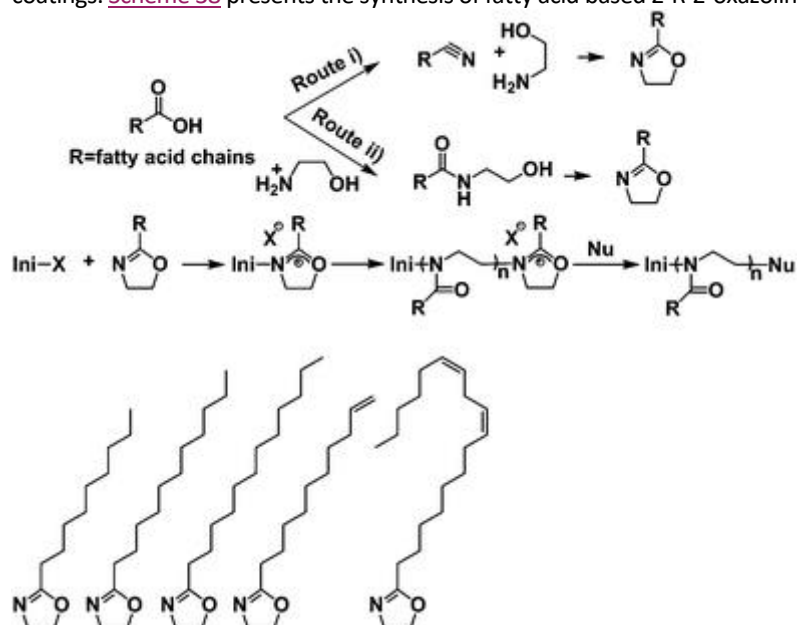
IV.6 Polyoxazolines

Poly(2-oxazoline)s (POx), which were discovered in 1966, are obtained by cationic ring opening polymerization of 2-R-2-oxazoline (ROx) monomers and can be regarded as pseudo-peptides or bioinspired polymers.¹⁹⁴ Depending on the R group, the properties of the POx can be specifically tuned. Indeed using short R chains (R = Me or Et, MeOx and EtOx monomers respectively), hydrophilic properties will be obtained while longer R chains will lead to hydrophobic POx. In addition, POx with methyl side chains, poly(MeOx), or ethyl, poly(EtOx), present a multitude of attractive properties such as high biocompatibility, low acute toxicity, no bioaccumulation and blood clearance, and they have been approved by US Food and Drug Administration (FDA).^{195,196} All these features open the possibility to prepare amphiphilic POx that can be used in several kinds of applications such as nonionic surfactants,¹⁹⁷ emulsifiers, antimicrobial materials when associated with quaternary ammonium salts, and in biomedical applications as drug carriers.¹⁹⁸ Vegetable oil derivatives have been used in two ways to lead to POx, either by synthesizing hydrophobic and crystalline POx from fatty acids and further amphiphilic POx by the combination with hydrophilic POx, or directly by combining hydrophobic fatty acid based segments with hydrophilic POx to achieve amphiphilic properties. The various methods are illustrated in Scheme 37.



Scheme 37 Different approaches to fatty acid based polyoxazolines and amphiphilic fatty acid segment/hydrophilic polyoxazoline compounds.

The synthesis of POx from vegetable oil derivatives has been widely explored and has recently been well reviewed by Hoogenboom.¹⁹⁹ Subsequently, selected points will be discussed in the present review. Fatty acid based ROx monomers can be synthesized following two major routes. The first is the condensation of nitriles with 1-amino-2-ethanol, and the second is a two-step condensation of acids with 1-amino-2-ethanol. Most of the studies on the synthesis of fatty acid based 2-R-2-oxazoline monomers have used the first strategy, which corresponds to the condensation of the fatty acid based nitriles at 120–140 °C using zinc(II) or cadmium(II) acetate as the catalyst.¹⁹⁹ Krause and coll. from Henkel KGaA have used the second strategy which starts with a condensation of the fatty acids with 1-amino-2-ethanol at 120–140 °C by removing the formed water, followed by a ring-closing reaction at 170–230 °C under vacuum with a titanium catalyst such as titanium(IV) tetrabutoxide or titanium(IV) acetylacetonate.²⁰⁰ POx from different fatty acids and thus with various side-chain lengths have been prepared in the literature, and it has been demonstrated that melting point values of POx with side-chains from 6 to 17 were in the range of 140–160 °C.^{201,202} The long fatty acid side chain based POx presented high crystallinity due to the packing of the R chains and were hydrophobic in nature which make them suitable for amphiphilic structures if combined with a hydrophilic block and for low surface energy and low adhesive coatings. [Scheme 38](#) presents the synthesis of fatty acid based 2-R-2-oxazoline monomers.



Scheme 38 Synthesis of fatty acid based 2-R-2-oxazoline monomers.

Amphiphilic POx can be obtained by coupling fatty acid based POx and poly(MeOx) or poly(EtOx) in order to obtain block copolymers, or by the copolymerization of ROx from fatty acids with MeOx or EtOx.²⁰³ These amphiphilic POx can then self-assemble into various structures targeting different applications.²⁰⁴ Among the corresponding literature, amphiphilic block copolymers from the 2-nonyl-2-oxazoline monomer (NonOx), a catalyst-functionalized monomer and the MeOx monomer, synthesized by Nuyken and coll. and used for micellar catalysis, can be mentioned.²⁰⁵ As an example of the wide range of catalyzed chemical transformations, block copolymers functionalized with a catalytic ruthenium(II) complex were successfully applied for aqueous ring-closing metathesis, as shown in Fig. 3.²⁰⁶

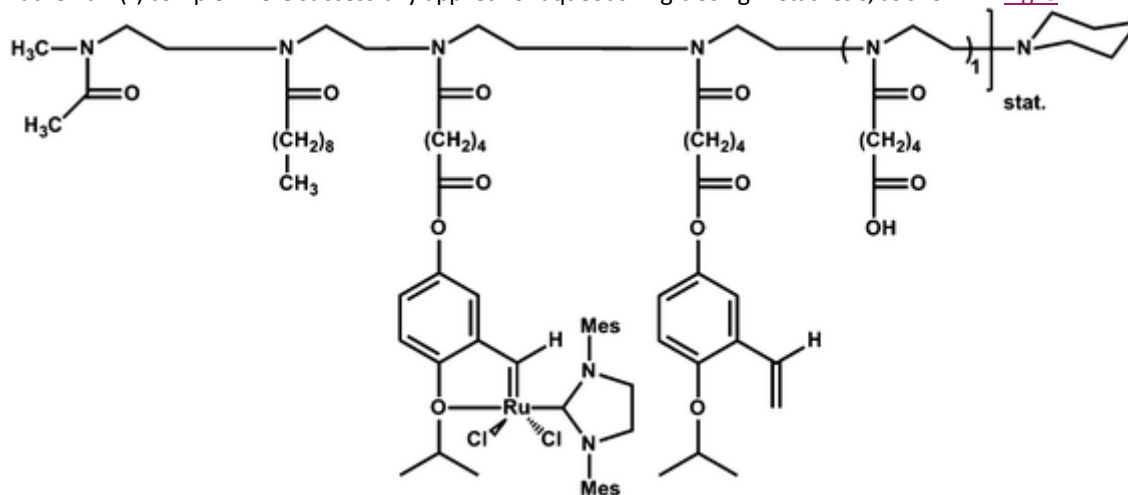


Fig. 3 Amphiphilic block copolymers from the 2-nonyl-2-oxazoline monomer (NonOx), a catalyst-functionalized monomer and the MeOx monomer.²⁰⁶

Cationic ring-opening polymerization allows the introduction of functional groups in POx during the initiation and the end-capping steps. For instance, Schubert and coll. demonstrated the use of propargyl tosylate as the initiator to polymerize the NonOx monomer, issued from capric acid which occurs in particular in coconut oil.²⁰⁷ They ended up with an alkyne end-functionalized poly(NonOx) that can be further reacted with different azide compounds by an azide-alkyne click reaction.

Unsaturated monomers based on undecenoic acid or oleic acid can be used to synthesize ROx monomers with unsaturations along the R group. Hoogendoorn and Schubert demonstrated a microwave-assisted cationic ring-opening polymerization on a soy-based 2-oxazoline monomer (SoyOx) obtained from Henkel.²⁰⁸ They managed to achieve full conversion after 10 minutes at 140 °C with a good control of the polymerization (\bar{D} around 1.1). The POx from unsaturated fatty acids allows further modifications on the double bonds present on the side-chains of the polymer backbone such as epoxidation,²⁰⁹ crosslinking and thiol-ene reaction.²¹⁰

Càdiz and coll. synthesized two ROx monomers from undecenoic acid and decanoic acid and then polymerized them to obtain fatty acid based POx.²¹¹ They further functionalized the pendant double bonds with an alcohol by the thiol-ene reaction with 2-mercaptoethanol to end up with polyols, which were then used to prepare polyurethane networks.

Fatty acid derivatives have also been used directly with hydrophilic POx to achieve amphiphilic properties. The functionalization of POx has recently been reviewed elsewhere including with fatty acid based derivatives.¹⁹⁶ These amphiphilic diblock copolymers were obtained *via* three methods: termination of the cationic ring opening polymerization,²¹² direct coupling,^{212,213} or using a fatty acid based initiator.

Using the latter strategy, an initiator containing both a fatty acid chain or a triglyceride segment and an initiating group such as halogenated derivatives, tosylates or triflates are needed. Long methylene chain based tosylates or triflates such as 1,2-di-dodecanoylpropyl-*p*-toluene sulfonate²¹³ or 1,2-*O*-dioctadecyl-*sn*-glycero-3-trifluoromethanesulfonate²¹⁴ respectively can be synthesized and used to initiate the polymerization of MeOx or EtOx monomers (see Fig. 4).

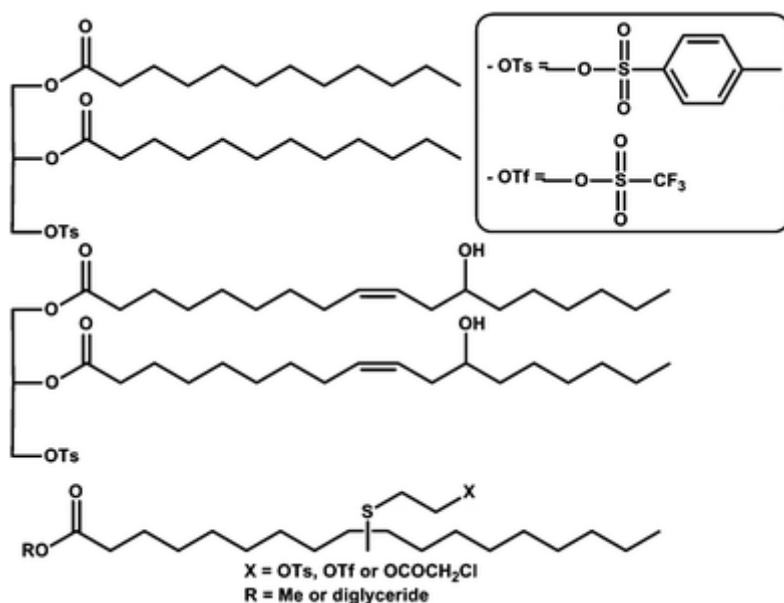


Fig. 4 Fatty acid based initiators for the polymerization of MeOx or EtOx monomers.^{213,214}

Robin and coll. have also synthesized nonionic surfactants based on vegetable oils and POx thanks to a castor oil based tosylate macroinitiator.¹⁹⁵ From this macroinitiator, poly(MeOx) of various molecular weights were prepared to investigate the influence of the hydrophilic POx length on the solution behavior of such nonionic surfactants. Narrow dispersities were achieved for the POx segment. Besides, it has been demonstrated that while increasing the POx hydrophilic chain length, higher values of CMC were observed. The average size of the aggregated nonionic surfactants suggested the formation of vesicles or nonspherical micelles. Very recently, the same group reported the synthesis and the self-assembly of amphiphilic polymers based on methyl oleate or grape seed oil and poly(MeOx).²¹⁵ The methyl oleate or grape seed oil was first hydroxylated by the thiol-ene reaction with mercaptoethanol, then further transformed into three kinds of macroinitiators with tosyl ($-\text{OTs}$), triflate ($-\text{OSO}_2\text{-CF}_3$) or chloride based ($-\text{OCO-CH}_2\text{-Cl}$) groups. Amphiphilic polymers were obtained from the latter macroinitiator after cationic ring opening polymerization of the MeOx monomer. They presented self-assembly behavior with aggregates of 4.3 nm and 10.2 nm for the fatty ester- and triglyceride-based polymers respectively.

IV.7 Poly(alkylacrylate)s/poly(alkylmethacrylate)s

When looking at the polymerization methods to synthesize polymers from fatty acids, mainly step growth polymerization was reported. Few examples of polymers obtained by chain-growth polymerization such as ROP of lactones, epoxides and oxazolines were even reported. Indeed, the unsaturations of fatty acids lack the required reactivity to consider efficient radical, anionic or cationic polymerizations. More reactive functions towards these polymerization methods can however be introduced in the structure of the fatty acid derivative. Indeed, acrylic and methacrylic functional groups can be easily incorporated in fatty alcohol structures by esterification with acrylic acid (or derivatives) and methacrylic acid respectively. These long chain acrylates and methacrylates then lead, by chain growth polymerization, to uncommon polymers with soft behaviors in comparison with shorter side chain polymers such as poly(methyl methacrylate) (PMMA). These acrylates and methacrylates are then potential monomers for controlled/living polymerization.

Regarding fatty acid-based acrylates and methacrylates, ATRP has been the most applied polymerization technique. The first example was reported by Beers and Matyjaszewski.²¹⁶ Indeed the polymerization of lauryl acrylate (LA) was investigated by ATRP using $\text{CuBr}/4,4'\text{-di}(5\text{-nonyl})\text{-}2,2'\text{-bipyridine}$ (CuBr/dNbpy) as the catalytic complex. Good control of the polymerization was achieved in almost bulk conditions (5 vol% toluene). N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA) was also used as the ligand instead of dNbpy. However PMDETA could not adapt to this monomer due to the poor solubility of poly(lauryl acrylate) in polar solvents, whereas PMDETA can only dissolve the catalytic complex in polar media. Polymerization of lauryl acrylate was also studied in ionic liquids using $\text{CuBr}/\text{PMDETA}$; however the heterogeneous nature of the reaction medium resulted in poor control of the polymerization.²¹⁷ Robin and coll. polymerized lauryl acrylate by ATRP using N -(n -octyl)-2-pyridylmethanimine (OPMI)

as the ligand of copper(I) bromide.²¹⁸ The reaction mixture was homogeneous at 130 °C in xylene and afforded a good control of the polymerization.

To vary the polymerization method, a promising environmental friendly route to poly(lauryl acrylate) was proposed by using single-electron transfer/degenerative chain transfer living radical polymerization (SET/DTLRP).²¹⁹ The polymerization was catalyzed by Na₂S₂O₄ and was conducted in aqueous media. In this way, α,ω -diiodo-poly(lauryl acrylate) was obtained which can be further used as a macro-initiator.

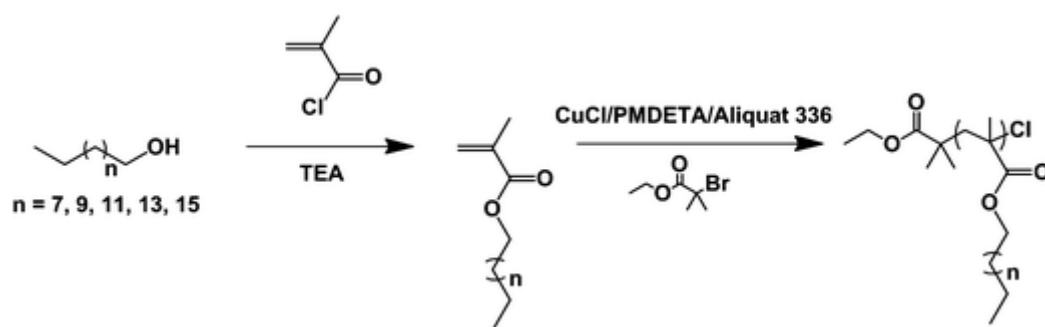
Nicol and coll. proposed the synthesis of block copolymers of lauryl acrylate with another fatty-acid based acrylate which is octadecyl acrylate (ODA) (also stearyl acrylate).²²⁰ ATRP was carried out and afforded good control of the polymerization. Thermal investigation of the so-formed diblock copolymers revealed semi-crystallinity of both blocks induced by the presence of long alkyl side chains in the polymer backbone. Moreover, phase segregation of both blocks was observed and led to interesting mechanical properties depending on the temperature.

The crystallinity and high hydrophobicity of the C18 side-segment of poly(octadecyl acrylate) (PODA) were already studied and it was beneficially used as a nucleating agent, rheology modifier, stabilizer in dispersions and smart gels. However these studies were carried out *via* conventional radical polymerization.

Other studies dealing with the use of ATRP to polymerize ODA were reported. For instance Matyjaszewski and coll. described the synthesis of block, statistical and gradient copolymers from ODA and *tert*-butyl acrylate.²²¹ The corresponding methacrylate monomers were also used in this study. Random and block copolymers of ODA with methyl methacrylate (MMA) as a comonomer were also reported by Holder and Harris.²²² These copolymers were used as comb-like stabilizers for dispersion polymerization of MMA leading to stable PMMA micro-particles. The same group described the synthesis of comb-like amphiphilic diblock copolymers composed of PODA as the lipophilic segment and poly(oligo(ethylene glycol) methyl ether methacrylate) as the hydrophilic segment.²²³ The properties of one of the diblock copolymers in aqueous solution were investigated and micelles were observed. In another example, PODA-*b*-polystyrene-*b*-PODA triblock copolymers were synthesized by ATRP using FeCl₂·4H₂O/PPh₃ as the catalytic system.²²⁴ The crystallization behavior of these copolymers was investigated and was related to the crystallization of PODA side chains. An increase of the crystallinity was observed with an increase of PODA block length.

Finally NMP was efficiently used for the synthesis of gradient and block copolymers of PODA and poly(methyl acrylate).²²⁵ Block copolymers were prepared by using a batch process and copolymer characterization revealed clear segregation of the two blocks. In the case of gradient copolymers, a semi-batch process was used and the authors observed a strong melting-point depression caused by the incorporation of amorphous methyl acrylate units in the polymer structure.

Fatty-acid based methacrylates were also used as monomers for controlled/living radical polymerizations. Similar to alkyl acrylates, lauryl methacrylate (LMA) and octadecyl methacrylate (ODMA) were the most investigated monomers. LMA was polymerized by ATRP following different reaction conditions, initiators and ligands.^{226–228} In the same manner as for poly(lauryl acrylate), the soft nature of poly(lauryl methacrylate) (PLMA) was beneficially used for the development, by ATRP, of hard–soft block copolymers comprising a PLMA middle block ($T_g = -60$ °C) and PMMA ($T_g = 110$ °C) or poly(*tert*-butyl methacrylate) (PtBMA) end blocks.^{229,230} The copolymers showed thermoplastic to elastomeric behaviors depending on the composition.²³¹ ATRP was also used for the synthesis of functionalized and block copolymers based on poly(octadecyl methacrylate) (PODMA).²²¹ Various applications were targeted by tailoring the chemical structure of the resulting polymers showing the great potential of PODMA based systems. For instance, PODMA synthesis by ATRP was initiated by a functionalized crown ether initiator leading to unusual self-assembly of the resulting PODMA in solvent mixtures of THF and water. The observed aggregates were characterized by porous morphologies suggesting drug delivery applications.²³² The same group copolymerized ODMA and 3-(trimethoxysilyl) propyl methacrylate by successive addition yielding diblock copolymers that self-assembled in a mixture of THF and methanol.²³³ Subsequent gelation led to organic/inorganic hybrid nanomaterials that present promising opportunities in drug delivery and catalysis applications. Matyjaszewski and coll. used ATRP and ROP to synthesize block or random copolymers composed of ϵ -caprolactone, ODMA and dimethylaminoethyl methacrylate units.²³⁴ The resulting copolymers were used as surfactants for the dispersion polymerization of L-lactide to form polylactide microspheres. ATRP was also applied to other long alkyl chain methacrylates that were obtained from fatty alcohols of various chain lengths (Scheme 39).²³⁵ Investigation of the thermal properties of these polymers revealed an increase of the melting point with an increase of the alkyl chain length, resulting in polymers with different physical properties.



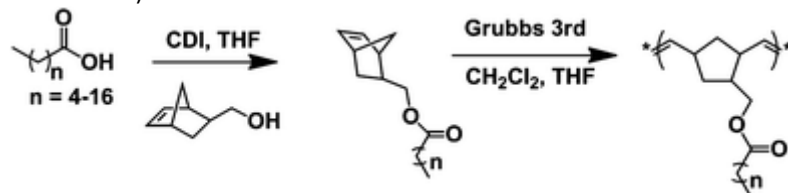
Scheme 39 ATRP of fatty acid-based methacrylates.²³⁵

RAFT polymerization was also applied to lauryl methacrylate in order to develop controlled macromolecular structures and thus allowing specific applications. For instance, ω -alkyne terminated PLMA was synthesized by the formation of an alkyne disulfide at the chain end. This functionalized PLMA was then reacted onto an azide-modified glass surface that resulted in a more hydrophobic surface.²³⁶ Finally, RAFT was also used for the synthesis of block copolymers composed of lauryl methacrylate and 2-(acetoacetoxy) ethyl methacrylate repeating units.²³⁷ Thermal properties of the copolymers were investigated after which micellization of the block copolymers was demonstrated in *n*-hexane.

In summary, it has been demonstrated that fatty-acid based acrylates and methacrylates can be useful monomers both for bulk and solution applications of the resulting polymers and copolymers. Indeed the high hydrophobicity of such polymers can provide suitable surface modifications in the case of bulk applications and provide an amphiphilic character when solution applications are needed. Numerous investigations on thermal properties of fatty-acid based polyacrylates or polymethacrylates showed that it is possible to take benefit of the low glass transition temperature and the low melting point of these polymers to target thermoplastic elastomer applications.

IV.8 ROMP by using fatty-acid functionalized norbornenes

It has been previously shown that ADMET is a method of choice to polymerize fatty-acid based monomers. It was also mentioned that ring-opening metathesis polymerization (ROMP) is not the most suitable method when using fatty acids as the feedstock due to the low ring strain of the resulting unsaturated cyclic monomers. However, partially bio-based monomers satisfying the ROMP requirements can be obtained by coupling fatty-acid derivatives with conventional unsaturated cyclic building blocks such as norbornene. Larock and coll. described the efficient functionalization of plant oil derivatives and their subsequent polymerization by ROMP leading to promising bio-based thermosets.^{238,239} Meier and Mutlu also took advantage of this strategy to synthesize various ester functionalized norbornenes by using fatty acids with different chain lengths (from C6 to C18) (Scheme 40).²⁴⁰ The polymers obtained had molecular weights up to 165 kg mol^{-1} with dispersities between 1.05 and 1.26. Reaction kinetics revealed a living behavior of the polymerization due to a faster rate of initiation than the rate of propagation (allowed by the use of Grubbs 3rd generation catalyst) and due to the limitation of secondary metathesis reactions. The thermo-mechanical properties of these polymers were highly dependent on the chain length of the fatty acid used; T_g decreased from $102 \text{ }^\circ\text{C}$ to $-32 \text{ }^\circ\text{C}$ (from fatty acids with chain length between 6 and 18 carbons). Crystallization ability was observed for polymers prepared from fatty acids with chain length between 14 and 18 carbons. The observed melting point decreases with increase in the chain length (from $30 \text{ }^\circ\text{C}$ to $6 \text{ }^\circ\text{C}$).

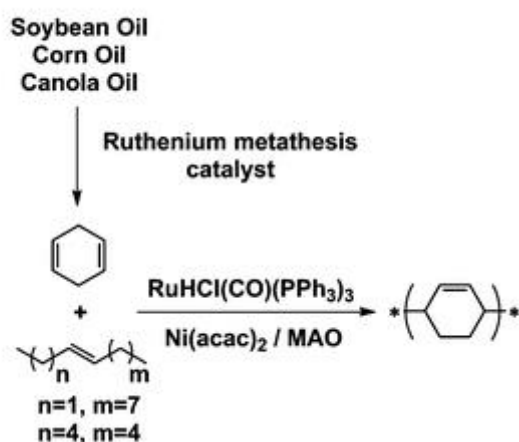


Scheme 40 Ring opening metathesis polymerization (ROMP) of fatty acid functionalized norbornenes.²⁴⁰

IV.9 Polycyclohexadiene

While most of the studies reported on polymerization of fatty-acid derivatives affording linear or branched aliphatic polymers, very few examples can be found on the synthesis of fatty-acid based cyclo-aliphatic polymers. By using an elegant route, Mathers and coll. succeeded in synthesizing 1,3-cyclohexadiene from different plant oils (soybean, corn and canola).²⁴¹ These substrates were chosen due to their high content of polyunsaturated triglycerides, which allow the production of volatile diene products when a suitable metathesis catalyst is used. In particular, 1,4-cyclohexadiene (1,4-CHD) was isolated from the reaction mixture by distillation. This compound was then subjected to isomerization using a ruthenium hydride catalyst leading to 1,3-cyclohexadiene (1,3-CHD) with good conversion (typically 65–70%). 1,3-CHD was then polymerized in bulk, hydrogenated D-limonene, and toluene, using nickel(II) acetylacetonate/methylaluminoxane as a catalytic system. The isomerization and subsequent polymerization were also examined as a one-step cascade reaction (Scheme 41). Semi-crystalline polymers were obtained with a melting point varying with the reaction conditions (in the range of 274–322 °C). Thermal stability investigation suggested a low processing window due to the small difference between the melting point and onset temperature of degradation. The great potential of such a material resides in its excellent physical properties as well as its ability to transform into conducting polymers and proton conductors.

Polyunsaturated plant oils :

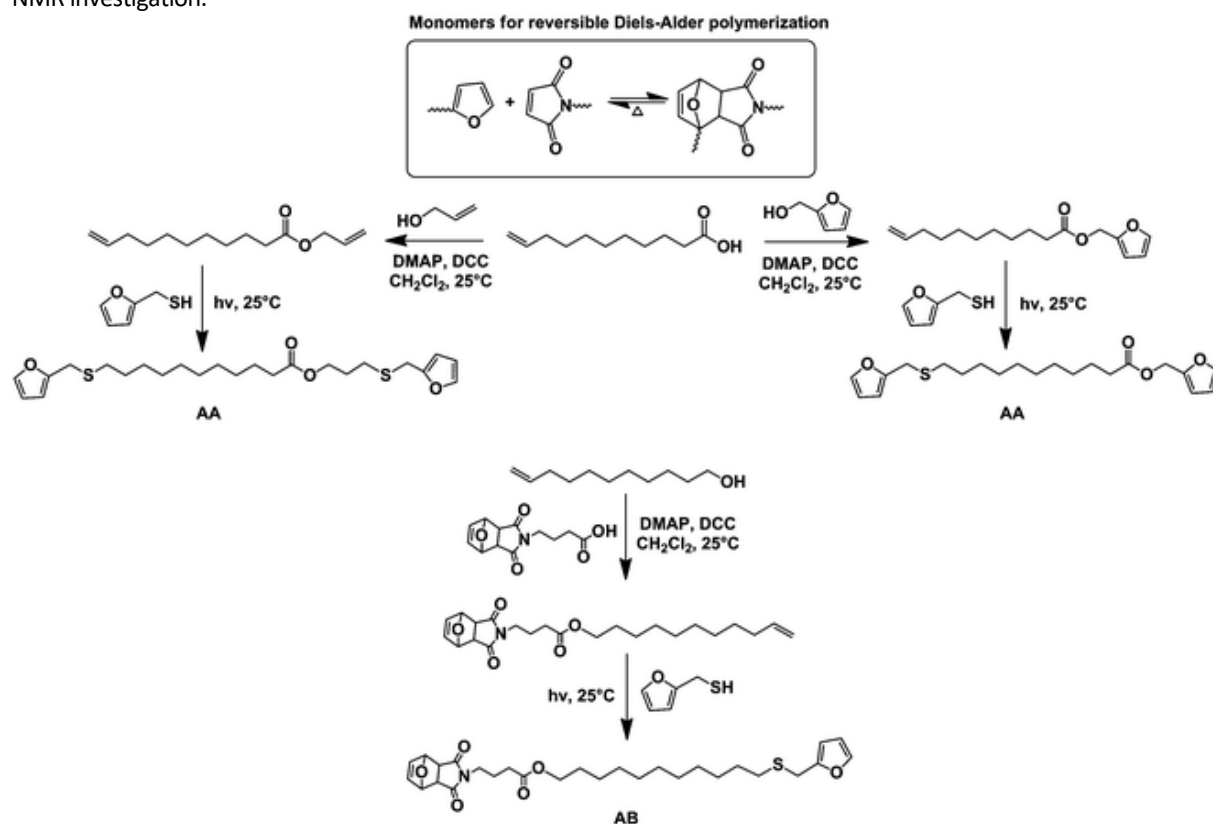


Scheme 41 Production of 1,4-cyclohexadiene followed by the one-pot isomerization and polymerization cascade sequence.²⁴¹

IV.10 Diels–Alder reversible polymerization

The use of renewable building blocks obtained from other biomass feedstocks (such as lignocellulosic materials), in combination with the use of fatty acid-based derivatives, can bring original and specific functions to the final polymer. For instance, furan derivatives such as furfural and 5-hydroxymethylfurfural represent two widely developed furan-derived monomers, which can be obtained from C5 and C6 carbohydrate resources. Starting from these two building blocks, a large range of strategic compounds are accessible such as 2,5-furandicarboxylic acid, which is used to mimic terephthalic acid,²⁴² and furfuryl alcohol, a precursor to a variety of resins, that has found numerous applications, especially in high-tech domains.^{2,243} Regarding the chemical structure of furan compounds, a pronounced dienic character is noteworthy, which makes them suitable for Diels–Alder (DA) reactions with dienophiles like maleimides.²⁴⁴ The interest of this reaction resides in the thermal reversibility of the DA reaction that allows the possible controlled depolymerization of thermoplastics and thermosets bearing such functional groups.^{245–248} Gandini and coll. investigated the functionalization of fatty acids with furan and maleimide moieties by a double click strategy.²⁴⁹ 10-Undecenoic acid and the corresponding alcohol were used as precursors for functionalization with furan and masked maleimide compounds by thiol–ene coupling and/or esterification (Scheme 42). The resulting monomers were then reacted by two DA polycondensation approaches. In a first example, monomers bearing two terminal furan rings were reacted with bis-maleimides while, in a second case, AB monomers bearing both furan and maleimide end-groups were self-polymerized. High conversions were reached after several days and the measured molecular weights were in the range of 6–10 kg mol⁻¹. The retro-DA reaction carried out at 110 °C for a few days showed the recovery of the starting monomers thus confirming the thermo-responsive character of such systems. The same group also used a 10-undecenoic acid platform to synthesize potential precursors for nonlinear DA polymerization.²⁵⁰ Two different approaches were retained in this work, namely the A₂ + B₃ system and the AB₂ system. Thus a bis-furan, a bis-maleimide, a tris-furan, a tris-maleimide and monomers bearing both furan and protected maleimide end groups (A₂B or AB₂) were

synthesized by a combination of thiol–ene reaction and esterification. The DA polymerization of $A_2 + B_3$ or $A_3 + B_2$ systems yielded highly branched or crosslinked materials depending on the A/B molar ratios, whereas A_2B or AB_2 systems yielded hyperbranched polymers. Feasibility of several DA/retro-DA cycles was proved both by UV and ^1H NMR investigation.



Scheme 42 Various monomers used in reversible Diels–Alder polymerization.²⁴⁹

V Conclusion

In this review, we have demonstrated that huge varieties of bio-based thermoplastic polymers can be obtained from fatty acid-based precursors. Among these, polyesters and polyurethanes testified the wide range of properties achievable that enable covering many applications.

These polymeric materials present well-defined structures and their thermo-mechanical properties can be easily tuned (for example for polyester and polyurethanes, T_g can vary from $-80\text{ }^\circ\text{C}$ to $160\text{ }^\circ\text{C}$ and T_m from $-30\text{ }^\circ\text{C}$ to $230\text{ }^\circ\text{C}$) by chemical modification and/or copolymerization. These strategies present important advantages in comparison to the direct polymerization of triglycerides that generally leads to ill-defined networks.

Nevertheless, one limitation could be the multi-step synthesis of the fatty acid precursors, which is not always compatible with the large-scale manufacture of cheap commercial polymers and also poses environmental concerns. Thus, it is most probable that high added value specialty polymers have to be targeted as far as fatty acid precursors are concerned. One main challenge will be the development of alternative synthetic pathways to these thermoplastics, starting directly from crude vegetable oils and/or minimizing the purification steps.

For some applications, these fatty acid-based thermoplastics can also lack some properties due to their purely aliphatic structure. Therefore, the use of other important biomass feedstocks (terpenes, carbohydrates) to broaden the properties and applications of vegetable-based thermoplastics also seems to be a promising field of investigation in the near future. Such polymeric materials remain scarce in the literature today but are exposed to a growing interest in the community.

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