sustainable chemistry

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Review

Sulfur-Containing Polymers Prepared from Fatty Acid-Derived Monomers: Application of Atom-Economical Thiol-ene/Thiol-yne Click Reactions and Inverse Vulcanization Strategies

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Abstract: This paper is review with 119 references. Approaches to supplant currently used plastics with materials made from more sustainably-sourced monomers is one of the great contemporary challenges in sustainable chemistry. Fatty acids are attractive candidates as polymer precursors because they can be affordably produced on all inhabited continents, and they are also abundant as underutilized by-products of other industries. In surveying the array of synthetic approaches to convert fatty acids into polymers, those routes that produce organosulfur polymers stand out as being especially attractive from a sustainability standpoint. The first well-explored synthetic approach to fatty acid-derived organosulfur polymers employs the thiol-ene click reaction or the closely-related thiol-yne variation. This approach is high-yielding under mild conditions with up to 100% atom economy and high functional group tolerance. More recently, inverse vulcanization has been employed to access high sulfur-content polymers by the reaction of fatty acid-derived olefins with elemental sulfur. This approach is attractive not only because it is theoretically 100% atom economical but also because elemental sulfur is itself an underutilized by-product of fossil fuel refining. The thiol-ene, inverse vulcanization, and mechanistically-related thiol-yne and classic vulcanization are therefore discussed as promising routes to access polymers and composites from fatty acid-derived precursors.

Keywords: sustainable polymers; fatty acids; thiol-ene; inverse vulcanization

1. Introduction

1.1. Motivation for this Review

Plastics pervade modern life [1–5], yet their accumulation in the environment is a threat to ecosystems globally [6–9] and only a small fraction of post-consumer plastics are recycled [10]. Strategies to use bio-derived precursors to prepare polymers and to assure the biodegradability or facile recyclability of polymers are at the forefront of sustainable chemistry and materials science [11–13]. Plant oils and their component fatty acids can be produced in all inhabited regions of the world, an important consideration for resilience and equity in resource distribution as it relates to sustainability. In this review, the focus is on plant oil-derived free fatty acids as precursors to organosulfur polymers. Free fatty acids are of interest because they are found in high percentages in waste products such as acid oil by-product of biodiesel production, used food grease waste, and low value products of animal fat rendering [14–22].

Preparing modern polymers from plant oil-derived precursors has been of interest for several decades [23,24], and there have been several insightful reviews covering various aspects of materials derived from triglycerides [25–31] and fatty acids [32–35]. The current review centers specifically on organosulfur polymers derived from fatty acids. These materials are especially attractive from a sustainability standpoint because of the high atom economy with which they can be prepared by the methods discussed in the next two sections. A review on this particular niche is timely because in the last few years several important advances have capitalized on the facile reversibility of S–S bond formation to access healable and readily-recyclable materials with high strength and chemical resistance. This new class of recyclable and healable fatty acid-derived materials has not been covered previously in the aforementioned reviews on fatty acid-derived polymers.

1.2. Sources and Classification of Fatty Acids

Fatty acids are generally obtained by the hydrolysis of triglycerides (Figure 1), the primary constituents of plant oils and animal fats. The typical fatty acid component breakdown for a variety of familiar sources is summarized in Table 1. Common fatty acids provide a plethora of possibilities for chemical modification. The carboxylate functionality can be esterified or undergo amidation, while unsaturated fatty acids also afford the possibility of functionalization at the olefin units. Ricinoleate, primarily found in castor oil, is unique among the structures shown in Figure 1 in that it also featuring an alcohol moiety, allowing additional modification at this site.

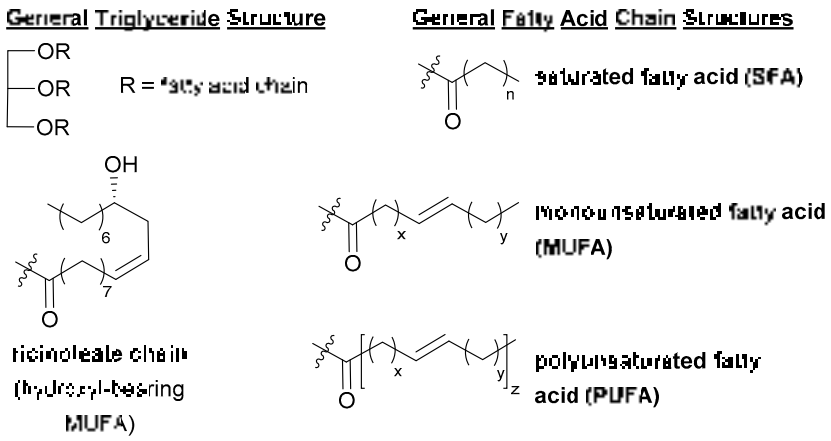


Figure 1. General structures for fatty acids derived from naturally-occurring triglycerides.

While the relative percentages of each class of fatty acids varies widely by species, it is notable that in a wide range of species ranging from tree-derived sources (olive oil) to flowers (sunflower and safflower oil), to underground legumes (peanut oil), the most common saturated fatty acid (SFA) component is palmitic acid (16-carbon chain), though coconut oil features predominantly lauric acid (12-carbon chain) as the SFA in its triglycerides. The most common monounsaturated fatty acid (MUFA) is generally oleic acid (18-carbon chain). Given that the olefin functionality plays a key role in the reactivity of fatty acids with sulfur species, oleic acid-derived monomers are the most well-studied for development of polymers discussed herein. The most common polyunsaturated fatty acid (PUFA) in common oils is diunsaturated linoleic acid (18-carbon chain with two olefins), though linseed oil is a common example in which linolenic acid (18-carbon chain with three olefins) is the most common PUFA. Throughout the course of the current review, fatty acids available from many of the sources shown in Table 1, as well the unique ricinoleate derivatives from castor oil, will be discussed.

Table 1. Fatty acid chain type compositions of some common plant oils.

Source	SFA Chains		MUFA Chains		PUFA Chains	
	Content (% of Total) [a]	Predominant Chain Length	Content (% of Total)	Predominant Chain Length	PUFA Content (% of Total)	Predominant Chain Length (Unsaturation) [b]
Coconut	92	12	6	18	2	18 (2)
Olive	15	16	74	18	10	18 (2)
Canola	8	16	62	18	32	18 (2)
Peanut	18	16	50	18	32	18 (2)
Safflower	9	16	14	18	77	18 (2)
Soybean	16	16	24	18	60	18 (2)
Corn	15	16	28	18	57	18 (2)
Sunflower	13	16	22	18	66	18 (2)
Linseed	10	16	19	18	72	18 (3)

[a] some values add up to more or less than 100% due to rounding to the nearest percentage. Numbers are reported from the published studies cited in the text. [b] number of olefin units in the most prevalent fatty acid chain of the PUFA component.

2. Applications of Thiol-ene and Thiol-yne Reactions

2.1. General Overview of Thiol-ene and Thiol-yne Reactions

The general thiol-ene reaction (Figure 2a) and closely-related thiol-yne reaction (Figure 2b) are 100% atom-economical click reactions, meaning that they can generally be accomplished under mild conditions with high yield and good functional group tolerance [36–38]. In either of these two reactions, an initially-generated sulfur radical undergoes addition across a C–C pi bond to form a new C–S bond via the mechanism shown in Figure 2c. The initiation can be affected by the use of a catalyst or by photoinitiation.

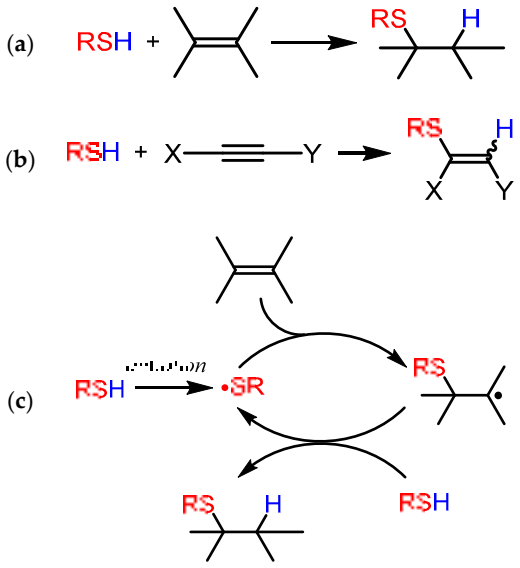


Figure 2. General net reaction for the thiol-ene (**a**) and thiol-yne (**b**) reactions, and a simplified mechanism for C–S bond formation (**c**).

In the context of applying these C–S bond forming reactions on the path to accessing fatty acid-derived organosulfur polymers, an olefin ultimately derived from an unsaturated fatty acid is employed as one of the requisite reactive moieties, while a variety of different thiols or dithiols can be employed as the sulfur source. The thiol-ene/thiol-yne reactions may be applied as part of the monomer synthesis, in post-polymerization modification, or to facilitate crosslinking of polymers. Examples for all of these possible variations will be described in the following section.

2.2. Applications of Thiol-ene Reactions to Fatty Acid-Derived Polymers

The first several studies discussed here involve the initial synthesis of α,ω-diols from fatty acids. Such diols are valuable monomers for the production of polyesters and polyurethanes. Türünç, et al., for example [39], recently detailed an optimized synthesis of castor oil-derived diol or α,ω-ester-alcohol monomers using the thiol-ene addition reaction (Figure 3). The sulfur-derivatized monomers were subsequently polymerized via condensation polymerization. One notable advantage of the process described in this study over prior work it that monomer synthesis could be affected using solvent-free techniques. Once prepared, the monomers were used to access structurally-diverse polymers. For example, polymerization of M1 with glycerol using TBD (triazabicyclodecene) as an initiator yielded a hyperbranched polymer structure, whereas linear polymers were obtained by copolymerization of M1 with M2, M3 with M5, or M4 with M5. These polymerizations afforded materials with good thermal properties such as melting points (T_m) between 50 and 71 °C and thermal stability up to around 300 °C as assessed by 5% weight loss observed in thermogravimetric analysis (TGA).

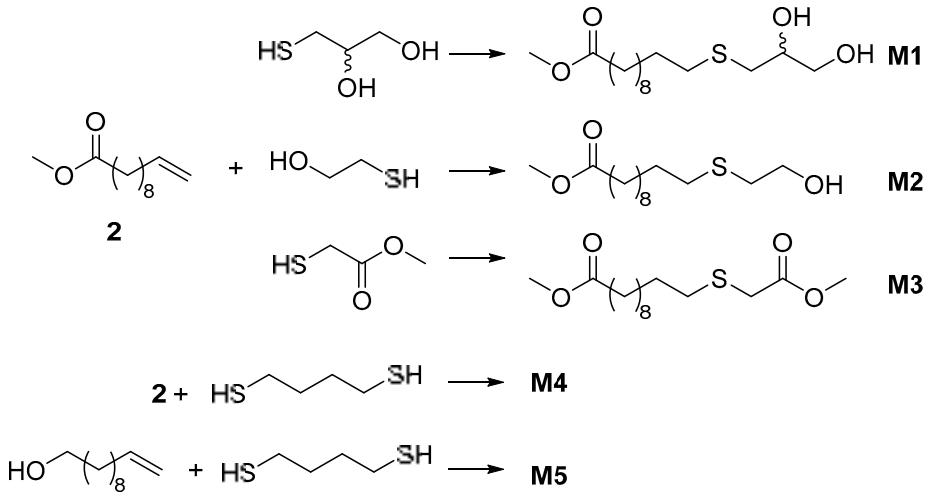


Figure 3. Monomer preparation from castor oil-derived compound **2** [39].

Another study [40] reports the preparation of thermoplastic polyurethanes. In this case the requisite sulfur-derivatized diol monomers were synthesized by the thiol-ene reaction of oleic acid or 10-undecenoic acid, which are major products of castor oil pyrolysis and saponification of sunflower oil (Figure 4a). These monomers were then readily polymerized with 4,4′-methylenebis(phenylisocyanate) in *N*,*N*-dimethyl formamide (DMF) using tin(II) 2-ethylhexanoate as a catalyst (Figure 4b). Polymers so produced exhibited M_n values in the range of 36–83 kDa. Thermal properties include glass transition temperatures (T_g) ranging from 8 to 56 °C and T_m values of between 104 and 124 °C from differential scanning calorimetry (DSC) analysis. TGA revealed high thermal stability as well, as manifest by thermal decomposition temperatures (T_d) above 269 °C. It should be noted that PU1 and PU3, both derived from 10-undecenoic acid, showed higher crystallinity than PU2 and PU4 due to the pendant methylene chains in the oleic acid backbone, which prevent close packing of the chains. Stress–strain curves were acquired to evaluate the mechanical strength of several of the materials in this study. PU2 and PU4 exhibited behavior similar to that of amorphous rubbers, whereas PU1 and PU3 showed more crystalline behavior. All polymers studied were able to withstand ≥300% strain before breaking. These properties make them competitive candidates, in terms of mechanical strength, for replacing traditional polyurethane resins. Perhaps the most interesting aspect of this work was the cytotoxicity study. In this case cytotoxicity was evaluated by the MTT assay (MTT = 3-[4,5-dimethylthiazole-2-yl]-2,5-diphenyltetrazolium bromide). This assay revealed that after

7 days, human fibroblast cell viability was not affected by the presence of the materials. This was striking, and indicates good preliminary promise for the use of these materials for biopolymer applications.

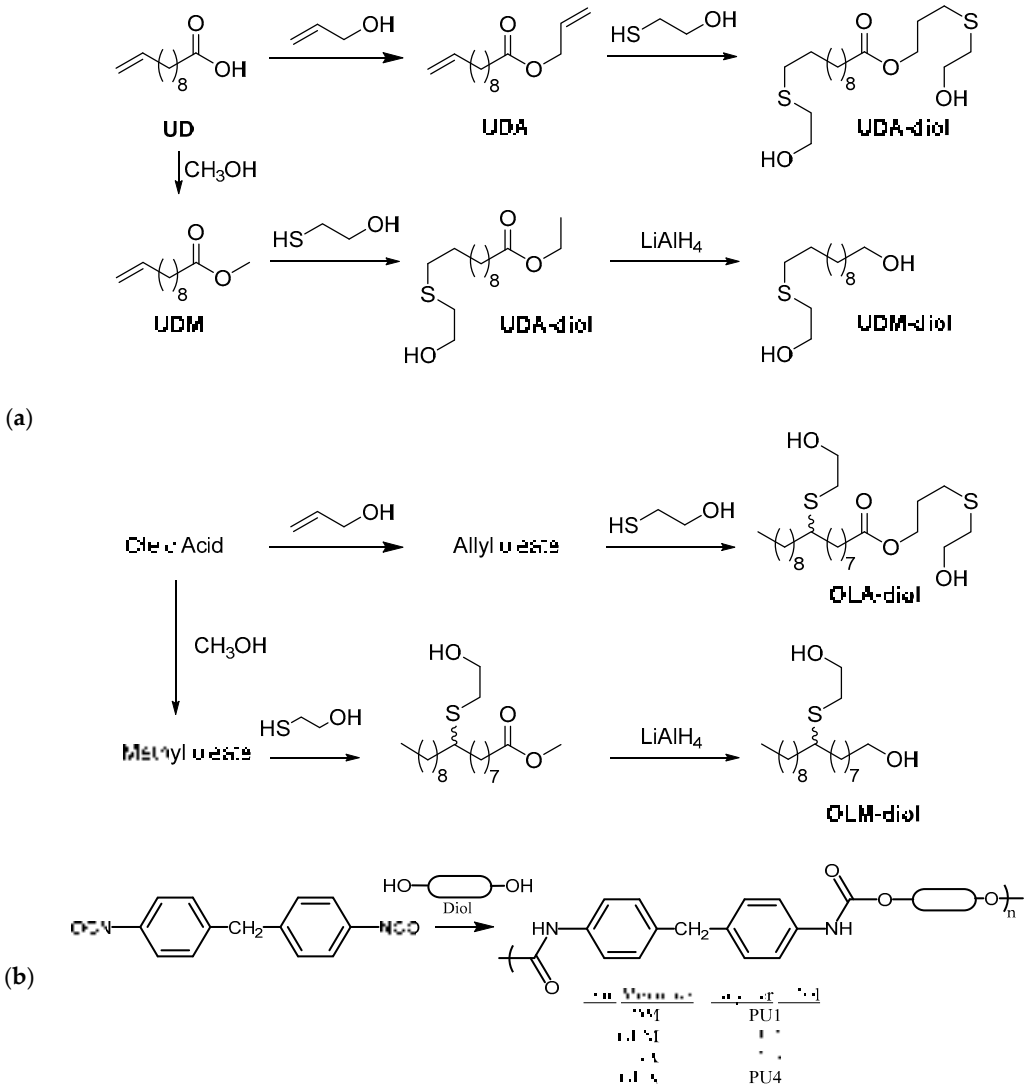


Figure 4. (**a**) Preparation of four diol monomers. (**b**) Utility of monomers in polyurethane preparation [40].

Desroches, et al. demonstrated that transesterification of canola (rapeseed) oil with ethylene glycol is a viable route for producing pseudo-telechelic diols (Figure 5) [41]. Quantitative thiol-ene reaction was then affected between the diols and 2-mercaptoethanol under mild conditions with UV light initiation. Step-growth polymerization of diols with methylene diphenyl-4,4′-diisocyanate (analogous to the reaction shown in Figure 4b) then afforded polyurethanes that boasted thermal properties (T_g = −3 °C) similar to those of commodity polyurethanes made from traditional diols (T_g = 8 °C) for use as coatings and binders.

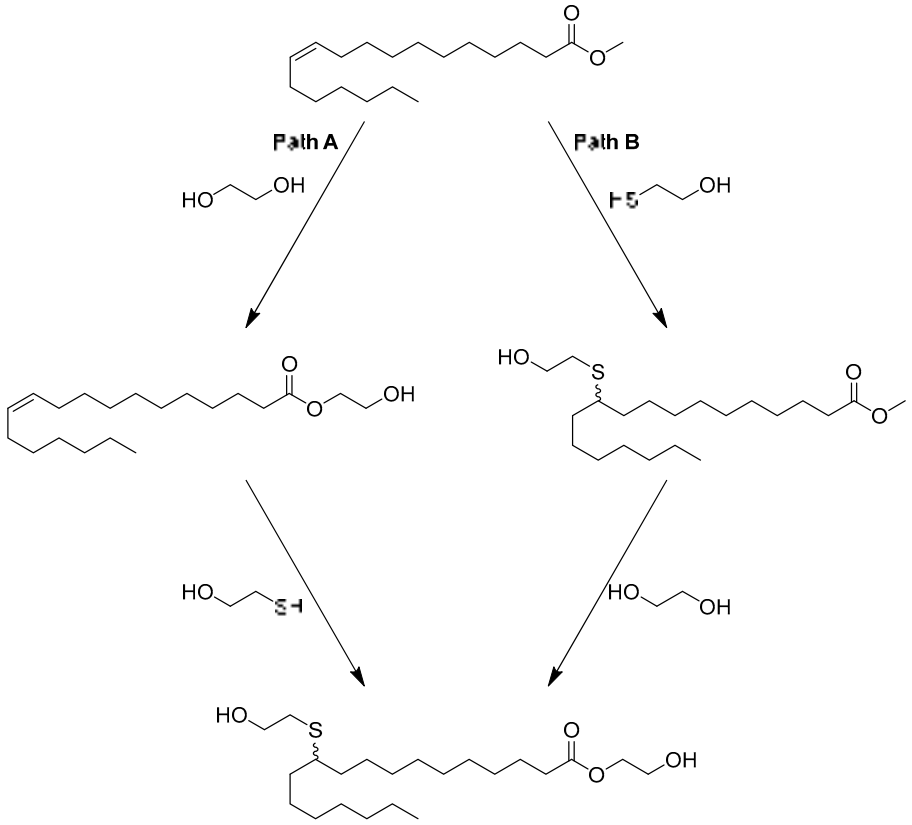


Figure 5. Routes to synthesize pseudo-telechelic diols.

In addition to the preparation of diol monomers from fatty acids discussed above, several strategies have been developed to access diester or dicarboxylic acid monomers. Diester and dicarboxylic acid monomers are attractive candidates for use in trans/esterification routes to polyesters or in amidation reactions to yield polyamides, for example. A recent example of facile diester production from fatty acid precursors comes from Meier, et al. who demonstrated the synthesis of an oleic-acid derived dimer **3** that can be used without its further purification to synthesize polyamides (Figure 6) [42]. The ability to use the monomer without purification is possible because its synthesis, affected by UV-initiated thiol-ene reaction of **3** with 1,2-ethanedithiol at room temperature, proceeded cleanly with approximately 98% conversion. Polyamides were then prepared via metal-catalyzed polycondensation of hexaminediamine, dimethyl adipate, and **3** (Figure 6). One of the drawbacks of some commercial polyamides is that they exhibit a sharp drop off in mechanical properties upon water uptake. Nylon-6,6, for example, exhibits 3.5 wt.% water uptake at a relative humidity of just 55%, accompanied by a precipitous drop in T_g from 100 °C when dry to 43 °C and a drop in tensile strength at yield from 80 MPa to 43 MPa [43]. Water uptake tests conducted on polymers shown in Figure 6 exhibit significantly lower water uptake than commercial polyamides at both 25 °C and 80 °C and also exhibited faster water release than does nylon-6,6.

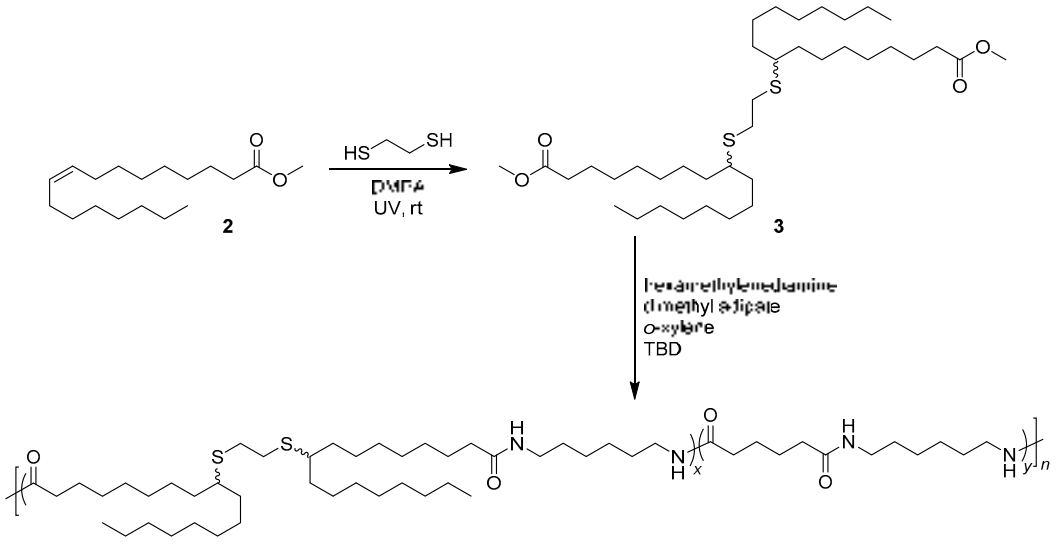


Figure 6. Preparation of dimer **3** and subsequent polymerization.

Another study utilized the thiol-ene reaction to produce dicarboxylic acid monomers containing two sulfur atoms per monomer with varying aliphatic chain lengths (2, 6, and 10 methylene groups between the sulfur atoms). These monomers then underwent polycondensation with diamines to yield fatty-acid derived, linear polyamides (Figure 7) [44]. A host of properties were characterized, most notably thermal and tensile properties, impact resistance, water absorption, and chemical stability. The authors found that increasing the spacing between amide units allows attenuation of inter-/intra-chain hydrogen bonding, which, while imparting physical strength to the polymers, can also be accompanied by brittleness and lower impact strength. Increased H-bonding also leads to higher melting temperatures, which can be an impediment to processability. More amide units in the polymer backbone also increase the propensity for water absorptivity, which can reduce the strength and potentially degrade the polymer. The synthesized polymers were thus more readily processible than typical commercial polyamides by merit of their lower T_g, T_c, and T_m values. The polymers also exhibited improvements in chemical and impact resistance, and advantageous low water absorptivity and high oxygen and water vapor permeation compared to commercial polyamides.

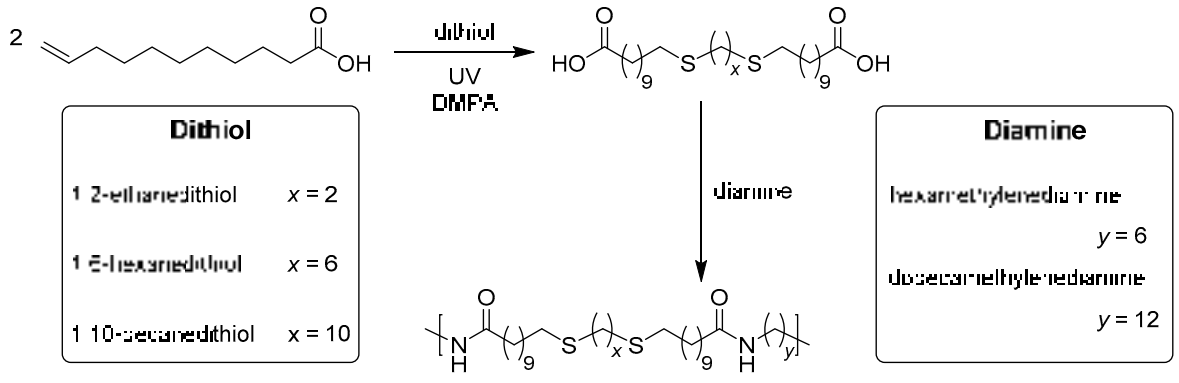


Figure 7. Preparation of dicarboxylic acid monomers and subsequent polymerization.

Employing linear bifunctional monomers of the type discussed so far in this section is only one of the approaches that has been surveyed for incorporating fatty acids into materials. Because the thiol-ene reaction employs an olefin substrate, several strategies have been enumerated to prepare monomers with olefinic end caps, side chains or in the backbone. Kempe, et al., for example, explored some cationic ring-opening polymerization of cyclic fatty acid-based monomers that can be facilitated

by microwave irradiation at 100 °C to form DecEnOx (Figure 8) [45]. This process leaves an unmodified terminal olefin unit poised for further modification. Post-polymerization modifications using the thiol-ene reaction in green solvents (methyl-THF or methyl laurate) result in low PDIs (1.22–1.26) and respectable M_n ranging from 4900–11,400 g/mol. Especially notable in this study is the ability to append a saccharide from the polymer backbone, a demonstration of the functional group tolerance and mild conditions possible for the thiol-ene reaction. The stark disparity between the polarity of the polymers modified to include alkyl chains or the saccharide also serves to demonstrate the range of materials accessible by this technique. Although their successful synthesis has been demonstrated, the full property sets afforded by these structurally-diverse materials has yet to be fully reported.

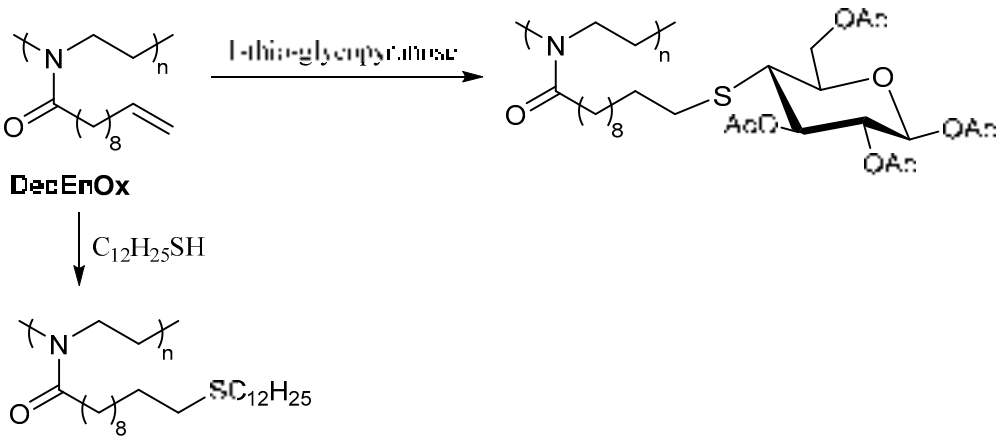


Figure 8. Post-polymerization modifications of DecEnOx using green solvents [45].

De and coworkers utilized RAFT polymerization of a methacrylate-functionalized oleic acid monomer (2-(methacryloyloxy)ethyl oleate) (Figure 9), resulting in polymers (PMAEO) with a narrow PDI, controlled molecular weights and defined end groups [46]. Of particular interest is the ability to further functionalize the polymer, as the alkene unit within the oleic acid side chain are unreacted following polymerization. Further functionalization with a variety of thiol compounds via the thiol-ene reaction, for example, was affected when excess of thiols was used. The excess thiol was required in this case because of the low reactivity of the internal olefins. Despite this lower reactivity, however, quantitative conversion was confirmed by ^{1}H NMR spectrometric analysis for some of the materials surveyed. The functionalization of the olefin sidechains provided a convenient avenue for the installation of a variety of additional functionalities into the polymer, resulting in a wide range of accessible properties. When 3-mercaptopropanoic acid was employed, for example, the resulting polymer was soluble in aqueous media. Epoxides were also readily installed by reaction of PMAEO with *m*-CPBA in CH_2Cl_2 at room temperature. Facile crosslinking of epoxide moieties upon their reaction with diamines was also demonstrated.

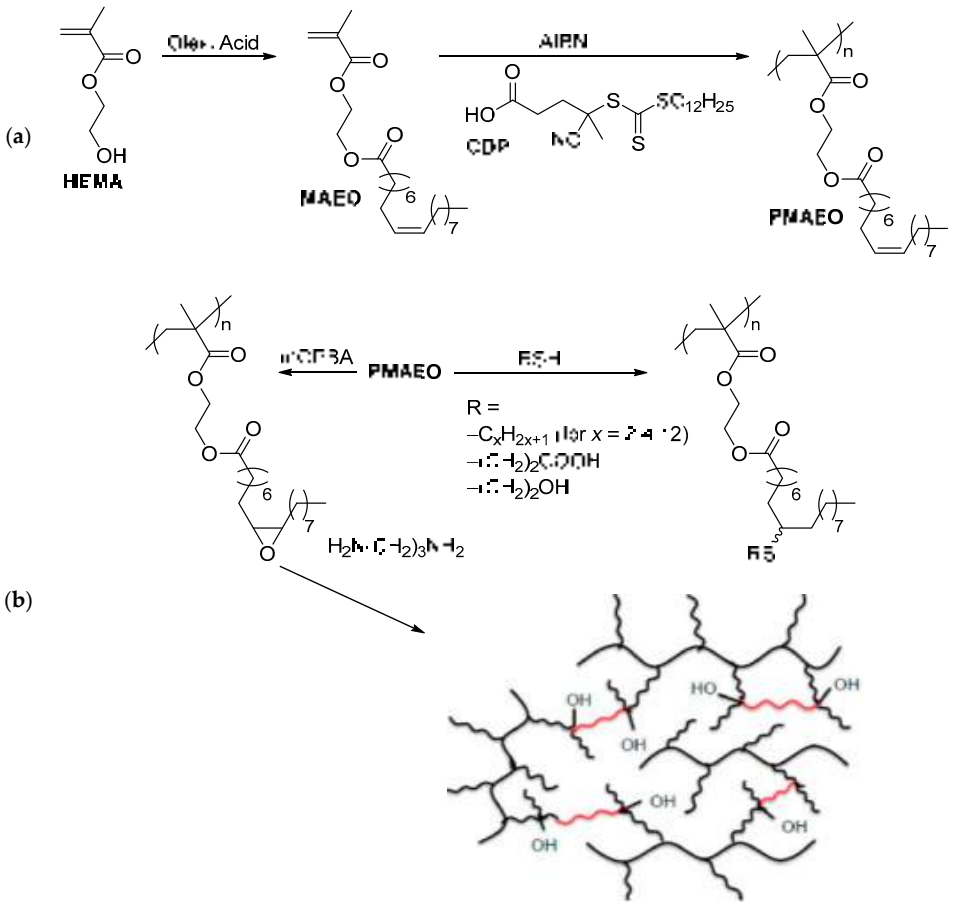


Figure 9. Synthesis of PMAEO (**a**) and post-polymerization modification via the thiol-ene reaction and epoxidation reaction. (**b**) Part of (**b**) is reprinted with permission from reference [46]. Copyright 2011 Royal Society of Chemistry.

Polyhydroxyalkanoates (PHAs), polyesters that are produced by certain bacteria strains, have recently emerged as an attractive alternative to petroleum-based plastics because they are biodegradable and can be synthesized from renewable sources. Despite the promise of these materials, the lack of chemical reactivity in the side chains has limited derivatization to access a wider application space. Levine and coworkers thus investigated an engineered strain of *Escherichia coli* that allows for the identity and quantity of repeat units to be controlled, opening the door to a panoply of new materials [47].

The focus of this particular study was on a polymers such as polymeric α,ω-diol PHBU (Figure 10) with unsaturated side chains that could be modified using the thiol-ene reaction. Three different thiols were incorporated, including one that allowed for crosslinking of the polymer. Decomposition temperatures of the polymers ranged from 288 °C for the unmodified polymer to 301 °C for the crosslinked polymer (using a 1:1 mole ratio of crosslinker to alkene). Changes in thermal properties among the polymers were unremarkable, with the exception of a change in melting temperatures for modified (116.4–134.0 °C) versus unmodified polymer (143.2 °C). However, mechanical properties were decidedly different between the crosslinked (X-PHBU, Figure 10, bottom) and non-crosslinked polymers. Tensile strength, elongation at break, and Young's modulus were determined for each material. These mechanical properties exhibit the greatest change upon comparison of as-prepared PHBU with the crosslinked derivative. PHBU had elongation at break of 89% and Young's modulus of 368 MPa, compared to values of 495% and 335 MPa for the thiol-crosslinked structure.

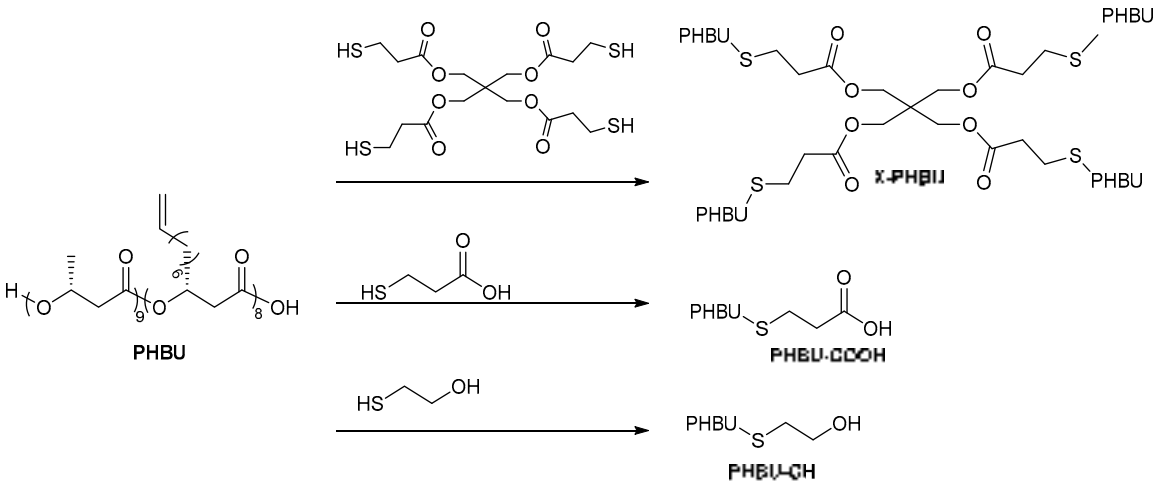


Figure 10. Post-polymerization modification of PHBU via the thiol-ene reaction yields three modified variations [47].

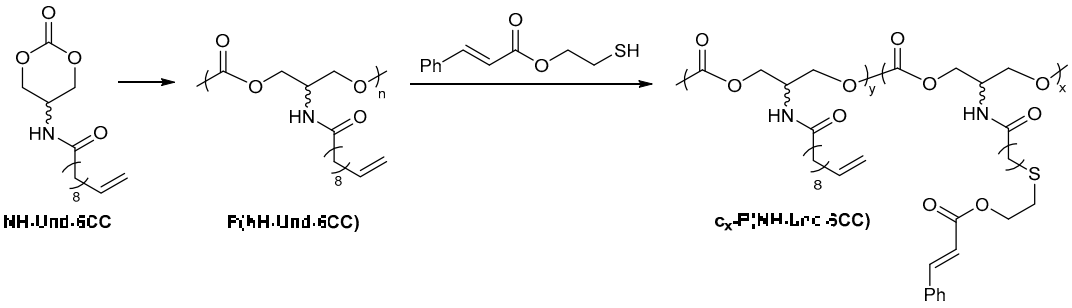
The primary mechanism of degradation of PHAs is hydrolytic cleavage of the polyester backbone. One of the goals of post-polymerization of the PHAs was therefore to tune the hydrophilicity of the surfaces of the polymers as a means of attenuation their degradation. This effort was moderately successful, as the water contact angles for PHBU-COOH and PHBU-OH were 6.4° and 8.1° lower than for PHBU, respectively.

Durand and coworkers sought to synthesize photosensitive polycarbonate derived from fatty acid-based starting materials. Polymers that could be selectively crosslinked and partially decrosslinked upon exposure to UV light were targeted (Figure 11a) [48]. Such materials provide a potential route to address the major issue of recycling of polycarbonates used in the biomedical field. Biomedical polycarbonates are often high strength, highly-crosslinked materials for which there is currently no viable method to reshape or recycle.

Methyl undecenoate was thus reacted with an amine functionalized diol, followed by intramolecular reaction of the resultant amide to form a 6-membered cyclic carbonate, NH-Und-6CC (Figure 11a), which then underwent ring-opening polymerization (ROP). Following ROP, the pendant alkene moiety was further functionalized via the thiol-ene reaction with a cinnamoyl-derivatized thiol. The percentage of cinnamoyl incorporated was controlled by tuning the reaction time. Up to 100 mol% substitution was achievable in 30 min.

The cinnamoyl group contains an internal alkene capable of photochemical [2 + 2] cycloaddition reaction when exposed to UV light with a wavelength of 365 nm. The [2 + 2] cycloaddition was thus used to affect crosslinking to strengthen and cure the material. When the crosslinked polymer is irradiated with 254 nm light, the crosslinks partially reverse, which allows the materials to be reshaped and recycled. Tensile testing was done to probe the mechanical properties of the crosslinked materials. As the cinnamoyl content increased, so did the Young's modulus and maximum stress at break. At 10 mol% cinnamoyl content, the Young modulus and maximum stress are 1.3 MPa and 0.5 MPa, respectively. When the cinnamoyl content is increased to 100 mol%, those values increase dramatically, to 1266 MPa and 35 MPa, respectively. As materials became more crosslinked, the percent elongation at break decreased from 156% in the 10 mol% cinnamoyl content polymer, to 3% in the 100 mol% cinnamoyl content polymer.

(**a**)



(**b**)



Figure 11. (**a**) Synthesis of polycarbonate derivatives containing cinnamate. (**b**) Photo demonstrating the flexibility of low cinnamate-content polymers, 30 mol% cinnamate shown. Part (**b**) is reprinted with permission from reference [48]. Copyright 2018 American Chemical Society.

Building on the work described above, Durand and coworkers also showed that commercially available castor oil derivatives can be leveraged to synthesize biologically-sourced polycarbonate network polymers [49]. Efforts in this paper were focused on post-polymerization modification of the dangling olefin moieties via the thiol-ene reaction to produce cross-linked materials exhibiting superior transparency and flexibility. The thiol crosslinkers were selected to include examples with aromatic spacers (1,4-benzenedimethanethiol, BDT) and aliphatic spacers comprising two chain lengths (1,6-hexanedithiol, HDT and 1,9-nonanedithiol, NDT) (Figure 12).

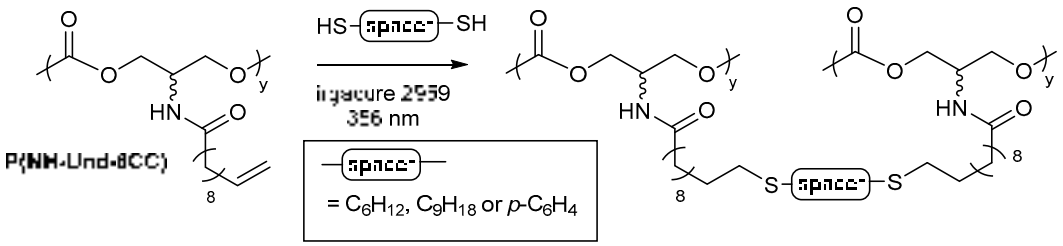


Figure 12. Thiol-ene reaction used to modify P(NH-Und-6CC) after polymerization using various thiols [49].

Mechanical properties were investigated by dynamic mechanical analysis (DMA). With increasing flexibility of crosslinking agents, the T_g of the materials increased: The T_g for polymers crosslinked by BDT, HDT and NDT were 8.8 °C, 15.1 °C, and 37.7 °C, respectively. This trend was also observed for the storage modulus and Young's modulus (1.3, 50, and 240 MPa, respectively), while the inverse was observed for elongation at break (190%, 76%, and 26%, respectively).

HDT-crosslinked material was selected for further evaluation of the extent to which crosslink density influences each property of the network. Theoretically, 0.5 equivalents of dithiol crosslinker is sufficient to crosslink all of the olefin units in the linear polymer. The amount of dithiol in the

crosslinking reaction was thus varied from 0.1 to 0.8 equivalents. The gel content increased predictably from 0.1 to 0.5 equivalents, and then slightly decreased with an excess of dithiol (89% gel content with 0.5 equivalents of dithiol compared to 83% gel content with 0.8 equivalents). The swelling ratio in CH_2Cl_2 also generally decreased as the dithiol content was increased, with the notable exception of 0.8 equivalents which significantly raised the swelling ratio without significantly compromising the gel content, attributable to a lower cross-linking density. The T_g increased from 5.3 to 15.1 °C as the crosslinker concentration was increased from 0.1 to 0.5 equivalents, decreasing to 7.4 °C upon addition of 0.8 equivalents of crosslinker. The storage modulus (ranging from 0.1–4.5 MPa) and Young's modulus (ranging from 0.8–50 MPa) likewise progressively increased with increasing crosslink density, with the same observable trend of values decreasing upon addition of excess crosslinking agent.

Moser and coworkers synthesized semicrystalline poly(thioether-ester)s utilizing the thiol-ene polymerization under mild, solvent-free conditions [50]. Monomers were prepared from 9-decenoic acid, which can be produced from oleic acid [51]. After esterification to yield terminal dienes, they were then reacted with dithiols (1,2-ethanedithiol or 1,3-propanedithiol) to yield linear polyesters (Figure 13). The presence of both a T_m and a T_g lead to the classification of these polymers as semicrystalline. Wide-angle X-ray scattering (WAXS) was thus used to determine the relative crystallinity. Polymer **6** was found to be the most crystalline, followed by **5**, **3**, and **4**. The inclusion of 1,3-propanedithiol as the crosslinking agent in polymers **5** and **6** lead to the greater crystallinity, as the additional methylene unit allows for greater chain flexibility when compared to 1,2-ethanedithiol. The T_g, as determined by DMA, ranged from −36.8 (polymer **6**) to −25.7 °C (polymer **3**), and T_m of the polymers ranged from 60.9 (polymer **5**) to 70.5 °C (polymer **4**).

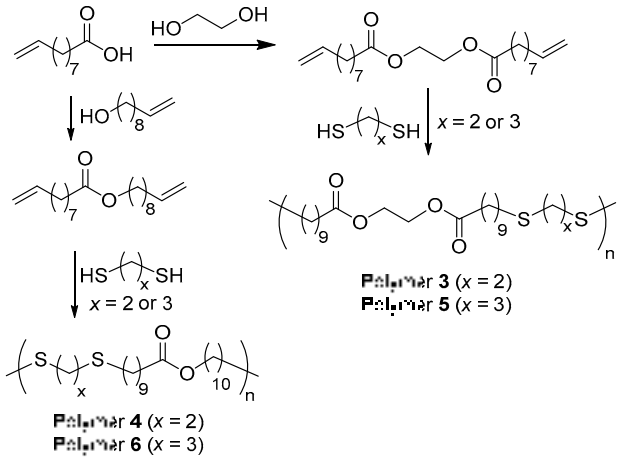


Figure 13. Preparation of polymers **3**–**6** [50].

Mechanical properties were probed using DMA from −60 to +60 °C. Storage and loss moduli, as well as tan δ at T_g and room temperature were reported for all polymers. Polymers **5** and **6** exhibited higher storage moduli values at both T_g and room temperature. These materials also exhibited higher loss moduli at both temperatures, suggesting that they are more efficient at dissipating energy through heat. Thermal and chemical stability as well as solubility were also reported. Using TGA, it was determined that all polymers were thermally stable below 300 °C. All polymers were soluble in chloroform and THF, but insoluble in more polar solvents, likely due to the long aliphatic chains present in the polymer backbone. The polymers were also subjected to acid and base challenge by soaking in acetic acid, sulfuric acid, and sodium hydroxide for seven days. All polymers were stable, meaning undissolved, in acetic acid and sodium hydroxide. However, when exposed to the oxidizing acid, the polymers were completely soluble, suggesting that they would be susceptible to other oxidizing agents.

2.3. Comparison or Combination of Thiol-ene and Olefin Metathesis Reactions

Monomers and polymers featuring side chain and endcap olefins described as substrates for thiol-ene modification in the previous section are often also attractive substrates for olefin metathesis reactions. Several studies have therefore examined the viability of using thiol-ene click reactions in tandem with olefin metathesis or have compared fatty acid-derived polymers prepared using thiol-ene versus metathesis routes as complementary approaches. In one such study [52], Türünç and coworkers sought to compare polymerization by thiol-ene reaction and ADMET as mechanisms to produce biodegradable polymers from renewable feedstocks with potential application as biomedically-relevant materials. Polymers produced by both techniques were fully characterized to assess their chemical stability when exposed to different solvents, acidic and enzymatic conditions. The polymers synthesized via ADMET proved to tolerate a wider range of functional groups (both esters and anhydrides could function as monomers). In contrast, the thiol-ene reaction could tolerate esters but not anhydrides (Figure 14). However, the thiol-ene reaction lead to polymers with higher molecular weights of up to 11,850 g/mol compared to a maximum of 9000 g/mol for those prepared by ADMET.

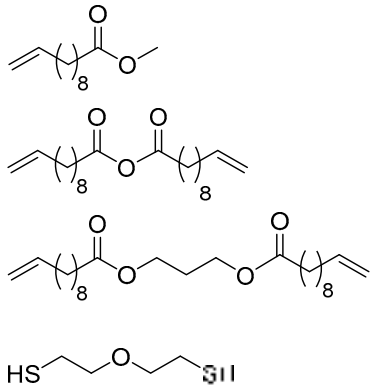


Figure 14. Structures of dienes and thiols probed, along with a chain stopper (topmost structure) [52].

In a related study [53], the same research group investigated copolymers synthesized from castor oil derivatives by ADMET or the thiol-ene reaction with the goal of elucidating an alternative to polyethylene (Figure 15). The polymers exhibited desirable melting points ranging from 40–80 °C. All polymers, with the exception of P3, exhibited degrees of crystallization values between 36% and 52%, which is higher than that reported for LLDPE [54]. On this basis, it was concluded that the thiol-ene reaction is a useful facsimile towards the synthesis of renewable polyethylenes.

A study by Unverferth and coworkers [55] also focused on post-polymerization modification, in this case of star-shaped polyesters prepared via ADMET polymerization of castor oil derivatives (Figure 16). Two main cores were used for the star shaped polyesters, one containing four arms and another containing six arms available for polymer growth. These two cores were then functionalized with either 10 or 20 repeat units per arm. Both internal and terminal olefins in the resultant structures were successfully modified using the thiol-ene reaction. Five different thiols were used in the post-polymerization modification of each star-shaped precursor. Modification extent and kinetics were easily quantifiable by ^{1}H NMR spectrometric analysis. Although internal alkenes reacted expectedly more slowly than terminal alkenes, quantitative consumption of all alkene units was achievable in all cases. It was also noted that no degradation of the polymer backbone occurred during the post-polymerization modification manipulations. Functionalization with a variety of different thiols allowed ready tuning of the polarity of the modified polymers. The effective polarity of each construct was thus assessed using RP-HPLC to determine the octanol-water partition coefficient.

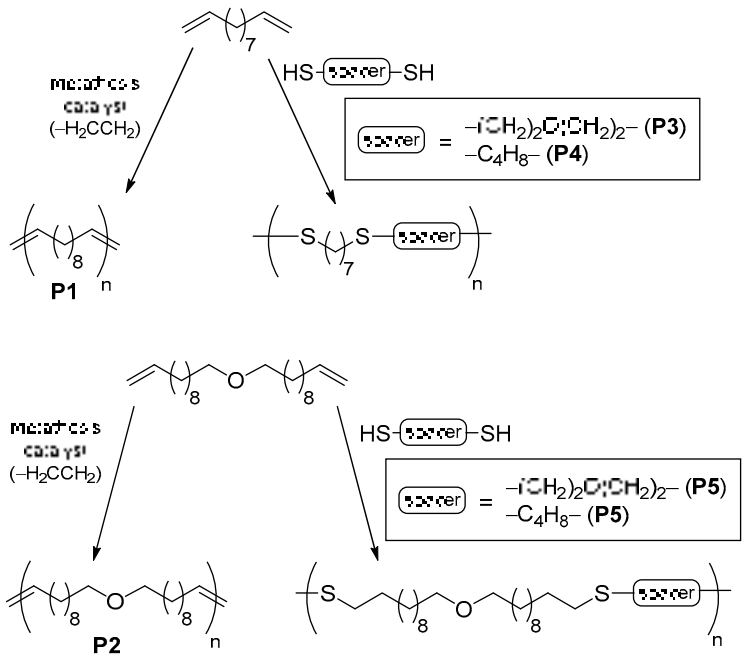


Figure 15. Synthesis of bio-derived polymers **P1**–**P6** [54].

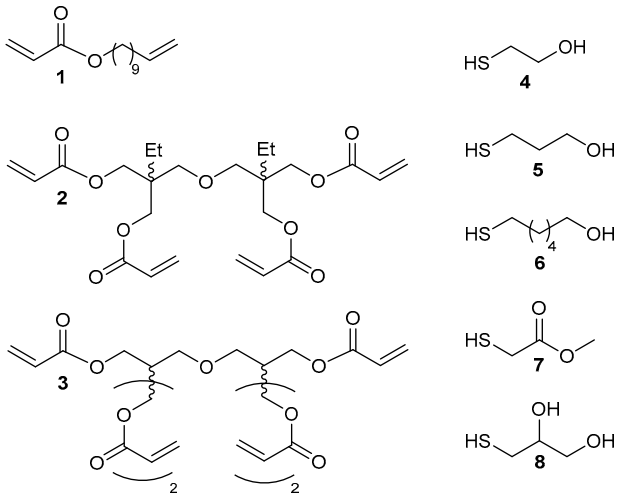


Figure 16. Dienes and thiols used to prepare star-shaped polymers [55].

Dannecker and coworkers aimed to synthesize sustainable polyethers via ADMET and thiol-ene polymerizations employing monomers derived from methyl oleate [56]. In some previous work, the authors had demonstrated synthesis of ether monomers using the Williamson ether synthesis; however, that approach was lacking in sustainability. In the updated strategy, the authors use $GaBr_3$ for the catalytic reduction of esters to yield ethers for polymerization, and the utility of greener polymerization solvents such as methyl THF and polarclean was established (Figure 17).

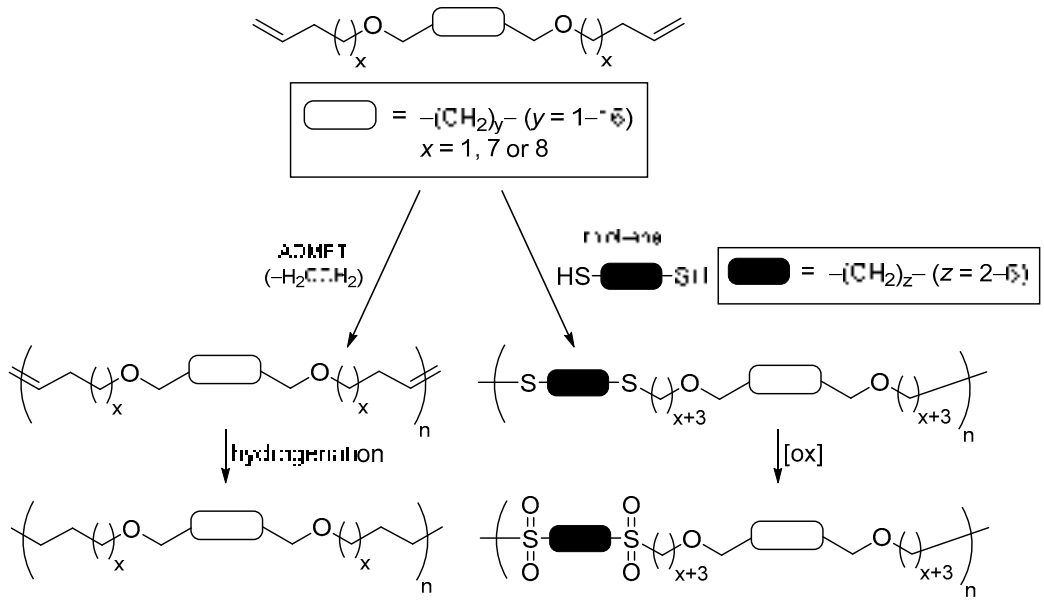


Figure 17. General synthetic scheme for comparison of thiol-ene and metathesis routes to polymers [56].

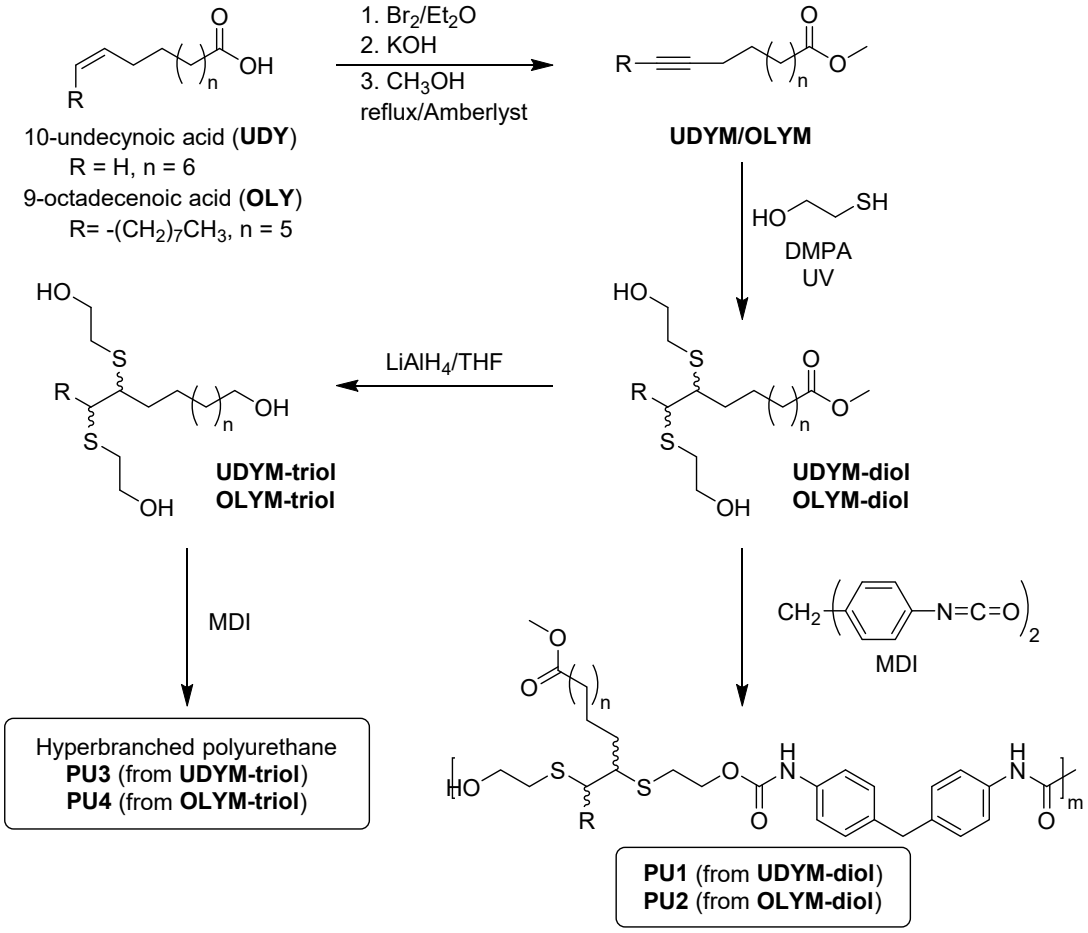
The thiol-ene polymerization was first attempted solvent-free in a microwave reactor with AIBN initiator at 80 °C. The number average molecular weights obtained by this route were low (M_n = 950 g/mol); this was thought to be due to poor mixing because of the high viscosity of the monomers at this temperature. It was determined that a solvent was necessary to accomplish high molecular weights. Methyl THF was chosen for this purpose on the basis of its sustainable nature, lower toxicity, and higher boiling point than the THF more commonly used in traditional polymer syntheses. The resulting polymers exhibited M_n increased by an order of magnitude, and after optimization, number average molecular weights greater than 15 kDa were achieved. The thiol-ene polymers were then oxidized by hydrogen peroxide solution to form sulfoxides and sulfones to improve their thermal properties.

For the ADMET polymerization, three different catalysts were screened for their ability to affect solvent-free polymerization. It was determined that the 2nd generation Hoveyda-Grubbs catalyst tolerated the conditions best, and with the addition of polarclean solvent, produced the highest M_n of 32 kDa. The resulting polymers were then hydrogenated to increase the melting temperatures.

2.4. General Applications of Thiol-yne Reactions to Fatty Acid-Derived Polymers

Given the natural occurrence of olefin moieties in a wide range of fatty acids, most of the work in the field has employed the thiol-ene rather than the thiol-yne reaction. However, there are a few studies in which modified fatty acid precursors have been utilized as substrates for thiol-yne elaboration towards polymer synthesis. In one such study employing the thiol-yne route, products of common reactions of fatty acids found in sunflower oil and castor oil were used as the initial starting materials (Figure 18) [57]. After installation of the requisite alkyne unit, the compounds were subjected to the thiol-yne reaction with 2-mercaptoethanol to yield diol derivatives. Subsequent reduction of the methyl ester using lithium aluminum hydride led to the target triols. Both diol and triol derivatives were exploited for use in polymer formulations to access target thermoplastic and thermosetting polyurethanes upon their reaction with methylenebis(phenylisocyanate) (**PU1** and **PU2** derived from diols; **PU3** and **PU4** derived from triols). The resulting polymers exhibited good thermal properties, with T_d values between 245 and 261 °C and T_g values ranging from 15–59 °C. **PU1** and **PU2** exhibited high strain upon breaking (1693% and 965%), but low Young's moduli (≤0.054 MPa), whereas **PU3** and **PU4** were much stiffer, exhibiting low strain at breaking of around 10% but high Young's moduli ranging from 89–143 MPa.

(**a**)



(**b**)

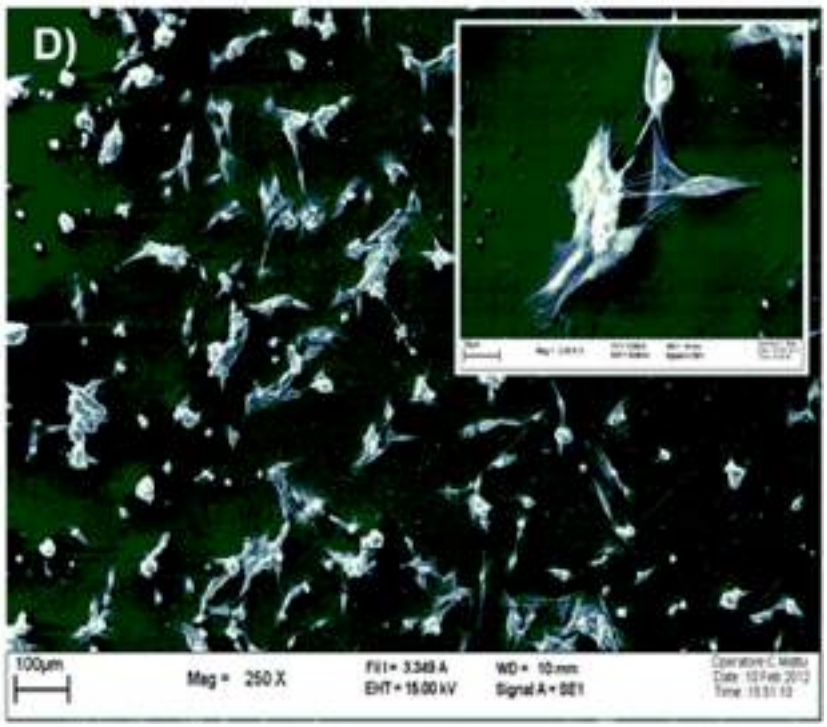


Figure 18. (**a**) Synthesis of polyols from sustainable starting materials. (**b**) Scanning electron micrograph image of MG63 cells cultured on PU3 demonstrates the viability of human cells on this substrate. Part (**b**) is reprinted with permission from reference [57]. Copyright 2012 Royal Society of Chemistry.

Polyurethanes have utility in tissue engineering and bone grafting, so the biocompatibility of the synthesized materials was investigated. Cell viability using an MTS assay (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) in an osteoblast cell line was monitored as a means of assessing the utility of these new materials in bone-grafting applications (Figure 18b). The materials showed no significant cytotoxicity, with all materials providing over 75% cell viability over a 24 h period. No difference in cell viability was observable between materials prepared from diols versus triols.

Beyazkilic and coworkers likewise described the modification of a fatty acid with a terminal alkyne, thus allowing for subsequent reaction with 2-mercaptoethanol via the thiol-yne addition to give monomer VSHA (Figure 19) [58]. Polyesters were then synthesized by combination of VSHA with monomers such as 1,4-butanediol and ε-caprolactone in varying feed ratios to yield di- and tri-block copolymers. Two different polymerization methods—traditional metal-catalyzed polycondensation and enzymatic polycondensation—were employed in this pursuit. While metal-catalyzed reactions are the predominant method used to synthesize polyesters in industrial settings, the inclusion of metals can have deleterious effects in the eventual use of the polymer. Even when a high loading (10–25 wt%) of metal catalyst was employed, the lipase catalyzed reaction still exhibited better kinetics and higher ultimate molecular weights.

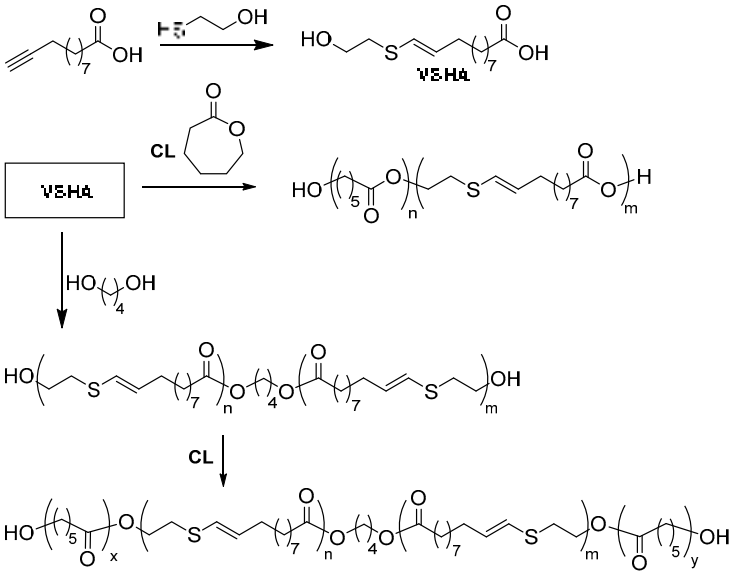


Figure 19. Synthesis of random polymer and triblock copolymer [58].

The alkene unit remaining in the polymer chain allowed for post-polymerization modification to be performed. Using 1,4-butane-dithiol and UV irradiation at room temperature, the polyester was successfully crosslinked within one hour, as confirmed by monitoring the disappearance of the C=C stretch via IR spectroscopy and ^{1}H NMR spectrometry. Surface modification of films prepared by solution-casting the triblock polyesters was also affected by reacting it with a fluorescent label (7-mercapto-4-methylcoumarin) as a convenient means of quantifying the extent of modification.

3. Applications of Vulcanization and Inverse Vulcanization

3.1. Inverse Vulcanization versus Classical Vulcanization

Vulcanization is a term that most commonly refers to the process discovered by Charles Goodyear in 1844 whereby olefin units in natural rubber are crosslinked with a small percentage of elemental sulfur (Figure 20a) [59]. The result of this process is the durable vulcanized rubber familiar in modern life as the black material of which most automobile tires are made. More recently, Pyun's group coined

the term inverse vulcanization [60] to refer to a process in which crosslinking of olefins is affected by their reaction with a majority component sulfur (Figure 20b), rather than as the minority component (<5 wt%) originally used in classic Goodyear vulcanization. Because they are comprised in large part by sulfur, materials prepared by the inverse vulcanization process are generally formulated as incorporating polymeric sulfur catenates, generally unstable at STP, stabilized by their entrapment within a crosslinked network. Mechanistically, both vulcanization and inverse vulcanization employ the addition of a sulfur radical across a C–C pi bond, much like the first propagation step of the thiol-ene reaction discussed in the previous section. In the inverse vulcanization and vulcanization reactions, however, sulfur radicals are generated by heating elemental sulfur above its floor temperature of 159 °C to induce thermal homolysis of S_8 rings (the typical sulfur allotrope at STP) and ultimate formation of polymeric sulfur radicals. Like the thiol-ene reaction, inverse vulcanization is also theoretically 100% atom economical, although some side reactions are sometimes observed. Elemental sulfur is also an attractive comonomer because it is produced as a fossil fuel refining by-product in a large excess for which there is currently no practical use. Another notable feature of these reactions is that vulcanization is used on large industrial scale in the rubber industry and, though not yet commercialized on industrial scale, inverse vulcanization has been demonstrated on kilogram scales [61].

Since the first articulation of inverse vulcanization in its modern embodiment in 2013 [60], this mechanism has proven broadly applicable to producing high sulfur content materials (HSMs) from a wide range of olefins for a plethora of applications [62–76]. In addition to petrochemically-derived olefins, many biologically-derived olefins have also been successfully exploited as comonomers with sulfur, including terpenoids [77–80]. Triglycerides [81–88], fatty acids [89–92], sorbitan esters [93], amino acid derivatives [94], guaiacol derivatives [95], and cellulose/lignin derivatives or lignocellulosic biomass [11,96–100].

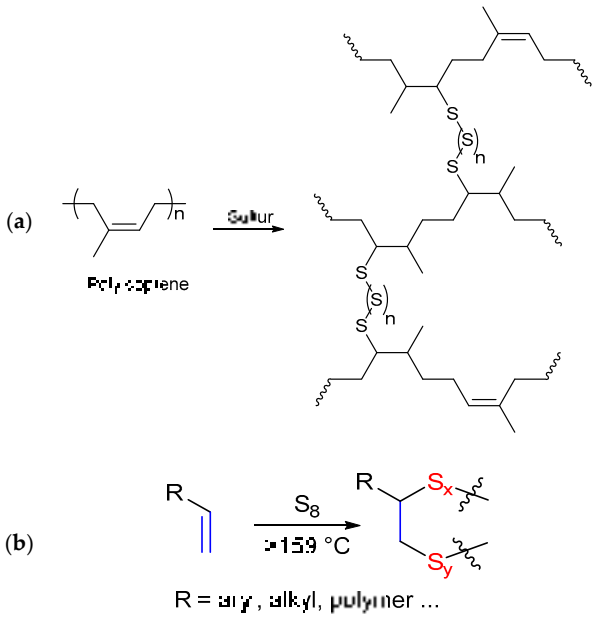


Figure 20. Vulcanization (**a**) and inverse vulcanization (**b**) processes. Reproduced from [63] (part (**a**)) and [94] (part (**b**)) under a Creative Commons 3 License (https://creativecommons.org/licenses/by-nc/3.0/).

HSMs resulting from inverse vulcanization are primarily comprised by S–S bonds, allowing for their facile recycling and thermal healability by merit of the thermal reversibility of S–S bond formation. The high sulfur content materials produced by the inverse vulcanization of some triglycerides have also been established not only to be biodegradable, but to even enhance the growth of food crops as timed-release sulfur fertilizer sources. All of the aforementioned properties make HSMs derived from

fatty acids tantalizing targets from a sustainability standpoint. In the last few years, several examples of such materials, as well as materials crosslinked by traditional vulcanization processes, have been reported. These materials are the subject of discussion in the final portion of this review.

3.2. Applications of Vulcanization/Inverse Vulcanization to Fatty Acid-Derived Polymers

Estolides are employed in many commercial applications, including cosmetics, inks, and emulsifiers in margarine, and they are also biodegradable. Dworakowska and coworkers thus investigated a one-pot polyesterification of fatty acid derivatives to form estolides as part of a broader study on the extent to which their properties could be improved through crosslinking by vulcanization or other radical routes [101]. The estolides proved readily crosslinkable using dicumyl peroxide or by their vulcanization to yield bio-based elastomers (Figure 21). Thermal and mechanical properties of the crosslinked networks were evaluated. TGA of the materials indicated high thermal stability, with a 5% decomposition temperature between 205 and 318 °C. Low glass transition temperatures were also reported (−69 to −54 °C), coupled with good tensile strength (0.11 to 0.40 MPa).

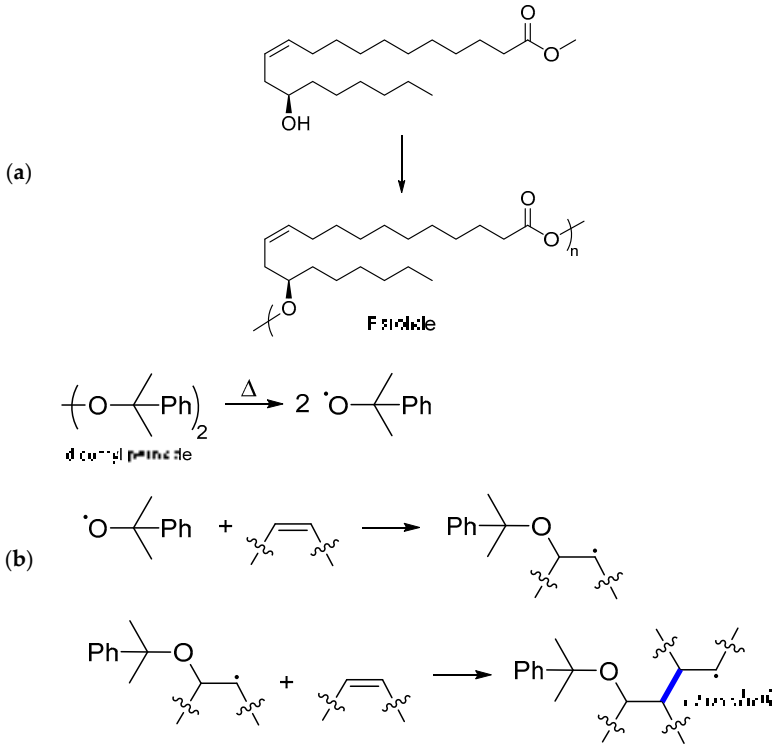


Figure 21. (**a**) Formation of estolide from methyl ricinoleate containing olefinic linkages in the backbone that can subsequently undergo radical crosslinked by vulcanization (analogous to Figure 20a) or by action of dicumyl peroxide (**b**).

In a similar study, Ebata and coworkers investigated castor oil derivatives as monomers for eventual inclusion into sulfur-vulcanized thermosetting elastomers (Figure 22) [102]. Such bio-derived thermosets were envisioned as potential replacements for conventional rubber monomers. The initial step of the process was to subject methyl ricinoleate to lipase-catalyzed condensation polymerization. This process afforded readily-processable polymers according to Figure 22. This method allowed some control over molecular weight, and polymers having M_w of 52 and 101 kDa were prepared to assess the influence of molecular weight on properties. Following their synthesis, these polymers were crosslinked with sulfur by addition of stearic acid, zinc oxide, carbon black, and other sulfur-based crosslinking agents (Figure 22). The cured materials could then be fabricated into films using a thermal press. The resulting films exhibited good hardness (up to 48 A), an ultimate tensile strength of up to

6.91 MPa, and elongation at break of up to 350%. The best physical properties were observed with the higher molecular weight polymer.

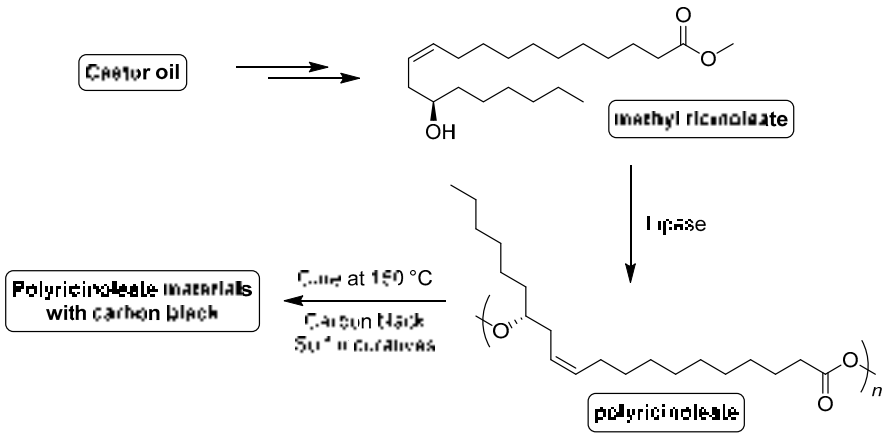


Figure 22. Production of polyricinoleate thermosetting elastomer.

Thus far, the studies discussed in this section have illustrated the toughening of fatty acid-derived polymers by traditional vulcanization by addition of small percentages of sulfur (or other sulfur-containing curatives). More recently, the utility of inverse vulcanization of fatty acids with majority component sulfur has been explored. For example, Smith and coworkers reported the inverse vulcanization of oleic acid and sulfur in varying ratios [92]. The inverse vulcanization of oleic acid and sulfur led to copolymers $\mathbf{ZOS_x}$, where x is the weight percent of sulfur in the monomer feed, varied from 8 to 99 (Figure 23a). Heating sulfur with organics at high temperatures can release H_2S gas, which is highly toxic even at low concentrations. In this study, the authors found that doing the reaction in the presence of ZnO effectively suppressed H_2S generation.

Infrared spectroscopy and ^{1}H NMR spectrometry were used to confirm the consumption of alkene units in the oleic acid starting materials, and thermal techniques, such as TGA and DSC, were used to show the presence of polymeric sulfur in the materials, as indicated by a T_g in the DSC at −40 °C. Perhaps the most interesting results of the study are indicated in the mechanical properties. Temperature scanning DMA in single cantilever mode was undertaken from −60 °C to +60 °C. It was found that with the addition of one percent of oleic acid into the materials ($\mathbf{ZOS_{99}}$), the storage modulus of the material increased almost 8-fold when compared to elemental sulfur. These materials also showed thermal healing ability; when the surfaces of the materials were scratched, the gentle heating of the materials at 100 °C for a short time allowed the scratch to heal (Figure 23b). The materials also showed the ability to be recycled at least four times without the loss of strength, as determined by the storage modulus.

The inverse vulcanization of technical grade and pure linoleic acid ($\mathbf{ZLS_x}$ and $\mathbf{ZPLS_x}$, respectively, where x = weight percentage of feedstock sulfur) was similarly probed by Smith and coworkers (Figure 24) [91]. Technical grade linoleic is a blend of many fatty acids, with the majority component being linoleic acid, followed by primarily oleic acid and a small percentage of short and long chain, saturated, and unsaturated fatty acids. A noteworthy aspect of this work was thus to compare how the blend of fatty acids performed compared to a pure linoleic acid sample as a monomer for inverse vulcanization. Realizing useful polymers from fatty acid mixtures would improve their affordability. The $\mathbf{ZLS_x}$ and $\mathbf{ZPLS_x}$ polymers were thus evaluated for physical and mechanical properties. The polymers were thermally stable at high temperatures (ranging from 231 to 273 °C), and the technical grade-derived materials boasted higher T_d than the analogous pure linoleic acid-derived materials. Some of the materials with higher organic content were crosslinked to such a degree that thermosets were formed, precluding their recyclability or thermal healing by the methods described.

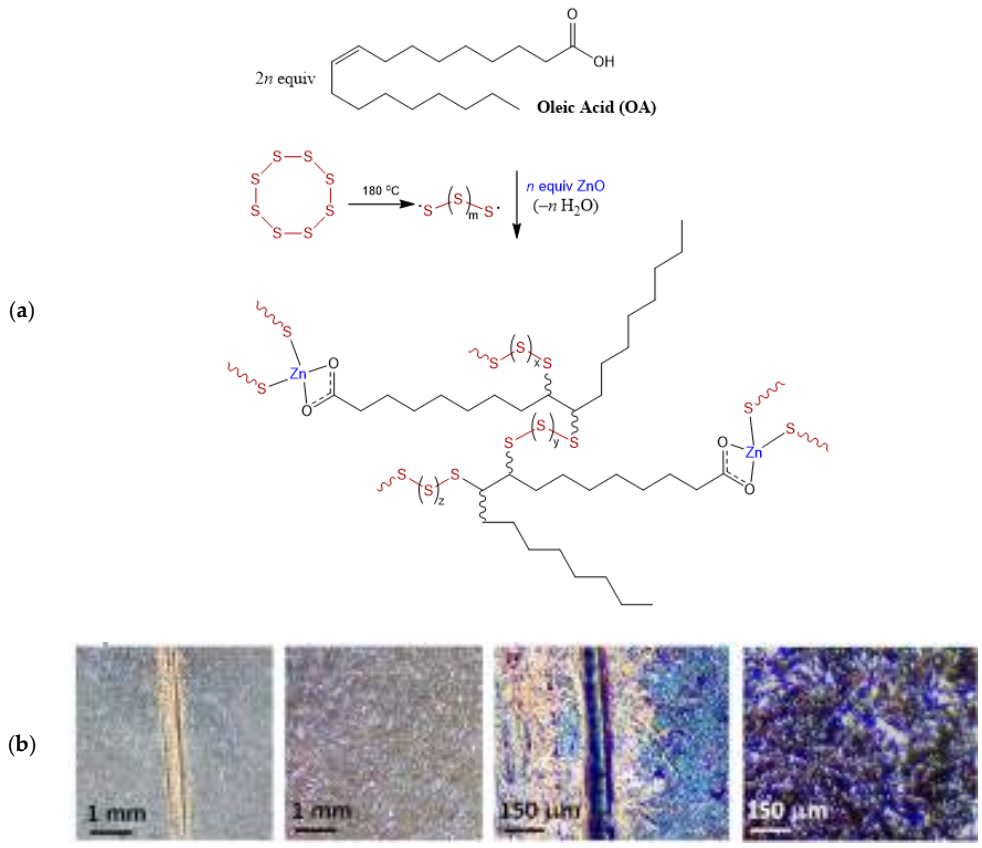


Figure 23. (**a**) Synthesis of $\mathbf{ZOS}_x$ materials. (**b**) Optical micrographs of $\mathbf{ZOS}_{96}$ before and after thermal annealing at 100 °C for 5 min. Reprinted with permission from reference [92]. Copyright 2019 John Wiley and Sons.

The $\mathbf{ZLS}_x$ and $\mathbf{ZPLS}_x$ polymers that were remeltable were subjected to DMA from −60 to +60 °C. As the sulfur content increased in the materials, the storage and loss moduli decreased. This is expected, as elemental sulfur is a weak and brittle material. Flexural stress–strain analysis was also performed on these materials at room temperature. While these materials exhibited moderate flexural moduli and strength, most interesting was that the materials could withstand over 20% of strain. In contrast, similar materials made from lignocellulosic waste can only be deformed by <3% strain before breaking.

In the work discussed above, Smith and coworkers noted that the synthesis of polymers using oleic acid and elemental sulfur could be carried out in the presence of zinc oxide to suppress H_2S gas evolution. Zinc oxide is not sustainably sourced, however, and thus an alternative was sought to function as the base/H_2S-supressing agent in this reaction [90]. For this purpose, Portland cement or Pozzalanic cements were considered to supplant the ZnO.

Portland cement (**PC**), along with fly ash (**FA**), ground granulated blast furnace slag (**GGFBS**), metakaolin (**MK**), and silica fume (**SF**) were reacted with oleic acid and elemental sulfur to form $\mathbf{YOS}_{90}$, (where **Y** is the cementitious material and all materials are comprised by 90 weight percent of feedstock sulfur). Each of the materials synthesized was remeltable and subjected to compressive strength and acid resistance testing. The compressive strengths of $\mathbf{ZOS}_{90}$, $\mathbf{FAOS}_{90}$, and $\mathbf{PCOS}_{90}$ were similar to that of ordinary Portland cement (OPC), with $\mathbf{PCOS}_{90}$ exceeding the strength of OPC. The other materials were less than 70% of the strength of OPC. Flexural strength and moduli were also evaluated using DMA, but these values were notable lower than that of OPC. One of the interesting findings in this study is that the materials are resistant to oxidizing acids like sulfuric acid, as assessed by strain-strain analysis of these materials before and after soaking in 0.5 M H_2SO_4 for 30 min. Two of the materials ($\mathbf{GGBFSOS}_{90}$ and $\mathbf{MKOS}_{90}$) experienced no loss in flexural modulus after the acid challenge (Figure 25). For comparison, after soaking OPC in the same acidic conditions it completely deteriorates,

and its flexural strength cannot be measured. The sulfur-bearing materials also experience enhanced flexibility after the acid challenge, with some able to experience up to ~30% strain before breaking.

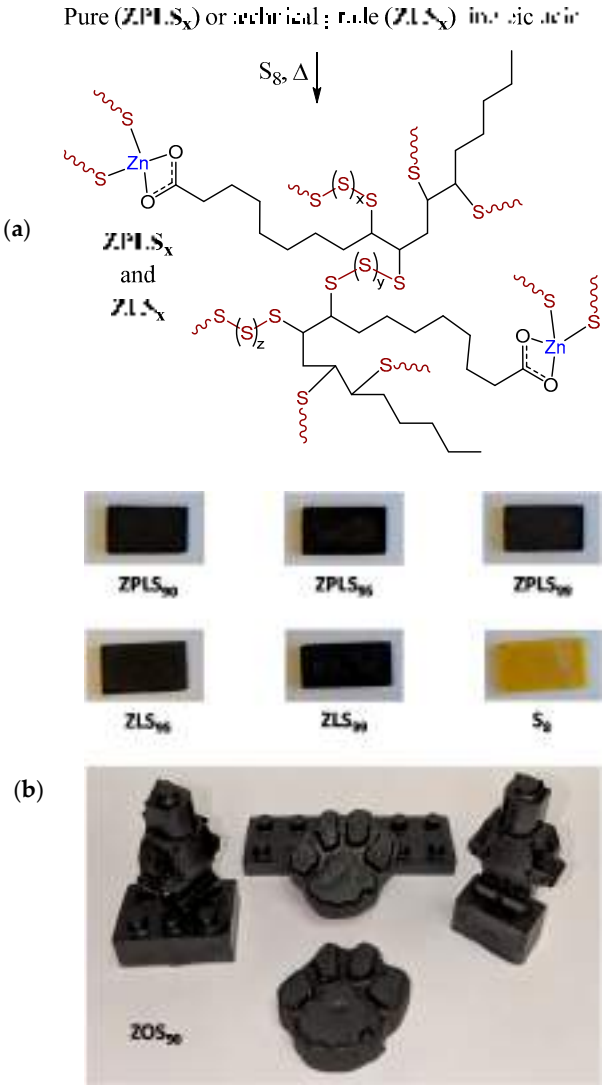


Figure 24. Preparation of **ZLS**$_x$ and **ZPLS**$_x$ (**a**) and photos (**b**) of the materials. Reprinted with permission from reference [91]. Copyright 2020 John Wiley and Sons.

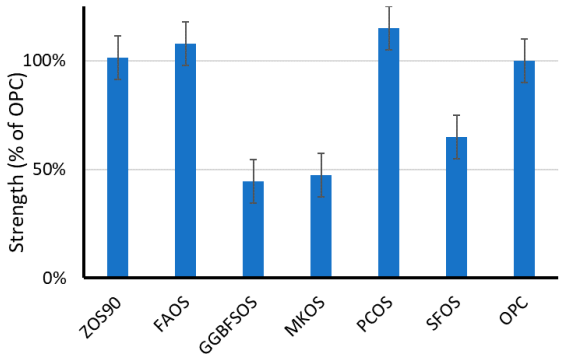


Figure 25. Compressive strength of sulfur cement materials, normalized to the strength of ordinary Portland cement. Reprinted with permission from reference [90]. Copyright 2020 Elsevier.

4. Recycling and Environmental Stability of Organosulfur Polymers

Approaches to recycle organosulfur polymers are in their nascent stages of development as compared to the well-studied routes to more widely-used petrochemical plastics. We have recently reviewed the chemical recycling routes to polyolefins and polyethylene terephthalate with comparison to some of the emerging, thermally recyclable high sulfur-content materials discussed herein [10]. Many organosulfur polymers can be thermally processed or healed by merit of the thermal reversibility of S–S bond formation [103–107]. The polymers prepared by inverse vulcanization, for example, can sometimes be recycled over a dozen cycles without loss in mechanical properties by simply melting the material down and recasting the material into new molds or by extrusion [63,91,92]. The ability of these high sulfur-content materials to retain their strength after so many thermal processing cycles is a notable advantage, as it stands in sharp contrast to the behavior of common the existing petrochemical plastics. Polyethylene terephthalate, for example, exhibits initial strain at break of 42% that plummets to only 0.7% after just the fifth thermal processing cycle [108].

However, the simple melt processing route to recycling organosulfur polymers is limited to the thermoplastics. Quite recently, however, thermal compression molding techniques have been developed whereby additive manufacturing and recycling of ground powders was demonstrated for thermosetting organosulfur polymers comprising large proportions of triglyceride comonomers [74]. A chemical approach that relies on amine- or phosphine-induced S–S bond metathesis has also proven highly effective for recycling organosulfur polymers that are not remeltable [73].

In addition to recycling of organosulfur polymers into new items, some efforts have been undertaken to reclaim organic and sulfur small molecular materials through pyrolytic disintegration of the polymers. Along with typical organic pyrolysis products (benzene derivatives, oligoolefins, ethylene, and propylene, for example), the ultimate fate of the sulfur from these species is generally SO_2, with some contribution of CS_2 [109,110]. Although SO_2 is toxic, it can be reclaimed as elemental sulfur through catalytic processes or it can be further oxidized to sulfuric acid [111,112].

In terms of the environmental stability and fate of organosulfur polymers, there is good evidence that higher sulfur content materials are quite stable to oxidation, as many have proven impervious to oxidizing acid [88,94,96]. Organosulfur coatings and treatments have even been used to protect metal and mineral cement installations in factories where oxidative damage from oxidizing acids are otherwise problematic [113–119].

However, little work has been done to elucidate the ultimate fate of any of the materials described herein via biodegradation mechanisms. This is clearly an area that deserves additional investigation if these materials are to have a place in green building technologies. Early studies have proven that using some organosulfur polymers as elements of time-release fertilizers could enhance the growth of food crops such as tomatoes that benefit from acidic soil [82]. This growth enhancement is attributable to the slow production of sulfuric acid by sulfur-metabolizing bacteria, providing one environmental fate of these materials. Much work has yet to be done in this area.

5. Conclusions and Outlook

The examples delineated in this review demonstrate the wide range of synthetic methodologies available for the modification of alcohol, alkene, alkyne, ester, and carboxylic acid sites in fatty acids. One of the critical hindrances to commercial applications for fatty acid-derived polymer production is that the internal alkenes that are present in most of the naturally-occurring unsaturated fatty acids have lower reactivity when compared to traditional olefin monomers such as ethylene, acrylate, and styrene derivatives. The development of new catalysts that are more active and that exhibit high tolerance for polar functional groups must be an area of continued development to access readily-prepared fatty acid polymers. Existing high activity metathesis catalysts with good functional group tolerance have proven to be some of the more successful in this regard, as illustrated in some of the examples discussed herein. The use of radical routes and click chemistry, as illustrated by the thiol-ene and

thiol-yne reactions herein, is another pathway to fatty acid polymers that holds great promise for ongoing development that does not require the development of new transition metal catalysts.

In addition to the development of protocols and catalysts noted above, and by carefully considering the foregoing examples in light of the current need for more sustainable and affordable materials having mechanical strength profiles on par with current commercial goods, several specific areas can be identified for further development. First, many of the fatty acid-derived polymers that have been reported to date contain olefinic linkages in their backbones or as side chains. All of these polymers that can be affordably produced should be exposed to vulcanization under different conditions (amount of curative and vulcanization time) to assess the potential improvements in strength. This approach has the potential to yield high toughness materials that will almost certainly be competitive with synthetic rubber based on the early studies discussed here. A drawback to this strategy is that, like traditional tire rubber, the materials may be difficult to recycle at their initial end of service. More easily-recyclable materials obtained by the inverse vulcanization of the olefin-bearing polymers with varying percentage of sulfur should thus also be targeted in future work. Such high sulfur-content materials may be considerably more environmentally benign given initial work on their use as fertilizers [82].

Perhaps the most obvious drawback of the majority of materials discussed herein is that they by and large require an isolated, pure fatty acid for their preparation, with the exception of some of the preliminary work described for technical grade fatty acid mixtures. Clearly, ethical and practical aspects must be weighed when considering the ramification of using food-grade precursors to prepare polymers when there is also a growing challenge to feed a growing global population. Tremendous advances in both economy and ecology of fatty acid derived polymeric material production could be achieved if crude waste materials that are high in free fatty acid content but that are no longer high value food sources—waste cooking grease, brown grease, trap grease, and acid oil, for example—could be leveraged as precursors to materials having useful property profiles.

Author Contributions: Conceptualization, A.D.S.; resources, A.G.T.; writing—original draft preparation, A.D.S.; writing—review and editing, all authors. All authors have read and agreed to the published version of the manuscript.

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