REVIEW

Click green chemistry for the synthesis of biobased polymers and networks derived from vegetable oils

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As we live in a time of heightening environmental issues, material science is required to prepare sustainable polymers through green chemistry ideals. Vegetable oils and their fatty acid derivatives are well regarded for their use in polymer chemistry. Click chemistry has drastically affected the synthesis of vegetable oil-derived polymers over the last twenty years. This review covers the most recent and relevant developments in click chemistry as a functionalization and polymerization method of vegetable oils and their derivatives. First, a quick overview is provided of the main macromolecular architectures and properties of the most commonly accessible vegetable oils, their most prevalent chemical modifications, and their prevalence in polymer families. It is followed by an introduction of the click chemistry reactions frequently developed on vegetable oils. The focus of the manuscript is the development of this efficient chemistry for the synthesis of polymer materials derived from vegetable oils.

Introduction

Living in these mediatized times, citizens are aware more than ever of how individuals and industrials contribute to environmental preservation. The topics of sustainability, recyclability, developing and utilizing renewable resources, waste management, and eco-friendly products are widespread due to rising environmental concerns. Consequently, a major responsibility lies on academics and industrials to develop solutions that address this global problem. In the field of chemistry, Anastas and Warner conceptualized the ideals of sustainable chemistry by developing the "12 Principles of Green Chemistry". Generally, the ideals of green chemistry are focused around different points such as (i) minimizing waste, (ii) using renewable feedstock and energy, (iii) using safe and environmentally benign substances and, (iv) atom economy.[1]

Biobased polymers, also described as biomass or renewably sourced polymers, refers to the origin of the carbon (and main atoms of the macromolecular chains). It is a material from which the starting components (building blocks or biopolymers) are directly extracted or derived from biomass (all the organic systems produced by living organisms). As such, biobased polymers present a positive C^{14} content. According to a 2019 European Bioplastics report, biobased polymers represent around 1% of the over 359 million tons of polymers produced annually. As the potential of these renewable polymers is high, the polymer industry must develop considerably to respond to the immense and global social concerns using greener chemistry principles on renewable feedstock.

Historically and presently, vegetable and animal origin oils and fats remain the most abundantly used renewable resource for the chemical industry.[2] Vegetable oils are prime candidates to replace fossil-based derivatives in polymer materials for a multitude of reasons such as (i) their universal availabilities, (ii) low toxicities, (iii) low prices and, (iv) their inherent chemical structures.[2-4] Fatty acids are based on linear carbon chains with different active groups such as hydroxyls, oxiranes, and double bonds along the chains, with carboxylic acid ends, to perform an affluent amount of chemistry.[5] Vegetable oils have been studied and explored in several different types of thermoplastics and thermosets syntheses, notably epoxy resins, polyamides (PAs),[6, 7] polyesters,[8] or polyurethanes (PUs).[5, 7, 9-11] Consequently, vegetable oils are the base of attractive building blocks for the synthesis of biobased polymers which can compete with fossil-based equivalents. Besides, some new macromolecular architectures linked to original biobased building blocks can be obtained, for instance, from a dimer of fatty acids.[9, 10, 12-16]

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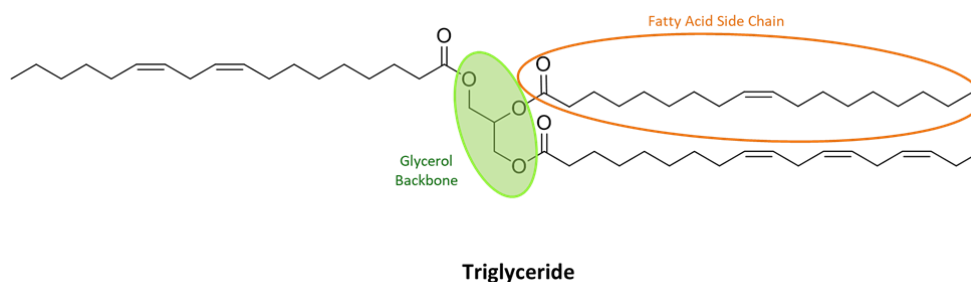† Footnotes relating to the title and/or authors should appear here.

A decade after establishing the principles of green chemistry, the concept of click chemistry was introduced by Sharpless and co-workers in 2001.[17] The use of click chemistry for the controlled synthesis of different macromolecular architectures gained substantial interest as these reactions adhere to the principles of green chemistry. Click chemistry consists of a wide range of reactions with many advantages. With regards to the synthesis of monomers and polymers from vegetable oils by click chemistry, the literature reports the use of different reactions, such for instance (i) triazolinedione (TAD) chemistry, (ii) Diels−Alder (DA) cycloadditions, (iii) thiol-ene addition (iv) thiol-yne addition, and (v) Cu(I)-catalyzed azide-alkyne reaction. Although the thiol-ene addition reaction dominates in the use of click chemistry in oleochemistry, the efficient application of the DA reaction,[18] and TAD click chemistry [19] to oleochemistry has recently been brought forth.

The most recent strategies for modifying oleochemicals into networks and polymers via click chemistry reactions are analyzed and highlighted in this review article. This state of art gives the general context of the oleo-chemistry towards polymer-based systems and the properties of vegetable oils-based materials. The most commonly accessible and prevalent glycerides and the standard chemistry performed on the primary moieties from vegetable oils are described. This part is followed by a section that describes the main click chemistry reactions used on vegetable oils. The article will focus particular attention on the recent uses of click chemistry to develop biobased macromolecular architectures with advanced properties. The purpose of the present review is to complement previous works and reviews with the latest results regarding triglycerides (TGs) and fatty acids (FAs) by click chemistry associated with applying several green principles to develop building blocks macromers towards the synthesis of biobased polymers. However, in the three subsequent sections, some generalities about TGs and FAs, the possible chemical modifications, and their prevalence in polymer families are presented, followed by a quick overview of the main click reactions.
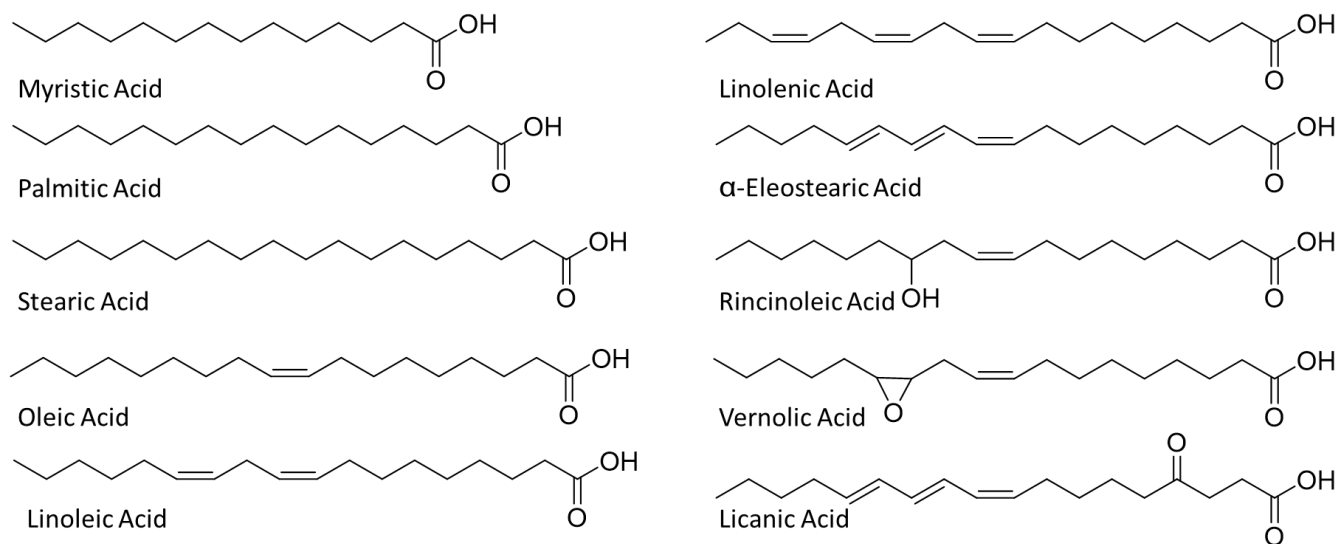
Triglycerides and fatty acids modifications

Vegetable oils mainly consist of TGs, which are depicted in Fig. 1. They are primarily obtained from vegetable oils, animal fats, or microalgae. They can be defined as esters of glycerol, consisting of three FAs (R_1, R_2, and R_3). These main structural elements tend to dictate the physical and chemical properties of the TGs. Main variations are (i) the chain length, which usually varies up to 24 carbons, (ii) the degree of unsaturation (number of double bonds per FA), and lastly, (iii) the stereochemistry of the double bonds.[20] Fig. 2, illustrates the chemical structure of the most common FAs. The FA composition of vegetable oils can vary according to the plant species (Table 1), crop type, season, and growing conditions.[21] Table 1 presents the main industrial vegetable oils, their composition, and their average double bonds per TG. It is also evidenced in Table 1 that palmitic, stearic, oleic, linoleic, and linoleic acids consist of the majority of the FAs from common vegetable oils. Of recent interest is the emergence of microalgae oil. In contrast to vegetable oils, microalgae oil does not compete with food or feed as it is grown in bioreactors rather than arable land.[22] They contain TGs with higher average chain length and higher number of double, allowing for increased reaction sites.

Oleochemistry is the term used to define the chemistry that can be performed on TGs or FAs. A simplified list of different reactions based on FAs is found in Table 2. This list exemplifies the richness of oleochemistry. The most important reactions related to the ester and double bond moieties have been thoroughly and largely reviewed during the last decades.[2, 6, 21, 23-25]

Fig. 1 General chemical structure of TGs, where R stands for a fatty hydrocarbon chain

Myristic Acid

Palmitic Acid

Stearic Acid

Oleic Acid

Linoleic Acid

Linolenic Acid

α-Eleostearic Acid

Rincinoleic Acid OH

Vernolic Acid

Licanic Acid

Fig. 2 Chemical structures of most common fatty acids

Table 1 Fatty acid profiles of the most industrially viable vegetable oils. Adapted with permission from [21, 26, 27].

Fatty Acid	Systematic name	Structure [C:DB] [a]	Formula	Canola	Corn	Cottonseed	Linseed	Olive	Palm	Rapseed	Soybean	High Oleic [b]
Myristic	Tetradecanoic acid	14:0	$C_{14}H_{28}O_2$	0.1	0.1	0.7	0.0	0.0	1.0	0.1	0.1	0.0
Myristoleic	Tetradecenoic acid	14:1	$C_{14}H_{26}O_2$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Palmitic	Hexadecanoic acid	16:0	$C_{16}H_{32}O_2$	4.1	10.9	21.6	5.5	13.7	44.4	3.0	11.0	6.4
Palmitoleic	Hexadecenoic acid	16:1	$C_{16}H_{30}O_2$	0.3	0.2	0.6	0.0	1.2	0.2	0.2	0.1	0.1
Margaric	Heptadecanoic acid	17:0	$C_{17}H_{34}O_2$	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0
Margaroleic	Heptadecenoic acid	17:1	$C_{17}H_{32}O_2$	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Stearic	Octadecanoic acid	18:0	$C_{18}H_{36}O_2$	1.8	2.0	2.6	3.5	2.5	4.1	1.0	4.0	3.1
Oleic	*Cis*-9-octadecenoic acid	18:1	$C_{18}H_{34}O_2$	60.9	25.4	18.6	19.1	71.1	39.3	13.2	23.4	82.6
Linoleic	*Cis,cis*-9,12-octodecdienoic acid	18:2	$C_{18}H_{32}O_2$	21.0	59.6	54.4	15.3	10.0	10.0	13.2	53.2	2.3
Linolenic	*Cis,cis,cis*-9,12,15-octadecatrienoic acid	18:3	$C_{18}H_{30}O_2$	8.8	1.2	0.7	56.6	0.6	0.4	9.0	7.8	3.7
Arachidic	Eicosanoic acid	20:0	$C_{20}H_{40}O_2$	0.7	0.4	0.3	0.0	0.9	0.3	0.5	0.3	0.2
Gadoleic	*Cis*-9-eicosenoic acid	20:1	$C_{20}H_{38}O_2$	1.0	0.0	0.0	0.0	0.0	0.0	9.0	0.0	0.4
Eicosadienoic	*Cis,cis*-11,14-eicosadienoic acid	20:2	$C_{20}H_{36}O_2$	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0	0.0
Behenic	Docosanoic acid	22:0	$C_{22}H_{42}O_2$	0.3	0.1	0.2	0.0	0.0	0.1	0.5	0.1	0.3
Erucic	*Cis*-13-docosenoic acid	22:1	$C_{22}H_{40}O_2$	0.7	0.0	0.0	0.0	0.0	0.0	49.2	0.0	0.1
Lignoceric	Tetracosanoic acid	24:0	$C_{22}H_{44}O_2$	0.2	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0
Average : #DB/triglyceride				3.9	4.5	3.9	6.6	2.8	1.8	3.8	4.6	3.0

[a] C represents the number of carbon atom and DB the number of double bonds in the fatty-acid chain [b] Gentically engineered high oleic acid content soybean oil (DuPont).

Table 2 Overview of main chemical modifications performed on FAs and TGs. Adapted with permission from [5]

Reaction Site	Reaction Name	Reaction Schematic
Main reactions on the carbonyl group	(Trans)esterification	
	Amidification	
	Reduction	
Main reactions on the carbon-carbon double bond	Epoxidation	
	Epoxide ring opening	
	Hydroformylation	
	Ozonolysis-Hydrogenation	
	Metathesis	
	Thiol-ene coupling	
	Diels-Alder cycloaddition	

FAs and FA esters are obtained by transesterification (e.g., alcoholysis) of TGs. Commonly, acid (sulfuric acid) and basic (sodium or potassium hydroxide) catalysts are used. In this way, biodiesel production, for instance, is mainly obtained by transesterification reactions of TGs and methanol to yield glycerol and FA methyl esters (FAMEs).[28] FAMEs are also be used as green solvents. [29] Moreover, glycerol can be used as a precursor for industrial commodities such as 1, 3-propanediol, and ethylene glycol,[24] to replace fossil-based derivatives. The FAs and FAMEs that yield from the saponification or alcoholysis process are often modified by esterification and transesterification reactions to obtain architectures of interest for several chemical reactions. An extensive range of chemical and physical reactions are used to alter the reactive chemical groups of FAs or TGs to develop new building blocks. For instance, a convenient way to achieve reactive

hydroxyl groups from carboxylic acids is their reduction using lithium aluminium hydride (LiAlH$_4$). This reaction is commonly used for the synthesis of polyols.[30]

As shown in Table 2, different reactions on the double bonds can be used, such as epoxidation, hydroformylation, ozonolysis, thiol-ene coupling (TEC), oxidation, Diels-Alder (DA), and metathesis of unsaturated oils. Based on FAs, TGs, and FAMEs, they yield effective modifications for the synthesis of biobased polymers.[23-25, 31] For instance, oxirane groups can be directly obtained by reaction of the double bonds of FAs or TGs with hydrogen peroxide, oxygen, or chemo-enzymatic reactions.[23] Industrially, the epoxidation of vegetable oils is carried out with peroxoacetic or peroxoformic acids.[32] Epoxy groups can be opened by different reagents (amines, carboxylic acids, thiols, alcohols, water, and hydrogen halides) or hydrogenation to yield secondary hydroxyl groups.[33] These modifications can, for instance, produce diverse polyols for the synthesis of PUs.[5]

Hydroformylation is used to convert an unsaturation into an aldehyde and then into a highly reactive primary hydroxyl group (Table 2). The reaction entails converting the unsaturation to a carbonyl moiety using carbon monoxide and hydrogen (syngas). Then, the aldehyde can be further converted into an alcohol moiety with Raney nickel under H$_2$ pressure at high temperatures.[34]

Ozonolysis is another powerful reaction that can yield primary hydroxyl groups (Table 2).[35] Oxidative scission on TGs or TAs produces molecules with terminal primary hydroxyls groups. Depending on the work-up conditions can also yield the formation of carboxylic acids and an aldehyde group. A prominent example includes the ozonolysis reaction of oleic acid using hydrogen peroxide to generate azaleic and perlargonic acids.[21]

Olefin metathesis allows the possibility to obtain valuable building blocks from TGs or FAs (Table 2). Generally, metathesis allows for the re-allotting of olefin moiety by the scission and the renewal of an unsaturation. The metallic catalyst plays a crucial role in the success of the reaction, and ruthenium-based-catalysts are the most efficient and selective.[36] A prominent example of the metathesis reaction is the cross-metathesis of methyl oleate with ethene to produce the bifunctional entity, methyl 9-decenoate.

Some reactions can be performed with physical treatments, as is the case for instance of the industrial production of the monomer to achieve PA11 (Arkema, France). Castor oil is a non-edible vegetable oil with the particularity of containing a high content of ricinoleic acid (greater than 90 % FA content).[37] Pyrolysis, a thermal treatment in the absence of air, decomposes organic biomass into lower molar masses (Mw) compounds. As shown in Scheme 1, the pyrolysis of methyl ricinoleate cleaves the molecule to produce methyl undec-10-enoate (MUDO) and heptaldehyde.[38] The monomer of PA11 is obtained from MUDO after hydrolysis, brominating the double bond with HBr and the addition of ammoniac to generate an amine-ending group. MUDO and its carboxylic acid counterpart, undecylenic acid (UDA), are molecules of high interest with its active terminal double bond. They are often used in the synthesis of monomers and polymers by click-chemistry, particularly in thiol-ene chemistry. Since TEC and DA cycloaddition are click chemistry reactions, they will be developed in the corresponding section.
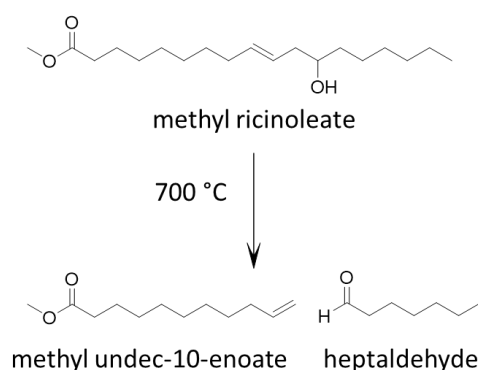
Scheme 1 Main pathway of methyl ricinoleate pyrolysis.

Vegetable oil-based polymers

Considering the variety of vegetable oils available and the myriad possibilities that chemistry offers to prepare polymers from vegetable oils, it is not simple to summarize all the possible derived polymers and their related properties. Nevertheless, vegetable oil-based polymers' performance compared to their petroleum-derived counterparts must rely not only on their sustainability but also on their properties. Herein, we have summarized the main groups of vegetable oil-derived polymers usually obtained (epoxy resins, PU, PAs, and polyesters), their advantages, disadvantages, and trends. Generally, given their long-chain aliphatic structure, vegetable oils are suitable for synthesizing hydrophobic polymers and complement well hydrophilic bioresources such as carbohydrates and proteins. Furthermore, vegetable oils are suitable for producing monomers with structures similar to fossil-based counterparts and can be interesting to achieve similar desire properties. More detailed information about each class of polymers derived from vegetable oils can be found in recent reviews on the topic.[6, 8, 39]

Epoxy resins are thermosetting materials used as protective coatings, adhesives, or composites due to their chemical resistance and mechanical, adhesion, or electrical properties.[40] For their preparation, resin precursors containing epoxy groups are treated with curing agents, such as amines or anhydrides, to result in cross-linked networks. Most of the commercially available epoxy resins are obtained using bisphenol A and epichlorohydrin.[41] However, the adverse health effects reported for bisphenol A have boosted the development of more sustainable epoxy resins. In this sense, epoxidized vegetable oils and vegetable oil-based curing agents represent an exciting option for the preparation of greener epoxy resins.[42] In terms of performance, biobased epoxies show comparable mechanical and thermal properties to their petroleum-derived counterparts.[40] The newer class of polymers known as covalent adaptable networks (CANs) and, most specifically, associative CANs or vitrimers, studied by Leibler's group, used a mixture of fatty dicarboxylic and tricarboxylic acids to cure diglycidyl ether of bisphenol A (DGEBA).[43] This work catalyzed the fields of designing recyclable and reprocessable thermosets known today as CANs.[44] Several recent works have involved FAs in CANs and are being readily explored.[45-48] This presents an interesting perspective of the role vegetable oils can play in this new class of polymers.

PUs are a family of polymers with exceptional properties for their application as coatings, adhesives, foams[49], or elastomers in the construction, biomedical,[50] or automotive industries. PUs are prepared by reacting polyols with polyisocyanates and usually incorporating a chain extender such as a low molecular weight diol or diamine. The properties of PUs can be controlled by the micro-phase separation of hard segments (HS), composed of polyisocyanates and chain extender, and soft segments (SS). Biobased PUs can be prepared from vegetable oil-derived polyols that impart flexibility to the resulting network,[51] and considerably decreasing carbon footprint.[52] The combination of soft and hard segments results in specific properties of PUs such as elasticity, mechanical strength, toughness, and degradation. Long-chain aliphatic PUs have been shown to have decreased melting temperature with increased distance between urethane groups due to the use of vegetable oil derivatives. The production of diisocyanates is environmentally harmful, and the Narine[53] and Cramail[54] groups have explored greener strategies from vegetable oil derivatives. Eccentric triglycerides resources such as microalgae-based polyols have in explored in the synthesis of PU foams.[55] Furthermore, many non-isocyanate polyurethanes routes to achieving polyurethanes using vegetable oils and derivatives that have been explored.[56-58]

Polyamides are a class of polymers commonly used as fibers for different applications, such as electric and electronic applications, or in the automotive or textile industry. They show great performance regarding heat and chemical resistance as well as toughness. Nevertheless, they generally show high-water absorption and poor low-temperature properties, which limit their application. Polyamides can be obtained by the polycondensation of amino carboxylic acids, from the reaction of dicarboxylic acids with diamines, or after the ring-opening polymerization of lactams.[59] Polyamides can also be obtained from vegetable oils. As previously stated, this is the case of the well-known PA11 that can be prepared from 10-undecenoic acid obtained after the pyrolysis of castor oil.[60] These long-chain polycondensates lower processing temperatures and allow for lower water absorption than classic short-chain polycondensates such as PA 6. There is a growing incentive to develop long-chain polycondensates derived from vegetable oils to bridge the gap between polyolefins and polycondensates.[61] Furthermore, further adding functional pendant side chains to long-chain vegetable oil PAs is being explored, yet attaining high MWs still seems challenging.[62]

Polyesters are biodegradable polymeric materials that possess an ester linkage that can be hydrolyzed and degraded under specific conditions. They are widely used in biomedical applications such as drug delivery or tissue engineering and found applications in packaging and elastomers.[6, 63] They are prepared via condensation polymerization of diols with dicarboxylic acids or diesters, intrinsic hydroxycarboxylic acids, or ring-opening polymerization of lactones, and acyclic diene metathesis (ADMET) polymerization. Long hydrocarbon chains

in polyesters can promote crystallization. Similar to PAs, physicochemical properties can be adjusted by controlling the ester group density. Consequently, vegetable oils and particularly FAs are raw materials for aliphatic polyester that vary in structure and properties, have received intense attention in recent years.[45] Moreover, long-chain polyester-based thermoplastic elastomers can be prepared.[64] Similar to PUs and PAs, exploring functional thermoplastic aliphatic polyesters with active side groups has been explored.[65] Given their biodegradable nature of ester linkages, researchers and industrials explore the use of biotechnology and, most specifically, enzymes to chemically recycle polymer to yield interesting monomers used in an upcycling approach.[66]

Besides the above-mentioned families of polymers, a variety of polyureas, polyacetals, polycarbonates, polyanhydrides (to name a few), UV or thermally cured-acrylate resins, [67-69] and composites[70] were also synthesized from fatty acids and their derivates. Unfortunately, long-chain vegetable oil-derived polymer physical properties do not compete with their commercial counterparts in most cases. Indeed, the renewable nature of vegetable oils allows for polymers to increase in sustainability, but another major drawback for the moment is their economic viability that renders their use often in niche added-value applications. Regardless, the varying composition of vegetable oils and their modification with different functional groups allows for a precise design of both linear and branched polymers with specific properties depending on the target application. Different examples will be presented in the different sections of this work.

Click Chemistry

Click chemistry was introduced by Sharpless and co-workers in 2001 and consists of a wide range of relatively fast reactions that are modular, wide in scope, giving high yields, being stereospecific, and generating mainly inoffensive by-products.[17] It is the high thermodynamic driving force of click reactions that allows them to achieve these characteristics. In line with several principles of green chemistry, the parameters of the reactions should include simple reaction conditions, readily available starting materials and reagents, the use of no solvents or benign solvents, and simple product isolation. Some common click chemistry reactions used on TGs and TAs are highlighted in Scheme 2 and then developed below. For a deeper mechanistic comprehension, recent literature presents several states of art.[19, 71-74] These common
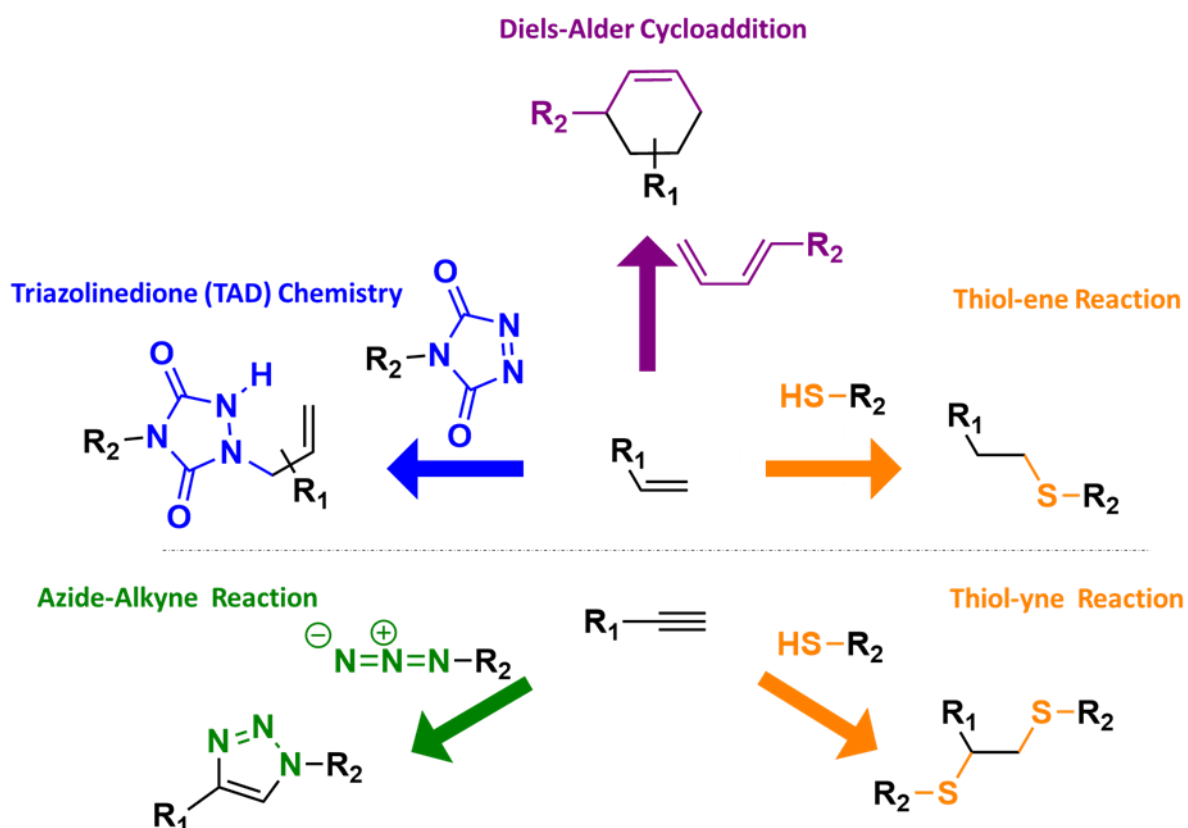

reactions based on click chemistry are diverse.

Scheme 2 Schematic representation of click chemistry reactions applied to TGs, FAs, and derivatives.

Diels-Alder cycloaddition

The DA cycloaddition (Scheme 2) consists of a chemical reaction between a conjugated diene and a substituted alkene, commonly termed dienophile, to form an adduct. Otto Diels and Kurt Alder first reported this reaction in 1928.[75] It is extensively used in organic chemistry to produce six-membered unsaturated rings with reasonable control over regio- and stereochemical properties.[76] The [4+2] cycloaddition takes place through a concerted mechanism. It is fascinating due to its thermal reversibility (retro DA reaction or r-DA), depending on the diene/dienophile couple.[77] The thermal reversibility is highly appealing in polymer chemistry for applications with recyclable or self-healing materials. All these benefits explain why the DA reaction for derivatives and polymer synthesis has bloomed over the last two decades and is now an established strategy for synthesizing macromolecular architectures. For instance, Gandini *et al.* have published several reviews in the previous decade, summarizing the most relevant results regarding the use of the DA reaction in polymer chemistry.[77-79]

One of the most well-known diene/dienophile couples used in polymer chemistry is the furan/maleimide system (Scheme 3). The main characteristic of this coupling is that the r-DA can be achieved at relatively low temperatures.[77] For instance, the DA reaction could occur around 65 °C, whereas the r-DA leading to uncoupling of the adduct is predominant at about 110 °C.[78] According to the corresponding chemical structures and conditions, these temperatures can vary. An interesting particularity of the furan/maleimide couple is based on the potential renewable character of the furan derivatives, leading to greener chemistry alternatives. The strong diene character of the furan ring renders it attractive in terms of reaction yield and kinetics. Although the furan/maleimide couple is the most famous couple for DA reaction, other diene/dienophile couples can also be used. Given the nature of the reaction, the DA reaction exemplifies several aspects of green chemistry, most notably waste prevention, atom economy, energy efficiency, and reduced use of derivatization. Furthermore, in the case of the furan/maleimide couple, reactions have been found to proceed well in bulk conditions without harmful catalysis, leading to safer chemistry conditions.
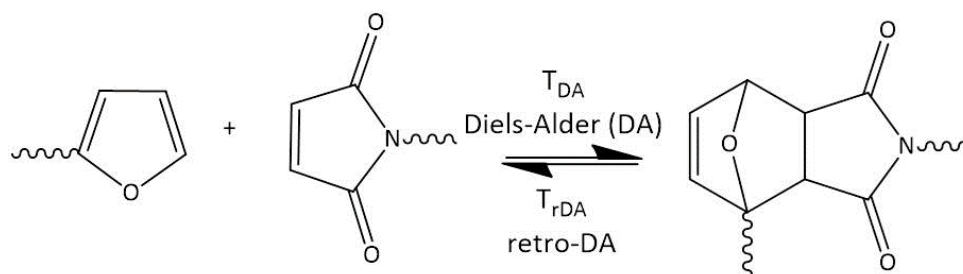
Scheme 3 Schematic of DA reaction and r-DA between furan and maleimide moieties.[80]

Triazolinediones chemistry

Recently, another example of click chemistry based on the reactivity of 1,2,4-triazoline-3,5-dione (TAD) has been added to the toolbox of chemists for polymer science. TADs are heterocyclic molecules with an azo group and two carbonyl functionalities, highly resembling maleimide dienophiles.[19] Within this electronic configuration, the azo group, is stabilized and the electron-withdrawing carbonyls coupled with the molecule conformation make them highly reactive.[81] The high reactivity of azodicarbonyl derivatives was first reported by Diels and co-workers in 1925.[82] However, the use of the most reactive TAD versions for the DA reaction was not reported until the 60s.[83, 84] TADs can take part in DA and ene-type reactions fulfilling the requirements of click chemistry reactions such as orthogonality and reversibility as well as high yields under mild reaction conditions (Scheme 2).[81] Comparing with maleimides, TADs show higher reactivity, reacting with dienes almost instantaneously at relatively low temperatures, and, in most cases, produce irreversible products.[19] Given the nature of the TAD chemistry, it complies in similar ways to several green chemistry principles as that of the DA reaction. Du Prez and co-workers have intensively developed these types of reactions in the last years. They have introduced the term "transclick" reactions.[81] These reactions have been defined as covalent linking processes that can be triggered to form a new bond with other available orthogonal partners, releasing one of the initially involved counterparts. Thus, this strategy could be applied to form dynamic bonds or the thermal exchange between clickable groups, contributing to the potential of developing self-healing and recyclable materials.

Thiol-ene reaction

The thiol-ene reaction, also defined as thiol-ene coupling (TEC), takes place between double bonds (enes), which can be either terminal monosubstituted or internal disubstituted enes, and thiol groups (Scheme 2). The reaction takes advantage of the labile sulfur-hydrogen bond.[85] Two reactions between thiols and double bonds have gained prevalence and possess many characteristics of click reactions: (i) the free-radical addition of thiyl radicals (generated from thiols initiated by light, heat, or radical initiators) to electron-rich or poor double bonds and (ii) the catalyzed (by a base or nucleophile) thiol-Michael addition to electron-deficient double bonds. Concerning the free-radical thiol-ene reaction, the reaction rate depends strongly on the structure of the thiol and the ene. Thiyl radicals tend to be added faster to electron-rich enes (terminal double bonds) than electron-poor enes (acrylates).[86] The use of TEC for monomer synthesis has been used for a wide range of polymers. For example, TEC has been used to synthesize AA, AB, and AB_2 type monomers for polycondensation or polyaddition to obtain polyesters, PAs, and NIPUs has been of recent interest. Moreover, the modifications by TEC to yield highly functional molecules has also been studied for applications such as polyols for PU synthesis, epoxy resin curing agents, monomers for coating applications, and plasticizers for PVC. Given the click chemistry nature of the thiol-ene reaction, it fulfills several principles of green chemistry such as waste prevention, atom economy, energy efficiency, reduced derivatives, and in some instances can be performed in bulk, reducing the use of solvents and increasing the safety of the applied chemistry.

Thiol-yne reaction

The thiol-yne reaction, otherwise defined as thiol-yne coupling (TYC), was re-introduced as a powerful tool for polymerization by Bowan and co-workers in 2009.[87] Their work demonstrated how readily accessible azide-alkyne building blocks could complement thiol-ene reactions. Essentially by the thiol-yne reaction, two thiyl radicals can react with alkynes to form thioether linkages, consequently saturating the alkyne bond (Scheme 2).[88] Similar to the free-radical thiol-ene addition, a radical source or UV irradiation can be used. Additionally, this reaction similarly follows green chemistry ideals of the thiol-ene addition, such as waste prevention, atom economy, energy efficiency, reduced derivatives, and typical azide-alkyne cycloaddition is no need for a potential toxic catalyst.

Huisgen 1,3-dipolar cycloaddition

One of the most appealing examples of click chemistry is the Huisgen [3 + 2] dipolar cycloaddition of alkynes and azides to yield 1,2,3-triazoles (Scheme 2).[76, 89] Molecules can be easily functionalized with alkyne and azide moieties under mild conditions. Moreover, their tolerance to a wide variety of functional groups and reaction conditions turns these coupling agents into attractive alternatives for polymer chemistry.[76, 90]

Sharpless and Meldal reported the copper-catalyzed version of the azide-alkyne cycloaddition (CuAAC).[91, 92] This reaction between azides and alkynes is high yielding and shows higher regioselectivity, resulting solely in 1,4-regioisomer, increasing the reaction rate up to 10^7 times, and avoiding the use of high temperatures.[76, 89, 90] Furthermore, water as a solvent proved to induce a beneficial kinetic effect on the reaction. The CuAAC reaction has been widely used in polymer chemistry to produce polymers with different macromolecular architectures such as linear or block copolymers, or dendrimers, circumventing common problems such as steric hindrance of reactive sites in a growing polymer chain [89, 90]. As a greener alternative to using a copper catalyst in the Huisgen 1,3-dipolar cycloaddition, the thermally driven version of this reaction has also been employed in polymer chemistry.[93] The thermal Huisgen 1,3-dipolar cycloaddition offers some advantages over the CuAAC, particularly in polymer chemistry where the removal of the catalyst entrapped within the polymer matrix becomes difficult. However, this version is non-stereoselective and forms both 1,4- and 1,5-disubstituted triazole rings.[93] Consequently, the Huisgen [3 + 2] dipolar cycloaddition abides by certain green principles such as waste prevention, atom economy, reduced derivatives, and also energy efficiency, as is the case of CuAAC.

Synthesis of building blocks and polymers by click reactions from TGs and FAs

The different click reactions previously presented have been applied to FAs and TGs to synthesize building blocks and biobased macromolecular architectures. Recent developments in this field are discussed in this section.

Diels-Alder (DA) cycloaddition

The DA reaction has been widely used in the last decades in oleochemistry, for example, in the dimerization of FAs.[94] The double bonds of vegetable oils have been used as dienes and reacted with anhydrides such as maleic anhydride, acrylic acids, or methacrylates.[40, 95-106] However, in some cases, to develop DA reactions on TGs or FAs, the incorporation of specific reactive functionalities such as furan or maleimide groups onto the TAs and TGs structures is required. For instance, the generation of furan compounds, such as furfural or 5-hydroxymethylfurfural, can open the way to different building blocks from glycerides functionalized with furan moieties.[79] Table 3 summarizes the different polymers that can be obtained using the DA reaction with vegetable oils.

Two approaches have been mainly applied to prepare macromolecular materials from the DA reaction as illustrated in Table 4.[18] One-way deals with the synthesis of thermally reversible linear, branched, or cross-linked polymers based on the polycondensation of building blocks incorporating both DA complementary moieties such as furan and maleimide groups. On the other hand, the thermally reversible cross-linking of linear polymers bearing pendant furan or maleimide moieties and using complementary maleimide or furan bifunctional cross-linkers has also been widely explored. One of the most interesting features of this reaction is the temperature control for the forward and r-DA reactions that allow for the decoupling of the DA reaction groups resulting in recyclable or self-healing cross-linked materials.

Ta**ble 3** Summary of vegetable oil derived polymers via DA reaction

Vegetable Oil	Type of polymer	Application	References
Tung oil	Biobased epoxy	Protective coatings Adhesives Castings Microelectronics	95 96 97
	UV-curable resins	Printed circuit boards Hydrophobic coatings UV-coatings for paints and varnishes	98 99
	Polymerized tung oil	Pressure-sensitive adhesives	101
	Glycerin ester of tung oil-modified rosins	Tackifiers for adhesives and rubbers Coatings	102
	Polyester resins	Microencapsulation Toughening agent	103
Sunflower oil	Renewable networks	Coating application with antibacterial properties	104
Soybean oil	Polyurethane	Self-healing materials	122
	Alkyd resins	Coatings	105
	Acrylated soybean oil	Coatings Flame retardant products	123)
Myrcene oil	UV-curable vinyl ester resing	Surface coating Radiation curable inks Printed circuit boards	106
Sunflower and rapeseed oil	Polyurethane	Adhesives Coatings Automotive Construction industry	118 120 121
Jatropha oil	Thermoreversible polymeric networks	Adhesive	124 125
Jatropha and Sunflower oil	Thermoreversible polymeric networks	Adhesives	126

Table 4 Schematic representation of the macromolecular materials resulting from DA reaction using vegetable oils and their derivatives from different approaches (A and B refers to furan and maleimide groups, respectively).

| Type of Macromolecular Architecture	Type of Reaction	Reaction Schematic	Refer
	AA + BB		114
Thermally Reversible Polymers	AB		114
	An + Bm (n or m > 2)		110, 1
Cross-linking of Linear Polymers	P-A + BB P-B + AA		87,12

Gandini and co-workers have extensively worked on the DA reaction with building blocks synthesis from TGs and FAs, followed by polymer synthesis.[77, 107-114] The first report for the preparation of vegetable oil-

based monomers was reported by these authors using UDA, derived from castor oil, that possess two reactive terminal sites available for the insertion of furan or maleimide moieties.[114, 115] In these works, two difuran monomers were prepared using esterification and thiol-ene reactions (Fig. 3-a & b). Another bifunctional monomer bearing both furan and maleimide groups was also prepared from 10-undecenol (UDC) using protective chemistry (Fig. 3-c). These monomers were polymerized by the DA reaction at 65 °C in 1,1,2,2-tetrachloroethane (TCE) using 1,6-bismaleimidohexane with the first two, whereas the bifunctional monomer was self-polymerized after deprotection. Raising the temperature to 110 °C allowed for the recovery of the monomers through r-DA depolymerization. The reported polymers obtained using difuran and bismaleimide (BMI) monomers had a low mass-average molar mass (Mw) of 7-9 kDa and T_g of about -30 °C. In the self-polymerized polymer, the Mw was 17 kDa with a T_g of -2 °C due to a stiffer macromolecular architecture.
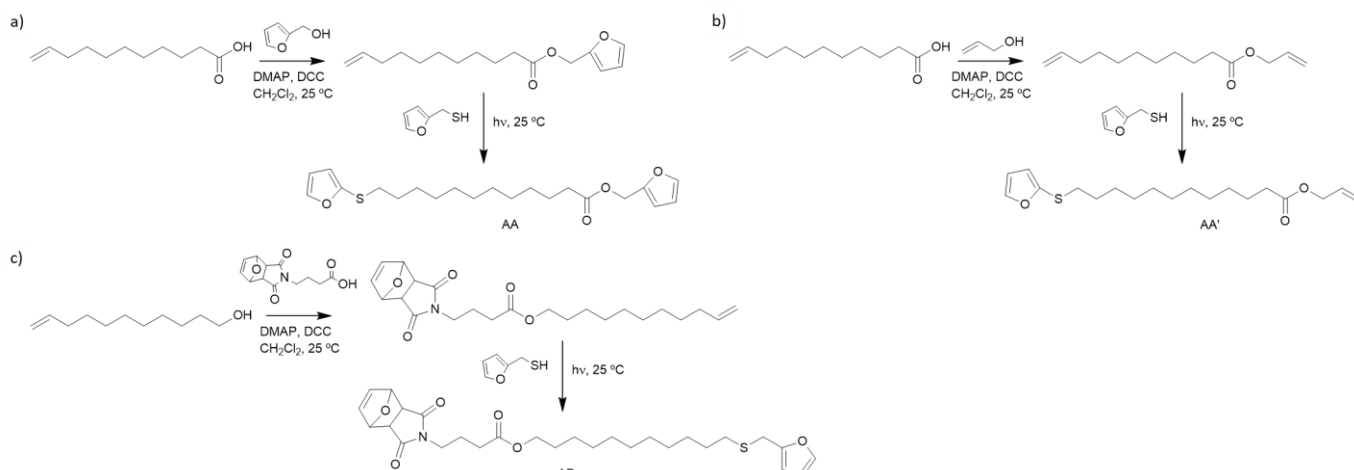
Fig. 3 (a) Synthesis of difuran monomer from 10-undecenoic acid, (b) synthesis of a second difuran monomer from 10-undecenoic acid and, (c) synthesis of protected AB macromonomer. Reproduced from ref. 114 with permission from John Wiley and Sons, copyright 2011.

In a more recent work by the same authors, non-linear polymers were prepared by employing trifuran, difuran, or BMI monomers (Fig. 4).[110] The trifuran monomer was polymerized with an aliphatic BMI, whereas the difuran monomer was polymerized with a trimaleimide, leading to the same types of macromolecular architectures. Both macromolecular structures showed Mw between 35 and 50 kDa and T_g around 0 °C when using a 0.5 trifunctional/bifunctional molar ratio. The authors reported that stoichiometric monomer conditions produced gels with T_g values of about 15 °C. On the other hand, the DA self-polymerization resulted in hyperbranched macromolecules with Mw between 50 and 70 kDa and T_g around 5 °C.
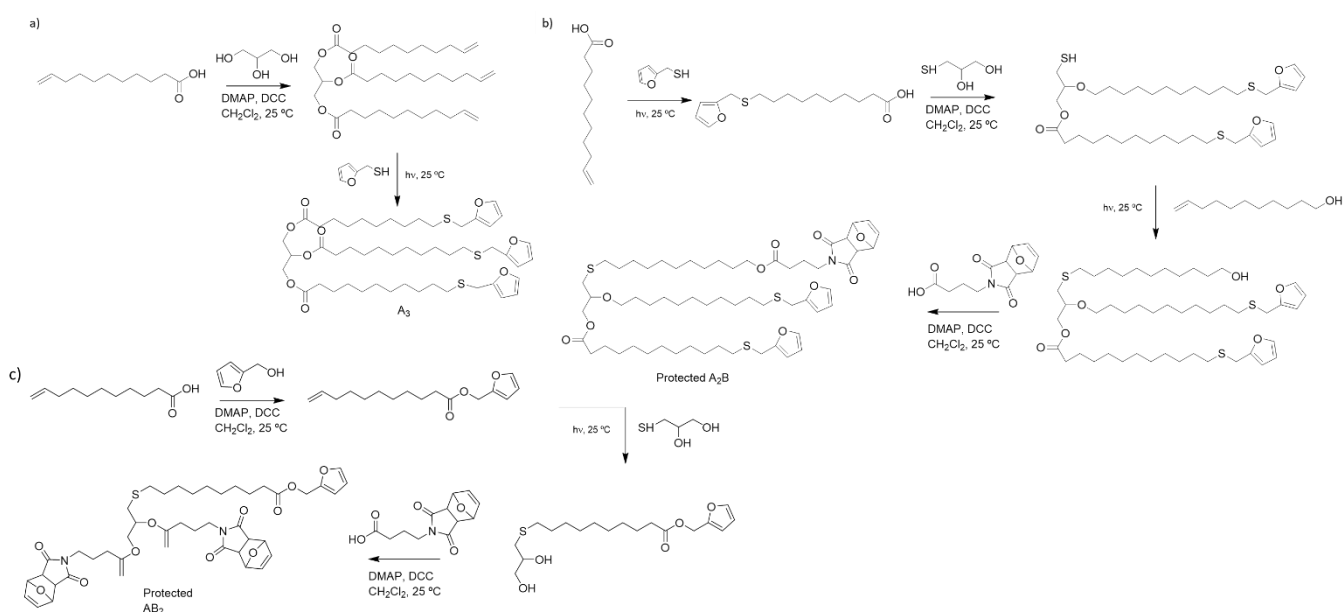
Fig. 4 (a) Synthesis of trifuran monomer based on 10-undecenoic acid, (b) synthesis of a difuran monomer bearing a protected maleimide moiety, and (c) synthesis of a monofuran monomer bearing two protected maleimide moieties. Reproduced from ref. 110 with permission from John Wiley and Sons, copyright 2013.

The same authors explored a simpler catalyst and solvent-free route to shift to greener synthetic routes to prepare vegetable oil-derived furan monomers. Epoxidized linseed oil was submitted to a reaction with furfuryl amine, resulting in the transamination of the three ester groups and the epoxy ring-opening induced by the primary amine, without solvent and catalyst.[116] Moreover, this reaction allowed the complete recovery of both the product and the excess reagent, fulfilling the principles of green chemistry. The resulting products incorporated available furan groups for DA polymerizations with BMIs. The DA polycondensation resulted in a mixture of linear and branched polymers with Mw between 35 and 40 kDa and T_g around 80-100 °C. However, in this case, the DA reaction was with organic solvent and was conducted in TCE. The same strategy was also applied to epoxidized soybean oil, and similar results were obtained.

On their continued efforts to develop greener processes, the reaction of commercial tung oil (TO) with maleimides under solvent-free conditions was also explored.[117] This oil contains three conjugated unsaturations that can behave as dienes for the DA reaction. The authors explored the reaction of this glyceride with methylmaleimide at 65 °C resulting in a stable adduct not able to undergo the retro DA reaction. When combined with different BMIs of varying flexibility, the DA crosslinking of TO resulted in gels with T_g values between -10 and 75 °C (Fig. 5-a). Again, the stability of these adducts was high and did not offer the reversibility of the previously reported systems. In another approach, the same transamination reaction reported for epoxidized vegetable oils was performed, and the resulting furan/triene difunctional DA dienes were cross-linked with the same BMIs (Fig. 5-b). In this case, the resulting polymers had one thermally labile furan/maleimide adduct in each monomer unit and a thermally stable one formed by a maleimide group with the α-eleostearic triene moiety; thus, the depolymerization was successfully achieved
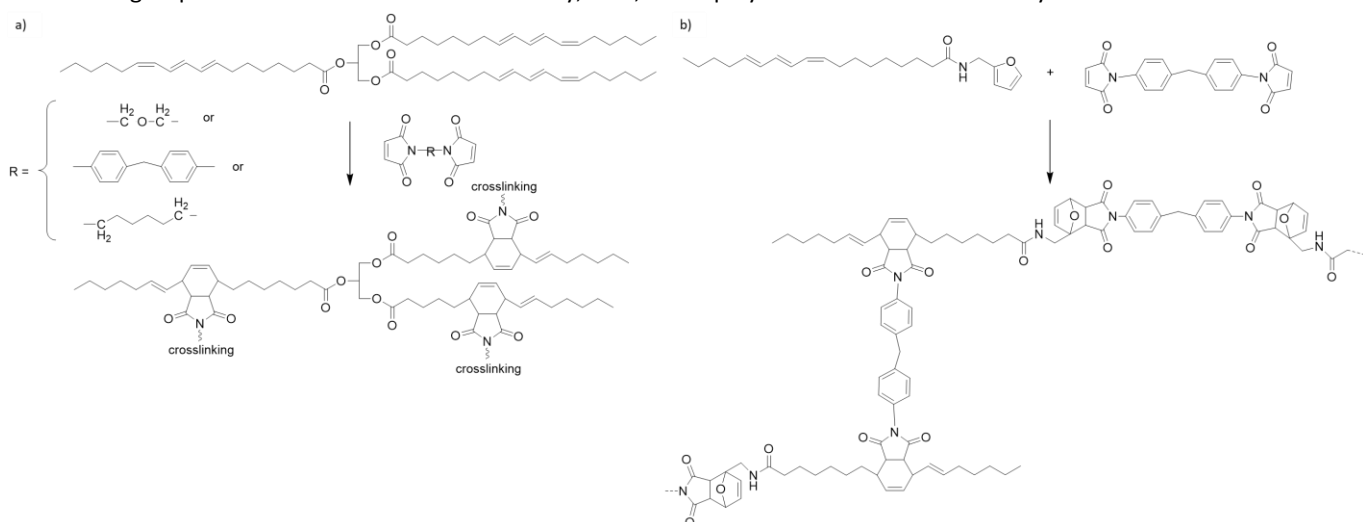

for the furan/maleimide adducts around 110 °C. The reported T_g was higher than in the previous system due to the amide-based hydrogen bonds responsible for the polymer stiffening.

Fig. 5 (a) The DA cross-linking reaction of tung oil with BMIs, (b) linear DA polycondensation of α-eleostearic furfurylamide with an aromatic BMI. Reproduced from ref. 18 with permission from John Wiley and Sons, copyright 2017.

In recent work, the DA reaction was employed to prepare reversible cross-linked PUs based on vegetable oils (Fig. 6-a).[118] A new diol containing pendant furan rings was synthesized and integrated into a linear rapeseed-based PU backbone which was then cross-linked by the DA reaction using a short polypropylene oxide BMI. In this study, octadec-9-enoic acid (OA) was used as the starting point to produce an oligomer with pendant furan rings through esterification using furan-2-ylmethanol. This type of esterification does not respect many ideals of green chemistry. Alternatively, it has been successful via chemo-enzymatic means that reduce waste and increase atom economy.[119] The esterified compound was epoxidized in situ using acetic acid, H_2O_2, and acid catalyst in toxic organic solvent (toluene) to produce an epoxidized product (FMOO). The acid-catalyzed ring-opening polymerization of FMOO finally produced an oligomer polyether diol (FO) in bulk (Fig. 6-b). Moreover, different biobased cross-linked PUs were prepared by varying the proportion of FO by polyaddition between a polyester polyol and toxic hexamethylene diisocyanate (HDI) and then evaluated. The T_g increased due to the cross-linking, and a more pronounced endothermic r-DA peak was observed when the amount of FO increased (Fig. 6-c). Regarding the mechanical properties, the tensile strength and Young's modulus increased due to the DA reaction. Reprocessing cycles were also performed, resulting in stable properties. Finally, self-healing was also studied by cutting the PU samples and

heating them at 120 °C for 1 h and cured at 60 °C for 2 days (Fig. 6-d). The initial heating produced the breakage of the crosslinks that were then healed during heating. In the following work, different PUs were prepared by varying the molar masses and chemical structures of the BMI cross-linkers to study their effect on the recyclability and healing capacity of the networks.[120]
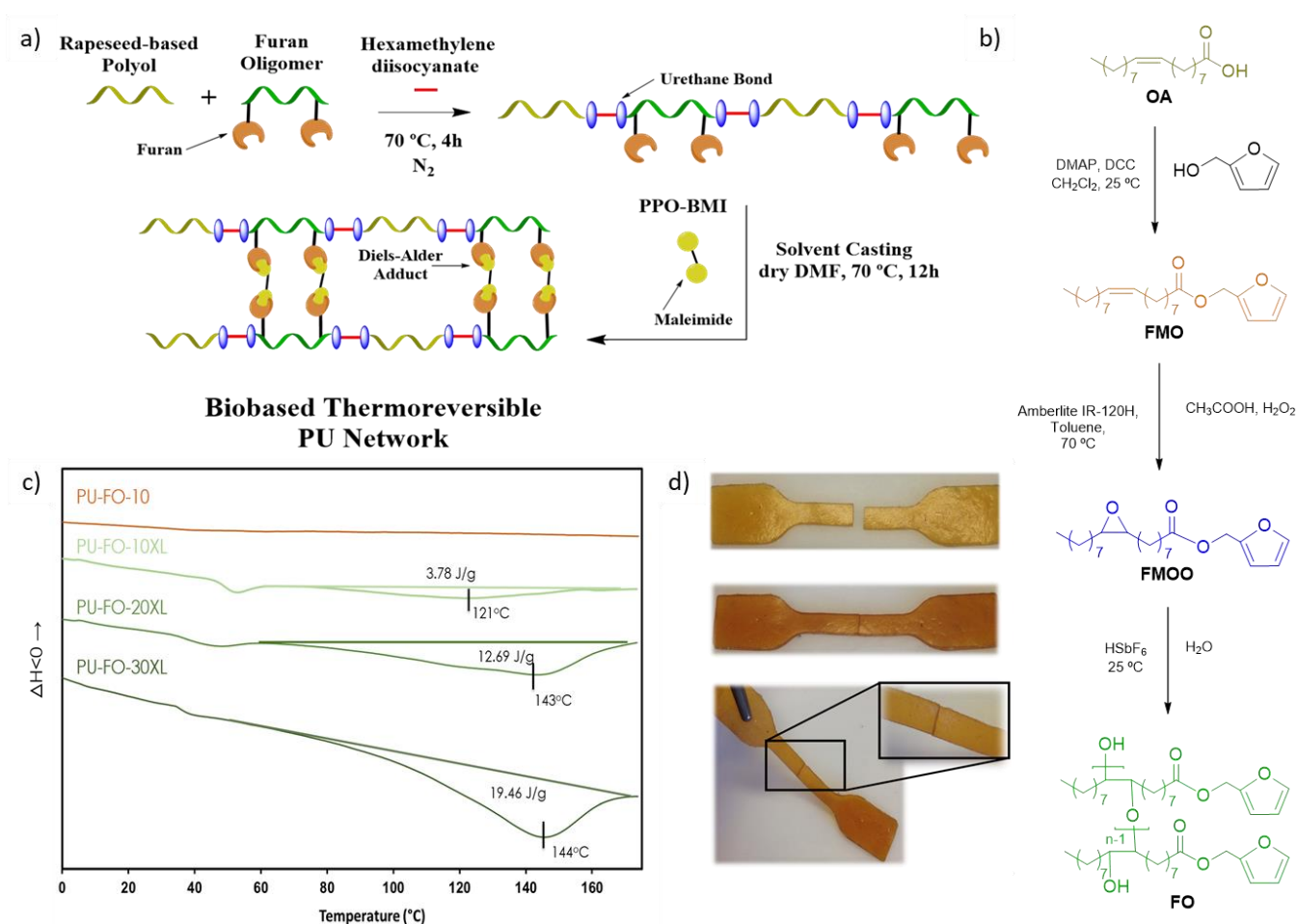
Fig. 6 (a) General scheme for the synthesis of thermoreversible PU-based systems, (b) reaction scheme of FO, (c) self-healing evaluation of the materials of (i) dumbbell sample cut in half, (ii) and (iii) healed dumbbell sample after heating 1 h at 120 °C and 2 days at 60 °C, and (d) thermograms of different PUs prepared. Reproduced from ref. 118 with permission from John Wiley and Sons, copyright 2019.

In an attempt to move to more sustainable materials, our group has recently reported the synthesis of a novel biobased BMI (methyl oleate BMI (MO BMI)) derived from sunflower oil for the cross-linking of PU networks via the DA reaction.[121] The biobased PUs were prepared by combining rapeseed-based polyol, HDI, and (furan-2,5-diyl)dimethanol) as the chain extender. This furan bearing chain extender was chosen to explore the cross-linking in the hard segment (HS) domain. The biobased MO BMI showed a softening effect for PU materials with an increased elongation at break, and a decrease in Young's modulus and tensile strength attributed to the aliphatic and branched long chains of the cross-linker. The mechanical properties were preserved at least two hot press reprocessing cycles when using MO BMI, showing good thermal recyclability and heat-induced self-healing.

Recently, self-healing PUs based on soybean oil polyol modified with furfuryl alcohol via the DA reaction with 1,5-bis(maleimido)-2-methyl pentane were prepared.[122] The recycling ability of PU was studied using a solubility test. The material was dissolved in organic solvent (DMSO) after heating at 180 °C due to the thermoreversibility of the DA reaction. The authors have shown the recyclability of these materials. The shape-memory properties of the obtained films were also positively evaluated. The films showed a shape recovery higher than traditional soy oil-based PU due to a more regular cross-linked network of the DA cross-linked PU due to one-to-one correspondence between furan and maleimide. Finally, the self-healing ability of the PU was investigated by cut, scratch, and tensile testing. Preliminary healing was achieved at 70 °C, whereas profound self-healing occurs at temperatures above 120 °C.

The DA reaction has also been used for the cross-linking of acrylated soybean oil (AESO), an easily polymerizable monomer used for different applications such as coatings or flame retardant products.[123] The

use of the DA reaction between furfuryl functionalized AESO, monofunctional N-phenylmaleimide, and a BMI, 1,1-(methylenedi-4,1-phenylene) has also been developed.[123] The materials showed one endothermic transition at temperatures between 103 and 134 °C, indicating that both the endo and exo adducts can be reverted at similar temperatures. The formation of the adduct resulted in more rigid materials with an increased T_g. Furan-functionalized fatty esters have also been prepared for network synthesis.[124] Methyl oleate, methyl linoleate, and jatropha oil were all epoxidized using in situ generated performic acid. Then, the epoxidized compounds were reacted with furfurylamine and cross-linked with BMIs through DA reaction. Furfuryl-amine functionalized jatropha oil was reacted with 1-1'-(methylenedi-4,1-phenylene) BMI. DSC showed the thermoreversibility. With a r-DA reaction occurring around 125°C. The high degree of cross-linking results in brittle materials. Finally, the authors explored the use of furan-functionalized jatropha oil for partial substitution of (1,4)-polyketone reacted with furfurylamine to improve the polymer properties and add a renewable character to the material. The addition of 10% of furan-functionalized linoleate resulted in increased thermal stability and temperature to achieve the reversible cross-linking of the network.

More recently, the modification of epoxidized jatropha oil with furfurylamine was also explored. Furfurylamine reacted with the ester groups present in the TGs backbones via ester bond cleavage by aminolysis leading to brittle thermally reversible polymers when cross-linked through the DA reaction. Results showed that side reactions were promoted using an excess of furfurylamine and higher temperatures, probably due to solvation behavior and reactivity changes. The use of 50% lithium bromide as catalyst improved the epoxide conversion, and the highest conversion was obtained when using equimolar amounts of epoxide and furfurylamine at 80 °C for 24 h. Different product mixtures were cross-linked with an aliphatic BMI via DA reaction. The products showed varying flexibility depending on the chain length, the number of furans attached, and cross-links.[125] Bearing in mind these results, the same authors explored the cross-linking of furan-functionalized jatropha and sunflower oils with aliphatic and aromatic BMIs. The thermal properties were also influenced by the type of oil employed, and sunflower-based polymers showed higher T_g values. The recyclability of the polymers through the retro-DA reaction was also demonstrated.[126]

Some other examples of the DA reaction involving different diene/dienophile couples for the modification or cross-linking of vegetable oils have also been reported in the literature. The use of the DA reaction to cross-link a biobased epoxy monomer with conjugated double bonds, glycidyl ester of eleostearic acid, synthesized from TO has been reported.[96] The DA reaction resulted in being more active than the ring-opening of epoxy and anhydride. The monomer was cured using both maleic anhydride, nadic methyl anhydride, and 1,1'-(methylenedi-4,1-phenylene)-BMI. The structures and cross-linking densities of the prepared thermosetting polymers can be tuned by varying the anhydrides and dienophiles structure. Microwave-assisted maleation of TO was investigated as a green approach based on DA reaction and free radical copolymerization without solvent and catalyst with low reaction time and high yields.[98] The obtained product was reacted with epoxidized glycidyl ester, epoxidized soybean oil, and epoxidized octyl soyate to produce fully oil-based epoxy resins. As another example of green chemistry, sunflower oil can also be used for the DA reaction with terpenes. In the presence of oxygen, DA reaction between β-myrcene or β-farnesene and sunflower oil to design novel biobased networks were also reported.[104] Sunflower oil takes part in the DA reaction and increases the flexibility of the system. The resulting materials showed different T_g, varying from 20 to 92 °C.

Triazolinediones chemistry

As mentioned earlier, TADs have become interesting compounds in organic synthesis and, more recently, in polymer chemistry. Biswas and co-workers were the first to report the reaction of TADs with soybean oil.[127] They reported the modification of a TG oil through the reaction with 4-phenyl-1,2-3-triazoline-3,5-dione. The increase in viscosity confirmed the formation of ene and DA reaction products between the TAD and the oil, giving an example of self-curing vegetable oils that could be used as additives in lubricants or as thickeners in a variety of formulations reducing the use of solvents or catalysts.

Du Prez and co-workers explored the use of TADs for the click cross-linking of vegetable oils at room temperature without catalysts.[128] First, the reaction was studied with natural FAs and monofunctional TAD moieties. Oleyl alcohol, elaidyl alcohol, methyl ricinoleate, 10-undecenoic acid, methyl linoleate, and methyl linolenate were used as model FAs and reacted with phenyl-TAD. Studies were also conducted with polyunsaturated FAs such as methyl linoleate and methyl linolenate. This strategy was then applied to cross-linking vegetable oils such as olive, sunflower, colza, corn, groundnut, pumpkinseed, soybean, and castor oils using a bifunctional TAD. Gelation took place within minutes, but the red color of the TAD compounds was observed for longer reaction times. The differences in the gelation time observed for the different oils were attributed to the reaction kinetics of the different FAs and the ene: TAD ratio. The T_g of the resulting materials ranged from 60 to 124 °C revealing the rigidity imparted by the aromatic TAD cross-linker. For the first time,

the same research group reported using TAD-based chemistry to prepare nanoparticles using vegetable oils as the starting compound.[129] Lipid-based nanoparticles can be used for different applications such as drug delivery, imaging, and therapeutics. By using vegetable oils, less toxic and biocompatible particles can be achieved, containing ester functionalities to improve their degradability and reducing their cost. Multi shape-memory materials have also been developed combining high oleic soybean oil and TAD click chemistry.[130] The double bonds of vegetable oil-derived polymers were cross-linked using TAD chemistry. The matrix is prepared by surface-initiated atom transfer radical polymerization of soybean amide methacrylate. Consequently, two types of cross-links were achieved; permanent TAD cross-links and dynamic physical cross-links were achieved by the hydrogen bonds from the vegetable oil and the TAD groups. Therefore, TAD cross-linking produces a permanent shape while the physical network ensures multi-responsive and multi-shape-memory properties. The heating of the samples results in the deformation of the material due to the decomplexation of hydrogen bonds. Upon cooling, the temporary shape is blocked. The hydrogen bonds can be eliminated by further heating, and the material recovers its permanent shape.

Thiol-ene reaction

Thiol-ene click reaction has been vastly applied to unsaturated TGs and FAs.[131, 132] This section describes the latest works based on TEC with three sub-sections: (i) building block synthesis, (ii) polymer synthesis, and (iii) polymers modifications.

Building blocks synthesis

TEC has been used to modify the physical properties of TGs and their derivatives (e.g., ramification,[133] increasing water dispersibility,[134]). However, these modifications will not be developed in this review. Table 5 presents a recent work summary of the monomers (AA, AB, AB$_2$) synthesized using TEC derived from vegetable oils and type final polymer achieved using these monomers. Table 6 summarizes the glycerides-derived polyfunctional architectures synthesized using TEC with the corresponding final polymers achieved in recent works.

Table 5 Summary of vegetable oil-derived AA, AB, and AB$_2$ type monomers synthesized using TEC.

Vegetable Oil	Derivative Used	Type of Monomer (AA, BB, AB$_2$)	Type of Polymer	Applications	References
Sunflower OIl	Enone derivative methyl oleate (EMO)	AB	Polyester	Biomedical	136
	Methyl oleate	AB	Polyamide	Biomedical	143
	Oleic acid	AA	Polyamide	Adhesives, inks, surface coatings	141
	Oleyl alcohol	AA	NIPU	Pharmaceutical	146
Castor Oil	Heptanal	AA	Polyester	Drug delivery	137
	Heptanal	AB	Polyester	Drug delivery	137
	10-Undecenol (UDC)	AA	NIPU	Coatings	145, 146
	10-Undecenol (UDC)	AB	Polyester NIPU	Biomedical	138,139 144

Methyl ricinoleate	AB$_2$	Polyester	Additive	140
10-Undecenlyamine	AB	NIPU	Adhesives	144
Undeclyenic acid (UDA)	AA	Polyamide	Automotive	142
		NIPU	Pharmaceutical	146
		PU (di-NCO)	Coating	148
Methyl undec-10-enoate (MUDO)	AA	NIPU	Coating	145
1-bromo-10-undecene	AA	NIPU	Pharmaceutical	146

    The use of synthesizing AB-type monomers for the synthesis of polyesters has been recently explored. Enone derivatives of methyl oleate (EMO) (methyl-9-oxo-10-octadecenoate and methyl-10-oxo-8-octadecenoate)[135] have been used to obtain a hydroxyester containing a ketone via TEC.[136] TEC was used to functionalize the EMO with primary hydroxyl groups using mercaptoethanol (ME) and octanethiol. The highest functionalization conditions for both reagents were achieved using a basic/nucleophilic catalyst at room temperature with stoichiometric equivalents. This respects several ideals of green chemistry, most notably such as atom economy and energy efficiency. As depicted in Fig. 7-a, the hydroxyester functionalized by ME was then used for polyesterification via enzymatic polymerization with lipase CalB to exploit safer catalysts rather than toxic organometallic catalysts. The ketone moiety found on the polymer backbone could be further modified via oxyamines (at room temperature) to yield oximes moieties as a functionalization strategy for ligands to be covalently immobilized, useful for biomedical applications. In a subsequent study, AA and AB monomers were synthesized for polycondensation using heptanal from the pyrolysis of ricinoleic acid (Scheme 1).[137] One-pot sequential modifications via Horner-Wadsworth-Emmons and thiol-Michael reactions modified heptanal to yield a branched diester (AA monomer) and a branched hydroxyester (AB monomer) (Fig. 7-b). Although these monomers require purification by column chromatography, they were used for polycondensation via enzymatic-catalyzed means to yield Mw of 15,000 kDa using polyethylene glycol as a co-monomer. The copolymers containing pendant moieties self-assembled into micelles in an aqueous solution, exhibiting potential behavior for drug delivery applications. The development of AB monomers via TEC for the synthesis of polyesters has also been explored. As depicted in Fig. 7-c, UDC was used to synthesize methyl 3-(11-hydroxyundecyl-thio-propanoate) (MHUTP), a hydroxyester.[138] MHUTP was obtained via TEC by a previously reported method,[139] where UDC was reacted with 3-mercaptopropionate, 2,2-dimethoxy-2-phenylacetophenone (DMPA) (photoinitiator) under UV in just minutes. MHUTP was used for polyesterification by lipase-catalyzed means, and the influence of reaction time and temperature on the Mw was studied. Methyl ricinoleate was also investigated as a co-monomer in polyesterification reactions. These acid-degradable polymers show potential in biomedical applications. Similarly, the synthesis of hyperbranched polyesters from methyl ricinoleate by modifying methyl ricinoleate into an AB$_2$ monomer via TEC using in ME in solvent-free conditions was performed.[140] Nevertheless, polycondensation took place with the use of hazardous catalysis such as Ti(OBu)$_4$.However these hyperbranched polymers high thermal stability and present themselves as a 'greener' additive to modify polymer performance. Other than this latter work, all previously mentioned monomers in this paragraph were further used for polycondensation via enzymatic catalysis. This further promoted and developed the use of CalB as an alternative to an

organometallic catalyst for the synthesis of polyesters by ideals that are in line with green chemistry principles.

Fig. 7 (a) Synthesis of polyketoesters using Novozyme 435 (Lipase CalB) followed by most modification by oxyamine. Reproduced from ref. 136 with permission from The Royal Society of Chemistry, copright 2014. b) Functionalization of heptanal for the synthesis of poly(β-thioether ester)s. Reproduced from ref. 137 with permission from Elsevier, copyright 2019. (c) Synthesis of poly(β-thioether ester) and poly(β-thioether ester-co-ricinoleic acid by enzyme-catalyzed transesterification. Reproduced from ref. 138 with permission from Elsevier, copyright 2019

Developing AA and AB monomers using TEC has also been used for the synthesis of PAs. Meier and co-workers developed a dimer FA to be used in PA and PUs.[141] The dimer FA was synthesized using methyl oleate, ethane-1,2-dithiol in a 1.9: 1 ratio, DMPA, and UV radiation at room temperature. As an alternative to the industrial established procedure of obtaining dimer FAs, the reported procedure does not require further purification, respects atom economy, and reduced the use of solvents. They observed that the dimerization of OA by TEC was much slower than methyl oleate. The developed dimer FA was used in collaboration with hexamethylenediamine and dimethyl adipate to synthesize PA with varying ratios of dimethyl adipate and dimer FA in copolymerization. PA synthesized using the novel dimer FA exhibited superior hydrophobic properties such as lower water intake than a similar commercial alternative such as Nylon 6,6 for application such as adhesives, printing inks, surfacing coating, lubricating oils, and corrosion inhibition. Similarly, Seppala and co-workers synthesized di-acids containing sulfur units within the backbone for the synthesis of PA.[142] The di-acids were synthesized using UDA and different length aliphatic dithiols via TEC using DMPA under UV radiation with the slight use of solvent. These diacids were used to synthesize PA with Mw approaching 55 kDa with higher dispersity and superior material properties such as higher impact resistance than conventional PAs, chemical resistance, increased ductility, and lower water adsorptions for applications such as the automotive industry. Furthermore, they used melt condensation for polymerization without the use of dangerous catalysis. Mostly recently, some authors synthesized PA via enzyme-catalyzed synthesis using AB-type functional monomer derived from methyl oleate.[143] It was found the using lipase
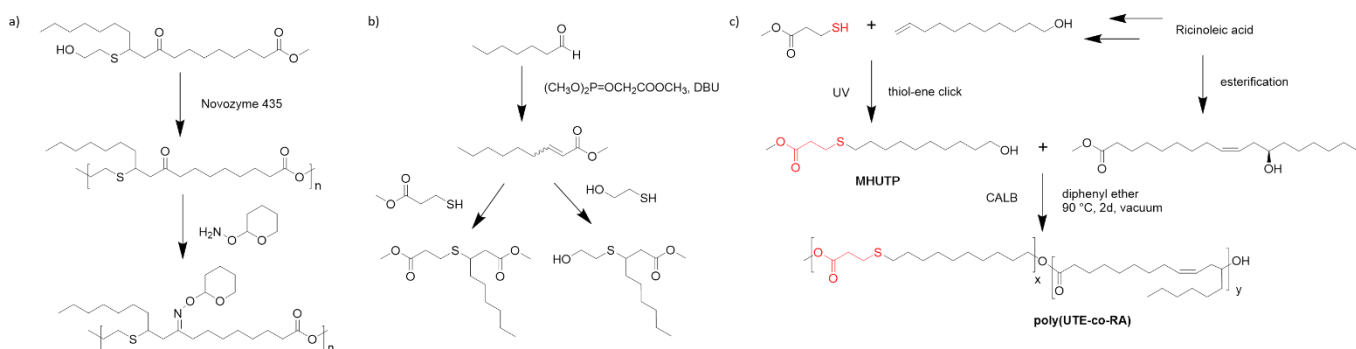
CalB was as effective as the previously used toxic catalyst using fewer mole equivalents interesting for biomedical applications.

Two different strategies were investigated for the synthesis of monomers using TEC to obtain NIPUs. NIPUs and non-isocyanate polyurea have been obtained by synthesizing AB monomers capable of transurethanization.[144] As depicted in Fig. 8-a, from castor oil, more specifically, UDA derivatives were used to synthesize two monomers with a carbamate and either a hydroxyl or amine final group. The synthesis of a cysteamine methyl carbamate (MMC) was obtained with two UDA derivatives, UDC and 10-undecenylamine via TEC. The reaction was performed in bulk, using DMPA under UV irradiation. NIPUs were synthesized by polycondensation using a conventional organometallic catalyst. Although this work circumvents the use of isocyanates for PU synthesis, dangerous reagents are used to synthesize MMC and the polymerization process and apply to the adhesive sector. In contrast, Cramail and co-workers synthesized various biscyclic carbonates to be reacted with diamines to obtain NIPUs by polyaddition. In an initial study, two different (bis) 6-membered cyclic carbonates (bis6CC) were synthesized using MUDO by a four-step synthesis of interest for coating applications.[145] As depicted in Fig. 8-b, the last step for the synthesis of the bis6CC, UndS b6CC, was accomplished via TEC using Und-6CC, 1,4-butanethiol under UV radiation. Although the synthesis of UndS-b6CC used TEC in its final synthesis step, previous reaction steps for both bis6CCs obtained required purification by chromatography, contradicting some aspects of green chemistry. In a continued work, the authors reported the design of (bis) 5-membered cyclic carbonates (bis5CC) from thioglycerol, FAs and sugar derivatives using TEC.[146] A panel of different bis5CC was obtained from derivatives of castor oil (UDC, 1-bromo-10-undecene, and UDA) and sunflower oil (oleyl alcohol) by following the same general procedure (Fig. 8-c). Although some of the synthesis did require the use of some dangerous solvents (DCM), in comparison to their previous work on the topic, the bis5CCs were obtained by rather direct means

without laborious purifications irrespective of green chemistry ideals. The bis5CCs were successfully polymerized using diamines to yield NIPU with Mw up to 14 900 Da that could be of interest for the pharmaceutical and biomedical sectors. In complement to this section, our group recently published a review on the synthesis of biobased cyclic carbonates for the synthesis of PHUs.[147]
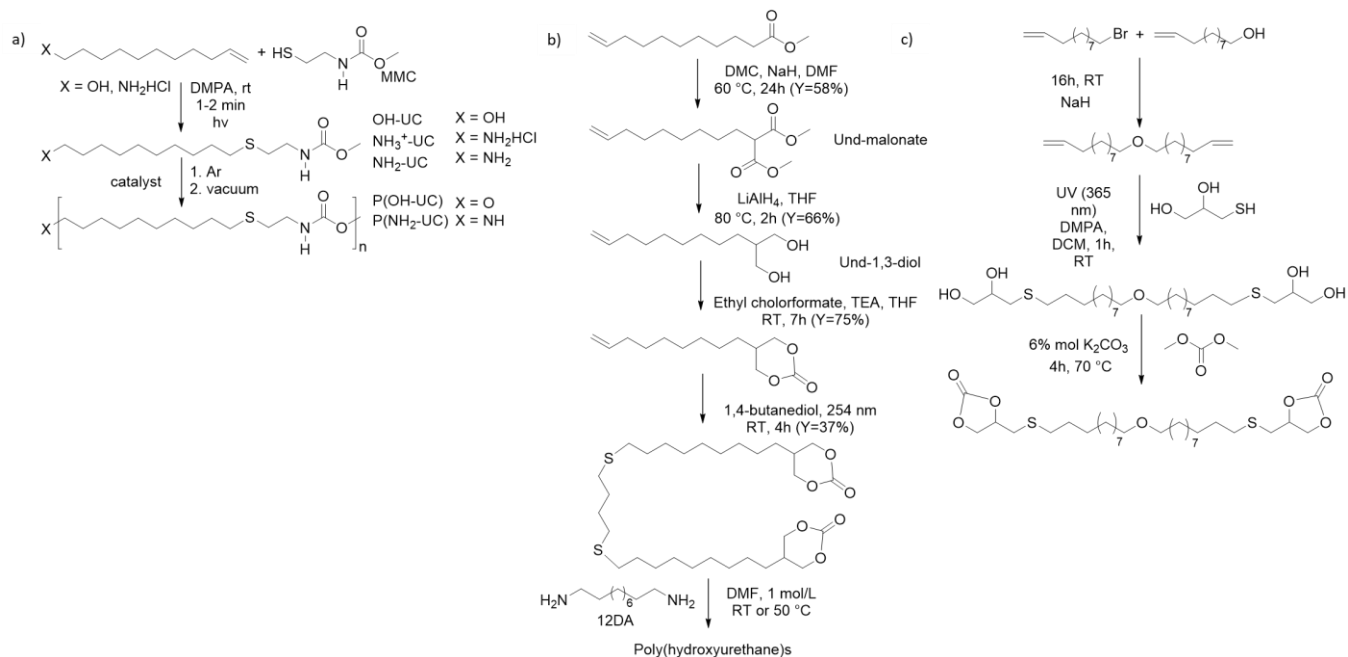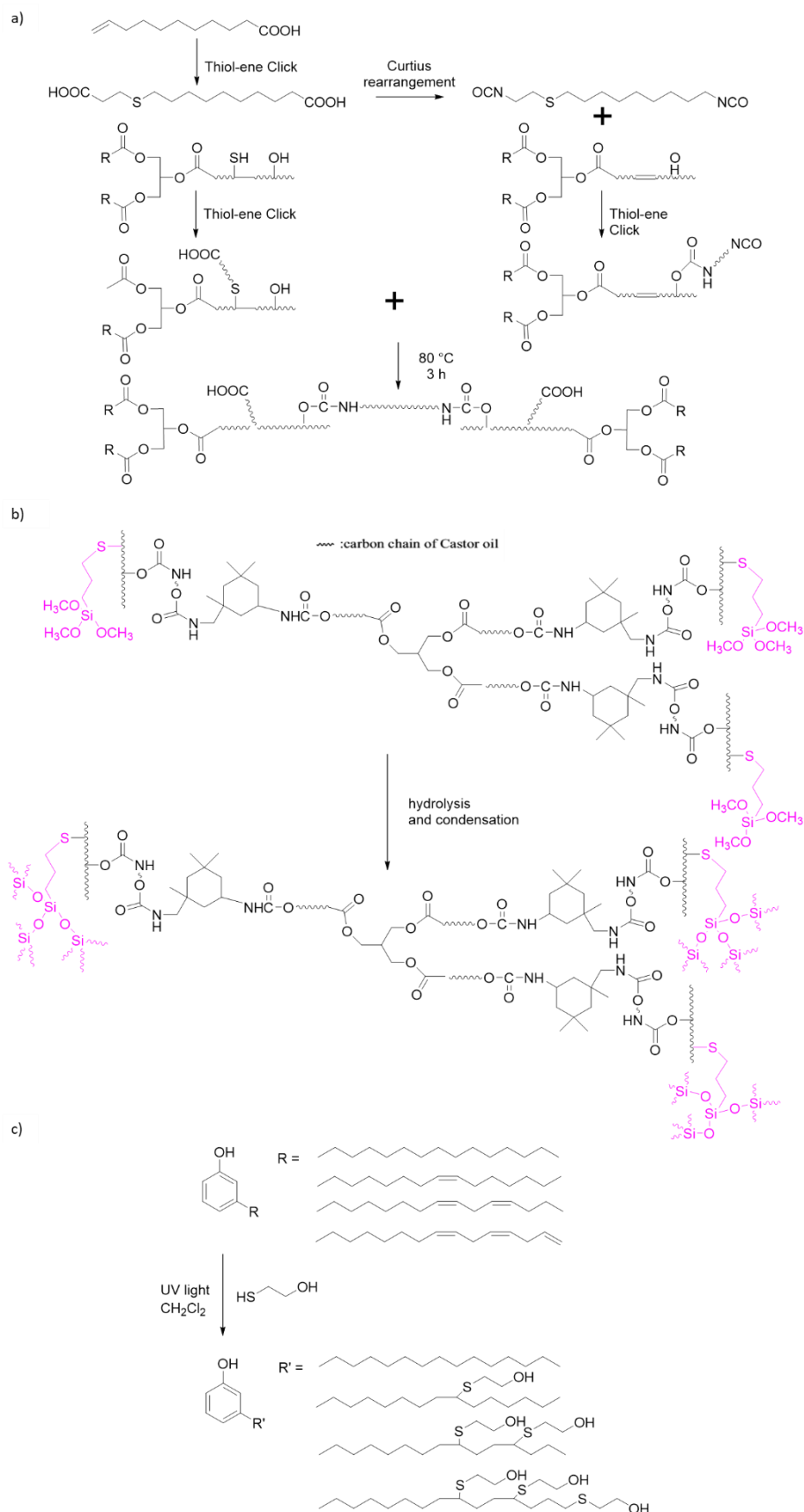

Fig. 8 (a) Thiol-ene addition of MMC to UDC and 10-undecen-1-amine chlorohydrate followed by the PU synthesis by polycondensation. Reproduced from ref. 144 with permission from Elsevier, copright 2016. b) Synthetic route to bis6CC and PHUs syntheses. Reproduced from ref. 145 with permission from The Royal Society of Chemistry, copyright 2014. (c) Synthetic route to bis5CC from FAs. Reproduced from ref. 146 with permission from The Royal Society of Chemistry, copyright 2017.

As PUs are a prominent polymer family, researchers have invested in developing building blocks from TGs and FAs via TEC to introduce reactive groups for PUs synthesis by classic polyaddition of hydroxyl and isocyanates groups. This requires the synthesis of or using reagents containing isocyanate moieties, a dangerous allergen for humans. These building blocks tend to be high in functionality, thus used for coating applications, and the recent literature on the subject is summarized in Table 6. Given its unique structure, castor oil and derivatives (most notably UDA) have been reported for the synthesis of monomers via TEC but as well as di-isocyanates. Derivatives for PUs synthesis using TEC have been developed for biobased waterborne PUs (WPUs) for coating applications.[148] As shown in Fig. 9-a, TEC was used to introduce carboxylic acid groups onto UDA and castor oil TGs. The modified UDA was then transformed from a di-carboxylic acid structure to a diisocyanate by Curtis rearrangement, and the modified castor oil was used as a hydrophilic chain-extender. Silanized castor oil achieved via TEC was also developed to be used as a functionalized polyol to be reacted with diisocyanates.[149] As depicted in Fig. 9-b, the functionalized silane PU then underwent silane moiety hydrolysis through a sol-gel process by utilizing the methoxysilane groups. The introduction of silane groups in the PU exhibited water-repellent surfaces, and the cross-linking nature of the PU with Si-O-Si units increased thermal stability and mechanical properties, interesting for coating applications. In their most recent work on the topic, the research group modified cardanol to achieve polyols for PU synthesis.[150] Cardanol is a by-product of the cashew processing industry and is extracted from cashew net shell liquid. Cardanol is a phenolic compound with a 15-carbon side chain in the meta position with varying degrees of unsaturation. The authors used ME to functionalize the cardanol fatty side chain with hydroxyl groups via TEC (Fig. 9-c). Similar to their previously mentioned work, they used a radical initiator, UV light irradiation, to react the unsaturations with the reagents, however, with the use of the hazardous solvent DCM. In this particular work, degrees of functionalization were varied according to reaction time. The polyols were then reacted with HDI to yield PUs with good thermal and hydrophobic properties. More recently, other research groups have solicited cardanol for the synthesis of polyols for PU synthesis. Upshaw and co-workers similarly functionalized the C=C bonds of the fatty side chains by TEC and went on to protect the phenolic group by alkoxylation (propoxylation) to improve the TEC reaction yield.[151] In other work, a panel of polyols from various chemical reactions (epoxide ring-opening and TEC using ME) have been synthesized, demonstrating varying PU properties concerning their hydroxyl content.[152] The similar method of functionalizing ME onto soybean oil [153, 154], and castor oil [155] via TEC were also exploited to obtain polyols for PU synthesis, also

without the use of hazardous solvents in line with the ideals of green chemistry, particularly for coating applications.

Table 6. Summary of lipid-derived polyfunctional architectures synthesized using TEC and the types of final polymers achieved.

Vegetable Oil or Derivative Used	Final Polyfunctional Macromolecule Achieved	Thermosets Achieved	References
	Silanized Castor Oil	PU/siloxane (SiPU) hybrid coatings	149
Castor Oil	Polyacetoacetate	Amine-acetoacetate	160
		Acrylic/aldehyde - acetoacetate coatings	162
	Polyol / Emulsifier	Waterborne PU	163
Undeclyenic acid (UDA)	Polyacids – Epoxy resin hardner	Acid cured epoxy coatings	158
Cardanol	Polyol	PU	150 - 152
	Polyol	PU	153 - 155
Soybean Oil	Polyacrylates	UV cured acrylate	159
	Polyacetoacetate	Amine-acetoacetate coatings	161
Rapeseed Oil	Polyamine	Amine cured epoxy coating	156
Grapeseed Oil	Polyamine	Amine cured epoxy coating	157

Fig. 9 (a) Synthesis of UDA-based diisocyanate and modified castor oil with carboxylic acid groups via TEC. Reproduced from ref. 148 with permission from Elsevier, copyright 2014. (b) synthesis of silicon cross-linked PUs, adapted from reference,[149] and (c) synthesis of polyols of cardanol via TEC. Reproduced from ref. 150 with permission from Elsevier, copyright 2015.

TEC can be used on TGs and FAs for the direct functionalization of reactive moieties in high functionality. Different architectures with high functionality have been used as curing agents for epoxy resins for coating and as plasticizers based on TEC. Recently, polyamines hardeners for the curing of epoxy resins have been synthesized from FAs of rapeseed oil,[156] or grapeseed oil,[157] and polyacids.[158] For coating applications, polyfunctional acrylates from soybean oil have been achieved,[159] and acetoacetate-modified castor oil and soybean oil to synthesize ambient curable films when reacted with amines,[160, 161] aldehydes or acrylates.[162] Furthermore, Upshaw and co-workers successfully functionalized mercaptanized soybean oil with hydroxyl, amine, isocyanate, isothiocyanate, epoxy, and silane terminal groups by TEC for applications such as foams, adhesives, coatings sealants, and elastomers. In a fascinating recently published study, biobased internal emulsifiers were synthesized using CO and cysteine derivative via TEC and used to obtain super tough WPUs.[163] More interestingly, these emulsifiers were achieved using flow chemistry conditions that yield productions rates up to 360 g/h.

Polymer Synthesis

The recent literature on TEC-based polymerizations can be subdivided into two main areas: linear polymerization using AA or AB-type monomers or polyfunctional architectures to synthesize thermosets. AA monomers consist of diene or dithiols, whereas AB monomers contain one diene and one reactive sulfur moiety. Given the particular structure of castor oil and its derivatives, they have been abundantly utilized. UDA is classically used in the synthesis of α,ω-dienes, whereas castor oil triglycerides for the synthesis of polyfunctional molecules.

Developing AA monomers from (most notably) UDA for TEC polymerization has led to obtaining polymer backbones containing amides, ethers, esters, and carbamates in addition to the thio(ether) bonds. Recently, interesting sustainable and ultra-strong elastomers via TEC of a diamide diene monomers derived from UDA and a di-thiol (3,6-dioxa-1,8-octanedithiol) have been developed.[164] First a diamide diene was developed by amidation of MUDO with 1,3-diamino-2-propanol to yield N,N'(2-hydroxypropane-1,3-diyl)bis(undec-10-enamide) (UDA-1). UDA-1 can be further reacted with butyric anhydride via the pendant hydroxyl group to yield 1,3-di (undec-10-enamido)propane-2-yl butyrate (BUDA), introducing a longer pendant group that can inhibit crystallization (Fig. 10). Polymerization took place by thio-Michael addition with varying amounts of UDA-1, BUDA, dithiol, azobisisobutyronitrile (AIBN) (radical initiator) at 70 °C for 12 h. The pendant polar hydroxyl and non-polar butyrate groups allowed for control structuring of hydrogen bonding and tuning of crystallization, whereas thioether bonds induced metal-ligand coordination. Unidirectional step-cycle deformation was applied to these materials and enhanced the tensile strengths to over 210 MPa while maintaining elasticity. This is mainly due to the rearrangement and alignment of crystalline microstructures. Furthermore, these materials exhibited aggregation-induced emission when observed with strong luminescence due to the formation of amide clusters with restrictive molecular motions. These ultra-strong biobased polyamides close the gap between polycondensates and polyolefins. Other research groups obtained α,ω-dienes via similar means. Such structures can be obtained by transesterification of MUDO or 9-decenoate (obtained from the ethenolysis of methyl oleate) and a diol (1,3-propanediol), or a diacid such as diethyl adipate by esterification using UDC.[165] The esters of these diene monomers were reduced via catalytic reduction to obtain ethers in the final polymer backbone when these dienes were polymerized with dithiols. The final polymers obtained present interesting biobased alternatives to polymer with properties similar to polyethylene. On the other hand, diene structures have been obtained by the transesterification of 9-decenoic acid by ethylene glycol or UDC to undergo photo-polymerization with various dithiols.[166] Most recently, Filippi and Meier have synthesized two renewable diene monomers bearing a carbamate or a urea moiety polymerized with renewable and commercially available dithiol monomers via thiol–ene step-growth polymerization with the slight use of solvents.[167] The dienes were synthesized from hydroxamic FA derivatives of UDA and oleic acid via the Lossen rearrangement in a one-step synthesis.
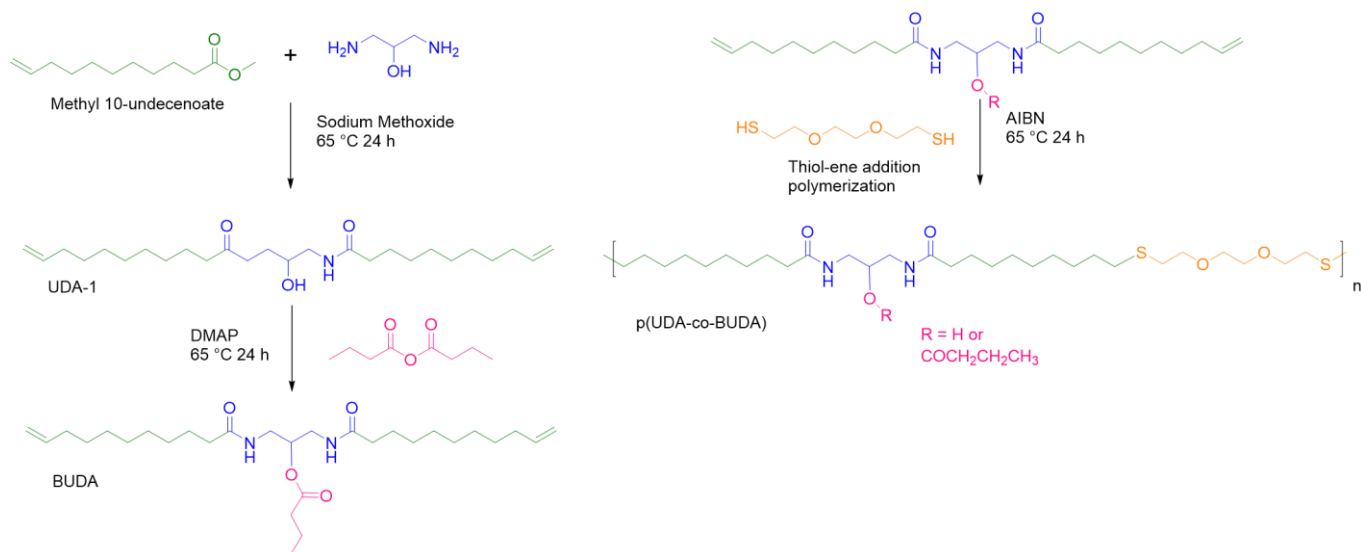
Fig. 10 Design of monomers UDA-1 and BUDA and functional PA via thiol-ene addition. Reproduced from ref. 164 from Springer Nature, copyright 2019.

UDA-based AA monomers with diene structures coupled with dithiols for TEC polymerization were mainly exploited to synthesize nanoparticles in miniemulsion. A diester diene monomer denoted DGU has been obtained by esterification of isosorbide and UDA (Fig. 11-a).[168] DGU was copolymerized by 1,4-butanethiol by thiol-ene miniemulsion polymerization. The organic phased consisted of DGU and an organic-soluble initiator (if used), whereas the aqueous phase contained distilled water and surfactants and was added to the organic phase to form an emulsion under vigorous stirring. This was followed by the addition of stoichiometric amounts of the dithiol followed by vigorous stirring to yield the final emulsion, and polymerization took place at 60-90 °C for 4 to 8 h. This resulted in poly(thioether-ester) nanoparticles in water. The same authors continued their work on thiol-ene miniemulsion polymerization by synthesis a different diester diene utilizing UDA but this time using 1,3-propanediol as the diol for transesterification (Fig. 11-b).[169] The developed nanoparticles exhibited the potential to be used for controlled release drug delivery vector for intravenous administration. The authors' most recent work on the topic consists of the development of a diene ester monomer, 2-(10-undecenoyloxy)ethyl methacrylate (MHU), synthesized by enzymatic esterification of UDA and 2-hydroxyethyl methacrylate.[170] MHU was used in two different synthesis routes: (i) the direct thiol-ene polymerization with a dithiol or (ii) a Michael addition with a diamine to yield a symmetrical diester diene used for thiol-ene polymerization when reacted with a dithiol. For the
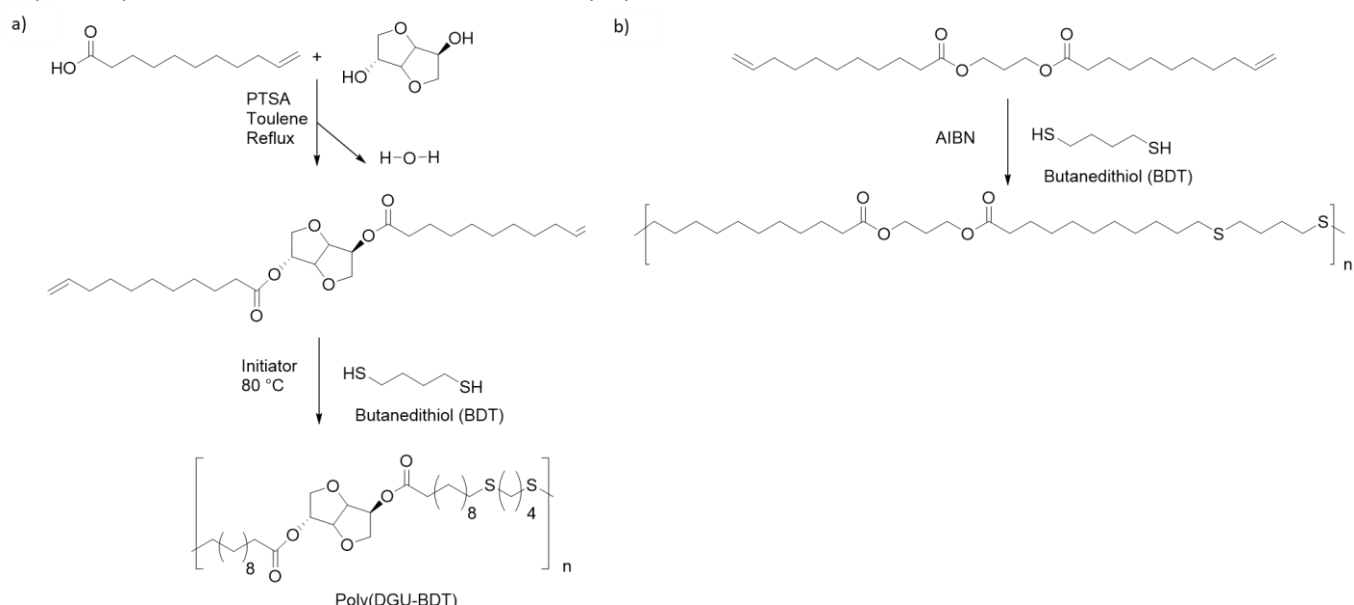

thiol-ene bulk polymerization of MHU and dithiol, the presence of methacrylate and an alkene group with

different reactivity led to a combination of step- and chain-growth polymerization. These systems present a high potential for drug delivery as antimicrobial and antioxidant compounds.

Fig. 11 (a) Dianhydro-D-glucityl diundec-10-enoate (DGU) synthesis followed by copolymerization with dithiol via thiol-ene polymerization. Reproduced from ref. 168 with permission from Elsevier, copyright 2018. (b) Synthesis of biocompatible polymeric nanoparticles via thiol-ene polymerization of a biobased monomer in miniemulsion exhibited blood compatibility properties. Reproduced from ref. 169 with permission from John Wiley and Sons, copyright 2017.

Developing AB monomers containing an alkene moiety at one end and a sulfur moiety at the other end for TEC polymerizations has also been explored. Du Prez and co-workers developed a thiolactone (five-membered cyclic thioether) derivative of UDA to yield an AB' precursor by two-step synthesis.[171] First, UDA was rendered more reactive and converted to its corresponding acid chloride and then reacted with DL-homocysteine thiolactone. It is important to note that the synthesis of this AB' monomer requires the use of dangerous chemical products ($SOCl_2$, DCM, and isooctane), nevertheless permitting high yields. The aminolysis of the thiolactone leads the AB' precursor to generate a pendant amide bond and an AB monomer with a free thiol moiety which reacts with terminal double bonds by radical thiol-ene addition to yield PA structures by UV radiation using DMPA at 40 °C. Different AB monomers were synthesized by the nucleophilic aminolysis of the AB' precursor using different primary amines, which led to diverse PA. The sulfide linkages of the polymer backbone could undergo oxidation to lead to sulfoxides and sulfones that consequently impact the final material properties. The use of diamines also obtained thermoset networks. Concretely, this sheds light on the possible design of high-performing PAs. More classically, other authors have developed a panel of AA and AB monomers by the esterification of functional carboxylic acids such as UDA, 11-mercaptoundecanoic acid, and lipoic acid by vinyl ether alcohols such as 1,4-butanediol vinyl ether and 1,6-hexanediol vinyl ether by enzymatic catalysis for coating applications.[172]

CO is highly utilized for the synthesis of thermosets using TEC to obtain UV-curable coatings. Functionalized sulfur moieties onto castor oil have been synthesized via the secondary hydroxyl group by esterification of 3-mercaptopropionic acid to yield a highly stable, self-initiated oligomer (CO-SH) for photoinitiator free UV coating (Fig. 12).[173] Thus, CO-SH simultaneously possessed double bonds and thiols moieties. CO-SH exhibited temporal stability with only a small conversion of double bonds when stored for 7 days at 80 °C or ambient temperature for 30 days. UV curable films were synthesized by photo-polymerization using CO-SH in conditions respective to green chemistry. Using the same modified castor oil, the authors developed UV-curable coatings with built-in flame retardancy for wood surfaces (Fig. 12).[174] Other authors used CO for the synthesis of hyperbranched urethane acrylate oligomer (CO20-IH).[175] A tetrathiol monomer (PETMP), photoinitiator, a reactive diluent (tripropylene glycol diacrylate), and CO-20-IH were used in varying amounts to synthesize by TEC UV-curable films. The UV-curable films exhibited acid
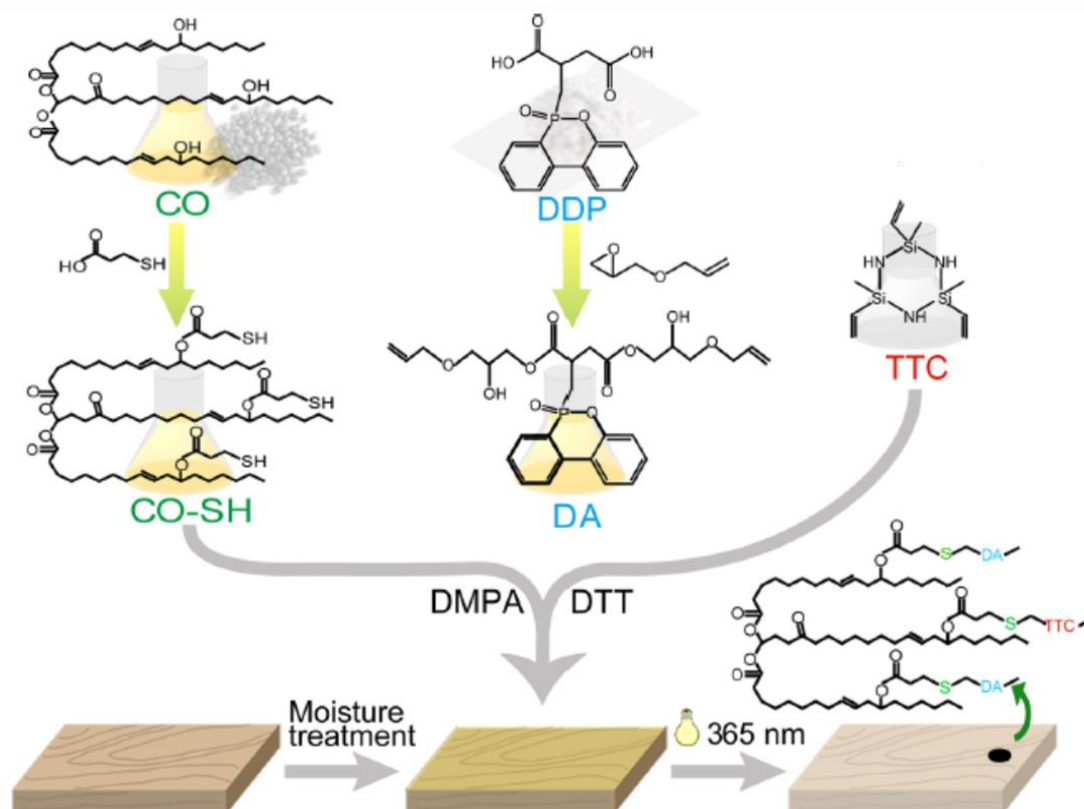
resistance, high hardness, and low water absorption. CO was primarily utilized to synthesize hybrid coatings with organic-inorganic covalent cross-linked network structures prepared via sol-gel and TEC reactions.[176] Furthermore, soybean oil,[177] and rapeseed oil,[178] have also been utilized to obtain polyfunctional molecules to obtain UV-curable coatings via TEC. Terminal double bonds were introduced onto these oils by epoxy ring-opening and were cross-linked by thiols varying in functionality and structure via TEC. Most recently, neat tung oil and hazelnut oil alongside dithiol derivatives of isosorbide were used to achieve photo-cured coatings.[179]

Fig. 12 Synthesis of CO-SH followed by synthesizing UV-cured films via TEC using DTT and TTC on wood surfaces . Reproduced from ref. 180 with permission from Elsevier, copyright 2019.

Chemical modifications of the polymers

The thiol-ene reaction for the post-polymerization modification of polymer architectures has become a significant, conventional, and easy tool for biobased polymers functionalization. Heise and co-workers were one of the first to exploit this concept on FA-derived polymers.[181] The authors synthesized polyesters using enzymatic ring-opening polymerization of globalide, an unsaturated macrolactone synthesized from hydroxyl FAs. A range of different thiols modified the polyester chains: butyl-3-mercaptopropionate, mercapto-1-hexanol, and *N*-acetylcisteamine are of great interest for biomedical applications.

Recently, several groups have continued using thiol-ene reaction for post-polymerization modifications. Some authors used the Steglich esterification to synthesize 2-(methacryloyloxy)ethyl oleate (MAEO) (a methyl acrylate derivative of OA), and it was polymerized by reversible addition-fragmentation chain transfer (RAFT) to yield poly(2-methacryloyloxy)ethyl oleate (PMAEO) with the aid of a chain transfer agent (Fig. 13-a).[182] The Steglich esterification requires using dangerous products such as N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and DCM, and perhaps other means of esterification could be favored to allow this reaction to adhere to green chemistry principles. The oleate side-chains of PMAEO were further modified via the thiol-ene reaction with AIBN at 60 °C in THF, with quantitative conversions (Fig. 13-b) for ethanethiol, butanethiol, dodecanethiol, 3-mercaptopropanoic acid, whereas ME gave approximately
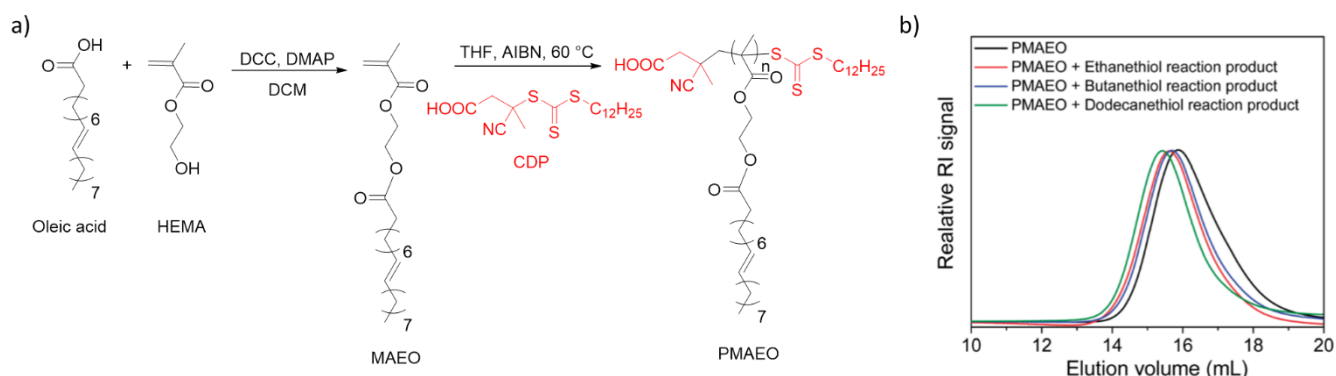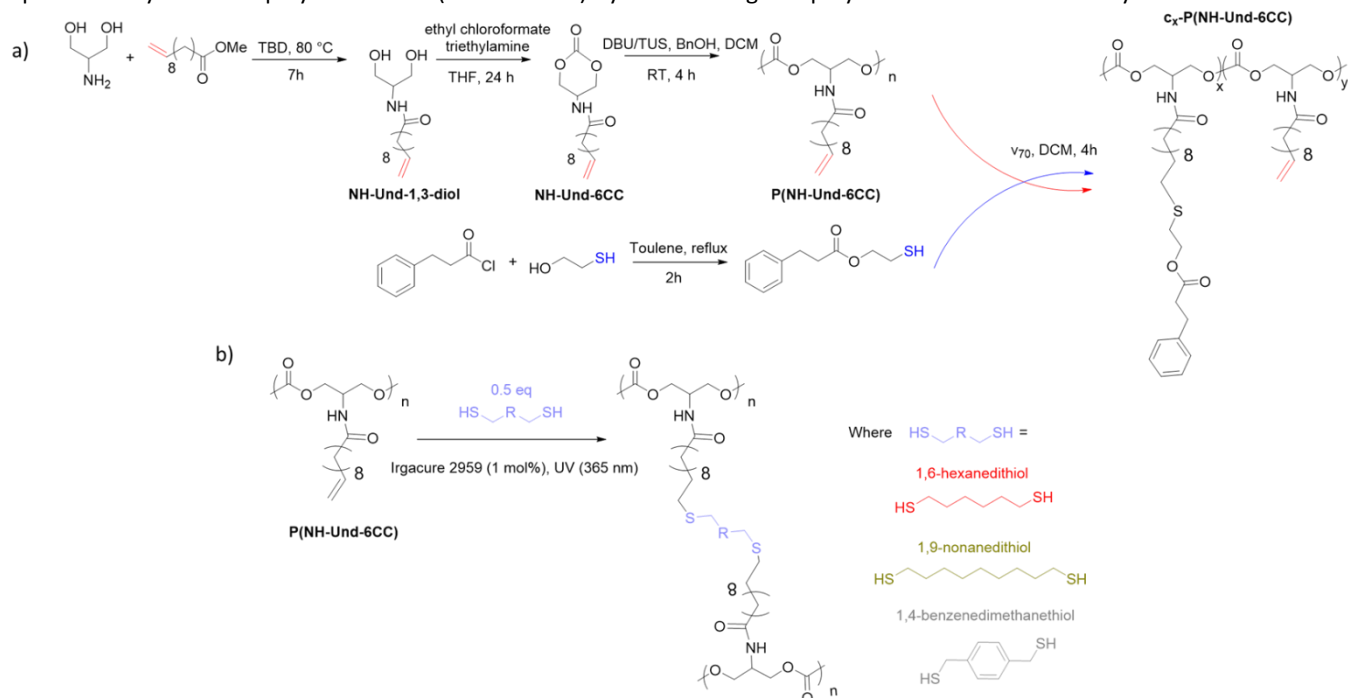

90% modified product. Interestingly, the modification of PMAEO by 3-mercaptopropanoic acid would render the polymer water-soluble interesting for paints and adhesive applications.

Fig. 13 (a) Synthesis of PMAEO by RAFT polymerization, (b) SEC based on RI curves of products from the thiol-ene reaction of PMAEO with different thiols. Reproduced from ref. 182 with permission from the Royal Society of Chemistry copyright 2014.

Cramail and co-workers have recently published on polymer modifications utilizing TEC. In the initial work,[183] a polycarbonate polymer is obtained using a synthesized carbonate monomer containing a pendant unsaturation originally derived from MUDO. As shown in Fig. 14-a, the carbonated monomer is obtained in two steps and further polymerized to yield P(NH-Und-6CC) polycarbonate. It is essential to highlight that synthesis of the carbonated monomer and subsequent polymer does require some dangerous solvents but adheres to other principles of green chemistry such as energy efficiency. The pendant unsaturation belonging to a fatty chain was functionalized via TEC by a synthesized cinnamate–thiol (Fig. 14-a) to yield a photoresponsive polycarbonate. TEC onto the polycarbonate took place using a radial initiator in DCM at 40 °C. Functionalization of varying cinnamate-thiol contents onto polycarbonates was achieved by varying the reaction time. Cross-linked polymers were achieved by utilizing the cinnamate moiety. When exposed to UV light, cinnamate groups switch from trans to cis conformation, and the cis-cinnamate groups undergo [2+2] cyclo-addition reaction. Consequently, the functionalized polycarbonates exhibited versatile mechanical properties ranging from rigid materials (lowest functionalized cinnamate content) to elastomeric networks (highest functionalized cinnamate content) with the potential of containing self-healing ability (due to the

reversibility of the cyclobutane ring formed by two cinnamate moieties. The authors went on to further exploit their synthesized polycarbonate P(NH-Und-6CC) by cross-linking this polymer back-bone via TEC by

Fig. 14 (a) Strategy to access cinnamate-containing aliphatic polycarbonates from FA derivatives. Reproduced from ref. 183 with permission from the American Chemical Society, copyright 2018. (b) Strategy for the synthesis of cross-linked polyester networks by TEC. Reproduced from ref. 184 with permission from the Royal Society of Chemistry, copyright 2019.

the pendant alkene bond and different dithiols (1,6-hexanedithiol, 1,9-nonanedithiol, and 1,4-benzenedimethanethiol) utilizing a radical initiator and UV light for 4 h with minimal use of hazardous solvents in comparison to their previous study, (Fig. 14-b).[184] The resulting polycarbonates exhibit[2]ed elastic properties influenced by the dithiols' structure or by the varied thiol/olefin unit ratio used. Moreover, pendant thiol groups were obtained when an excess of dithiols was used, which can be utilized for further modifications.

In recent work, TEC is used to modify poly (3-hydroxyalkoanoate)s (PHAs) biopolymer using UDA, octanoic acid, or soybean oil as substrates to yield poly(3-hydroxy undecenoate) (PHU), poly(3-hydroxy octanoate-co-undecenoate) (PHOU), and poly(3-hydroxy octanoate-co-soybean oil polymer (PHOSy).[185] With these different substrates, hydroxyl and carboxyl moieties are functionalized onto these biopolymers via the thiol-ene reaction to improve the mechanical properties and enhance the hydrophilic character of PHAs. Thiol-ene photo click reactions occurred using a radical initiator, the biopolymer, and the thiol (3-thio glycerol or mercaptopropionic acid) in DCM under UV for 4 h. Different techniques confirmed the functionalization of the PHAs, and this enhanced hydrophilic is vital for medical and physicochemical applications.

Thiol-yne reaction

There has been limited use of thiol-ene/yne coupling (TEC/TYC) in oleochemistry. Nevertheless, as will be described in the next section, modifications can be brought on to FAs to yield attractive architectures containing alkyne bonds. Unfortunately, this procedure does not respect all the ideals of green chemistry.[186, 187] Several scientific works using TEC/TYC have been recently published, e.g., the synthesis of PU,[188-190] and functional comb-like polymers.[191] The most recent work has continued work utilizing TEC/TYC to synthesize PUs and polyesters.

The majority of work in oleo chemistry explored by the TEC/TYC includes the synthesis of polyols for PUs. OA and α,ω-diacids have been converted into propargylic esters. As is often the case for the functionalization of lipids with alkyne moieties, the esterification of lipids reported herein does not respect several green chemistry principles (use of solvents and dangerous reagents). The propargylic esters were then modified by TEC/TYC using ME to synthesize two different polyols using DMPA as the radical initiator and UV radiation.[192] These polyols were then utilized for the synthesis of PUs using methylene diphenyl diisocyanate (MDI). The reported polyols did not possess dangling chains; consequently, the T_g is increased compared to PUs using vegetable-based polyols with dangling chains. More recently, the use of sunflower oil modified by TEC/TYC to synthesize hyperbranched polyols for thermoset PUs have been reported.[193] Generally, alkyne groups

were functionalized onto sunflower oil-derived TGs by the ring-opening of epoxides using propargyl alcohol. Although functionalization of TGs took place by epoxy ring-opening, this still ensued the need for dangerous catalysts and the use of solvent; however, it is a reaction that occurred at ambient temperature. TEC/TYC was utilized to functionalize primary hydroxyl groups onto the propargyl modified oil using ME, UV radiation at room temperature for 12 h to yield a polyol. The polyol and the subsequent PUs were synthesized using isophorone diisocyanate (IPDI) and HDI, with varying NCO/OH ratios. The biobased PU used to synthesize transparent films useful for the coating industry.

    Different research groups have pioneered the use of the TEC/TYC in oleochemistry. Recent works in the field are focused on the synthesis of polyols for PUs and polyesters. Concerning utilizing TEC/TYC in PUs, the authors have focused their efforts on synthesizing polyols that could further endure post-polymerization modifications. In an initial study,[194] the authors synthesized a vinyl-sulfide-containing diol (VSD) from UDA by the pathway described in Fig. 15-a, utilizing successive bromination, dehydrobromination, esterification, reduction, and hydrothiolation. VSD was reacted with MDI to yield PUs. This PU was modified by a thiol-ene reaction using 7-mercapto-4-methylcoumarin (Cm-SH), DMPA (dissolved in ACN). In follow-up work,[195] intermediate reaction products to yield VSD, methyl 10-undecynoate (MUDY), and 10-undecynyl alcohol (UDYO) were reacted with 3,6-dioxa-1,8-octanedithiol and DMPA at room temperature for 1 h under UV radiation to yield different new polyols (Fig. 15-b). The polyols were reacted with MDI. The PUs were further
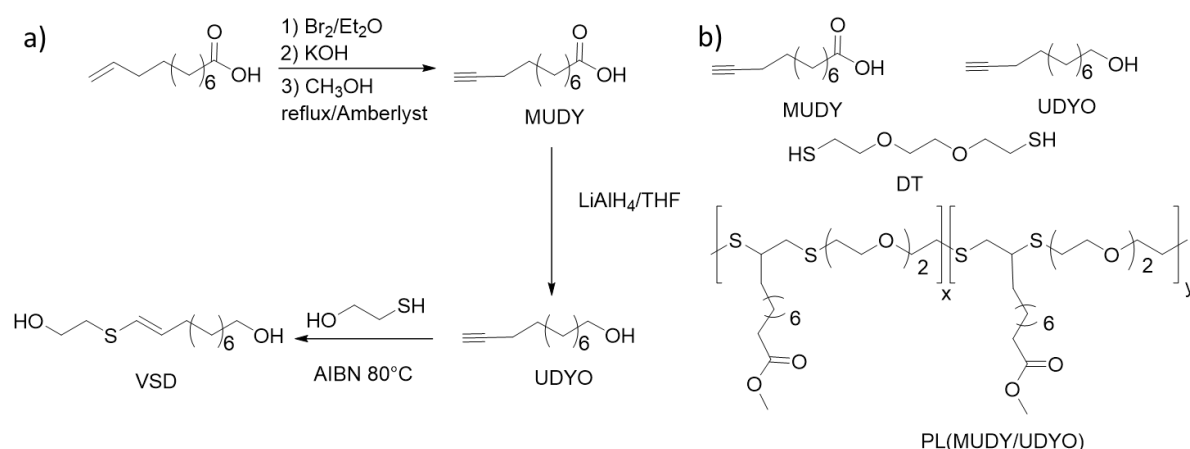
modified by the pendant ester moiety by aminolysis using poly(propylene glycol) monoamine (Jeffamine M-600) followed by iodine complexation. These modifications enhanced the hydrophilicity of PUs to impart antimicrobial properties. These PUs could be used in applications such as medical devices, protective clothing, antimicrobial filters and bandages. Lastly, synthesized diols from UDC based on allyl and propargyl groups were achieved,[196] and then polymerised with IDPI. The alkene and alkyne groups were reacted with thioglycerol via UV radiation using DMPA, to enhanced hydrophilicity. The PUs exhibited highly tunable thermal and mechanical properties, which make them suitable for a large range of applications.

Fig. 15 (a) Synthesis of VSD. Reproduced from ref. 194 from Scivener, copyright 2013. (b) Synthesis of polyols by TEC/TYC using MUDO and UDYO. Reproduced from ref. 195 with permission from John Wiley and Sons, copyright 2014.

    Some authors have used TEC/TYC for the synthesis of polyester in recent publications. In the initial work,[197] 10-undecynoic acid is used to synthesize vinyl sulfide-containing hydroxy acid (VSHA) (Fig. 16-a) using ME and AIBN at 80 °C and was obtained in moderate yields. The polycondensation of this monomer is performed via metal and enzymatic catalyzed means to yield polyesters (PVSHA). Higher Mws were obtained via enzymatic polymerizations. Enzymatic copolymerizations of diblock (VHSA and e-caprolactone (EL)) and triblock of (VHSA, EL, and BDO) were also obtained (Fig. 16-b). More interestingly, VHSA containing polymers could be further reacted via the thiol-ene reaction with (i) ME to yield pendant hydroxyl groups, (ii) 1,4-butanethiol to yield cross-linked materials, or (iii) 7-mercapto-4-methylcoumarin to modify the surface of polyesters. In a follow-up study,[198] VHSA and a ketone-containing hydroxy ester (KHE) (derived from methyl oleate) were used to synthesize a series of copolyesters via enzymatic polycondensation.[136] As depicted in Fig. 16-c, polyesters could be modified after polymerization via the thiol-reaction in VHSA containing segments and via oxyamine for KHE containing segments. Polyesters designed in such a fashion are interesting for biomedical applications.

Fig. 16 (a) Synthesis of VSHA, (b) copolymerization of VSHA with EL and BDO. Reproduced from ref. 197 with permission from John Wiley
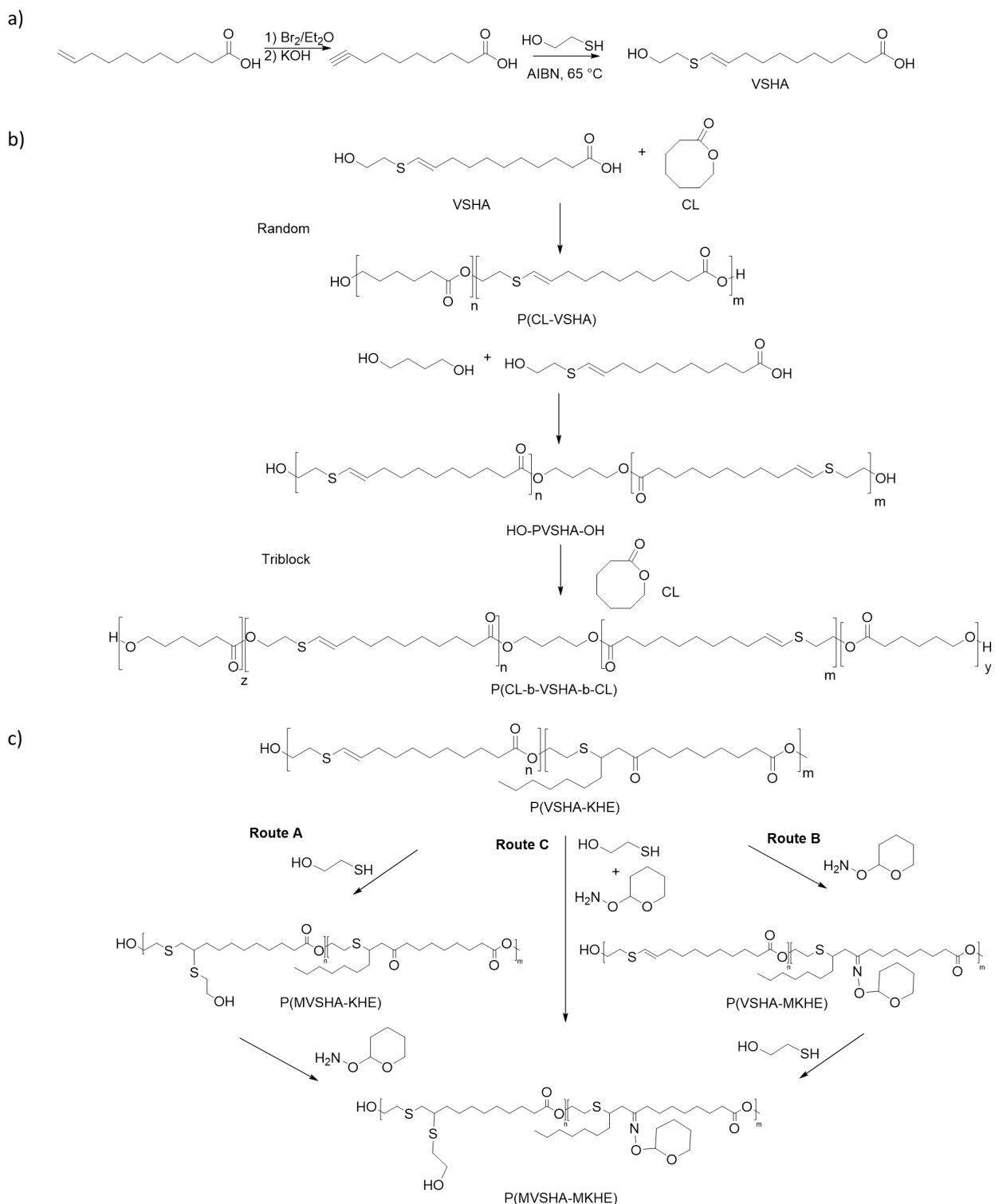
and Sons , copyright 2014. (c) Post-polymerization modification of VSHA-KHE copolymers. Reproduced from ref. 198 with permission from Elsevier, copyright 2015.

Huisgen 1,3-dipolar cycloaddition

Huisgen 1,3-dipolar cycloaddition represents an efficient method to produce polymers from vegetable oils. The FA chain of epoxidized soybean oil can be functionalized with azide groups by ring-opening nucleophilic addition of sodium azide to the epoxy group.[199] Later, this strategy was applied to achieve highly cross-linked biobased polymers through the copper-catalyzed and the thermal polyaddition of alkynylated (ASBO) and azidated soybean oil (AzSBO).[200] In this work, two different approaches were studied. First,

alkynylated soybean oil was polymerized by a CuAAC reaction with diazide linkers. Then, azidated soybean oil underwent thermal polymerization with dyne moieties and ethynylated soybean oil at 100 °C. The functionalization of epoxidized soybean oil (ESBO) with azide and alkyl groups is shown in Fig. 17-a. For this first approach, ASBO was polymerized with 1,6-diazidohexane and α,α'-diazido-p-xylene at room temperature using copper sulfate and sodium ascorbate as catalysts. The polymerization resulted in highly cross-linked polymers. AzSBO was in turn polymerized with 1,4-dethynylbenzene and 1,7-octadiyne and with ASBO. The CuAAC results in a 1,4-disubstituted 1,2,3-triazole, whereas the thermal driven reaction is supposed to be non-stereoselective and results in the formation of both 1,4- and 1,5-disubstituted 1,2,3-triazole rings. The T_g of the polymers obtained by the CuAAC reaction was higher than that of the polymers obtained by thermal polymerization. It was shown that the catalyst-based and solvent-free route was better than the pathway based on CuAAC.

New building blocks from castor, canola, corn, soybean and linseed oils were also used on this thermal-driven click reaction.[89] The azidated vegetable oils underwent a step-growth polymerization with ASBO under solvent and catalyst-free conditions (Fig. 17-b). The azidated oils also showed much higher viscosities than the epoxidized oils, attributed to stronger intermolecular hydrogen bonds in the azidated ones. The sol fraction and the swelling degree of the materials decreased with the increasing number of azide functionalities in the monomer. Different behavior from azidated castor oil was also observed, showing a higher T_g and elongation at break despite its lower cross-linking density. The higher degree of H-bonding due
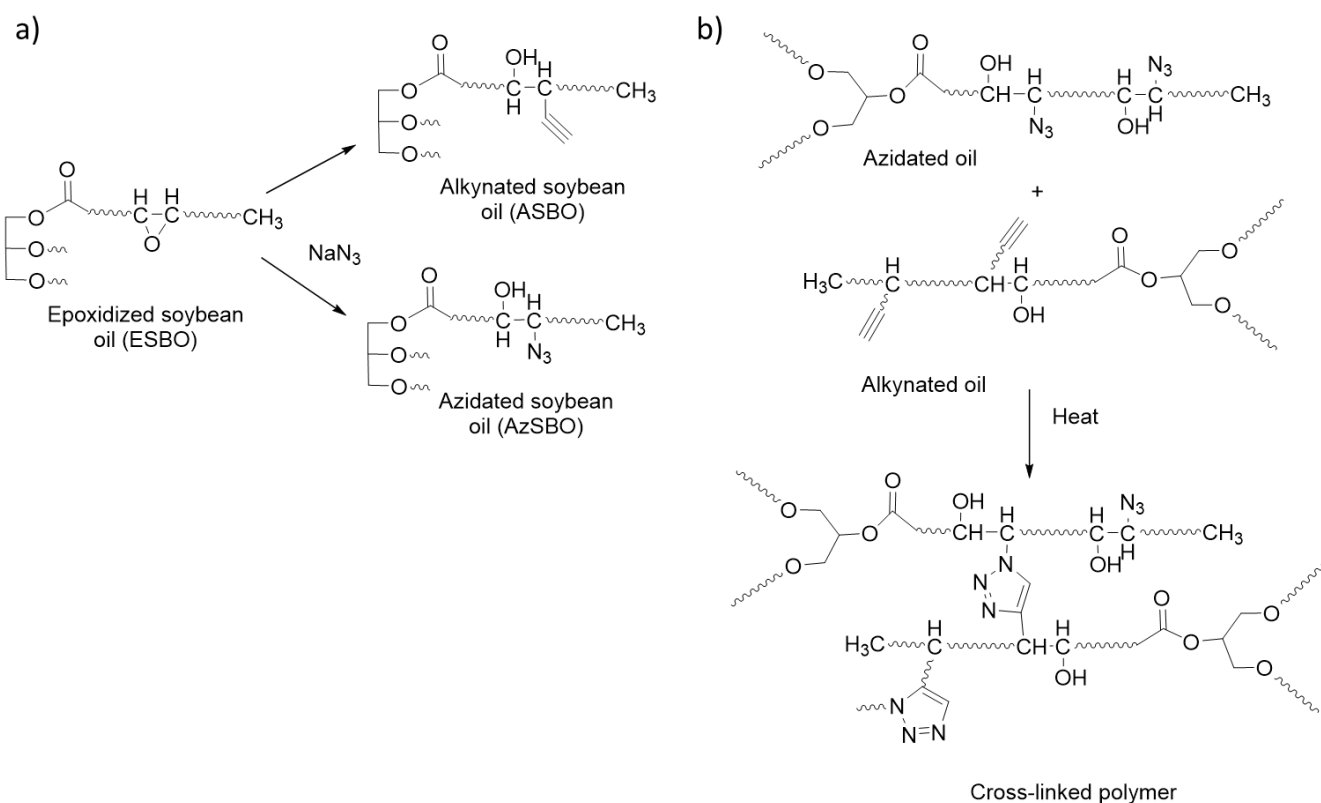
to additional hydroxyl group per FA chain could explain this behaviour.[93]

Fig. 17 (a) Introduction of terminal alkyne and azide groups on FA chains. Reproduced from ref. 89 with permission from the American Chemical Society , copyright 2010. (b) Cross-linking of vegetable oil-based polymers via triazole rings. Reproduced from ref. 200 with permission from the American Chemical Society , copyright 2012.

More recently, the use of photo-induced CuAAC reaction was applied to polymerize soybean oils at ambient conditions.[201] In this way, the reaction was achieved without solvent with rapid polymerization rates at low temperatures, in good agreement with green chemistry principles. As reported above, azide and alkyne groups were introduced into ESBO by simultaneous ring-opening between epoxides with sodium azide and propargyl alcohol. These multifunctional azides and alkynes were polymerized in the presence of a photoinitiator and Cu(II)Br2/N, N, N', N'', N''-pentamethyldiethylenetriamine. The photoinitiator forms reactive free radicals that can reduce Cu(II) into Cu(I) to catalyze CuAAC.

The use of the Huisgen cycloaddition has also obtained polytriazoles with melt-processing properties without solvent or catalyst. Three thermoplastic polytriazoles were obtained from diester dialkynes and a diazide monomer derived from OA.[202] The mechanical and thermal properties of the polymer are influenced

by the chain length of the ester employed. The use of these materials is crucial in applications where no traces of solvent or catalyst can be present, and due to their potential biocompatibility and biodegradability, they found applications in the biomedical and pharmaceutical fields. Polytriazoles have shown excellent coating properties due to their high thermal stability, good mechanical properties, and chemical resistance because of the presence of the 1,2,3-triazole five-membered ring, with a high dipole moment and the ability to form hydrogen bonds.[203] ASBO has been tested with two different propyfunctional urethane monomers to prepare high-performance coatings with efficient biocidal activity for biomedical applications. For ASBO preparation, ESBO was reacted with sodium azide in the presence of 1-methylimidazolium tetrafluoroborate as a catalyst. Propyn-terminated urethane monomers were prepared by reaction of propargyl alcohol with isocyanate monomers. All the materials prepared in this study showed only one T_g, between 58 and 80 °C, indicating the phase mixing of the soft segment from soybean oil-derived structures and hard segment from 1,2,3-triazole rings and urethane linkages.

Huisgen reaction was also used to prepare vegetable oil-based polyol used in PUs for wound dressing applications.[204] PUs were prepared from a mixture of castor oil and soybean oil-based polyol containing 1,2,3-triazolium rings (QTSBO). Of the reaction steps required to attain QTSBO, azidated soybean oil and propargyl alcohol via the Huisgen reaction was used to achieve primary hydroxyl groups. The resulting PU materials showed good tensile strength properties for wound dressing applications. Moreover, the presence of 1,2,3-triazolium rings provided antimicrobial activity against different bacterial and fungal strains.

PUs has also been elaborated from 1,2,3-triazole modified soybean oil-based polyols with good antibacterial and antifungal properties to be used as coatings for medical devices.[205] Sodium azide was used to introduce azides to ESBO, and 1-methylimidazolium tetrafluoroborate was selected as the catalyst at 65 °C. Then, various alkynes (phenylacetylene, propargyl alcohol, and N, N-dimethylpropargyl amine) were used to conduct the cycloaddition in the presence of copper sulfate and sodium ascorbate as the catalyst couple (Fig. 18). The alkylation of tertiary amine-containing polyol to obtain quaternary ammonium salt-containing polyol to impart biocidal activity to the PU has been performed. The polyols reacted with IPDI and mixed with PEG (molar mass of 1000 Da) to produce PUs. The results showed that incorporating the triazole groups resulted in higher storage modulus at glassy state, T_g, and thermal stability and hardness of the PUs. However, lower adhesion strength and hydrophilicity were also observed.
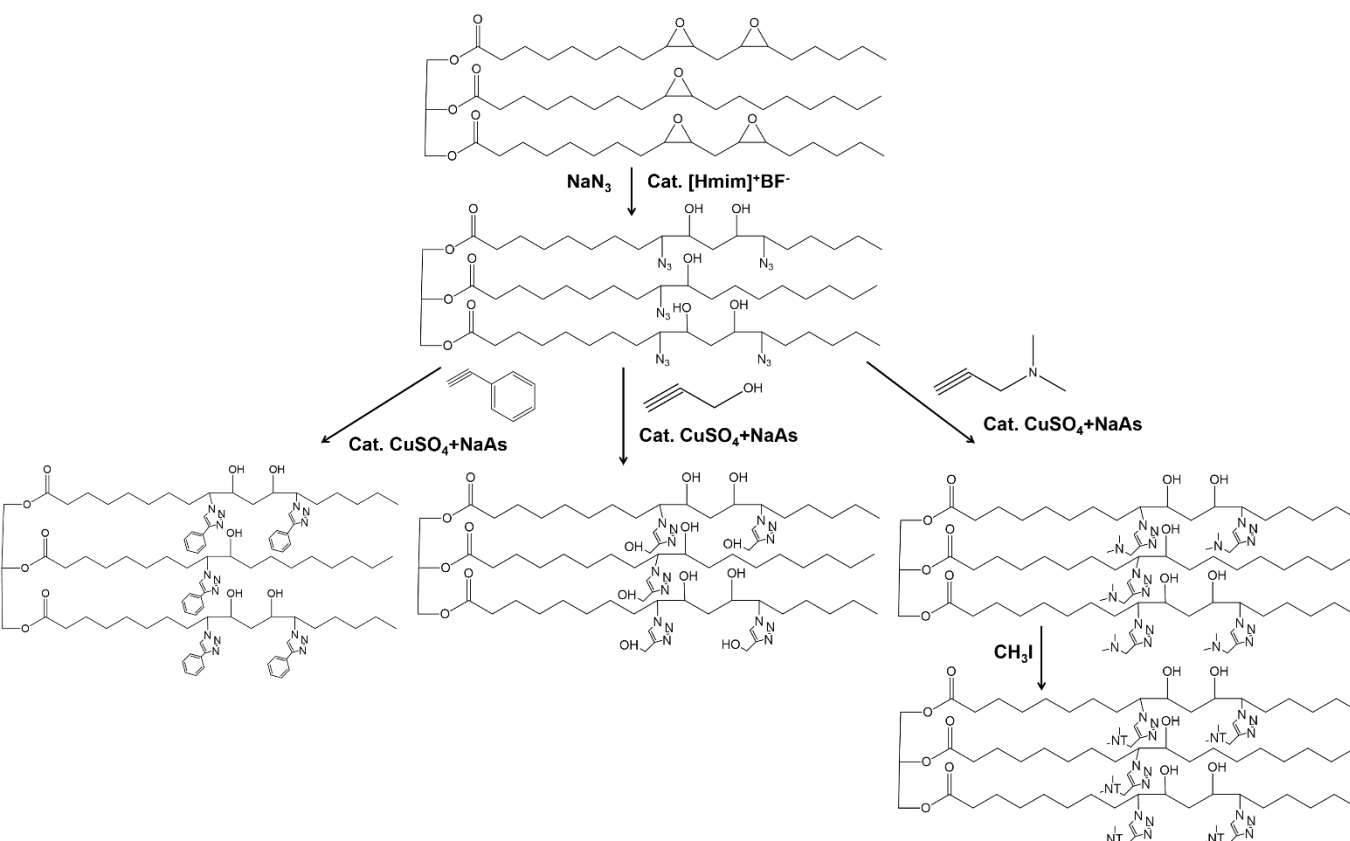
Fig. 18 Preparation of polyols from ESBO using Huisgen cycloaddition. Reproduced from ref. 205 with permission from the American Chemical Society , copyright 2013.

Copper-catalyzed Huisgen cycloaddition has been tested for the cross-linking of waterborne polymer systems to improve their mechanical properties, adhesion strength, and water/solvent resistance when compared with traditional coatings and adhesives.[90] Clickable alkyne or azide-functionalized monomers were incorporated into WPUs, polyester dispersions (PED), or polyacrylate emulsions. The authors observed that click reactions take place mainly on the particle surface, and after the polymer diffusion process, further cross-linking can occur. Click cross-linked WPU improved the tensile strength and Young's modulus, whereas the water absorption decreased. The improved mechanical properties were associated with a limitation of the mobility of the chains. PED cross-linked films showed higher tensile strength and increased T_g. Moreover, clickable groups are still available for further functionalization. The authors claimed that this strategy could replace the use of hardeners, reducing the cost of the preparation of the coating.

Conclusions

Although vegetable oils have historically been the most abundantly exploited renewable resource for the use of organic chemistry and polymer science, the production of sustainable polymer trails behind that of fossil-derived ones. Many different strategies have been developed to transform these triglycerides and their derivatives into functional building blocks and biobased polymers, and lately, an emphasis on doing so by green chemistry has been increasingly important and rightly so. In agreement with these ideals, this review presented the latest results of the utilization of click chemistry for the synthesis of derivatives, biobased polymers, and macromolecular networks to yield greener materials with advanced properties from vegetable oils. This review puts particular emphasis on examining the recent literature on the subject and whether the chemistry to synthesize these materials truly abides green chemistry principle or not.

Click chemistries are efficient and clean reactions from a green chemistry standpoint; nevertheless, functionalizing vegetable oils with the required moieties necessary for click chemistry does not always abide by green chemistry ideals. Thiol-ene addition has classically been the most predominately used of the click chemistry reactions used on fats and oils. Nevertheless, we comprehensively cover the emergence of the Diels-Alder reaction and triazolinedione chemistry to synthesize advanced sustainable polymers. These two types of chemistry have been utilized to develop covalent adaptable networks, which ties into the holistic approach of designing recyclable thermosets. Click chemistries are powerful reactions that have proven their ability to contribute to the synthesis of sustainable polymers. This review should inspire the further uses of these reactions to develop novel biobased macromolecular architectures derived from vegetable oils.

Click chemistry reactions have permitted considerable progress to functionalize monomers or polymers to achieved vegetable oil-derived epoxy resins (coatings), polyurethanes, polyamides, and polyesters. In many instances, these biobased polymers trail behind fossil-based counterparts and polyolefins in physicochemical properties and economic viability. Although considerable research has been presented on the chemistry to achieve elaborate biobased polymers using click chemistry, a current shortcoming of this field is the lack of critical thermal and mechanical characterization required to determine prosperous routes. In terms of economic availability, applying click chemistry on second and third-generation resources (such as cardanol and microalgae) to achieve high purity, low-cost monomers should be explored. Furthermore, chemical design should be explored in combination with processing to achieve competitive physical properties. In this vain, biobased polymers will be increasingly competitive by including click chemistry in the following strategy: to synthesize biobased polymers or analogs to replace commercial polymers or design novel polymeric materials with unique structures, properties (such as prolonged lifetimes), and innovative processing. More broadly, sustainable polymers from biomass are increasingly relevant globally, and collaboration across several fields, material science, chemistry, material processing, and biology, is required to discover new active components to be used as raw materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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