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Polymer Chemistry

Thiol–Ene Click Chemistry**

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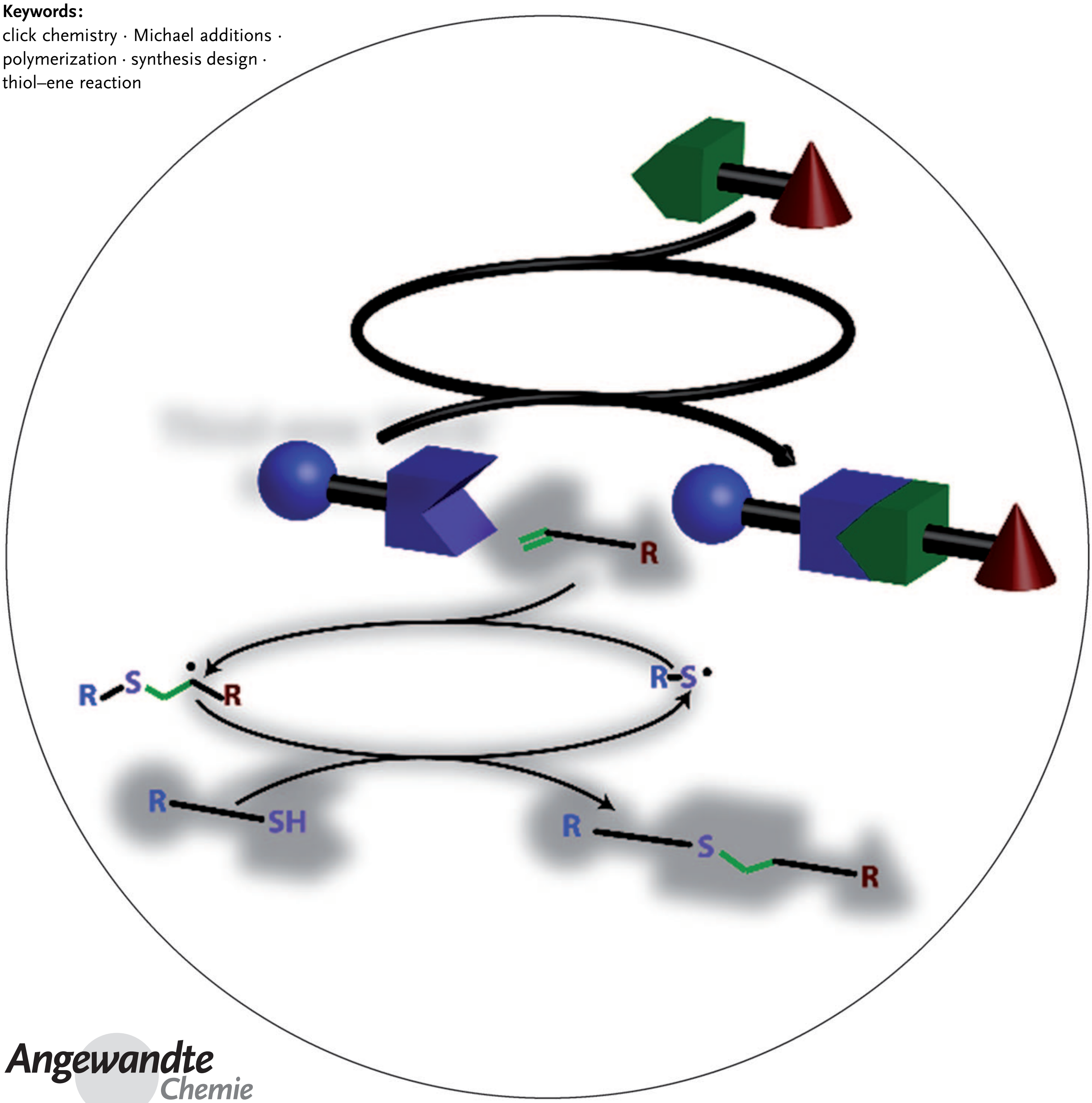


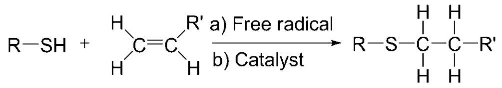
Following Sharpless' visionary characterization of several idealized reactions as click reactions, the materials science and synthetic chemistry communities have pursued numerous routes toward the identification and implementation of these click reactions. Herein, we review the radical-mediated thiol–ene reaction as one such click reaction. This reaction has all the desirable features of a click reaction, being highly efficient, simple to execute with no side products and proceeding rapidly to high yield. Further, the thiol–ene reaction is most frequently photoinitiated, particularly for photopolymerizations resulting in highly uniform polymer networks, promoting unique capabilities related to spatial and temporal control of the click reaction. The reaction mechanism and its implementation in various synthetic methodologies, biofunctionalization, surface and polymer modification, and polymerization are all reviewed.

From the Contents

1. Click Reactions: Introduction

In 2001, Sharpless et al.[1] described a new concept for conducting organic reactions, which was based upon the premise that organic synthesis should take advantage of the long history of development and progress during the 20th century and focus attention on highly selective, simple orthogonal reactions that do not yield side products and that give heteroatom-linked molecular systems with high efficiency under a variety of mild conditions. Several efficient reactions, which are capable of producing a wide catalogue of functional synthetic molecules and organic materials have been grouped accordingly under the term click reactions. Characteristics of modular click reactions include a) high yields with by-products (if any) that are removable by non-chromatographic processes, b) regiospecificity and stereospecificity, c) insensitivity to oxygen or water, d) mild, solventless (or aqueous) reaction conditions, e) orthogonality with other common organic synthesis reactions, and f) amenability to a wide variety of readily available starting compounds. Molecular processes considered to fit all or most of these criteria include certain cycloaddition reactions, such as the copper(I)-catalyzed 1,3-dipolar cycloaddition of azides and alkynes, and nucleophilic ring-opening reactions. Copper-catalyzed azide/alkyne click reactions in particular have received the most attention, with applications extending to the synthesis of biomedical libraries, dendrimer preparation, synthesis of functional block copolymers, cross-linking of adhesives for metal substrates (copper/zinc), synthesis of uniformly structured hydrogels, derivatization of cellular surfaces, the in situ preparation of enzyme inhibitors, and many others.[2–5] Extensive literature reports of the use of azide/alkyne chemistry[2–5] have clearly demonstrated the tremendous applicability and value of quantitative and orthogonal click chemistry, whilst at the same time clearly pointing out the need for additional click reactions that are able to be implemented and exploited for synthetic and materials development.

Based on the premise established for click reactions, and as exemplified by the azide–alkyne chemistry, we focus attention on the relatively weak sulfur–hydrogen bonds of thiols that result in a plethora of chemical reactions with nearly quantitative yields, with an ability to initiate these reactions by a variety of methods under mild conditions. Highly efficient reactions of thiols with reactive carbon–carbon double bonds, or simply "enes", were noted in a much cited article in 1905, which clearly indicated that the general concept of reactions between thiols and enes was well known in the early 1900s.[6] During the last century, two thiol reactions of particular note emerged (generalized in Scheme 1): thiol–ene free-radical addition to electron-rich/electron-poor carbon–carbon double bonds, and the catalyzed thiol Michael addition to electron-deficient carbon–carbon double bonds.



Scheme 1. General thiol–ene coupling by a) free-radical and b) Michael addition reactions. In both idealized reactions, a single thiol reacts with a single ene to yield the product.

The reaction of thiols with enes, whether proceeding by a radical (termed thiol–ene reaction) or anionic chain (termed thiol Michael addition), carry many of the attributes of click reactions. These attributes include achieving quantitative

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[**] This manuscript is dedicated to Charles Hoyle, who passed away on September 7, 2009, while working on revisions to this manuscript. His work on thiol–ene chemistry and his passion and enthusiasm for that chemistry was legendary. He was a dedicated husband, father, and advisor, and a brilliant scientist who is missed by all who knew him.

yields, requiring only small concentrations of relatively benign catalysts, having rapid reaction rates with reactions occurring either in bulk or in environmentally benign solvents over a large concentration range, requiring essentially no clean up, being insensitive to ambient oxygen or water, yielding a single regioselective product, and the ready availability of an enormous range of both thiols and enes. This exceptional versatility and its propensity for proceeding to quantitative conversions under even the mildest of conditions makes thiol–ene chemistry amenable to applications ranging from high performance protective polymer networks to processes that are important in the optical, biomedical, sensing, and bioorganic modification fields. Accordingly, both the thiol–ene radical and thiol Michael addition reactions are now routinely referred to in the literature as thiol click reactions.

The chemistry of thiols, whether radical- or catalyst-mediated, is certainly influenced by the basic structure of the thiol. Four prominent thiol types typically encountered in literature reports include alkyl thiols, thiophenols, thiol propionates, and thiol glycolates (Figure 1a). Both types of thiol click reaction are extremely efficient; radical addition has been known to proceed by an efficient step-growth chain process for several decades.[7,8] There have been several reviews of thiol–ene radical chemistry and polymerization,[9–11] the latest being in 2004. By 2004,[11] it had been plainly and extensively demonstrated that thiol–ene networks serve as benchmark polymer materials that can react to form highly uniform glasses, elastomers, and adhesives. Any non-sterically hindered terminal ene is capable of participating in the radical-mediated thiol–ene process, with electron-rich (vinyl ether) and/or strained enes (norbornene) reacting more rapidly than electron-deficient enes. Cross-linked polymers formed from these systems are the most ideal homogeneous network structures ever formed by free-radical polymerization, with narrow glass transition regions[10] and extremely low polymerization shrinkage stress.[11]

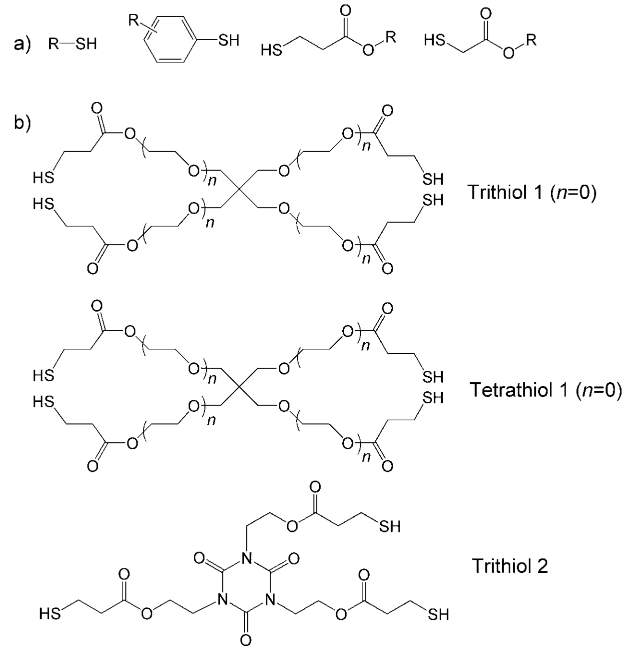


Figure 1. a) Common alkyl thiols. (b) Typical multifunctional thiols used in thiol–ene polymerization processes.

Many of the basics of thiol–ene chemistry were well defined by the early 2000s, and their use for relatively simple materials applications, such as protective coatings and films, were amply touted. However, there remained a tremendous potential for incorporating thiol–ene chemistry into a wide variety of newly emerging technologies. The particular benefits of the thiol–ene reaction in the molecular and spatial control of polymer structure had yet to be fully realized. Furthermore, there still remained significant questions about the kinetics of the free-radical thiol–ene reaction that, when answered, would suggest many innovative applications. Accordingly, this Review focuses on the free-radical thiol–ene reaction, which has been a particular focus of our research for almost a decade, though we will also present selected thiol Michael addition reactions as appropriate to place the thiol–ene reaction in the broader scheme of thiol click reactions. The mechanism of the reaction and recent advances in thiol–ene kinetics will be presented, along with a host of new applications based upon the rapid, highly efficient nature of the thiol–ene reaction.

Charles E. Hoyle studied chemistry at Baylor University (B.S. 1972) and completed his doctorate with Professor Fred Lewis at Northwestern University on small-molecule photochemistry. After researching at the University of Toronto with Jim Guillet, he joined Armstrong World Industries in Lancaster, PA in 1978, where he investigated polymer photodegradation and photoinitiated polymerization. In 1983, he was appointed to the University of Southern Mississippi, where he focused on all aspects of polymer photochemistry, and in particular thiol–ene reactions. Professor Charles Hoyle passed away on September 7, 2009 during the finalization of this manuscript. He will long be remembered by his students, colleagues, and the professional community at large.

Christopher N. Bowman studied Chemical Engineering at Purdue University (B.S. 1988) After receiving his Ph.D. in 1991, he was made Assistant Professor at the University of Colorado in Denver in 1992. He has focused on the fundamentals and applications of cross-linked polymers formed by photopolymerization reactions, and is currently the Patten Endowed Chair of the Department of Chemical and Biological Engineering, is a Clinical Professor of Restorative Dentistry, and serves as Co-Director of the NSF/Industry Cooperative Research Center for Fundamentals and Applications of Photopolymerizations.

2. Thiol–Ene Click Reactions: Basic Description

2.1. General Characteristics of Radical Thiol–Ene Click Reactions

2.1.1. Overview

Classical radical-based photopolymerization involving acrylates and methacrylates offers both spatial and temporal control by means of a chain-growth mechanism, and this polymerization is widely utilized for a range of applications, from coatings to dental materials, contact lenses, and photolithographic processes.[12,13] There exists significant interest in expanding these technologies for applications in nanotechnology, biomaterials, high-resolution lithography, selective functionalization of preformed linear polymers, surface functionalization, electro-optics, ultra-low-stress networks, and high-impact energy-absorbing thermosets. Unfortunately, classical photopolymerization reactions are plagued by several critical problems, including inhibition by oxygen,[14–16] complicated volume relaxation and stress development,[17,18] complex polymerization kinetics,[19–21] and the formation of highly heterogeneous polymers/networks.[22–24]

As has been described,[9–11] light-mediated thiol–ene radical reactions effectively combine the classical benefits of click reactions with the advantages of a photoinitiated process, which can be activated at specific times and locations, resulting in a powerful method for chemical synthesis and tailorable materials fabrication. In the case of multifunctional thiols and enes, of which representative structures of typical, commercially available molecules are depicted in Figure 1 and 2, cross-linked polymer materials with high conversions are formed. The overall simplicity, robustness, and mechanism of the thiol–ene photopolymerization reaction addresses each of the critical limitations of traditional photoinitiated systems by forming a homogeneous polymer network through a controllable combination of step-growth and chain-growth processes, with significantly simplified polymerization kinetics, reduced shrinkage and stress, and insensitivity to oxygen inhibition. These distinct advantages have made the thiol–ene photopolymerization reaction the focus of extensive fundamental research and also practical implementation in a number of novel applications in the last few years. Through spatial and temporal control of the photoinitiation component, the overall rate, extent, and occurrence of the thiol–ene click reaction have been successfully manipulated to obtain polymeric materials with an exceptional range of properties. Thiol-ene radical reactions have recently been extended to a variety of synthetic processes for basic chemical synthesis, polymeric materials modification, and fabrication of a wide range of polymeric materials and new applications, which include optical displays, nano-imprinting, holographic diffractive materials, microfluidic devices, high-impact energy-absorbing devices, complex surface patterns, optical switching arrays, and functionalized linear polymers.

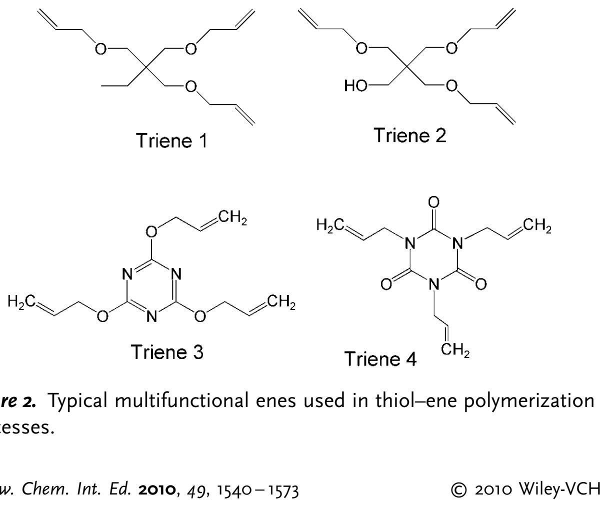

Triene 1
Triene 2
Triene 3
Triene 4

Figure 2. Typical multifunctional enes used in thiol–ene polymerization processes.

Thiol–ene networks have a tremendous advantage over traditional networks in that they form rapidly and quantitatively under ambient atmospheric conditions to yield nearly ideal, uniform polymer networks that are not plagued by the heterogeneity common in conventional radical photopolymerization reactions. Figure 3 presents the stark contrast in network structures and the resulting glass transition behavior that are achieved in a typical photopolymerized thiol–ene network in comparison with a conventional dimethacrylate-based network. The entire glass transition occurs over a total range of 30–50 °C for the thiol–ene polymer network, compared to more than a 200 °C range for the heterogeneous methacrylate network. This exceptional network uniformity imparts highly desirable mechanical behavior, particularly in the areas of energy absorption, for which these materials are employed in the vicinity of their glass transition (Section 3.8).

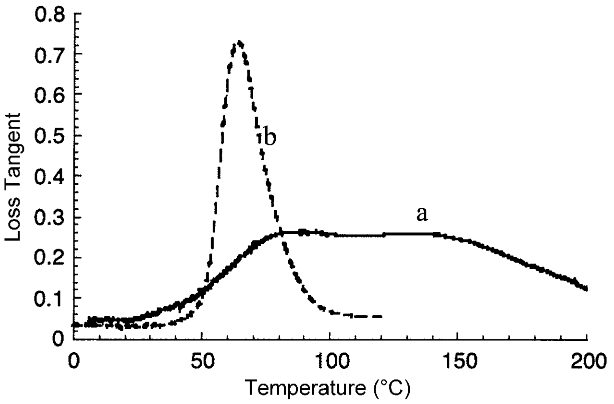
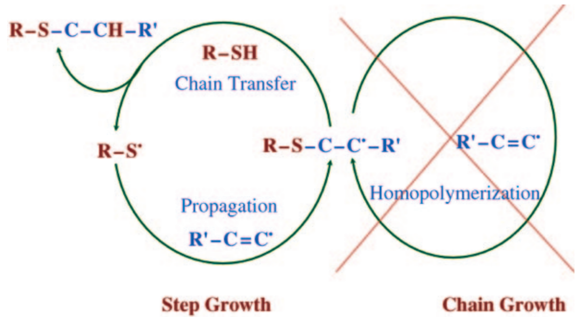


Figure 3. Loss tangent as a function of temperature for photopolymerized films from a) a mixture of the dimethacrylate made from the diglycidyl ether of bisphenol A and methacrylic acid (70 wt %) and triethyleneglycol dimethacrylate (30 wt %), and b) stoichiometrically mixed tetrathiol 1 ($n = 0$)/triene 4 (----). Reproduced from Ref. [200] with permission from Elsevier.

2.1.2. Free-Radical Thiol–Ene Kinetics

The ideal thiol–ene radical reaction revolves around the alternation between thiyl radical propagation across the ene functional group and the chain-transfer reaction, which involves abstraction of a hydrogen radical from the thiol by the carbon-centered radical (Scheme 2). In the ideal purely step-growth thiol–ene reaction, no homopolymerization (i.e., chain growth), in which the carbon-centered radical propagates through the ene moiety, occurs; conversions that



Scheme 2. The idealized free-radical thiol–ene reaction with alternating chain transfer and propagation. Note that an analogous mechanism also applies to the thiol–Michael addition reaction when undergoing an anionic chain process if the radicals are replaced by their anionic counterparts.

approach 100 % are obtained unless mass-transfer limitations prevent such from being achieved. The net reaction, therefore, is simply the combination of the thiol and ene functional groups, which causes the molecular weight and network structure to evolve in a manner that is identical to other step-growth polymerization reactions whilst simultaneously enabling all of the benefits of a rapid, photoinitiated radical-mediated process.[10,11,25–30] The addition of the thiol across the ene double bond (Scheme 2) is exothermic, with reaction enthalpies ranging from $-10.5\ \text{kcal mol}^{-1}$ for the electron-rich vinyl ether double bond to $-22.6\ \text{kcal mol}^{-1}$ for the electron-poor double bond of an *N*-alkyl maleimide.[31] For a given thiol, electron-rich enes polymerize much more rapidly than electron-poor enes (see references [10] and [11] for a detailed discussion involving a wide range of enes). Reduced rates and conversions are obtained for 1,2-substituted internal enes, which is presumably due to steric considerations and a reversible addition of the thiyl radical to the internal ene.[32,33] For ideal thiol–ene reactions, such as those observed for norbornenes and vinyl ethers,[26] no homopolymerization or chain growth is observed, thus implying that the overall rates of chain transfer and propagation must be essentially identical.

One of the great challenges of the thiol–ene reaction for many years had been in delineation of the rate-determining step and detailed kinetics of the two-step sequential chain process presented in Scheme 2. Because of the cyclical nature of these two steps, and the requirement that their overall rates are equal, if one of the reaction steps is inherently slower and possesses a lower kinetic constant, that reaction step becomes the rate-limiting step in the reaction process, and the relative concentration of the two radical species reflects that difference. The following relationships (1) to (3) summarize[34] the

$$\begin{gathered} k_{CT} \cong k_P \\ [\text{R-S}^\bullet]/[\text{R-S-C-C}^\bullet\text{-R}'] \approx 1 \text{ and } R_p \alpha [\text{R-SH}]^{1/2}[\text{R}'\text{-C=C}]^{1/2} \end{gathered} \tag{1}$$

$$\begin{gathered} k_{CT} \ll \text{k}_\text{p} \\ [\text{R-S}^\bullet]/[\text{R-S-C-C}^\bullet\text{-R}'] \ll 1 \text{ and } R_p \alpha [\text{R-SH}]^1 \end{gathered} \tag{2}$$

$$\begin{gathered} k_{CT} \ll \text{k}_\text{p} \\ [\text{R-S}^\bullet]/[\text{R-S-C-C}^\bullet\text{-R}'] \gg 1 \text{ and } \text{R}_\text{p} \alpha [\text{R}'\text{-C=C}]^1 \end{gathered} \tag{3}$$

expected overall reaction rate (R_p) behavior in the cases for which 1) the kinetic constants of the two reactions are approximately equal [Eq. (1)], 2) chain transfer is the slow reaction[Eq. (2)], and 3) the thiyl radical propagation is the slow reaction[Eq. (3)]:

where k_{CT} is the chain transfer rate constant, k_p is the propagation rate constant, [R-SH] is the thiol concentration, [R′-C=C] is the ene concentration, [R-S•] is the thiyl radical concentration, and [R-S-C-C•-R′] is the carbon-centered radical concentration. In each case, the reaction is first order overall in the monomer concentration; however, the detailed dependence is dictated by the nature and reactivity of both radicals and the chemical nature of the thiol and ene functional groups. Thiols with less abstractable hydrogen atoms, such as alkyl thiols, will tend to have reduced chain transfer rates [Eq. (2)], and therefore rate-limiting chain-transfer reactions, whereas enes that are less reactive will tend to cause the propagation reaction to be slow and rate limiting [Eq. (3)].[26] References [9–11] provide insight into the role of the thiol type (see Figure 1 a) on thiol–ene reactivity and kinetics. The ene structure dictates whether the reaction is chain-transfer-limited and first order in thiol concentration, as is the case for allyl ethers, to being propagation-limited and first order in ene concentration, as is the case for vinyl silazanes.[26] Norbornene and vinyl ethers have very similar propagation and chain transfer rates, and resulted in half-order dependence on both the thiol and ene concentration.[26] Indeed, a large range of thiol and ene functional groups have been evaluated both by conventional and high-throughput methods[33,35–37] and ranked according to their relative reactivity, with norbornenes and vinyl ethers being the most reactive and methacrylate, acrylonitrile, styrene, maleimides and conjugated dienes (in order of decreasing reactivity) the least reactive. This work complimented previous reports on the relationship between thiol–ene kinetics and the thiol and ene functional types.[9–11] Roper et al. found terminal enes to be the most reactive, with internal 1,2-substituted enes exhibiting a much lower overall reaction rate.[33]

Because of the unique reaction mechanism and the extremely rapid termination reaction in these systems, classical experimental techniques and their corresponding analysis are not suitable for detailed kinetic analysis. Therefore, Reddy et al. developed a modified rotating-sector-like experimental technique and a corresponding analysis method for evaluating the kinetics of alternating chain-transfer and propagation reactions. The propagation and chain-transfer kinetic constants range from 10^5 to $10^6\ \text{L mol}^{-1}\text{s}^{-1}$, and the exact values depend significantly on the monomer structures.[34,38] In contrast to conventional photopolymerizations, for which chain-length issues, diffusion and reaction diffusion limitations to termination, low conversion gelation and vitrification all complicate the kinetics and limit the final conversion, the thiol–ene photopolymerization kinetics remain consistent over a much greater range of polymerization. This near-ideal behavior, resulting from delayed gelation, relatively low molecular weight oligomeric species up until gelation, and generally lower cross-link densities has been modeled[38–41] in regards to both the kinetics and evolution of the polymer network structure.

The original photoinduced thiol–ene photopolymerizations utilized abstraction-type photoinitiators, such as benzophenone; these utilized the excited triplet state of the benzophenone to abstract a hydrogen from the thiol and thus initiate the polymerization.[10,11,28] Visible-[42,43] and ultraviolet-light-sensitive[44] type I initiators with excellent photoinitiation efficiency are better choices owing to improved initiation efficiency. The selection of appropriate excitation wavelength and monomer combinations can also eliminate the need for an initiator entirely.[29,30,45,46] Initiator-free thiol–ene photopolymerization reactions[46] have enabled traditional curing of optically clear films and also the production of large, transparent, almost crack-free samples to be produced, including spheres of various sizes up to 25 cm and tubes of lengths up to 60 cm in size.[46] This task is nearly impossible to achieve with conventional photoinitiators or other photopolymerized systems. An additional advantage of initiatorless photopolymerizations is the ability to polymerize thick samples without the generation of any colored or volatile by-products. When monomeric species are responsible for absorption and initiation, the absorbing species are bleached by the polymerization reaction, enabling the final polymer product to be transparent, even at the initiating wavelengths. The photoinitiator-free polymerization behavior and thick-film polymer samples thus produced are presented in Figure 4; the initiation and subsequent polymerization rate when initiated at 254 nm is quite high, with the polymerization complete in relatively short exposure times.[29] Although the thiol–ene reaction has primarily been the subject of photoinitiation, this reaction is a radical-mediated process, and as such, any technique that is appropriate for generating radicals in conventional polymerizations is also suitable for initiating it. Indeed, thiol–ene polymerizations induced by thermal initiators, as demonstrated by Cook and co-workers, are not uncommon.[47]

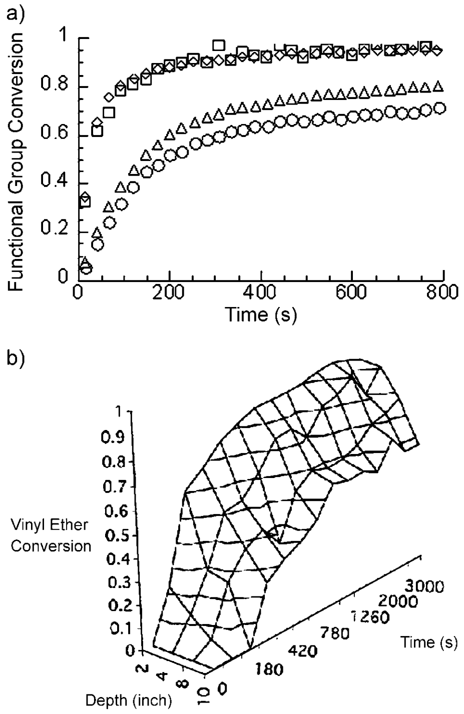
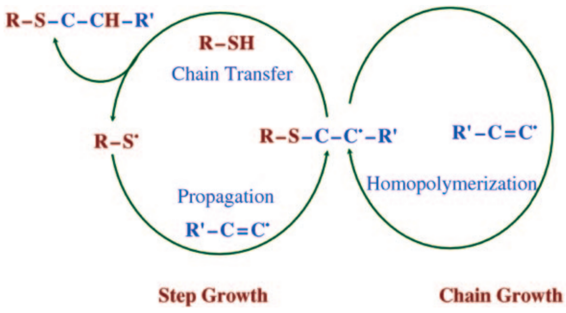


Figure 4. (a) Reaction progress for photoinitiator-free polymerizations (1:1 functional group mixture): a) Tetrathiol 1 ($n=0$) (□) with triethyleneglycol divinyl ether (◇) and tetrathiol 1 ($n=0$) (○) with triene 2 (△), b) tetrathiol 4 with triethylene glycol divinyl ether shown additionally with the degree of curing. Reproduced from Ref. [29] with permission from the American Chemical Society.

In summary, and in contrast to conventional free-radical chain-growth polymerizations, the kinetics of thiol–ene free-radical polymerization are quite simple in most cases until high functional group conversions are attained. However, as will be discussed in Section 2.1.3, the use of multiple enes with a single multifunctional thiol, and in particular in cases where one of the enes can undergo both homopolymerization and the thiol–ene reaction, does lead to quite complex kinetics and enables the production of highly cross-linked polymer structures with controlled structures.[48] Whilst this behavior complicates matters from a fundamental chemical kinetics point of view, it presents a unique opportunity to tailor polymer networks that is not otherwise possible and which enables the achievement of highly desirable physical and mechanical properties.

2.1.3. *Binary Thiol–Acrylate and Ternary Thiol–Ene–Acrylate Photopolymerizations*

In an effort to extend the physicochemical property range of thiol-containing polymers and polymerizations, the mechanisms, kinetics, and network properties of mixed-mode photopolymerizations have been investigated.[38,45b,48–55] Two distinct approaches have emerged: binary processes involving multifunctional thiols and traditional (meth)acrylates, and ternary systems comprising a thiol, a (meth)acrylate, and an ene that is incapable of homopolymerization. Both approaches involve complex interplay between the various propagation and chain-transfer rates to control the polymerization process and the polymer properties. As shown in Scheme 3, two different reaction cycles are possible: the first involves alternation of chain transfer and propagation, and the second incorporates addition and chain-growth mechanisms. The relative rates of these cycles, which are dictated by



Scheme 3. Cycles showing reactions of thiol–acrylate and thiol–ene–acrylate polymerization, where the active carbon-centered radical can now participate in either chain transfer or an additional propagation reaction.

the chemical properties of the thiol, ene and (meth)acrylate, the component concentrations, and the relative rates, ultimately tailor the final network structure and mechanical/physical properties to a level not achievable by classical photopolymerization processes or even by binary thiol–ene polymerizations.

By combining (meth)acrylates and thiols, a broad range of material properties are accessible from the large number of commercial (meth)acrylates that are available. In comparison to conventional (meth)acrylate homopolymerization, the presence of the thiol imparts profound beneficial attributes. Even a relatively small amount of thiol, typically in the 1–10 wt% range, is sufficient to reduce oxygen inhibition significantly, even in films that are only a few micrometers thick.[56] This behavior enables (meth)acrylates to be cured without the need for a nitrogen atmosphere, expensive initiator combinations, or the extremely high light intensities that are frequently required to overcome oxygen inhibition in purely (meth)acrylic polymerizations. Furthermore, the presence of the thiol delays the gel point conversion and reduces shrinkage. This combination facilitates an improvement in the shrinkage stress that arises during the polymerization and improves the achievable resolution in lithographic applications.[57] For relatively small amounts of thiol (typically 5–20%), these benefits are achieved without significant reductions (Figure 5) in the modulus or glass-transition temperature of the pure (meth)acrylate,[56] whilst at the same time increasing the polymerization rate by over an order of magnitude depending on the oxygen level. The (meth)acrylate polymerization rate enhancement by low concentrations of thiols in the presence of oxygen has been exploited by Crivello and co-workers[58] to polymerize a thiol–acrylate mixture with a visible LED (ca. 470 nm) light source. Furthermore, Pojman and co-workers[59] found that the start time for initiating frontal polymerizations of trimethylolpropane triacrylate (TMPTA) was lowered by an order of magnitude when only 10 mol% thiol was added. Other investigators have demonstrated that the enhanced ability to overcome oxygen inhibition and the control over the network structure facilitates the implementation of thiol–(meth)acrylate polymerization in the formation of hydrogels and tissue engineering matrices, for which polymerizations in the presence of oxygen are necessitated by the clinical environment and the requirement for cell viability.[60–63] Also, the addition of multifunctional thiols to pigmented diacrylates in air[64] results in much higher polymerization rates, thereby reducing the photoinitiator concentration required to obtain a fast, high-conversion polymerization process with a rate acceleration of a factor of about 10. This benefit has tremendous implications for rapid photocuring of highly pigmented systems in which extremely high photoinitiator concentrations are traditionally required to achieve rapid rates.

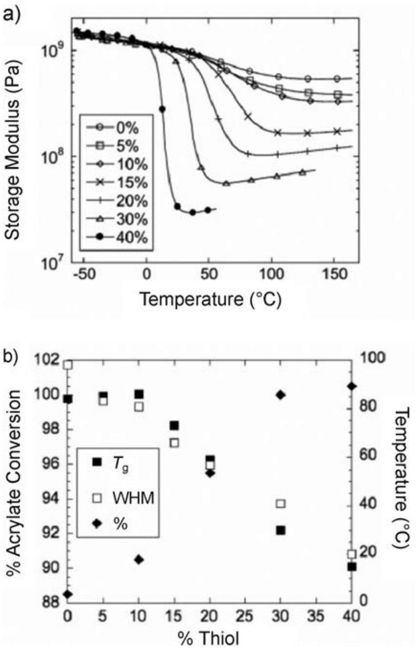


Figure 5. a) Storage modulus as a function of temperature for films photopolymerized from various amounts of tetrathiol 1 ($n=0$) in 1,6-hexanedioldiacrylate. Light intensity 10 mW cm^{-2}, Irgacure 651 concentration 0.1 wt%. b) Glas transition temperature T_g (○), width at half maximum (WHM; □), and acrylate conversion (◆). Reproduced from Ref. [56].

Despite numerous advantages, the binary thiol–acrylate polymerization process is still limited. Although acrylates readily react with the thiol, and the polymerization rate is only minimally affected by the presence of the thiol, the photopolymerization of methacrylate monomers is slowed relative to their acrylate counterparts by the presence of the thiol, thus frequently limiting the final conversion and reducing the desired benefits of the binary combination. Furthermore, for thiol–acrylate polymerizations, the relative kinetics of the chain-transfer and homopolymerization reactions are largely fixed, with little variation as a function of the specific acrylate and thiol utilized.[65] For certain thiol–(meth)acrylate compositions, this limitation results in residual unreacted thiol at the completion of the reaction. In contrast to these binary compositions, ternary thiol–ene–(meth)acrylate systems have been found[38] to overcome these deficiencies of binary systems, thus opening up opportunities for a wide range of advanced materials. In these ternary systems, several opportunities exist for manipulation of the polymerization and polymer properties that are not possible with binary systems. Okay and co-workers[34,40,48,53] modeled the network structural evolution for all combinations of binary and ternary thiol–ene–(meth)acrylate systems and demonstrated that simple changes in the relative concentrations of the species,and the copolymerization reactivity of the ene functional group, could be utilized to control the conversion at the gel point, the cross-linking density, and the network homogeneity of the resulting polymer. Reddy et al. independently measured the kinetic constants for each of the reactions involved in various ternary copolymerizations of thiols, allyl ethers, vinyl ethers, acrylates, and methacrylates, and used these values to predict the complex polymerization kinetics and polymer structure of the ternary system.[54] This work demonstrated that the ternary system was far less sensitive to the functional group stoichiometric ratio, and that nearly equivalent glass transition temperatures T_g could be achieved in a thiol–allyl ether–methacrylate system as for the pure methacrylate system (80 °C vs. 85 °C), whilst reducing the half-width of T_g from 100 °C to 55 °C.[45] Thus, T_g remained constant but the network heterogeneity was significantly lowered.

Along with the uniform, single-phase copolymerization that is possible with ternary systems, the presence of two distinct polymerizable double bonds also enables polymerization-induced phase separation to occur under appropriate conditions. In this process, one of the two vinyl groups preferentially polymerizes early in the reaction, forming a cross-linked network that, if the two materials become incompatible, can cause the second unreacted monomer to phase-separate. Such behavior has been observed for the copolymerization of thiol–allyl ether–methacrylate systems,[51,52] in which the methacrylate both homopolymerizes and copolymerizes with a small amount of the thiol in the initial stages of the reaction, followed by a thiol–ene polymerization of the thiol and allyl ether in the later reaction stages. Ultimately, this behavior results in a significant decrease in the polymerization shrinkage stress; this decrease would not occur in a single-phase polymerizing system. Such behavior is not possible without the presence of at least the two polymerizable double bonds, and it is virtually unique among polymer networks.

The thiol–vinyl ester–acrylate system, in which conjugated vinyl ester and acrylate groups are present on the same reactive species, namely vinyl acrylate, gives rise to unique polymerization behavior. The decrease in electron density on the acrylate and concomitant increase in electron density of the vinyl ester group afforded by the conjugation results in a system in which acrylate homopolymerization and thiol–ene radical chain processes occur simultaneously with little or no vinyl ester–acrylate or thiol–acrylate reactions.[45b]

There are numerous recent experimental and theoretical examples[38,53,66] of ternary thiol–ene–ene systems in which neither of the ene components is a homopolymerizable (meth)acrylate. In this situation, each of the distinct thiol–ene reactions will have different rates that control the network formation, and each ene will have a distinctly different chemical structure, both of which dictate the final properties of the network. For example, a thiol–allyl ether–maleimide network has exceptionally high thermal stability owing to the presence of the succinimide structure in the network.[66]

2.1.4. New Thiol or Ene Monomers for Photocuring

One of the salient features of thiol–ene chemistry is the ready availability of commercial thiols and enes. Moreover, owing to the relative ease of synthesis of new multifunctional thiols and enes, there is a large propensity for developing new monomer systems. For example, allyl ether functionalized biodegradable unsaturated polyesters have been reported[67] for use as the ene component of thiol–ene photocurable systems. Additionally, new low-molecular-weight thiols have been used in the synthesis of linear polysulfides.[68]

Particularly intriguing is the ability to make functional thiols and enes from renewable resources. Indeed, enes synthesized from natural products are very effective as reactive components in thiol–ene systems.[69–71] As thiol–ene reactions take place much more readily and under benign conditions, the potential exists for using this chemistry for applications where environmentally friendly, sustainable materials that can be processed with low energy expenditure under ambient conditions, and even in sunlight, are desired. These applications, including large-scale implementation for coatings, films, and other thermoset and thermoplastic polymer applications, are an incredible untapped potential for future expansion of thiol–ene polymers.

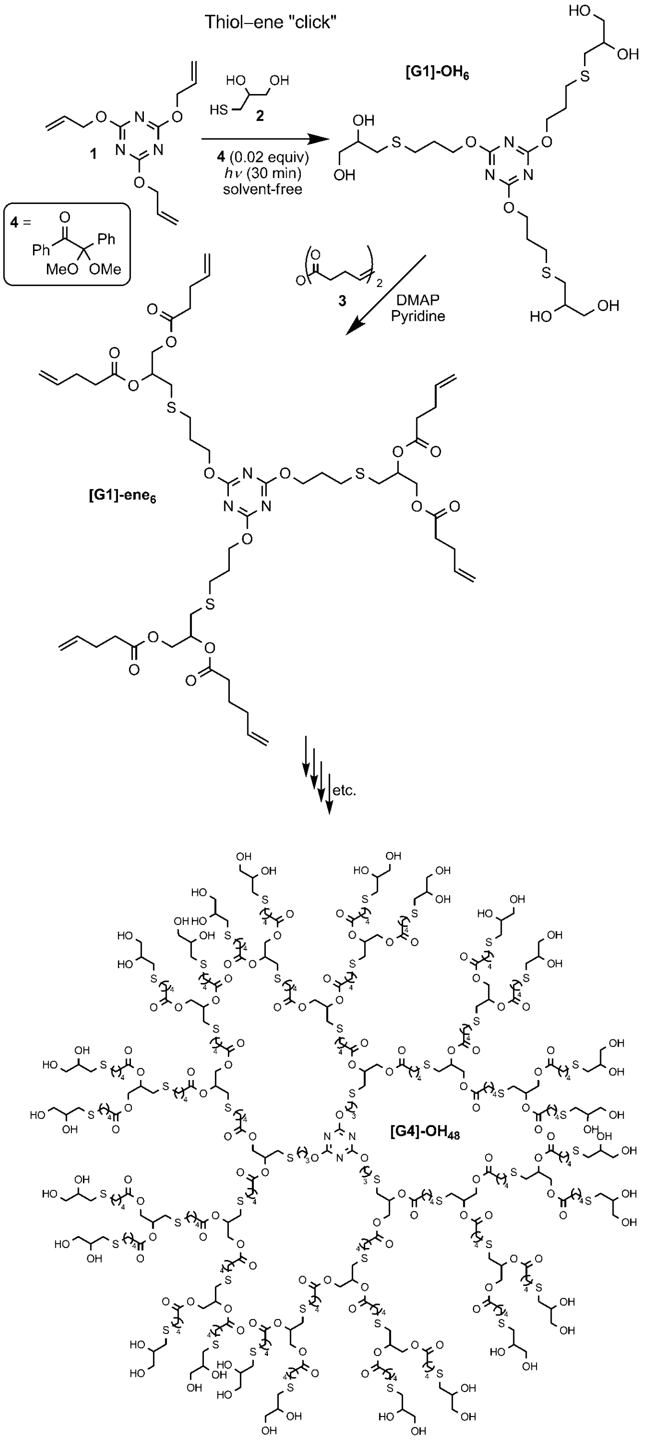
The types of enes amenable to thiol–ene radical reactions have also been extended to include an array of multifunctional systems with non-traditional architectures. For example, 6-, 8-, 16-, and 32-functional allyl amine dendrimers,[72a,b] 3- and 4-functional vinyl esters,[73] and nominally 16-functional vinyl esters synthesized by a secondary-amine-catalyzed Michael addition reaction (the last case in quantitative yield) were photopolymerized in a thiol–ene radical chain process with tri- and tetrathiols. In the case of the multiallyl dendrimers and vinyl ester functionalized prepolymers, the reactions were very rapid, leading to essentially quantitative conversions. Similarly, the photoinitiated free-radical thiol–ene reaction between 64-functional hyperbranched thiols and either hyperbranched 32-functional allyl ethers or 14-functional norbornenes proceeded with near quantitative conversions in relatively short times[74] despite the high functionalities of each component. These reactions[72–74] involving dendrimers or hyperbranched thiol and ene monomers clearly demonstrate the effect of cyclization; that is, multiple thiol–ene reactions between a single hyperbranched thiol and a single hyperbranched ene. This breakdown in the traditional gel-point conversion prediction in which multiple cyclization reactions occur between two interacting molecules leads to increased gel-point conversions, higher overall functional group conversions, and lower cross-linking densities.

Whilst the use of thiol–ene radical chain processes has yielded many types of networks with mechanical and physical properties that are tunable over a vast range, the incorporation of crystallinity into thiol–ene networks had proven to be elusive until a recent report by Johansson, Malmstrom and co-workers.[75] As pointed out by the authors, incorporation of crystallinity into thiol–ene networks has the potential of decreasing oxidative and chemical degradation whilst improving physical and mechanical properties and opening up a number of possible new applications.

The synthesis of telechelic dithiol polyesters,[76,77] and their incorporation them into thiol–ene networks[75] allows the formation of semicrystalline networks with controllable melting points. This outcome opens up a tremendous new opportunity for creating semicrystalline networks by independent structural control of the thiol and ene components.

2.1.5. Synthesis of Dendrimers and Other Functional Species

Thiol–ene radical reactions have been used in the synthesis of glycodendrons[78] and poly(thioether) dendrimers.[79] In the former case, an efficient thiol–ene radical reaction was used to couple a tetraene with mercaptoethanol during an efficient synthesis of a heptasaccharidic glycodendron. In the latter case, the synthesis of a fourth-generation 48-functional polyol (Scheme 4) was accomplished by a divergent approach featuring rapid, efficient sequential thiol–ene radical coupling reactions involving a triallyl triazene core (triene 3) and thiol glycerol to give a hexafunctional polyol, followed by a base-catalyzed esterification between the pendant alcohols and 4-pentenoic anhydride to yield a hexafunctional ene. The thiol–ene click/esterification sequence was continued, ultimately leading to a 48-functional alcohol and corresponding 48-functional enes.[79] As shown in Scheme 5, the 48-functional ene was reacted with a variety of functional thiols to yield dendrimers with selective chain-end functional groups. This pathway allows dendrimers to be functionalized with virtually any type of end group, provided that a thiol with the desired pendant chemical group is available, thereby utilizing the orthogonality of the thiol–ene coupling reaction.



Scheme 4. Synthetic method for 48-functional polyol dendrimer using sequential thiol–ene radical and esterification reactions. Reproduced from Ref. [79] with permission from the American Chemical Society.

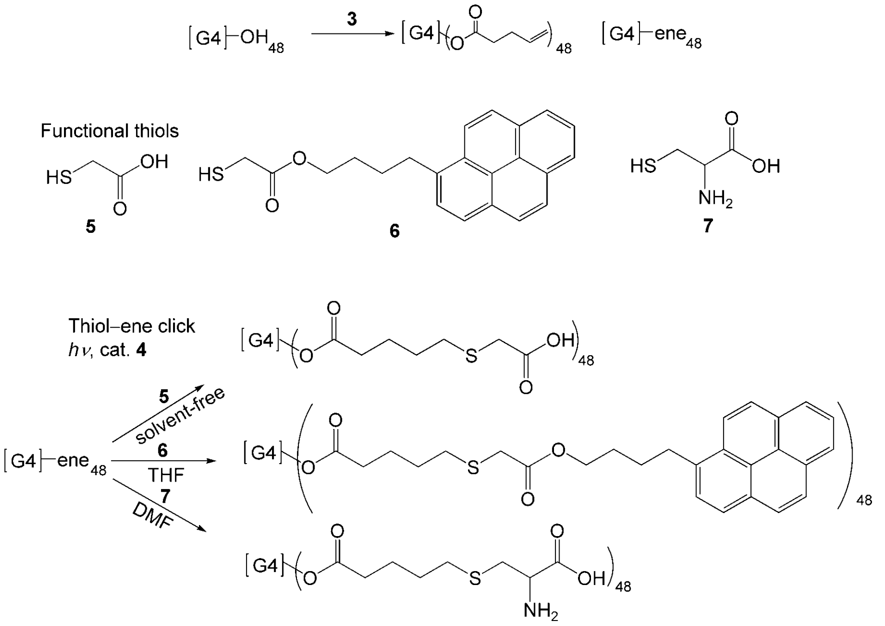
Apart from the dendritic species described in Scheme 4 and 5, the thiol–ene reaction is useful in several other high-yielding synthetic procedures.[80–82] Specifically, photoinitiated thiol–ene radical reactions have also been used to synthesize species such as modified cysteines (**7**), terpyridine lanthanide-ion-scavenging ligands functionalized with trimethoxysilane pendant groups,[81] and thioether linkages that are non-immunogenic between glycopeptides antigens and bovine serum albumin.[82]

2.1.6. Enthalpy Relaxation

One critical aspect of the high uniformity of thiol–ene networks is the propensity for extensive sub-T_g relaxation processes; that is, enthalpy and volume relaxation processes that lead to changes in mechanical, physical, surface, optical, and electronic properties. Figure 6 shows the relaxation that can occur when a material is cooled below T_g. The continuous plot below the T_g is depicted as either the actual kinetically controlled volume (V) or enthalpy (H), and the dashed line represents the equilibrium volume or enthalpy that would be obtained if sufficient time were allowed for complete network relaxation at a given temperature. The enthalpy relaxation is easily seen in the differential scanning calorimetry (DSC) scan of a thiol–ene network held at a temperature below T_g for a given period of time, as shown in Figure 7.[83] The large endotherms just prior to T_g reflect the extent of the relaxed enthalpy, which increases with sub-T_g aging time. Such large endotherms are not present for more traditional heterogeneous network structures. Rigid structural units and higher network cross-link density were found to effectively reduce and thus control enthalpy and volume relaxation.[83]

2.2. General Characteristics of Thiol–Michael Addition Click Reactions

Apart from the traditional thiol–ene free-radical reaction, thiol–vinyl reactions between a thiol and an electron-deficient ene also occur readily (Scheme 1). Depending on the substrate, this reaction has been referred to as a thia-Michael (192),[84] conjugate,[85] bioconjugation,[86] thiol–Michael,[87] thio-Michael,[88] Michael addition,[89] Michael type addition,[90] sulfa-Michael addition,[91] or more recently thiol–maleimide (i.e. thiol–ene) click[92] and thiol-based click[93] reaction. We simply refer to this click reaction as a thiol–Michael addition reaction, with the proviso that the ene is electron-deficient, such as (meth)acrylates, maleimides, α,β-unsaturated ketones, fumarate esters, acrylonitrile, cinna-



Scheme 5. Thiol–ene photoinitiated free-radical reaction of a 48-functional ene dendrimer with selective monofunctional thiols.

mates, and crotonates. Traditionally, a wide variety of catalysts have been used to initiate the thiol–Michael addition reaction, including strong bases, metals, organometallics, and Lewis acids.[94] In recent reports,[89,92] thiol–Michael addition reactions where the ene is a maleimide, that is the thiol–maleimide click reaction,[92] used a tertiary amine (triethylamine) as catalyst in THF to effectively functionalize degradable polyesters,[92] or in 1,4-dioxane to synthesize block copolymers by reactions between polymers selectively end-functionalized with maleimide and thiol groups (Scheme 6).[89] In one case, no catalyst was used when the reaction was conducted in a highly polar solvent with high dielectric constant (DMF) for the synthesis of nanoparticle surfaces functionalized with water-soluble linear acrylate-based copolymers.[93] These efficient reactions proceed with high conversions under mild conditions, and serve as models for the efficient use of thiol–ene click chemistry to generate a range of functionalized materials.

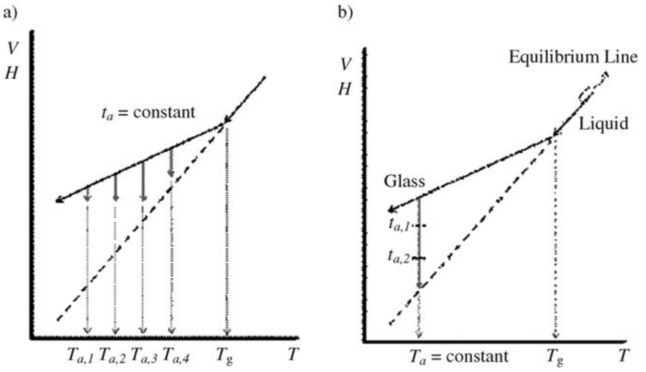
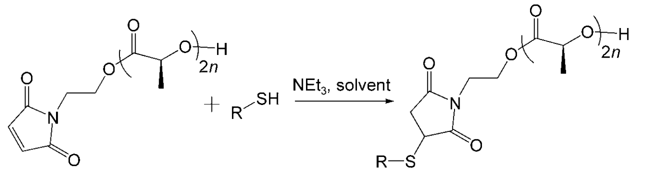


Figure 6. a) Isochronous and b) isothermic sub-T_g annealing methods. Reproduced from Ref. [83] with permission from the American Chemical Society.



Scheme 6. Thiol–Michael addition of electron-poor maleimide-terminated poly(lactic acid) and functionalized thiols. RSH represents a variety of aromatic, alkyl, and aliphatic thiols.

During the last few years, a strategy of using primary or secondary amines[73,95–98] or even more powerful and efficient nucleophilic alkyl phosphine catalysts[99–101] has emerged as a model for extremely efficient thiol–Michael addition reactions between electron-deficient enes and several types of thiols. The use of primary amines, which act as nucleophilic catalysts rather than as simple bases, was first noted in an article in the 1960s[102a] and was not followed up for use in materials applications until 2003 in a landmark patent.[102b] The primary/secondary amine and phosphine nucleophilic catalysts are particularly efficient, and provide a simple, highly efficient process for catalyzing thiol–ene reactions between thiols and acrylates and other electron-deficient enes. The reactions proceed with high conversion by an extremely efficient anionic chain process that is analogous to the mechanism for the radical reaction in Scheme 2, except that the radicals depicted there are anions and the mechanism for generation of the initial thiolate anion involves the addition of the nucleophilic catalyst to the electron-deficient alkene, followed by a subsequent proton abstraction of the thiol (Scheme 7a). In contrast to the thiol–ene radical

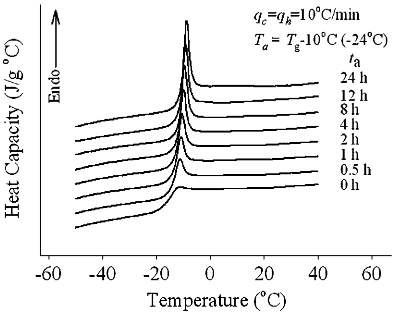
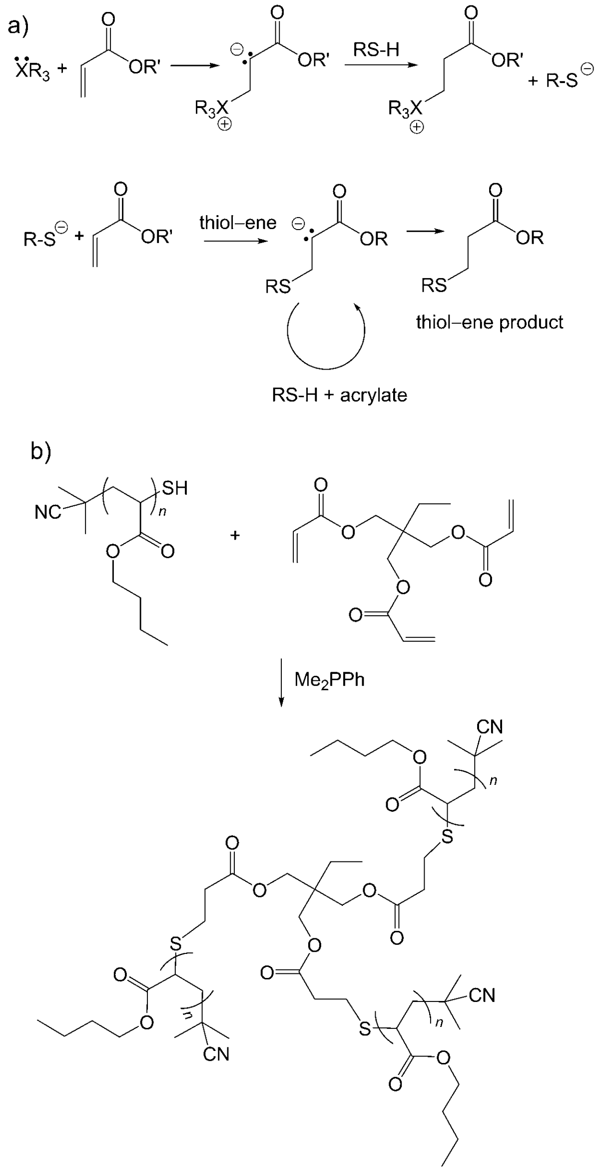


Figure 7. DSC scans of a film made by photopolymerization of a stoichiometric mixture of trithiol 1 (n = 0) and triene 1 after annealing for different times. Annealing temperature T_g−10 °C, DSC cooling/heating rates 10 °C min^{-1}. Reproduced from Ref. [83] with permission from the American Chemical Society.



Scheme 7. a) Mechanism for the nucleophile-initiated thiol–Michael addition process, where XR_3 is the nucleophilic catalyst. b) Star polymer synthesis using dimethylphenylphosphine.

process, there are no anionic coupling processes that terminate the chains for the thiol–Michael reactions once initiated. These essentially quantitative thiol–Michael addition reactions proceed at room temperature on the order of minutes or even seconds in many cases, and they have been used successfully for the rapid functionalization of existing polymers,[101] or the synthesis of linear[100] and multi-arm star polymers[99] (Scheme 7b) with no detectable by-products.

3. Thiol–Ene Click Reactions: Applications

As indicated in Section 1, thiol–ene click chemistry can be effectively applied to a large number of applications, ranging from optical components and adhesives to high-impact energy-absorbing materials. This section will focus on an overview of potential applications primarily for thiol–ene free-radical chemistry, and to a very limited extent thiol–Michael addition reactions. The description of the thiol–Michael addition reactions will be limited to those systems that are used to complement thiol–ene free-radical reactions.

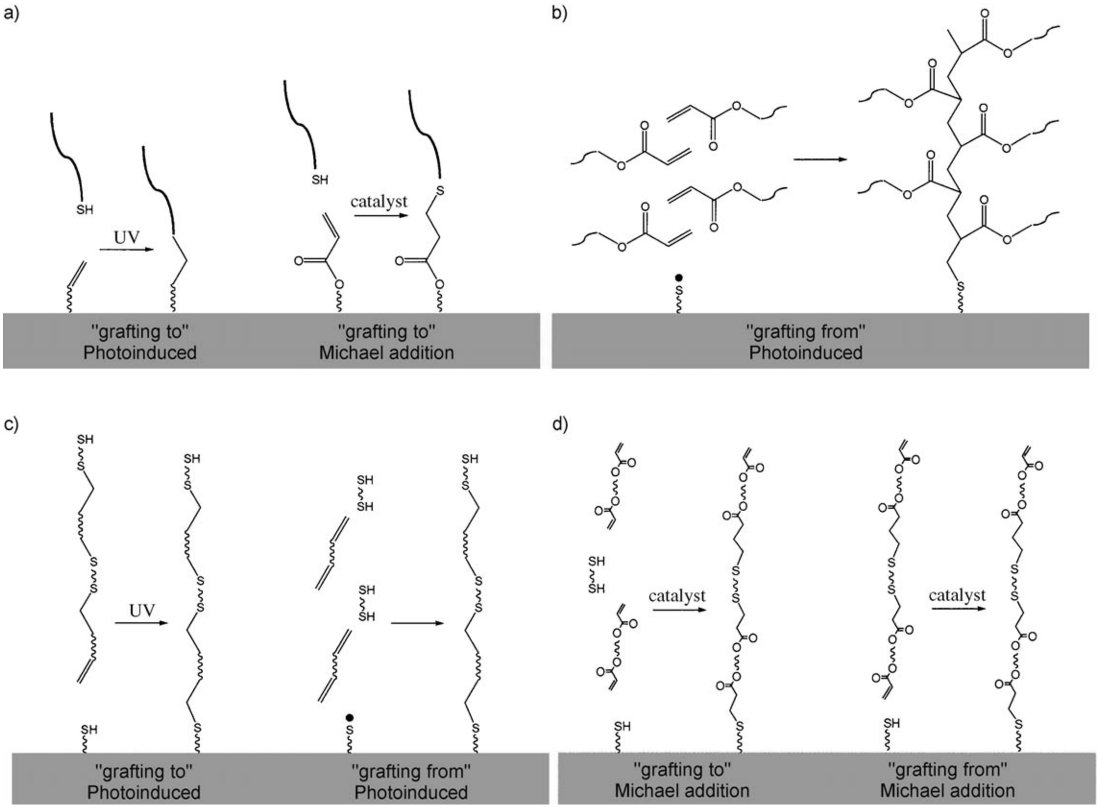
3.1. Substrate Surface Modification

The ability to use patterns to alter surfaces simply by light exposure has made the thiol–ene reaction a popular surface modification reaction. Surface modification approaches that utilize the thiol–ene reaction are as varied as the surfaces that are modified and the ultimate intended use of the surface modification. General approaches, shown in Scheme 8, include 1) a "grafting from" approach that utilizes thiol–ene substrates that contain initiators or residual thiols to induce grafting reactions (Scheme 8b),[103–105] 2) a "grafting to" approach that utilizes either Michael addition or photoinduced coupling reactions (Scheme 8a),[97,106–113] and 3) a combination of "grafting to" and "grafting from" approaches in which either photoinduced free-radical or thiol–Michael-addition-based polymerizations are performed in conjunction with and coupled to the surface (Scheme 8c,d).[96,97,107,114–117]

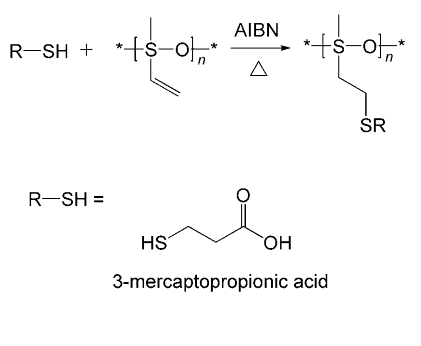
We first consider an example of the control over the attachment of acrylate chains afforded by the "grafting from" approach using a unique nanopatterning process.[103] The surface chain density of linear polymers formed by polymerization of monoacrylates from thiol–ene networks in "grafting from" reactions is controlled by the concentration of excess thiol groups used to form the initial base thiol–ene network. Similarly, the average molecular weight of the grafted chains was controlled by a chain-transfer agent added to the solution in contact with the surface of the thiol–ene substrate.

In a different "grafting from" process, photoiniferters were incorporated into the thiol–ene networks.[104] The photoinitiated controlled living radical polymerization of a hydrophobic semi-fluorinated acrylate and a hydrophilic poly(ethylene glycol) acrylate from iniferter sites within the thiol–ene networks led to the efficient attachment of linear polymers that were patterned by a lithographic process. This ability to precisely and spatially control the surface properties of thiol–ene networks opens up the potential for applications that include controlled adhesion, protein attachment, sensory responses, and fluorescence patterning.

The "grafting to" reactions have been utilized to modify surfaces for several purposes, including friction reduction by grafting of linseed oil onto aluminum[108,112] and attachment of biologically relevant compounds.[106–107] In other photoinitated "grafting to" processes, the radical chain reaction of thiols with ene-modified polymer substrates also yields materials with specific properties not achievable by other methods.[110,111,113] For example, thiopropionic acid and thiol alkanes with varying alkyl chain lengths (such as dodecanethiol in Scheme 9) were attached to poly(vinylmethylsiloxane) by a photoinitiated radical chain process to give responsive surfaces with wettability (determined by the contact angle with water) that could be recycled rapidly.[110,113]



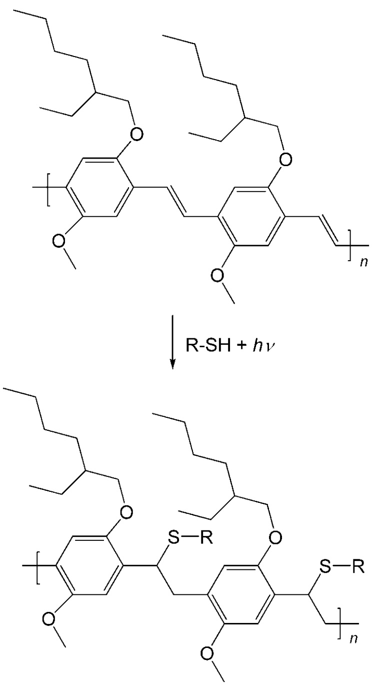
Scheme 8. Several surface-modification approaches enabled by thiol click reactions: a) "grafting to" approaches that utilize both thiol–ene and thiol–Michael addition coupling reactions (shown here for one type; the functional groups may be reversed), b) photoinduced "grafting from" approach using thiyl radicals produced photolytically on the surface to initiate acrylate polymerization, forming the surface-attached polymer graft, c) combination of "grafting to" and "grafting from" radical processes, and d) a combination of "grafting to" and "grafting from" thiol–Michael addition processes. For (c) and (d), the surface modification includes aspects of both grafting methods, as surface groups react with both small, monomeric species early in the reaction and oligomers and polymers at later stages of the reaction.



Scheme 9. Functionalization of cross-linked poly(vinylmethylsiloxane) by a thiol–ene radical chain reaction with 3-mercaptopropionic acid and dodecanethiol. Other alkane thiols were also used. AIBN = 2,2′-azobis(isobutyronitrile).

This approach provides the unique opportunity to adjust the surface of an otherwise extremely hydrophobic polymer to rapidly respond to an environmental stimulus. To extend the thiol modification of polymer films to optical polymer systems (Scheme 10), a simple alkanethiol was attached to the ene units in a polyphenylvinylene substrate that, when blended with host polymers, can be used to tune the emission characteristics of polymer light-emitting diodes.

Further to using the "grafting from" approach for photopatterning of surfaces that contain excess thiol groups,[103] several of the photoinitiated "grafting to" approaches also have the ability to photopattern the graft location and extent, thus utilizing the relative simplicity with which enes can be uniformly reacted to thiol-functionalized surfaces.[106,107,109] These thiol-terminated surfaces are formed by several methods, including the use of thiol-terminated silanes that form a self-assembled monolayer (SAM).[107,109] Although the intent is often to provide uniform surface coverage, there are distinct advantages in patterning surfaces or coupling reactions in a variety of ways. The most common approach is to pattern the radical generation by controlling the irradiation exposure in radical mediated polymerizations and coupling reactions[106,109] that can be readily extended to three dimensional control within thiol–ene networks and gels.[61] This effort has been particularly important in controlling the grafting of proteins in which the spatial distribution and organization of the surface chemistry on both the micro- and nanoscale are important in manipulating the desired biological function.[106] For protein and peptide attachment, the key benefit of the thiol–ene grafting reaction is that it is



Scheme 10. Photoinitiated radical chain reaction between ene groups of poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and an alkanethiol.

bioorthogonal with olefins on the surface directed to react specifically and exclusively with the thiols in the protein.

The combination of “grafting to” and “grafting from” surface modifications has been achieved through the implementation of both thiol–ene radical chain reactions and thiol–Michael addition reactons in the presence of a thiol-terminated surface;[96,97,107,114,115,117] several modifications involve the use of thiol-terminated silane-based SAMs.[97,107,114,115] These thiol–ene reactions that combine “grafting from” and “grafting to” approaches can also be patterned.[114,115] In general, the combination of “grafting from” and “grafting to” approaches involves careful characterization of the grafting reaction kinetics and molecular weight distributions achieved in linear polymer grafts formed by thiol–ene photopolymerization[96] and in thiol–acrylate Michael addition reactions that result in linear polymer grafts.[117] The click and step-growth nature of these reactions are exploited to control the molecular weight in a self-limiting manner, as small manipulations of the stoichiometric reactant ratio in a diene–dithiol polymerization self-limit the maximum achievable polymer molecular weight. This approach facilitates the formation of low-polydispersity, high-density grafted polymer chains even at low to intermediate oligomer/polymer molecular weights. Controllable, uniform grafted polymer films of thicknesses less than 10 nm have been obtained. Film thickness gradients were also achieved ,either with composition gradients or light intensity gradients, where corresponding orthogonal gradients were used to fabricate a complex two-dimensional gradient in film thickness and grafted polymer chain density.[97,107]

3.2. Thiol–Ene Click Reactions for Photolithography and Microdevice Fabrication

The step-growth mechanism of the thiol–ene reaction and the accompanying delay in gel point, uniform network formation, and lower shrinkage and shrinkage stress that are achieved, and also low oxygen inhibition, make thiol–ene reactions ideal for photolithography and microdevice fabrication. The delay in gel point results in more distinct photolithographic features as the gel fraction increases dramatically over a small conversion range. It is accompanied by a more rapid increase in the cross-link density and modulus of the gelled polymer than is observed in conversions immediately following the gel point in traditional photopolymerizations. The ability to overcome oxygen inhibition leads to higher fidelity in the reproduction of photolithographically patterned features, which also possess more distinct boundaries and walls. In particular, thiol–ene photopolymers have been used extensively to fabricate microfluidic devices[118–124] or to contribute to the performance,[125] alter the surface chemistry,[109] or control the material properties[57,110,111,113] of various microfluidic and other microdevices.

Along with direct photolithographic applications, thiol–ene reactions are highly effective in the fabrication of microdevices with nanoscale feature control through various types of nanoimprint lithography.[103,105,126–129] For step- and flash-lithographic methods,[103,127–129] the thiol–ene photopolymerization is performed while a mold with nanoscale features is impressed on the liquid monomer mixture. After polymerization the mold is removed, and the nanoscale features of the mold are reproduced in the thiol–ene polymer. The process can be rapidly repeated to fabricate multiple identical devices. Polymer features resulting from such a process are shown in Figure 8: a thiol–ene polymer produced with nanoscale features is subsequently exposed to an additional thiol–ene grafting reaction that further decreases the feature size.[103] The thiol–ene system is also suitable when partially cured to a soft, post-gelation polymeric material that was mechanically imprinted by a mold and subsequently exposed to light to complete the curing process.[105,126] This approach alleviates any problems with interpenetration of the thiol–ene polymer with the PDMS molds, thus enabling facile removal of the thiol–ene polymer after complete molding and polymerization.

Thiol–ene microfluidic materials are characterized by their exceptional solvent resistance,[119,124] rapid curing, and strong adhesion to metal and glass substrates.[118,119] Microfluidic devices have also been fabricated using multiple thiol–ene polymer layers (Figure 9), each of which is partially cured prior to lamination and subsequently re-exposed to light to complete the polymerization.[120] This approach is particularly useful for fabricating complex three-dimensional microfluidic devices that contain multidimensional channel networks. In one approach, device manufacture was simplified significantly by employing a commercially available thiol–ene optical adhesive (Norland)[118–120] to serve as the photoresist material that was patterned and developed into the microfluidic device. In a particularly fascinating account of using thiol–ene click reactions to fabricate highly structured

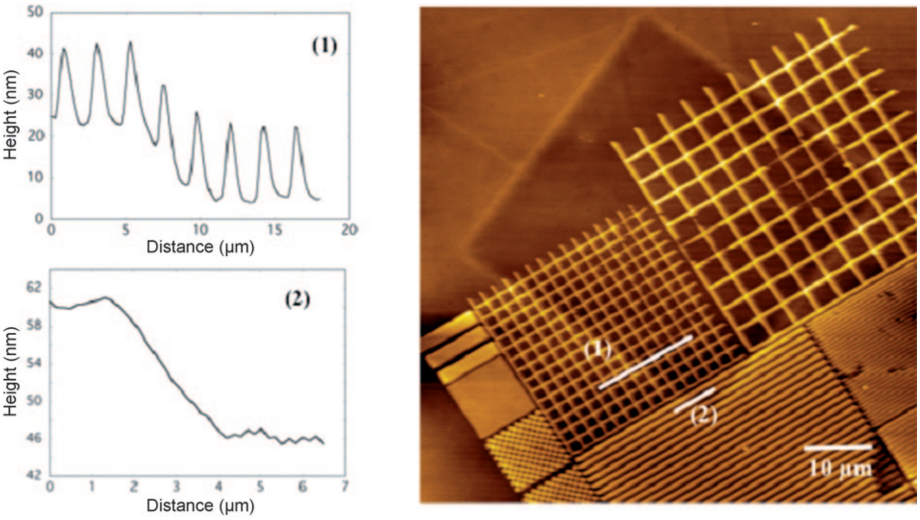


Figure 8. AFM image and height profiles along lines 1 and 2 of a secondary micropatterned polymer layer containing triethylene glycol divinyl ether and tetrathiol 1 ($n=0$) (thiol/ene = 0.35:1, 0.01 wt% *N*-(2,3-dimercaptopropyl)phthalamidic acid (DMPA) used as a photoinitiator) polymerized on a nanopatterned replica formed using triene 4/tetrathiol 1 ($n=0$) (thiol/ene = 1.1:1) through a photomask with 50 µm × 50 µm squares for 3 min. Reproduced from Ref. [103].

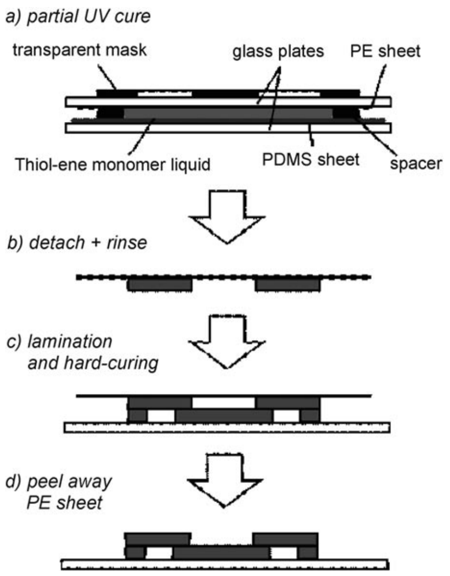


Figure 9. Flow diagram of the fabrication process for microchannel microfluidic devices. Adapted from Ref. [120].

materials for microfluidic, magnetic, optical, or electromechanical applications, pillar arrays with highly regular long-range ordering were fabricated.[57] Figure 10 depicts the use of photoinitiated thiol–ene radical polymerization of a tetrathiol/trivinyl ether mixture to lock-in long-range ordering of pillar structures that spontaneously form upon subjection to an electric field in a capacitor plate rearrangement.[57] The photoinitiated thiol–ene based pillars form rapidly in the presence of oxygen and resist merging, which was noted by the authors to be remarkable.

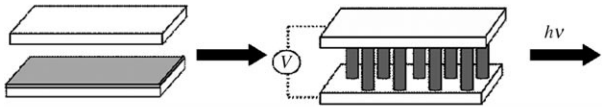


Figure 10. The electrohydrodynamic instability phenomenon in a thiol–ene resin system before photointiaited free-radical polymerization to lock in the pillared structure. An electric field destabilizes the film, amplifying undulations until they span the capacitor gap to form a regular pattern. Adapted from Ref. [57].

3.3. Formation of Nanostructured Networks

The highly uniform structure of thiol–ene networks is ideal for rapid fabrication of nanostructured components, as attested to by the narrow thermal and mechanical transitions. For example, fumed hydrophilic silica SiO_2 nanoparticles (40 nm), fumed titania (TiO_2 hydrophilic 21 nm particles), and multiwall carbon nanotubes have been incorporated into thiol–ene networks by photoinduced frontal polymerizations.[130] Modified polyhedral oligomeric silsesquioxane (POSS) and gold nanoparticles have also been incorporated into photopolymerized thiol–ene networks;[131,132] however, the density of nanoparticles that can be incorporated into the network is limited by aggregation. Apart from dispersion of non-functionalized nanoparticles into the thiol–ene networks, functionalized nanoparticles, such as silica with thiol/acrylate groups,[133] vinyl-functionalized POSS nanoparticles,[132] and thiol-functionalized zirconium and halfnium oxoclusters (Figure 11),[134,135] have been incorporated chemically into thiol–ene networks by virtue of participation of the functionalized nanostructures in the free-radical reaction process. Furthermore, polymer nanocapsules have been formed using photoinitiated thiol–ene reactions involving the reaction between alkyl or oligoethylene oxide based dithiols and functionalized rigid hosts.[136] These polymer nanocapsules have tailorable surfaces for targeting subsequent drug delivery.

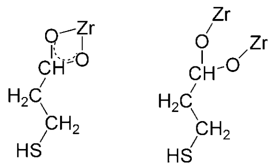


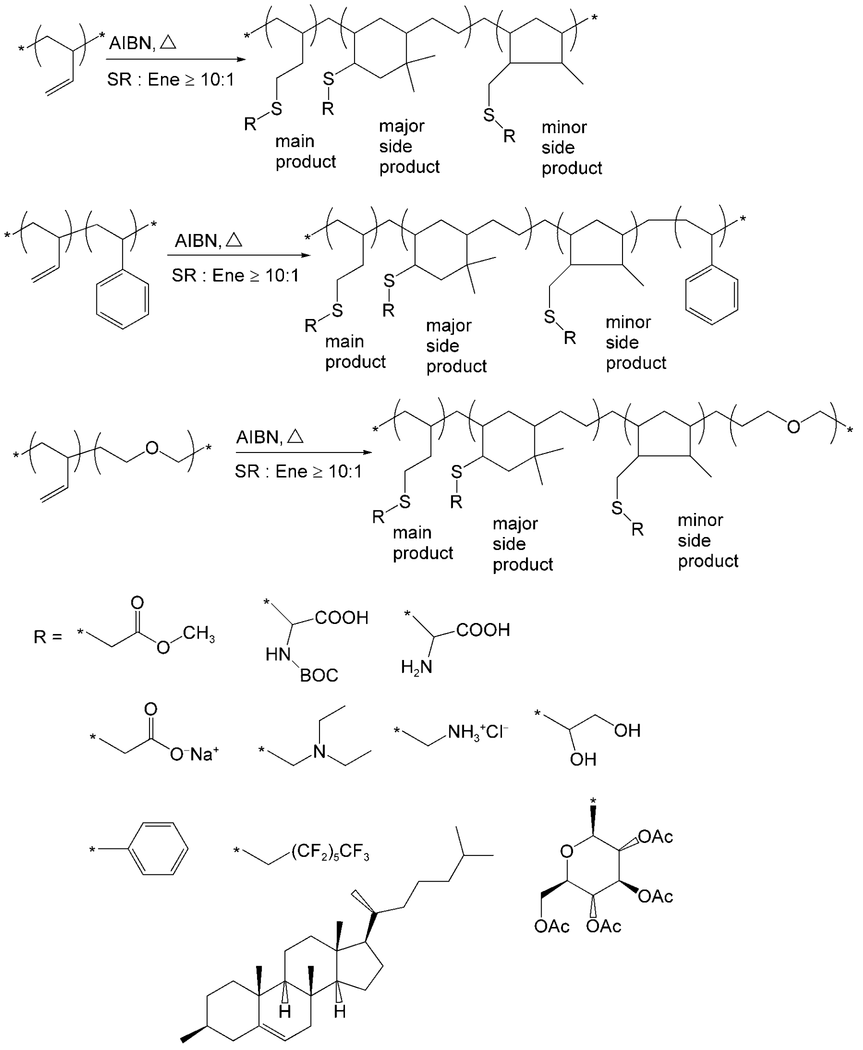
Figure 11. Representative structural units of zirconium oxoclusters formed with mercaptopropionic acid and mercaptopropionate groups.

Potential applications for thiol–ene-based nanostructured networks include optical components, electronic components (such as wires, resistors, circuit components), and in the case of 5–10 nm gold nanoparticles, clear films with rapid electrostatic discharge (ESD) rates.[131] Decreased burn rates,[132] hard coats with improved surface properties,[134] and cluster-based self-assembled monolayers[135] have also been reported. Improvements in mechanical hardness, abrasion resistance, thermal decomposition temperature with increased char, rubber storage modulus, glass transition, and sub-T_g enthalpy relaxation were reported in several cases; however, large increases in these basic properties are generally not found simply by incorporation of nanoparticles into the thiol–ene matrices.

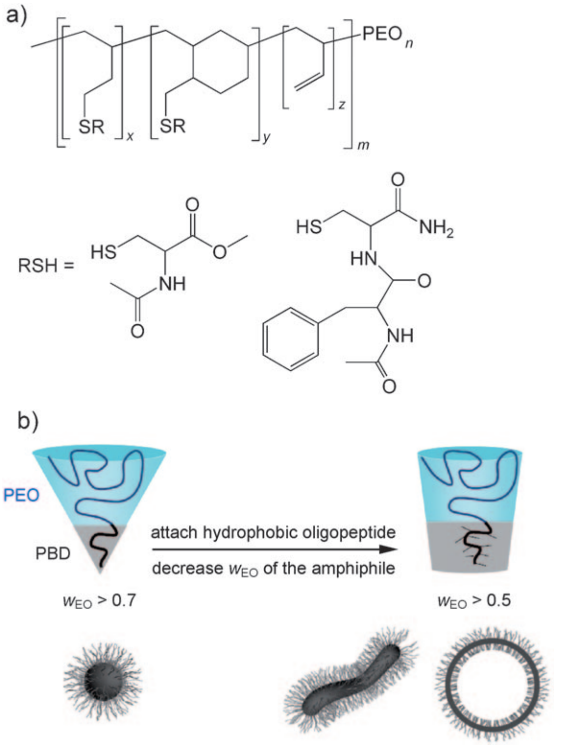
3.4. Polymer Functionalization

Although it is extremely important to be able to control and selectively modify existing polymer types to attain a desired specific material property, this outcome has often proven particularly difficult to achieve with conventional polymer modification techniques. The major problem in modifying or altering existing polymers using traditional chemical reactions is low-yield side products that require removal and lead to longer reaction times. One of the greatest opportunities for using thiol–ene click chemistry is for rapid, high-yield modification of existing polymers to tailor physical, mechanical, optical, solubility, and other key properties over a wide range. Accordingly, the use of monofunctional thiols with tethered functional groups has been shown to provide a facile, clean, and efficient method to alter the chemical and physical properties by reactions of thiols with polymers that have either end or side-chain functional groups. In recent years, significant effort has been expended toward polymer functionalization using thiol–ene free-radical reactions.[111,113,116,137–158] This development will allow the properties of preformed polymers to be modified and tuned over an extensive range under very mild reaction conditions. In fact, sunlight can be used as an effective tool to initiate the thiol–ene free-radical polymer functionalization process.[158]

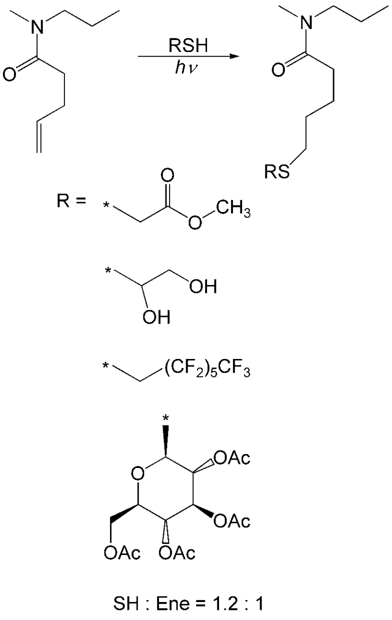
Schlaad and co-workers have shown that polybutadiene polymers and related copolymers that have abundant concentrations of readily accessible ene functional groups were derivatized with thiols by free-radical chain reactions. Free-radical click reactions between polybutadiene and the corresponding polybutadiene copolymers with functionalized thiols to provide significant changes in the chemical and physical characteristics of the substrate polymer are shown in Schemes 11–13. For hydrophobic polybutadiene and polybutadiene copolymers (Scheme 11), thiols with functional hydrophilic acid,[140,142] primary amine,[140,142] tertiary amine,[142] cysteine derivatives,[142,144,147,158] amino acid,[140,144] dihydroxy,[142] glucose,[140,145,158] non-hydrophilic esters,[142,158] cholesterol,[158] benzyl,[142] and semi-fluorinated[142] groups were all effectively attached to the polybutadiene backbone. When hydrophilic groups were attached, the functionalized hydrophobic polybutadiene and polybutadiene copolymers behave as amphiphilic or water-dispersible polymers that exhibit a wide range of properties and are responsive to temperature, pH, and electrolyte concentration. These products have applications ranging from controlled encapsulants for drug delivery to biologically important micelles and vesicles.[138,140,142,144,145] In the case of polybutadiene–poly(ethylene oxide) block copolymers, functionalization of the polybutadiene block (Scheme 11) via the thermal thiol–ene radical reaction with



Scheme 11. Generalized structures of 1,2-polybutadiene, 1,2-polybutadiene-*block*-polystyene, and 1,2-polybutadiene-*block*-polyethylene copolymers modified by the thiol–ene reaction. Representative RSH structures are shown that have been reported for modification of one or more of the 1,2-polybutadiene and 1,2-polybutadiene copolymers.



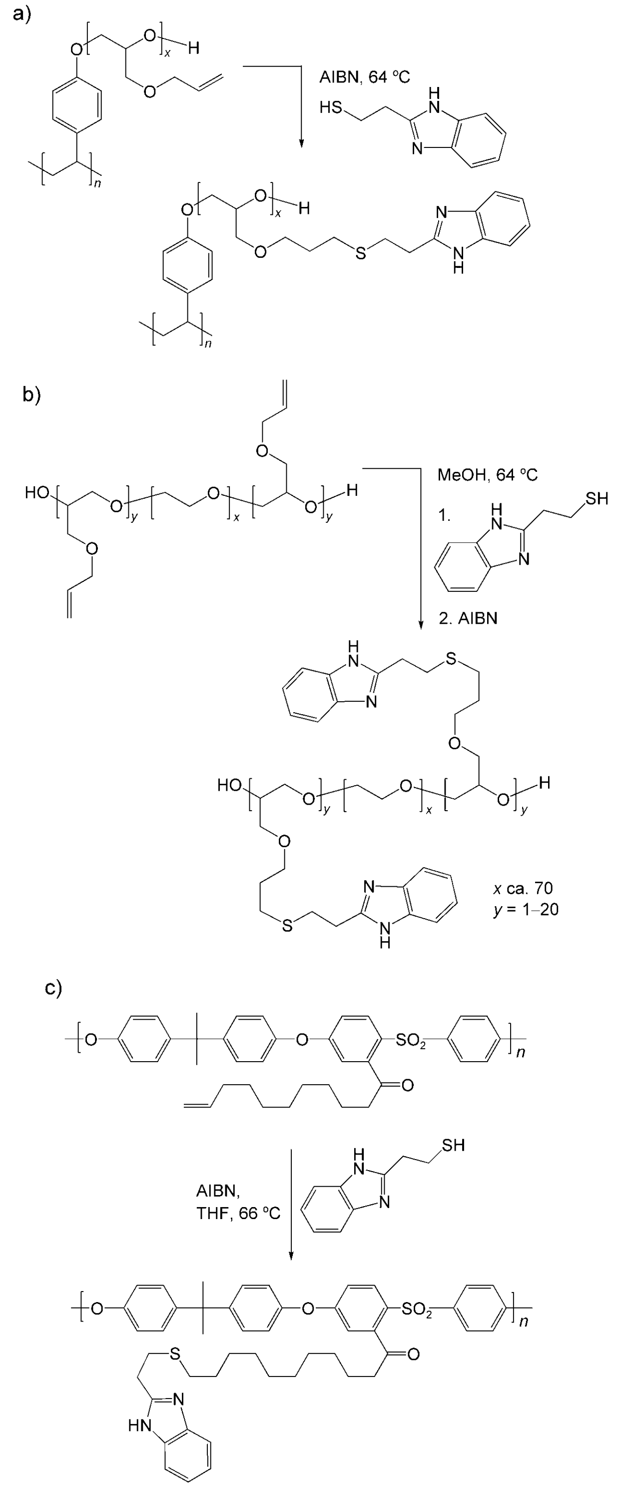
Scheme 12. a) Generalized structure of a polybutadiene-*block*-poly(ethylene oxide) copolymer modified by the thiol–ene click reaction between ene side groups and the hydrophilic and hydrophobic thiols. b) Morphological change from a spherical micelle to a worm-like micelle and vesicle upon functionalization of the polybutadiene-*block*-polyethylene-oxide copolymer with the hydrophobic peptide unit by the thiol–ene reaction. w_{EO} = weight fraction of the poly(ethylene oxide) block. Reproduced from Ref. [146].



Scheme 13. Functionalization of poly(2-(3-butenyl)-2-oxazoline) by the thiol–ene radical reaction with hydrophilic and hydrophobic small molecule thiols.

hydroxy, amine, and semifluorinated groups resulted in polybutadiene–poly(ethylene oxide) block copolymers, which formed aggregates in dilute solution that resembled micellar structures (clusters, cylindrical, or compartmentalized cores).[141,143] The carboxylate-modified polybutadiene–poly(ethylene oxide) copolymers exhibited stimuli-responsive properties, which could render the block copolymers in a glass-like state, thereby reducing the propensity to desorb from the surface. In a particularly interesting adaptation (Scheme 12), the butadiene block sequence of a polybutadiene–poly(ethylene oxide) copolymer was functionalized with a simple cysteine amide derivative and a hydrophobic oligodipeptide. The functionalization with the oligodipeptide by a radical chain process involving the thiol group resulted in structures that are worm-like micelles or vesicles (Scheme 12) depending upon the relative butadiene and ethylene oxide block lengths. Unfortunately, in the examples presented in Scheme 11 and 12, the free-radical thiol–ene addition reaction was accompanied by an intramolecular cyclization reaction that reduced the thiol functionalization yield by introduction of the hydrocarbon cyclic ring structure as a repeat unit.[139] To eliminate the problems associated with the cyclization reaction in the thiol addition to the ene functional side group in polybutadiene and polybutadiene copolymers, thiols were reacted with side-chain enes[139,149,150,151] that were configured geometrically such that carbon-centered radicals on the side chain were spatially unable to react with neighboring ene groups. Polymers with ene side groups that are incapable of cyclization between neighboring enes include polyoxazoline bearing ene side groups (Scheme 13),[139] polyhydroxystyrene with comb-like side chains obtained by attaching a polyglycidyl ether with allyl ether ene groups (Scheme 14 a),[151] tri-block copolymers consisting of a poly(ethylene oxide) center block with poly(glicidyl ether)-bearing allyl ether ene side groups attached by a reaction between terminal hydroxy groups of the parent macroinitiator (Scheme 14 b),[149] and a polysulfone[150] derivatized with a side-chain alkene (Scheme 14 c). As shown in Scheme 13, the photoinitiated thiol–ene reaction of the allyl ether bearing polyoxazoline proceeded rapidly to give polyoxazoline in high yield functionalized with ester, alcohol, perfluorinated alkane, and glucolpyranose, but without the cyclization side reactions that occur for the polybutadiene-functionalized systems. The comb polymer,[151] block copolymer,[149] and polysulfone[150] in Scheme 14 were derivatized with a benzimidazole-bearing thiol using a thermal thiol–ene radical reaction to produce intrinsically proton-conducting membranes with a conductivity that depended upon the concentration of the tethered benzimidazole groups. The basic polysulfone structure in Scheme 14 c[150] is noteworthy, as it consists of a high-performance backbone with excellent thermal and mechanical properties that make it potentially useful as a fuel-cell membrane. The results shown in Scheme 13 and Scheme 14 clearly point out the tremendous potential of using the near quantitative thiol–ene radical reaction to derivatize side groups of several types of polymer structures.

The side chain enes on hydroxy-terminated polybutadiene were modified by a thermal thiol–ene free-radical reaction to



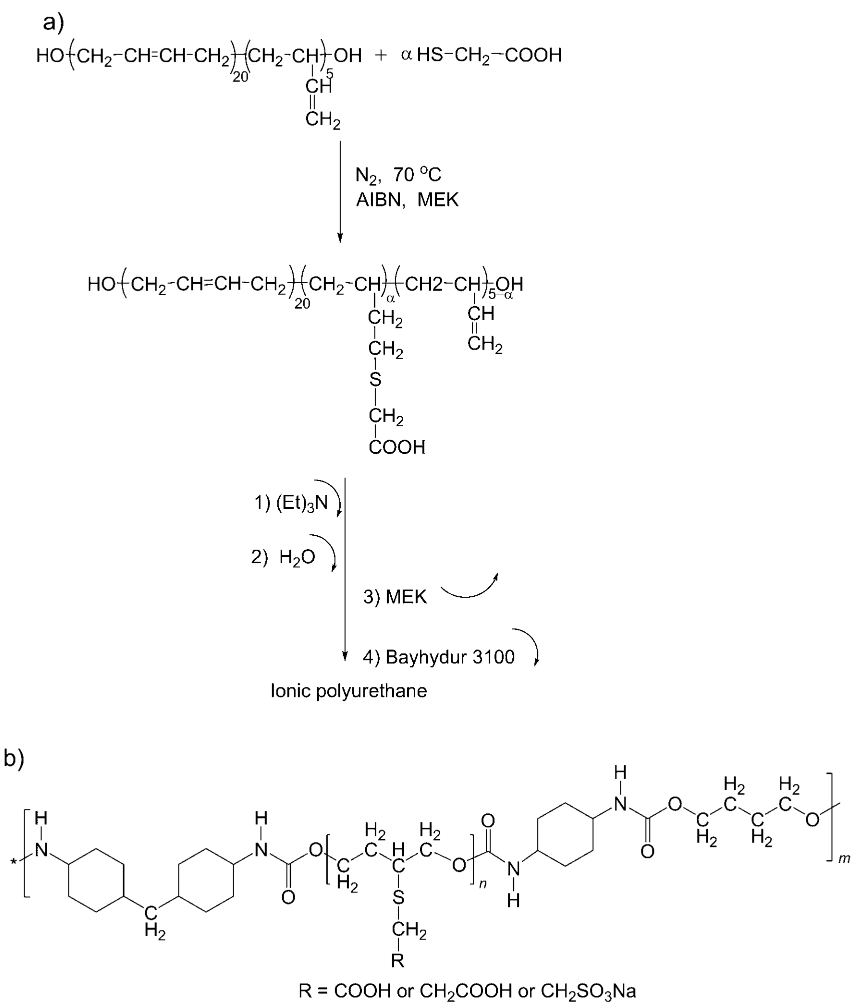
Scheme 14. Thiol–ene reaction of 2-(2-benzimidazoyl)ethanethiol with a) polyhydroxystyrene having attached polyglycidyl ether bearing allyl ether ene groups, b) triblock copolymer consisting of a polyethylene-oxide center block and poly(allyl glycidylether)end blocks, and c) a polysulfone derivatized with ene side groups.

give an acid-modified polymer. This product was reacted with a polyfunctional isocyanate to create a unique water-dispersible polyurethane without the use of the traditional chain extender (Scheme 15a). This approach removes problems associated with ionic groups in the hard segment.[159] Other polyurethanes with ene groups incorporated into the 1,4-polybutadiene main-chain soft segments were modified by a thermal thiol–ene radical reaction to give soft segments with carboxylic acid and sulfonate ionic groups (Scheme 15b).[148] These biocompatible segmented polyurethanes have been suggested for use in targeted cell adhesion and potential tissue repair.

In one noteworthy report, David and Kornfield[160] found that that 1,2-polybutadiene could be functionalized using a thiol–ene radical reaction in which benzoyl- or acetyl-protected thiols were formed by a deprotection reaction followed by a thermally initiated free-radical reaction. The radical chain reaction, induced after the deprotection step, was not inhibited by water, thioesters, disulfides, or other solvents. This outcome clearly illustrates the tremendous extended latitude for functionalizing polymer structures bearing ene side-chain reactants, in this case the simple alkenes of 1,2-polybutadiene, with such derivatives as cyanobiphenyl mesogens, carbazoles, dinitrobenzoates, *para*-hydroxybenzoates, and pyridinyl groups.

Campos, Hawker and co-workers[157] recently reported a strategy for extending polymer side chain and single end-group functionalization to asymmetric telechelic polymers with terminal thiol and azide end groups. This approach provides the opportunity to functionalize a wide range of polymers with side chain and terminal enes/azides selectively (Scheme 16). Essentially any functional group chemically linked to a small molecule thiol (several representative examples are shown in Scheme 16) can be coupled to either side-chain or terminal enes. Furthermore, the thiol/azide telechelic polymers can be functionalized with separate end groups, thus providing a facile, efficient method for selectively placing a wide range of different chemical groups on either polymer end in any combination that can be envisioned, provided that small-molecule thiols and azides with the desired functional groups are available. Extension of this strategy to a wide range of ene-bearing polymers provides an efficient, relatively low-cost, benign synthetic method for obtaining new high-performance polymeric materials in quantitative yields with little need for purification.

Thiol–ene reactions involving a thiol-functionalized trimethoxysilane group and the ene structural units in low- and high-density polyethylene[152] and the terminal unsaturation of polypropylene have also been reported.[153a,b,154] The resultant triethoxysilane-derivatized polyolefins could be post-cured with moisture to form composite-type structures. Other end-modified polymers, including mono-, di-, and trivinylsilyl-functionalized poly(ethylene oxides)[155] were reacted with thioglycolic acid to form water-soluble polymers with carboxylic acid and alcohol terminal groups, with the suggested potential of sequestering cationic substrates for dispersion in aqueous media.[155] Wheat gluten protein polymers[156] have also been conjugated by a thermal free-radical thiol–ene reaction between the thiol groups on the protein and hydroxybutyl vinyl ether and maleate esters bearing ethylene oxide groups.



Scheme 15. a) Synthesis of thiol-functionalized water-soluble polyurethane (MEK = methyl ethyl ketone), and b) polyurethane functionalized with mercaptopropionic acid groups by a thiol–ene reaction between a polyurethane (formed between a hydroxy-terminated polybutadiene and an aliphatic difunctional isocyanate) and mercaptopropionic acid.

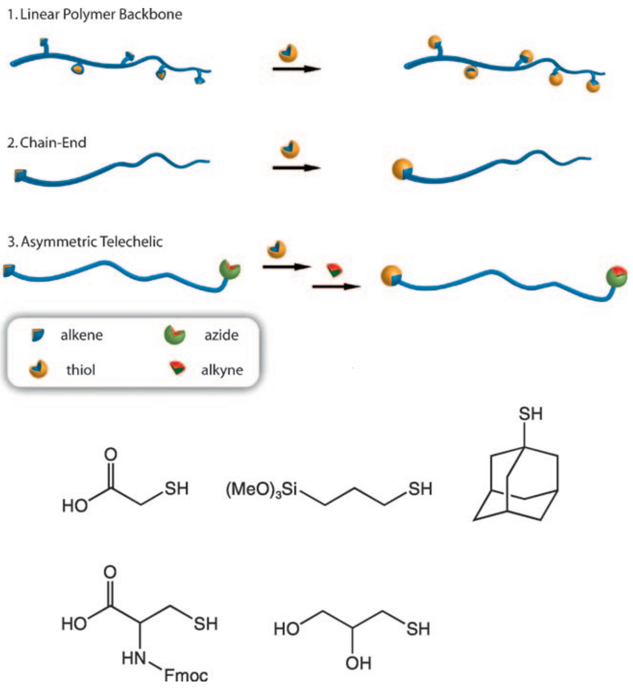
3.5. High-T_g and Hybrid Networks

As thiol–ene networks are characterized by flexible sulfide bonds, applications that require a high-T_g material, such as dental restoratives, optical components, automotive/aerospace repair resins, and other applications, are not readily achievable using most traditional thiol–ene combinations. Three recent approaches have been reported to remedy this problem and produce high-T_g thiol–ene networks.[161–163] The first approach uses norbornenes (Figure 12), which provide high-T_g networks ($> 80\,°C$) owing to mobility restrictions.[161] Along with having high T_g values, these networks exhibit relatively low moisture uptake, which is presumably due to the high hydrocarbon content.[161] In other work, multifunctional thiocarbamate oligomers (Figure 13) were synthesized by reacting aliphatic and aromatic diisocyanates with a tetrafunctional thiol.[162] The T_g values, devived from dynamic mechanical analysis, of sequential photocured/thermal cured films had values greater than 90 °C as a result of extensive hydrogen bonding. These networks exhibited excellent hardness and impact values, which is consistent with the presence of the carbamate groups. In a third approach, by using a dual-cure process involving a sequential thermal amine-catalyzed thiol–epoxy reaction followed by a photoinitiated thiol–ene reaction, it was possible to establish a procedure that resulted in high conversions and correspondingly high-T_g networks.[163a–d] The potential of this dual-thiol-based chemistry provides another clear method for making multicomponent networks with properties that are not achievable with simple thiol–ene systems. The use of hybrid thiol–ene/epoxy systems in which dual photoinitiated thiol–ene radical and epoxy cationic systems has been greatly expanded in a set of comprehensive reports from Soucek and co-workers that clearly demonstrate the potential for expansion into a wide range of applications.[163b–d] Other hybrid systems involving photopolymerization of divinylsiloxane-terminated polysiloxanes and a trithiol followed by thermal curing of a cellulose acetate butyrate system to form an interpenetrating polymer network with two distinct glass transitions have also been reported. These stategies open up the way for a wide range of IPN systems formed by sequential thiol–ene/thermal cure combinations.[164]

3.6. Optical Networks (HPDLCs)

One of the most prolific uses of thiol–ene radical polymerization processes focuses on the formation of a separate liquid-crystalline phase that forms from an original homogeneous single-phase mixture as the polymerization proceeds.[165,166a,b] The polymer-dispersed liquid-crystalline (PDLC) phases that are formed are characterized by electroactive liquid-crystalline-rich phases and highly cross-linked network phases.[165,166a,168–170] Recent advances based on thiol–ene materials for PDLCs,[41,166a,167,171] and advanced kinetic[164,166a,167] and light-scattering techniques[170] for in situ evaluation of phase separation and morphology development, have led the way to the development of a procedure for advanced, rapidly switching PDLCs. In a variation on traditional PDLCs, ferroelectric liquid crystals[41,172–175] have also been incorporated into thiol–ene networks.

Holographic polymer-dispersed liquid-crystalline composites based upon the use of UV[42,165,176–183] or visible[42,184] CW laser-initiated photopolymerization of a commercially available (Norland) thiol–ene system have also been fabricated using a traditional cyanobiphenyl mixture as the liquid-crystal



Scheme 16. Functionaliztion of three types of polymer structures using thiol–ene and alkyne–azide click reactions. Fmoc = Fluorenylmethoxycarbonyl. Reproduced from Ref. [157] with permission from the American Chemical Society.

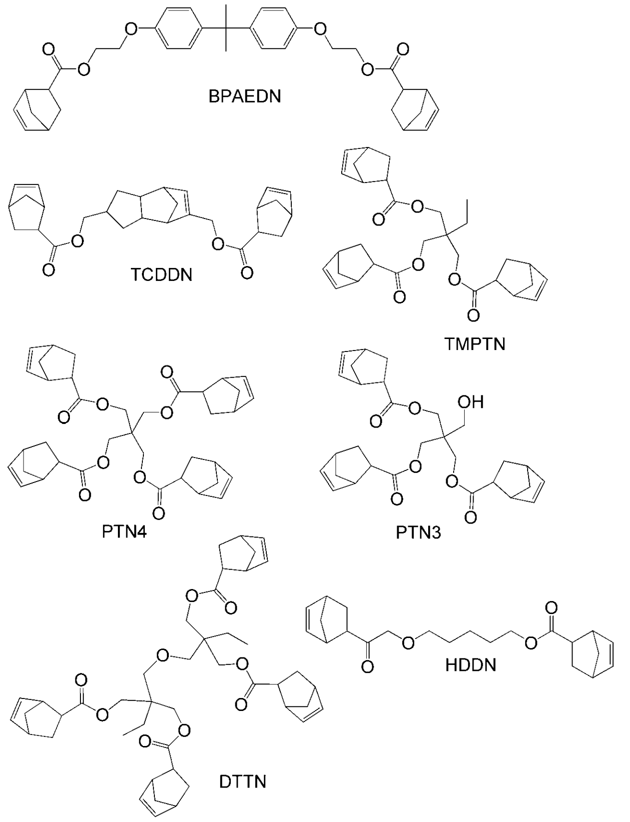


Figure 12. Representitive structures of multifunctional norbornenes.

component. Diffraction gratings (see Figure 14 for a typical TEM micrograph) based upon liquid-crystalline thiol–ene systems are very efficient, as determined by both experimental[142,166,176–179,181–184] and theoretical analyses.[181] Compared to diffraction gratings based on multiacrylates, thiol–ene-based holographic PDLCs (HPDLCs) are characterized by outstanding diffraction efficiency, low switching voltages, and high switching speeds, as well as exceptional control of droplet structure and size. Thiol–ene-based systems have set the standard for high-performance HPDLCs suitable for many optical and electronic applications, including reflection and transmission gratings, photonic crystals, photonic lasers, hierarchical nanostructured devices, ferroelectric liquid-crystal devices, spectrometers for biological and chemical sensors, and switchable photomasks.

In accordance with the advantages of three component systems outlined in Section 2.3, a ternary thiol–ene–acrylate system has also been evaluated. As the acrylate concentration increased, the HPDLC network optical switching properties and diffraction efficiency were found to decrease owing to introduction of heterogeneity into the network structure associated with contributions from the acrylate homopolymerization reaction.[176]

Further to using small-molecule liquid-crystalline components to form the phase-separated refractive nanostructure of HPDLC thiol–ene networks, other reports have shown that introduction of patterned, crystallizable poly(ethylene glycol) components[177,178] into the thiol–ene networks[177,178,185] results in diffraction grating efficiencies that are temperature-switchable. This method opens up an important route for chemical functionalization and corresponding patterning to create materials that are thermally, optically, and magnetically

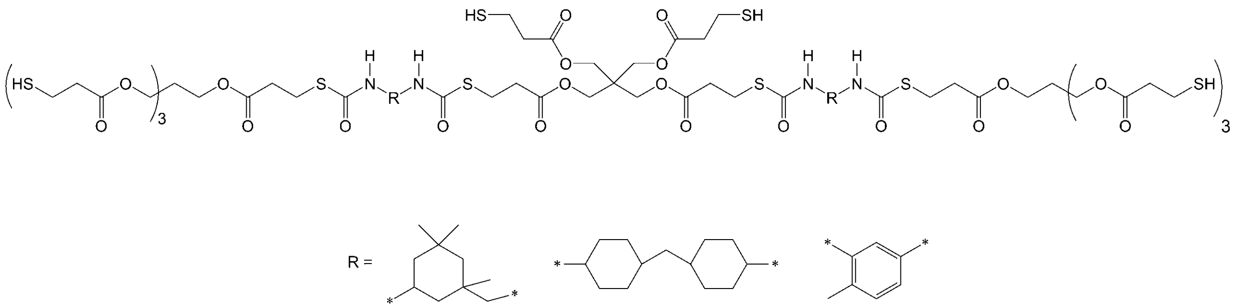


Figure 13. Typical structures of thiol end-capped oligomers made by reaction of tetrathiol 1 ($n = 0$) with suitable diisocyanates.

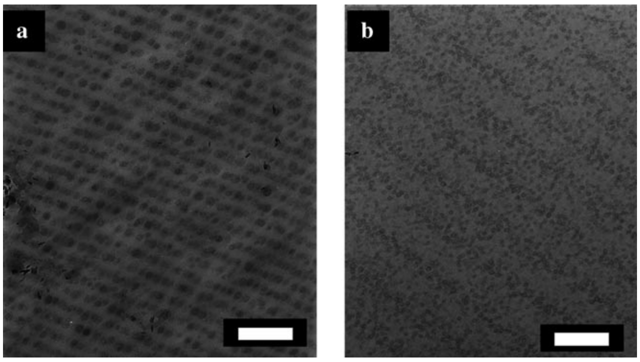


Figure 14. TEM examination of polymer/LC morphology in HPDLC reflection gratings based on two different thiol–ene networks. Scale bar: 500 nm. Reproduced from Ref. [165] with permission from the American Chemical Society.

switchable.[177,178] In other work, the combination of holographic patterning in the thiol–ene system and corresponding block copolymer self-assembly can result in nanolayered layered structures with a unique combination of nanostructuring on the 5–100 nm scale, thus offering additional opportunities for fabricating hierarchical nanostructured devices.[185]

Two particularly intriguing applications for HPDLCs have been reported.[186,187] The first uses multiple layered (stacked) thiol–ene HPDLCs with different wavelength band notches that allow for switchable wavelength transmission/reflection filtering devices for data transmission, or detectors for various chemical/biological species with distinct absorption or transmission signatures.[186] The second employs a thiol–ene HPDLC reflection grating as a photomask to spatially modulate a visible laser source by an electric field for use in lithographic applications.[187] This dynamic photomask (Figure 15) allows computer control over the patterning of the photoresist by spatial control over the photomask reflection pattern.

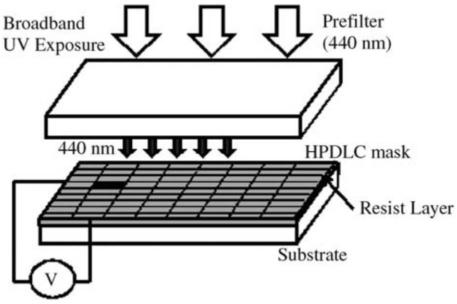


Figure 15. Photomask exposure unit based on a HPDLC reflection grating modulated by applied voltage. Adapted from Ref. [149].

3.7. Initiating and Sustaining Frontal Thiol–Ene Polymerizations

Thermally initiated free-radical frontal polymerizations are essentially non-linear self-propagating chemical wave fronts, initiated photolytically or thermally, which occur by generation of heat at a wave front that propagates through a thermally sensitive polymerizable medium. As shown in Figure 16, there is monomer in the path of the propagating front and polymer where the front has traveled. This method of polymer generation is characterized by extremely low energy input, high conversion, and rapid propagation to give materials with essentially no limitations on thickness. In some cases, photofrontal polymerization have been reported for thiol–ene systems in which the sample initiator bleaches and the reaction follows the bleaching path.[122,130,188,189] However, in the case of free-radical propagating fronts, the front is initiated with light by virtue of a photoinitiator that begins the polymerization process at the surface, followed by a thermally propagating wave sustained by a peroxide or azo thermal radical source.

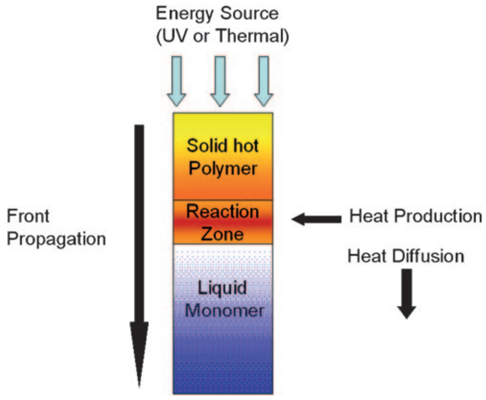


Figure 16. Depiction of a frontal propagating wavefront initiated either thermally or with UV light. Thiol is incorporated into the polymerizing resin system to assist in the initiation process in the presence of oxygen.

One of the major problems with traditional free-radical frontal polymerizations is oxygen inhibition, which requires long exposure times with high intensity sources to initiate the front. As described in Section 2.1, oxygen inhibition is negligible in thiol-based systems. This reduction in oxygen inhibition is important in initiating chemical wave fronts, as illustrated by two recent examples. The first involves an equimolar mixture of a trithiol and a triallyl ether with both photoinitiator and thermal initiator present.[190] The parameters that govern the thiol–ene frontal polymerization have been mathematically modeled[39] and the requirements for sustaining a thiol–ene thermally propagating front are described in terms of such critical parameters as reactant concentration. Alternatively, a small amount of a multifunctional thiol can be added to a di- or triacrylate to aid both in initiating the front in the presence of oxygen as well as increasing the frontal propagation rate.[59,190] However, if the concentration of thiol increases beyond a threshold value, the basic overall polymerization rate and resulting heat exotherm are reduced, and the front is extinguished.[59]

Finally, the photofrontal thiol–ene polymerization fronts alluded to above[122,130,188,189] have been utilized to control the height of photopolymerized systems by variation in the light dose delivered to the sample. A theoretical approach has been developed[122,189] to describe the process and aid in fabricating cured networks with excellent dimensional control over the three-dimensional structure formed with applications in films and microfluidics.

3.8. High-Energy Absorbing Materials

The ability of polymeric materials to absorb and dissipate energy efficiently at a given temperature is defined by the temperature dependency of the mechanical loss tangent upon application of a repetitive force to a material. The loss tangent substrate of the material, tan δ, is a function of temperature and the oscillating frequency of the applied force. One of the salient features of thiol–ene networks is the very narrow width of the tan δ peak as a function of temperature,[49,50,191,192] with full-width at half-maximum (FWHM) values for tan δ versus temperature plots typically on the order of 10–15 °C with correspondingly higher values of the tan δ peak maximum. As pointed out in Section 2.1, these very narrow FWHM values are consistent with chemically uniform cross-linked networks with few dangling chain ends and the elimination of microgels prevalent in conventionally polymerized networks. Such narrow tan δ versus temperature plots are not found for other similar polymer networks.

Taking advantage of the structural control afforded by the thiol–ene polymerization process, a series of high-energy-absorbing thiol–ene and thiol–ene–acrylate mixtures[49,50,191,192] were photopolymerized to give high-energy-absorbing networks with glass transition temperatures near ambient temperature. The multifunctional ene structured components in Figure 17 were designed to contain bisphenol A and/or urethane units that not only provide for high energy absorption at the tan δ peak maximum ($>$ 90%), but also impart additional improvement in physical and mechanical properties, such as higher percent elongation at break, tensile stress at break, and fracture toughness.[49,191] Incorporation of the bisphenol A structure has also been shown to lead to enhanced energy absorption owing to contributions from sub-T_g relaxation modes in the thiol–ene–acrylate ternary systems,[49] whilst the urethane groups provide hydrogen bonding[30] that leads to improvement in elastomeric properties. These high-energy-absorbing materials have tremendous potential in personal protection devices, such as mouthguards, helmets, and shoulder/knee pads. In another approach to developing energy-absorbing materials, a combination of a rapid radical thiol–ene polymerization followed by a slow vinyl ether cationic homopolymerization resulted in energy-dissipating networks with glass transition temperatures between those of the individual photopolymerized thiol–vinyl ether and vinyl ether networks.[193] One remaining future challenge is to create thiol–ene systems that exhibit ultra-high-energy absorption over a wider temperature range.

3.9. Photo-Cross-Linking Functional Polymers

There are a large number of applications that require linear polymers to be cross-linked as a means to improve mechanical and physical properties. Two recent examples[194,195] clearly show that thiol–ene radical processes are appropriate to cross-link existing polymers that are functionalized with either an ene or thiol component. In the former case, Lim et al. reported that hot-melt adhesives could be prepared by the rapid photoinduced reaction of ene functional groups on styrene–butadiene–styrene block copolymers using trimethylolpropane mercaptopropionate as a trithiol cross-linker.[194] The resulting cross-linked adhesives exhibited increases in the temperature for adhesive failure and corresponding decrease in peel strength. In the second case, a thiol-functionalized vinylidene fluoride based elastomer was cross-linked photolytically with 1,6-hexadiene.[195] Both thiol–ene cross-linking reactions were rapid and much more efficient than traditional thermally catalyzed cross-linking scenarios for linear polymers. The use of thiol–ene

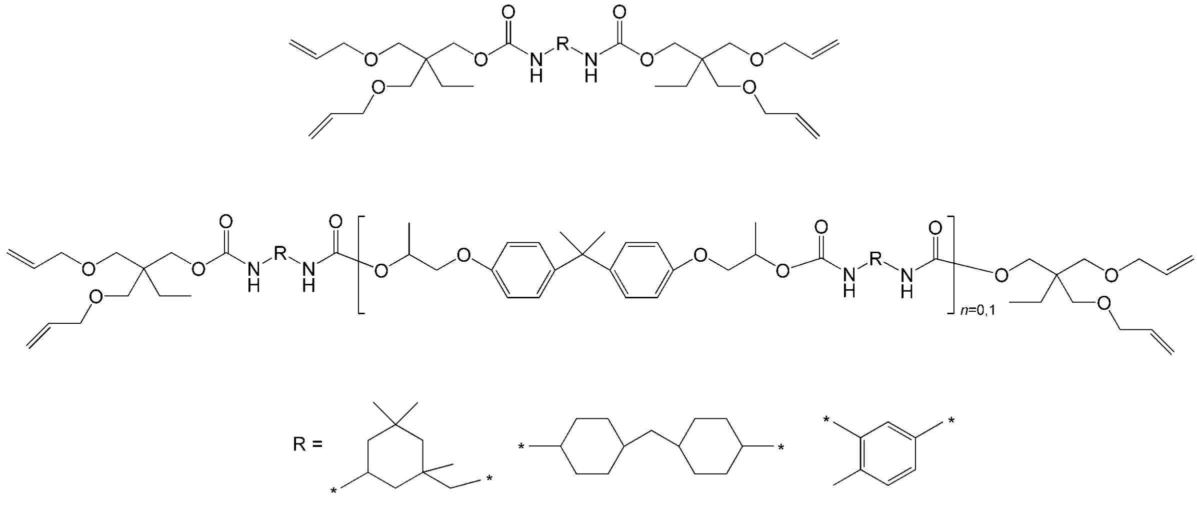


Figure 17. Ene structures containing carbamate linkages synthesized from diisocyanates and a difunctional allyl ether with a reactive hydroxy group.

radical coupling for cross-linking preformed polymers rapidly at low temperature using a benign photoinitiator is a tremendous opportunity for thiol–ene chemistry, and it is expected that the future will see many new developments in this arena with several potential applications. For example, a polyferrocenylsilane[196] functionalized with pendant ene groups was cross-linked by a photoinitiated reaction with a multifunctional thiol. The resulting metallopolymer network with silica spheres serves as an efficient photonic crystal based switching device with potential for use in flat-panel displays. Finally, thiol–ene cross-linking reactions have also been reported for ene-functionalized polyurethane dispersions,[197] as well as interpenetrating polymer networks involving a mixture of a trithiol and vinyl-terminated poly(dimethylsiloxane) combined with cellulose acetate butyrate.[197]

3.10. Formation of Low-Stress Networks

An elusive goal in obtaining photopolymerizable and photocontrollable homogeneous network structures with correspondingly reduced stress and homogeneous network structures is readily achieved using thiol–ene free-radical polymerization. The uniform, step-growth nature of the thiol–ene photopolymerization and the delayed gelation that results gives rise to three dramatic differences in material properties: 1) the magnitude of the polymerization shrinkage, 2) the development of reduced stresses resulting from both the lower shrinkage and the delayed gelation, and 3) the formation of a homogeneous polymer network with outstanding mechanical properties and a very narrow glass transition. This combination of ideal mechanical properties makes these materials exceptional candidates as energy-absorptive materials, dental materials, glassy coatings, and optical materials.

Based on the mechanism shown in Scheme 2, each ene double bond reacts with only one thiol-containing monomer rather than the two monomers that are generally coupled to each double bond in a traditional chain-growth radical photopolymerization. This difference implies less contraction of the Van der Waals distances separating monomers as the polymer forms, and the density difference between monomer and polymer is thus reduced for the thiol–ene polymerization in comparison to (meth)acrylate polymerizations. Patel et al.[199] reported that for (meth)acrylate double bonds, the shrinkage associated with the polymerization reaction is approximately 22–23 $cm^3\,mol^{-1}$ per reacted double bonds. In contrast, recent work[200] indicates that the shrinkage in the thiol–ene reaction is between 12 and 15 $cm^3\,mol^{-1}$ per reacted double bonds. The highest shrinkage values in the thiol–ene reaction were for double bonds from triallyl triazine trione, which experiences a small but significant amount of homopolymerization. These results confirm that the reduced shrinkage in the thiol–ene system results from the uniform polymer architecture that is a function of the photopolymerization step-growth process.

Apart from reduced shrinkage, the stress accompanying polymerization is also reduced in thiol–ene reactions. The formation of a glassy polymer during photopolymerization is always accompanied by stress development, as the post-gelation shrinkage that occurs imparts a permanent, irreversible strain that, when coupled with the highly cross-linked structure that resists deformation, leads to stress development. This stress development is enough to cause cracking in some materials, and is a major cause of failure in dental composite restorative materials.[201] Because of both the reduced shrinkage and the delayed gel point, the stress that arises in the thiol–ene photopolymerization is significantly reduced from that of conventional polymerization. Figure 18 presents a comparison of the shrinkage stress measured by a tensometer as a function of the double-bond conversion (allyl ether or methacrylate) measured simultaneously by near infrared spectroscopy.[200] The stress in the methacrylate polymer, which is used as a representative composition for current commercial dental restorative materials, arises at much lower conversions, reaches a higher absolute value, and the overall sample achieves lower double bond conversion than does the thiol–ene analogue.

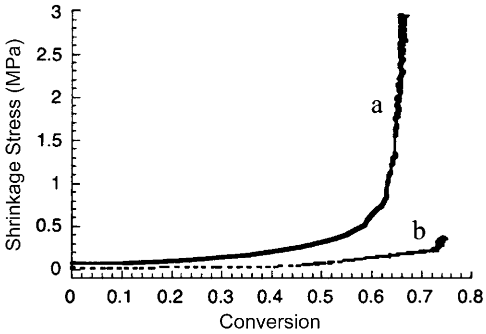


Figure 18. Polymerization shrinkage stress as a function of ene conversion in a) a mixture of dimethacrylate synthesized from the diglycidyl ether of bisphenol A and methacrylic acid (70 wt%) and triethyleneglycol dimethacrylate (30 wt%) (——), and b) stoichiometrically mixed tetrathiol 1 ($n=0$)/triene 4 (----). Samples contain 0.3 wt% camphorquinine (CQ) and 0.8 wt% ethyl-4-dimethylaminobenzoate (EDAB) and were cured with 580 $mW\,cm^{-2}$ visible light for 60 s. The thiol–ene polymer exhibits delayed gelation, which delays the initial stress rise, reduced shrinkage, and achieves an overall higher double bond conversion and much lower stress value. Reproduced from Ref. [200] with permission from Elsevier.

This array of advantages, which is even further improved by oligomerizing the thiol–ene mixture prior to polymerization,[202] all arises because of the distinct mechanism of the thiol–ene reaction. As such, these materials have significant potential in several high-T_g, high modulus applications, such as dental restoratives,[203] for which a low stress material is required.

In a closely related system, an oligomeric thiol prepared by an acrylate–thiol Michael addition reaction was copolymerized with a triallyl triazine ene that is chemically different from the acrylate used to synthesize the thiol.[98] The networks formed by the photoinitiated radical oligomeric thiol–ene reaction are much more uniform, as attested to by the FWHM temperature spread from plots of tan δ versus temperature, than the networks produced by direct photoinitiated radical polymerization of the ternary thiol–ene–acrylate ternary mixture of the same concentrations.

In a recent approach to further alleviating the stress in thiol–ene networks, allyl sulfide moieties[204–206] were incorporated into the polymer backbone. These moieties are capable of reacting with thiyl radicals, formed either during or at any point following polymerization, to reversibly fragment and reform the backbone and cross-link structure. As such, they alleviate network stresses and strains, deform in response to non-uniform irradiation fields, and respond to an irradiation stimulus to recover the initial shape.

3.11. Hydrogels and Biomaterials Applications

The robustness and simplicity of the thiol–ene photopolymerization and thiol–acrylate polymerizations occurring either by Michael addition reactions or photopolymerization have led to their widespread use in a number of biological applications. The ease of formation and reasonable reaction times under ambient conditions and insensitivity to the presence of water and oxygen have facilitated the application of these reactions in the biomaterials area, and particularly in controlled drug delivery, tissue engineering, and hydrogel formation. Two distinct approaches have emerged to form these highly capable biomaterials: Michael addition reactions and photopolymerizations of either thiol–ene or thiol–acrylate components. Both reaction types are generally performed in aqueous media, with one or both components in the reaction frequently containing poly(ethylene glycol) (PEG) cores and the thiol component often being a multicysteine-containing peptide.

The utilization of the thiol–acrylate Michael addition reaction to form hydrogel biomaterials was pioneered by Hubbell and co-workers[207–210] for controlled drug-delivery applications. In particular, these hydrogels were readily formed in an aqueous environment from PEG-containing multiacrylates or vinyl sulfones[211] and a variety of thiols, and particularly those from cysteine units in peptide sequences. These materials could be made hydrolytically or enzymatically degradable and provide zero-order drug release over several days. The hydrolytic degradation mechanism was identified as being associated with cleavage of the acrylate esters following their reaction with the thiol. Control of the polymerization reactivity was achieved by changes in the peptide structure, particularly the nature of the amino acids adjacent to the cysteine units, whilst changes in the network swelling and degradation kinetics were manipulated by changing the monomer functionality and by changing the molecular weight of the PEG multiacrylates. Niu et al.[212] utilized a similar approach to react PEG–poly(propylene oxide)–PEG triblock copolymers that were end-functionalized with acrylates and thiols to form a thermosensitive hydrogel material.

Anseth and co-workers extended the work of Hubbell and co-workers by taking similar thiol- and acrylate-containing monomers and photopolymerizing them in the mixed-mode thiol–acrylate polymerization[59,60,213] for hydrogel formation and as potential tissue-engineering matrices. Owing to the rapid photoinitiation and the mixed-mode step-chain growth polymerization, the polymer-network structures were formed more rapidly with greater cross-linking density than their Michael addition counterparts. Work has also focused on the inclusion of methacrylate-functionalized peptide sequences to manipulate cell behavior within the hydrogel.[63] Others have produced hydrogels from a pure step-growth thiol–ene reaction by replacing the acrylate moieties with allyl ethers and observing the changes in degradation and other network properties.[214] Finally, hydrogels based upon the thiol–ene network produced by reacting vinyl sulfone derivatized insulin with Trithiol 1 ($n = 0$; Figure 1) were also reported to be effective drug-release systems.[215]

3.12. Applications in Optics and Electronics

Owing to the high refractive index of sulfur and its ease of incorporation into organic materials, one of the most prevalent uses of thiol–enes for the past two decades has been in electrooptics. The photoinduced thiol–ene click reaction is readily initiated by a wide range of light sources and initiating systems, making it easy to fabricate optical components using low-, medium-, and high-pressure mercury lamps, CW and pulsed lasers, steady-state and pulsed xenon lamps, and a wide range of LEDs. A large number of electrooptical references can be found in the Review of thiol–enes in 2004.[21] Since 2000, hundreds of articles and patent applications, the majority dealing with Norland Optics photoocurable thiol–ene systems, have appeared in a wide array of journals. The applications of this technology are far too extensive to cover in detail in this Review, but apart from those already presented, applications extend to dielectric layers,[216,217] flexible display components,[218–225] photonic crystals,[226,227] molding/stamping/imprinting,[228–234] grating components,[235,236] lens components,[237–240] prism beam stearers,[241] optical waveguides,[242–245] lithography,[246,247] patterning,[248] waveguide cladding,[249] nanofiber high-oxygen-barrier networks,[250] nanopillars,[251] microbridges,[252] microfluidic devices,[253] and plasmonic crystals sensors.[254] Probably the largest singe use of Norland thiol–ene-based photocurable systems has been in the fabrication of PDLCs and HPDLCs and related liquid-crystalline optical devices.[255–291] There is little question that thiol–ene-based systems will play a key role in future advances in the optical photonics field.

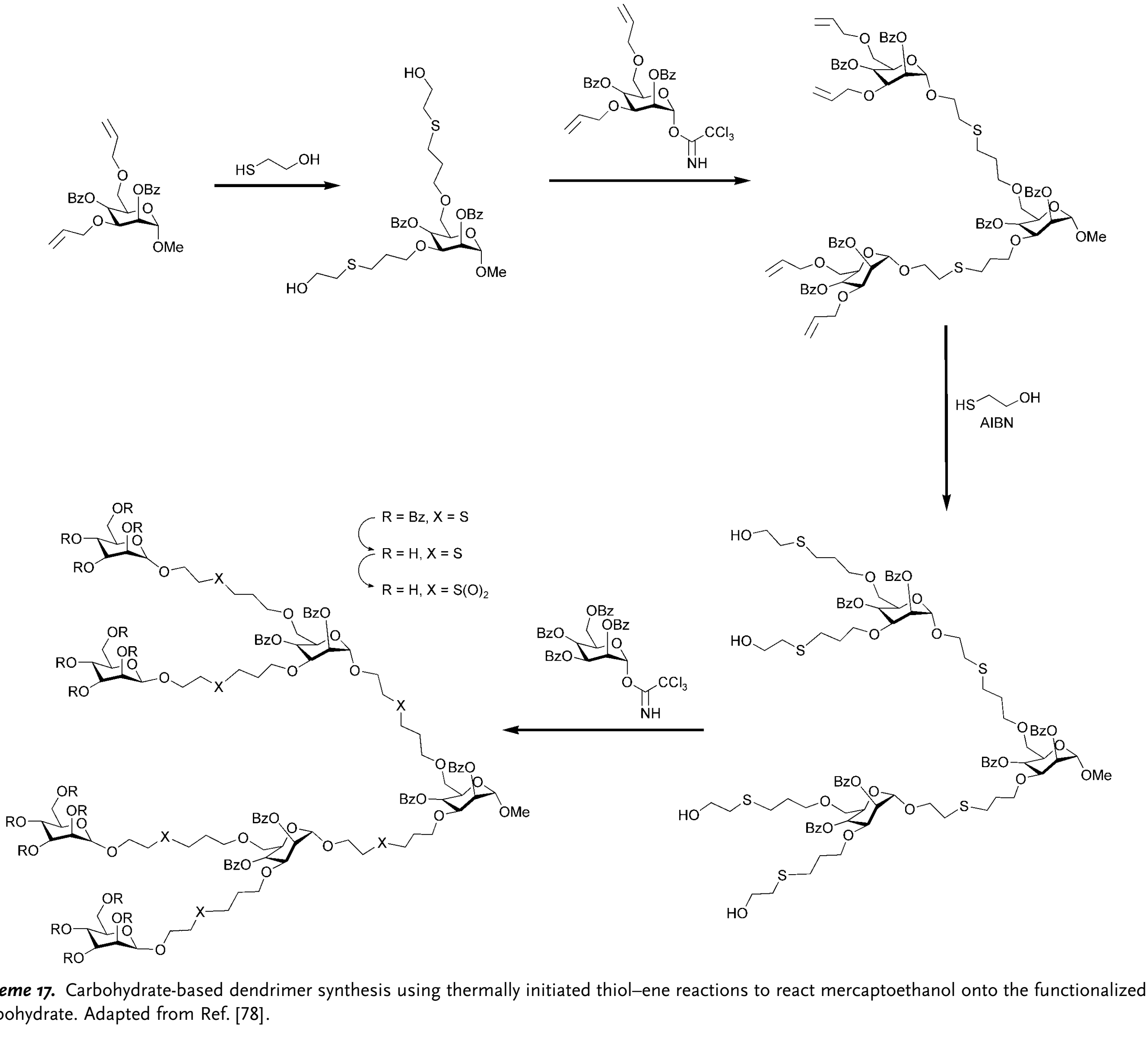
3.13. Bioorganic Thiol–Ene Functionalization

As indicated throughout this Review, the powerful capabilities of the radical-mediated thiol–ene reaction are exemplified in numerous functionalization and polymerization reactions; however, their prevalence in the area of bioorganic functionalization is a significant insight into the future of these reactions. The selectivity, ease of implementation, and high yields associated with the thiol–ene reaction are a perfect marriage with the requirements of biomaterials applications. Numerous accounts exist in the literature on the implementation of the thiol–ene reaction to functionalize biological materials and biological molecules, and to incorporate biological molecules into other synthetic materials and molecules.[78,80,147,156,292–303] These functionalization reactions have included highly successful thermal and photochemical radical generation mechanisms and also Michael Addition reactions.

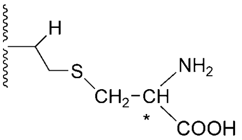
Unlike many other thiol–ene reactions, the implementation of thermally sensitive radical initiators, such as AIBN, has been prominent in the functionalization of biological materials.[78,80,147,156,292] For large-scale syntheses, the need to uniformly functionalize large volumes of material limits to some extent the viability of photoinitiation, where uniform extended exposure of large volumes is limited both by reactor design and light attenuation. Therefore, to achieve uniform bulk radical generation, elevated temperatures and thermal initiators have regularly been used. Similar uniform bulk radical generation and successful functionalization is also readily achieved by redox initiation for thiol–ene functionalization reactions without the need for elevated temperatures.

As shown in Scheme 17, one recent example of the thermally initiated thiol–ene biofunctionalization reaction was implemented by Heidecke and Lindhorst,[78] who were successful in reacting mercaptoethanol with terminal double bonds in sequential generations of dendrimer synthesis. The core of the dendrimer was a carbohydrate monomer, and yields up to 94 % were reported for the thiol addition to the terminal allyl ether. The synthesized glycodendron and systematically varying structures akin to it were subsequently evaluated for their effectiveness in preventing bacterial adhesion.

A second exciting direction in thermally initiated thiol–ene functionalization reactions is the implementation of the amino acid cysteine as the reactive thiol in functionalization reactions. Passaglia and Donati[147] recently functionalized styrene/butadiene copolymers with various cysteine derivatives as a means to generate optically active polymeric materials that contain amino acid residues. The resulting product (Scheme 18) is a mid-chain functionalization of the internal enes in the SBR copolymer, although the terminal



Scheme 17. Carbohydrate-based dendrimer synthesis using thermally initiated thiol–ene reactions to react mercaptoethanol onto the functionalized carbohydrate. Adapted from Ref. [78].



Scheme 18. Thermally initiated thiol–ene reaction of the amino acid cysteine with a styrene–butadiene copolymer, resulting in copolymers functionalized by the L-cysteine ethyl ester. These results demonstrate the utility of cysteine as a monomer in the thiol–ene reaction, enabling various reactions of cysteine and cysteine-containing peptides. Adapted from Ref. [147].

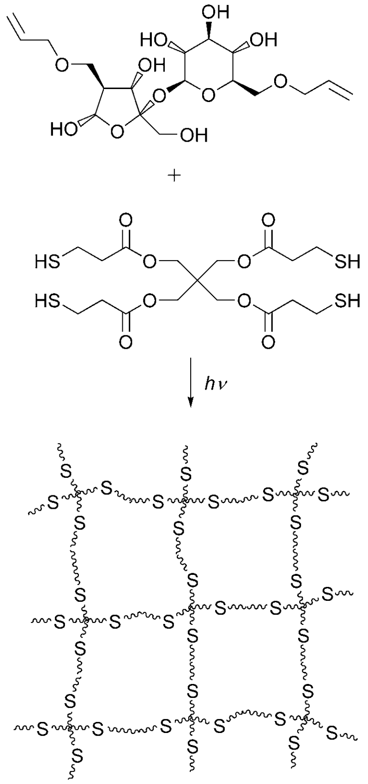
vinyl groups of model compounds were found to be significantly more reactive, as expected.

The work of Donati et al. points to an exciting future possibility for thiol–ene bioorganic functionalization and polymerization in which naturally occurring enes and thiols are utilized, such as the thiol in cysteine, to incorporate biological molecules into polymeric materials, thus synergistically combining the advantages of each. Recently, Anseth and coworkers have exploited this possibility by incorporating entire peptide sequences with terminal cysteines into hydrogel networks:[61a] The functional capability of the peptide is preserved when it is incorporated into the polymeric hydrogel material. In this instance, the peptide was chosen as a cysteine-terminated fluorophore. This peptide was incorporated into the network by exposure to a photoinitiator and a photomask, and fluorescence only occurred in the regions that were exposed to light. Further to direct radical-mediated thiol–ene coupling,[293] other work in this area has demonstrated that peptides are readily incorporated into thiol–acrylate polymerizations[294] and through Michael addition to thiolated surfaces.[107]

A great deal of additional work has been done in regards to the photoinduced coupling of thiols and enes in bioorganic systems.[61a,75,82,106,293–301] As shown in Scheme 19, Ortiz et al.[296] have developed a novel approach that utilizes the photoinduced thiol–ene reaction to fabricate sucrose-containing polymers. In this approach, conventional, multifunctional thiol monomers were photopolymerized with diallyl ether functionalized sucrose molecules to form a polymer network. Upon initiation by *N*-(2,3-dimercaptopropyl)phthalamidic acid (DMPA), the polymerization reaction was completed in less than 20 seconds, with nearly 90 % functional group conversion and nearly equivalent conversions of both the allyl ether and thiol, as necessitated by the step-growth nature of the reaction.

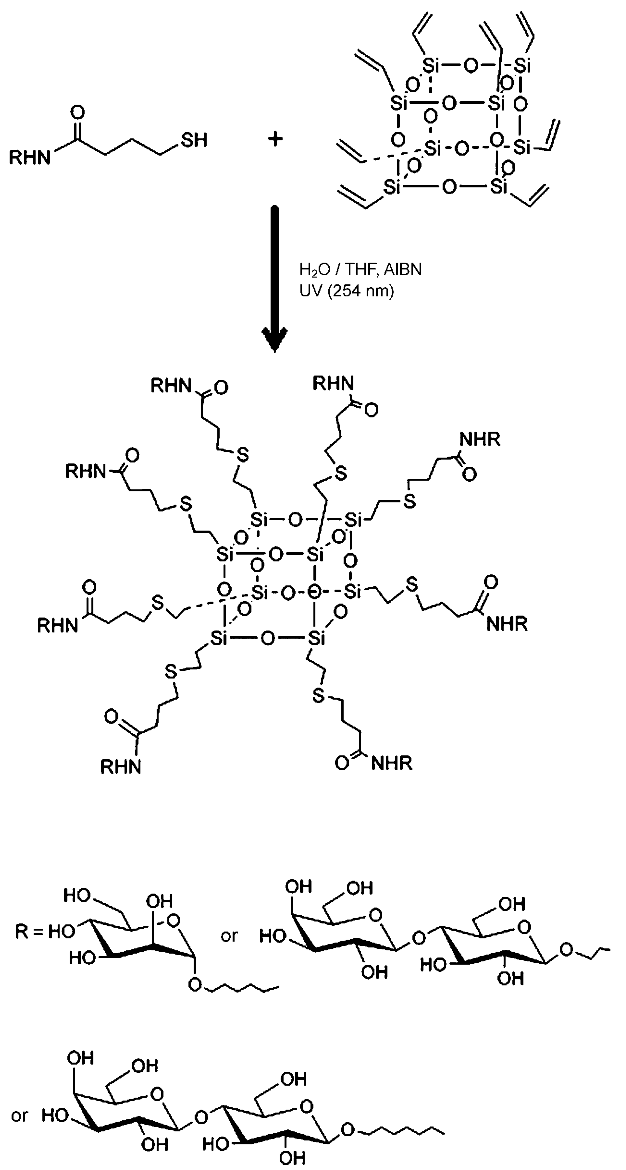
Gao et al.[298] combined the thiol–ene functionalization reaction with polyhedral silsesquioxane (POSS) chemistry to form an octafunctional carbohydrate (Scheme 20). Each of the eight silicon atoms in the POSS structure was functionalized with an allyl unit that was subsequently reacted with a thiol-terminated sugar residue, either mannoside or lactoside, to yield the carbohydrate-functionalized POSS. This POSS-based glycocluster is expected to have differential solubility, adhesive, and adsorption properties, as the authors demonstrated in a preliminary manner.

In bioorganic systems, the necessity for orthogonality in reactions and approaches is critical, and the reaction media is generally a complex mixture that contains any number of various chemical functional groups and species. As noted by Waldman and co-workers[106] in referring to the thiol–ene photoinduced functionalization, "…*this photoreaction can be considered to be bioorthogonal, unlike other photochemical methods used previously*…" Waldman was particularly interested in and focused on immobilization of proteins on surfaces. As a variety of methods exist for preparing uniform or non-uniform but patterned thiol-terminated surfaces, he chose to specifically functionalize biotin or a biotinylated protein with an allyl functional group and perform the photoinduced thiol–ene coupling of the protein to the thiolated surface (Scheme 21). The protein density on the surface could be controlled by the exposure time, and the protein was able to maintain its activity following coupling to the surface. The level of molecular control and orthogonality of this coupling reaction enables it to be used to design and tune biological material properties, and even form gradient structures.

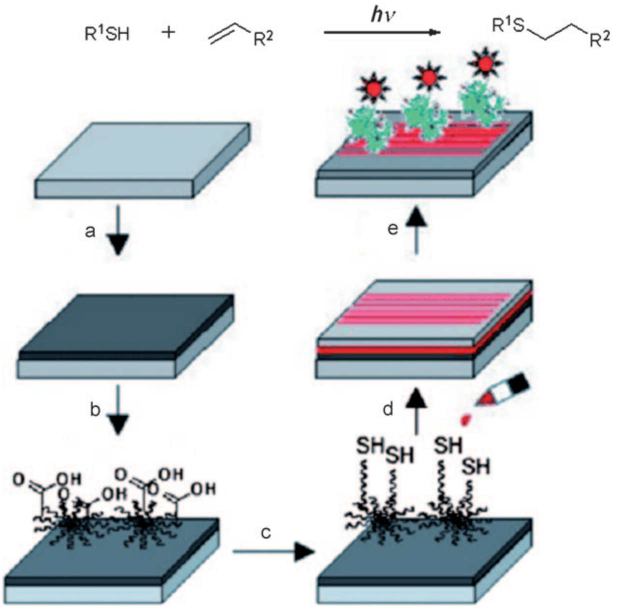


Scheme 19. Photoinduced thiol–ene polymerization of allyl ether functionalized sucrose molecules to form hydrogels. Adapted from Ref. [296].

Additional protein conjugation work by Wittrock et al.[82] has focused on the development of vaccines. Glycopeptide antigens are coupled to a protein core, in this case bovine serum albumin (BSA), which serves as a carrier for the antigens (Scheme 22). By forming an allyl-functionalized BSA core and reacting with thiolated glycopeptides, it was possible to achieve an average of eight glycopeptides per BSA molecule following photoinduced thiol–ene coupling. The authors cite the precise control afforded by the click reaction as one of the most promising aspects in regards to creating future vaccines based on this approach.



Scheme 20. Reactions of thiol-functionalized sugars and ene-functionalized POSS cores to form mannose- and lactose-derivatized POSS molecules. Reproduced with permission from Ref. [298].

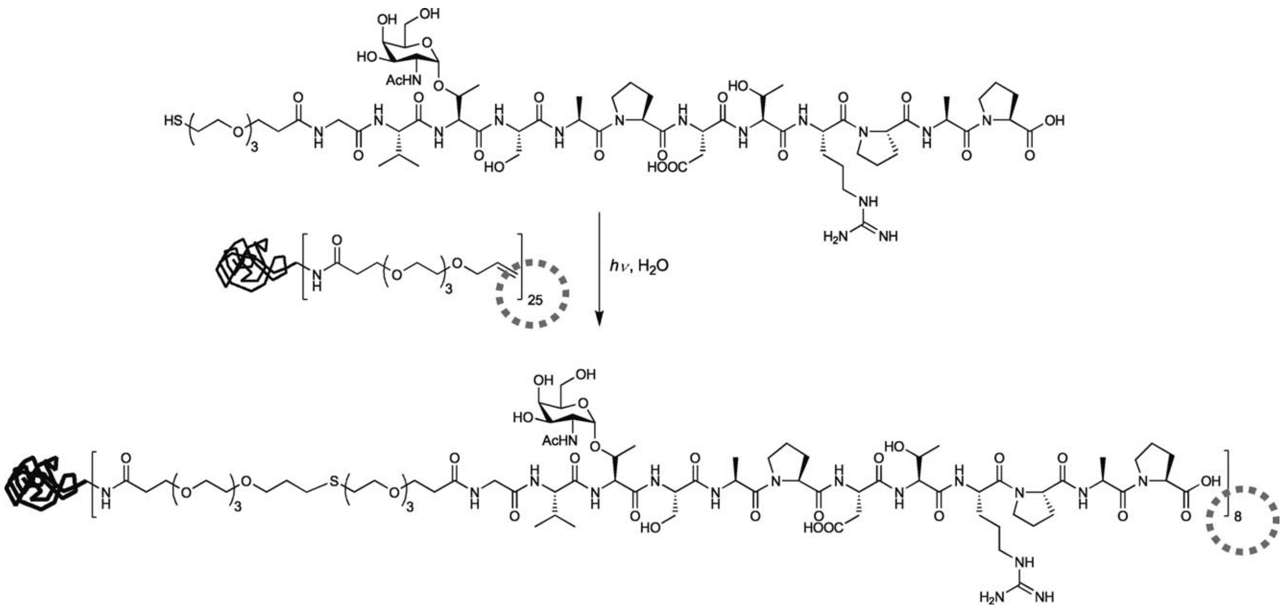


Scheme 21. The photoinduced thiol–ene coupling of proteins to surfaces with precise control of grafting density and position. a) Plasma-enhanced silanization, b) dendrimer attachment, c) thiol derivatization, d) photopatterned thiol–ene reaction to spatially control the patterning of the target ene-functionalized molecule, and e) mask removal. Reproduced from Ref. [106].

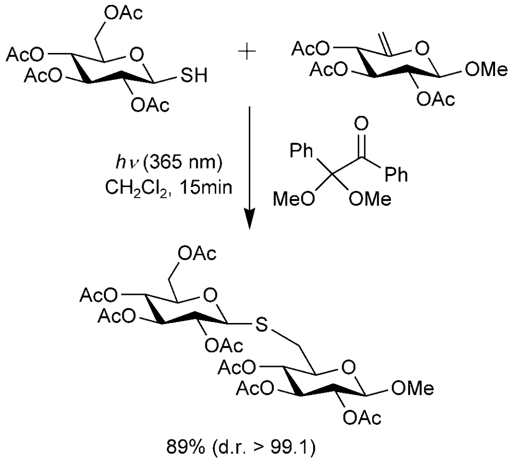
Building on the goal of creating molecules with advanced applications in medicine, Dondoni and co-workers[299] have recently utilized the photoinitiated thiol–ene reaction to create lead compounds as new drug target molecules: They created a technique for creating dimers and higher molecular weight oligomers of sugar molecules by reacting combinations of thiol-containing sugars and ene-containing sugars (Scheme 23). This approach has the potential for creating a library of compounds that mimic carbohydrate structures in a controlled manner. The reaction products were obtained in good to excellent yields and found to have diastereoselectivities of up to 99%; the reactions were performed without deoxygenation, and the only significant impurity was found to be the disulfide product. The authors note that the use of long-wavelength ultraviolet light or visible light (or even sunlight) has significant benefits associated with it in comparison to almost any other potential process that could be used.

In one final example of the powerful nature of the thiol–ene reaction for biomedical applications, Stenzel and co-workers[300] recently implemented thiol–ene reactions as a means for forming micellar structures appropriate for controlled drug delivery (Scheme 24). The common theme of utilizing thiol–ene reactions for creating sugar-moiety-containing small molecules, oligomers and polymers is continued in this work, where the authors were able to synthesize well-defined side-chain functionalized polymers, including block copolymers, containing controlled substitution levels and organization of vinyl side groups. These side groups were subsequently reacted with glucothiose by a photoinitated reaction to form well-defined sugar-functionalized polymer structures. Block copolymers of PEG–methacrylate and glucose-functionalized PHEMA were found to form thermoreversible micelles that could be used to encapsulate drugs for triggerable release.

Although the thiol–ene reaction itself has been demonstrated to be highly capable and functional in bioorganic systems, recent work by Anseth and co-workers[295] and Haddleton and co-workers[101] provides significant insight into the future directions of this field. Both of these groups combined multiple click reactions for bioorganic functioanlization, one being a thiol–ene reaction and the second a Huisgen click reaction. The incredible potential of these reactions in combination is particularly apparent for materials science applications involving biological systems and biomaterials. Anseth and co-workers developed techniques for



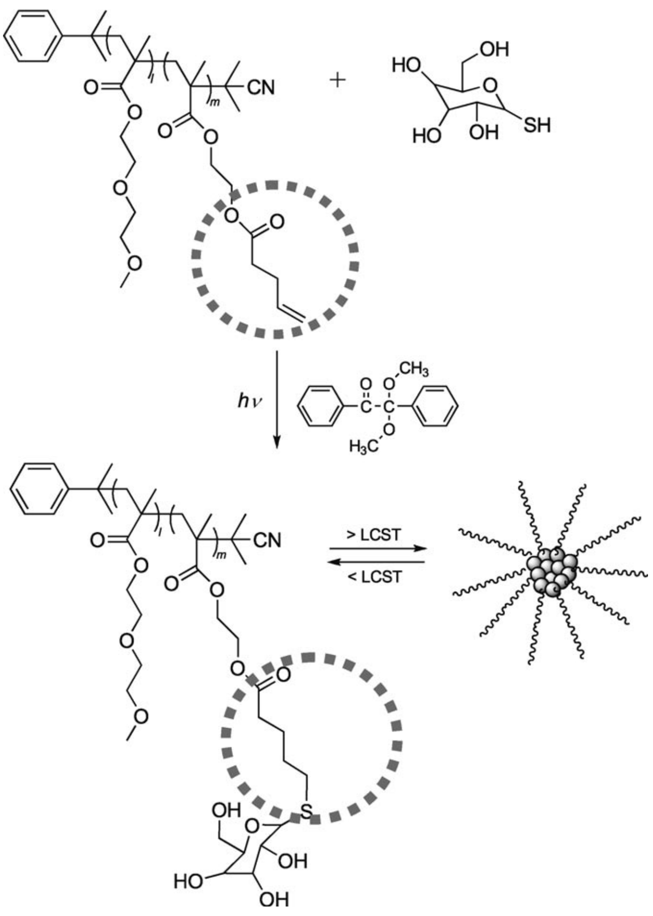
Scheme 22. Photoinduced thiol–ene coupling of glycopeptide antigens to a desired protein core for ultimate vaccine development. Reproduced from Ref. [82].



Scheme 23. Utilization of thiol–ene reactions to create a library of target compounds for drug development by the formation of an array of dimers and oligomers based on thiol- and ene-functionalized carbohydrate structures. Reproduced with permission from the American ChemicaL Society from Ref. [299].

copper-free synthesis of hydrogels through the Huisgen click reaction followed by photopatternable thiol–ene coupling of peptides that control cell behavior. Haddleton and co-workers utilized the thiol–Michael addition reaction to end-functionalize polymers having terminal ene groups that contained alkyne side chains, which were subsequently reacted with azide-containing sugars to yield glycosylated polymer backbones.

Finally, whilst the radical-mediated thiol–ene reaction is of great value in bioorganic functionalization reactions, it is not the only thiol–ene click reaction used in this manner. The thiol–Michael addition reaction has also been prominently featured in a range of bioorganic functionalization reactions,



Scheme 24. Formation of amphiphilic molecules that lead to micellar structures based on thiol-functionalized sugars and ene-functionalized copolymers. The relative hydrophilicty of the resulting structure is controlled by the degree of functionalization, with control afforded by the thiol–ene click reaction. Adapted from Ref. [300].

occurring with many of the same benefits, though under different reaction conditions compared to the radical-mediated thiol–ene reaction.[88,91a,101,107,302–303]

3.14. Odor, Toxicity, and Shelf Life

As with any chemical system, there are issues that must be resolved regarding both basic research and applications. Certainly, thiols have distinct odors, which may be prohibitive in some cases whilst acceptable in others. Furthermore, thiols may have toxicity considerations for some uses. The Aldrich catalogue lists LD50 for oral toxicities for several monothiols: 1-hexanethiol 1254 mg kg^{-1}, 3-mercaptopropionic acid 96 mg kg^{-1}, ethyl 2-mercaptoacetate as 178 mg kg^{-1}, 1-thioglycerol 645 mg kg^{-1}, 2-mercaptoacetic acid 114 mg kg^{-1}. Higher functional thiols reputedly have LD50 values of 1000 mg kg^{-1} or greater: Material safety data sheets should be consulted when using thiols, and proper precautions taken.

The shelf life of certain thiol–ene mixtures is very short in some cases, but can be controlled to a great extent for many systems by taking proper measures to ensure adequate performance after storing as discussed in references [10] and [11] and key references therein. Interestingly, thiol–ene formulations based on as-received commercial multifunctional secondary thiols have exceptional shelf lives.[304]

4. Outlook

The click chemistry paradigm is embodied in a single word: simplicity, and particularly simplicity that leads to ubiquitous implementation. The original alkyne–azide reaction has clearly achieved implementation across a broad spectrum of organic chemistry reactions whilst simultaneously spawning interest in a number of other reactions that also embody the click paradigm. In this Review, the photoinitiated thiol–ene radical reaction has been presented together with its enormous advantages, including ease of implementation, high yield and conversion, rapid reaction rates, and photoinitiation capability, which make it unique in its potential in both polymer science and molecular synthesis. The thiol–Michael addition reactions, when initiated by powerful nucleophilic catalysts, are also very efficient, and these are thought to occur by an anionic chain process that has little or no termination reactions that could otherwise reduce its efficiency and rate. The latter can be best thought of as a radical thiol–ene reaction that does not self-terminate, can occur at ambient conditions, and is oblivious to oxygen, water, or other reactive protic species.

As demonstrated in Section 3, there are a wide number of emerging applications that have been advanced by thiol–ene chemistry during the past 4–5 years. However, we have only focused on the more prevalent implementations of thiol–ene reactions. Their broader exploitation and utilization across many diverse fields, with several hundred papers and patents published in just the last five years (only some of which are cited herein) that in one way or another implement the thiol–ene reaction in different applications too numerous to present is the strongest evidence of their potential, their utility, their advantages and their simplicity. The click nature of the thiol–ene reactions, both free-radical and anionic chain processes, and the rapid generation of highly uniform networks with variable refractive index and high clarity, have made it the method of choice for use not only by chemists but also by a wide array of physicists, biologists, chemical engineers, electrical engineers, mechanical engineers, information storage engineers, and optical design engineers.

Adaptation and advances in thiol–ene radical chemistry continue to be reported,[292,297,299–301,305–312] and extend to new patterning/lithography procedures,[310,312] functionalization of advanced synthetic[301,309] and biologically relevant polymers/peptides,[292,297,300] generation of new homogeneous[304,308] and hybrid[311] network structures, functionalized microspheres[306] and nanoparticles,[307] stabilization/functionalization of capsules and multilayer systems,[305] and the high-yield synthesis of thiodisaccharides using conventional and sunlight sources.[299] This intriguing use of sunlight, along with a report cited in Section 3.4 for modification of linear polymers,[158] has the potential for being a very important resource for chemical and materials synthesis. Recent new reports of thiol–Michael addition reactions,[313–318] several of which take advantage of the powerful phosphine[315,317] and primary amine[316] nucleophilic catalysts, involve reactions of RAFT polymers that lead to nanoparticle modification,[314] end group functionalization and block/grafted copolymers,[313,315,307] and the synthesis of three-arm star polymers.[316] The recent implementation of the related photoinitiated thiol–yne free-radical chain reaction has been shown to exhibit essentially the same outstanding characteristics as its thiol–ene counterpart, with the benefit of adding quantitatively two aliphatic thiols per yne unit,[319–322] thus providing the click synthesis of a wide range of highly functional multimers, highly refractive optical materials, and water-soluble end-functionalized polymers. All of this activity attests to the tremendous potential for applying thiol–ene chemistry to an expanding number of frontiers in chemistry, biology, physics, and engineering.

There are pressing needs that remain for continued evaluation of the thiol–ene reaction mechanisms and their dependence on the ene and thiol structures, continuing development of novel thiol- and ene-based materials, and extending the thiol–ene click reaction to an even more expanded range of applications. Moreover, seqeuential reactions that combine thiol–ene and thiol–Michael addition reactions, along with the thiol–yne reactions, should open up many new pathways for the rapid and efficient synthesis of a wide range of chemical and material species. It is expected[323–325] that thiol–ene click chemistry has the potential to expand into all areas of science and engineering for creating and functionalizing polymers and surfaces for applications in a wide range of disciplines that involve high-performance materials. The future appears to indeed be bright for both radical- and catalytically mediated thiol–ene click reactions.

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