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Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers

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ABSTRACT: Polymer networks possessing reversible covalent cross-links constitute a novel material class with the capacity for adapting to an externally applied stimulus. These covalent adaptable networks (CANs) represent a trend in polymer network fabrication toward the rational design of structural materials possessing dynamic characteristics for specialty applications. Herein, we discuss the unique attributes of CANs that must be considered when designing, fabricating, and characterizing these smart materials that respond to either thermal or photochemical stimuli. While there are many reversible reactions which to consider as possible cross-link candidates in CANs, there are very few that are readily and repeatedly reversible. Furthermore, characterization of the mechanical properties of CANs requires special consideration owing to their unique attributes. Ultimately, these attributes are what lead to the advantageous properties displayed by CANs, such as recyclability, healability, tunability, shape changes, and low polymerization stress. Throughout this Perspective, we identify several trends and future directions in the emerging field of CANs that demonstrate the progress to date as well as the essential elements that are needed for further advancement.

1. Introduction

Polymer networks have been variously described as “branching to its extreme”[1] or, perhaps more precisely, as “indefinitely large polymer structures”.[2] Covalently cross-linked networks, or thermosets, are extensively used as structural materials in a vast array of applications ranging from coatings to composites to biomaterials. Additional chemical functionality is readily incorporated into these networks by the inclusion of the desired functional groups in monomers that are present during material fabrication; however, once set, these covalently cross-linked networks are, almost by definition, not readily amenable to any modification of their physical state or chemical structure. To address this significant shortcoming, recent synthetic strategies have incorporated reversible covalent bonds into these networks either within the cross-links or the backbone structure to facilitate adaptability in these otherwise intractable materials. Herein, we define covalent adaptable networks (CANs) as those networks which contain a sufficient number and topology of reversible covalent bonds so as to enable the cross-linked network structure to respond chemically to an applied stimulus. This response, which is generally a change in the stress and/or shape (strain) of the material, is achieved without necessitating any irreversible degradation of the network structure, being capable of maintaining the initial bond density while allowing the material to rearrange. These CANs are therefore “smart” materials capable of responding to a stimulus with a change in the physical structure, state, and/or shape of the network.

While characteristics of traditional thermosets are ideal for many applications, where dimensional stability, environmental resistance, and permanence are required, the recycling, reuse, and postpolymerization manipulation of such materials are limited. The applications of CANs are those that require or benefit from the thermal, mechanical, and other properties of a network, but not the permanence of a typical thermoset. The potential for CANs as a reversible adhesive or as a crack-healing material has far-reaching implication into a variety of technologies, from microelectronics[3−6] to nonlinear optics[7,8] to dental materials. Furthermore, CANs inherently have the ability to incorporate other chemical functionality postpolymerization, providing a flexible scaffold that is readily modified to incorporate new and important mechanical and chemical properties. This material design feature, which is often employed in supramolecular science, allows network adaptation toward chemical and environmental cues, yielding a dynamic response property that embodies the emerging field of “smart” materials.

Since the first conclusive structural determination, polymer networks have been traditionally characterized as being either chemical or physical gels owing to their covalent bond structure or connectivity associated with physical associations, respectively. Indeed, this convenient designation has provided the framework for generalizing the physicomechanical behavior of these network types; for example, chemical gels are often characterized by their inability to be melted, molded, mended, or otherwise permanently deformed. Nevertheless, this distinct classification is limited in its applicability as there are several material types, such as Diels−Alder networks, that are classically defined as a chemical gel though under certain circumstances they exhibit behavior more akin to that of physical gels, depending on the time scale of the experiment and the temperature. It is clear that material classification based on bond type, without consideration to bond dynamics, is insufficient to provide an accurate gauge of the network’s mechanical behavior and characteristics. The presumed intransient chemical gel behavior is based on the presumed static nature of the linkages which constitute the network. For those chemical gels which have reversible covalent linkages due to the inclusion of bonds for which the bond structure is covalent yet exhibiting dynamic reversible chemistry, the network behavior depends, even

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qualitatively, on the time scale of the evaluation relative to the average time scale of the bond reversibility.

When considering the characteristics of a strong versus a weak gel, de Gennes argued that the essential difference is the stability of the cross-links.[9] For strong gels, the cross-links are stable for all relevant experimental time scales and stresses, while the cross-links in weak gels are formed by a reversible reaction.[9] Implementation of reversible covalent or physical linkages into supramolecular structures constituted a class of material that Skene and Lehn termed "dynamers";[10] thus, as a network forming material, dynamers are simply weak gels. CANs are uniquely classified by their potential to demonstrate weak gel adaptability via reversible covalent chemistry where the reversibility may be inherent in the nature of the cross-links or triggered by an externally applied stimulus. For example, in the absence of irradiation, photoreversible CANs remain a strong gel while exposure to irradiation transforms the material, transiently, into a weak chemical gel. Other CANS, such as thermoreverible CANS, are by definition weak chemical gels on an infinite time scale but practically only demonstrate observable weak chemical gel characteristics at elevated temperatures. In practice, only a small group of the thermoreversible reactions truly form CANs as most of the thermal reversion processes are essentially depolymerization mechanisms that irreversibly degrade the network structure, removing the potential for the network to adapt while simultaneously retaining its topology and cross-link density.

In this Perspective, we describe several areas of development in the field of CANs while also outlining their unique material

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properties. The chemistries used to produce networks of these types are reviewed along with the advantages and disadvantages of each approach. Particular focus is given to the relative degree to which the polymer is capable of adapting as dictated by the molecular rearrangement mechanisms that are incorporated into the network's chemical structure.

2. CAN Structure and Fabrication

Chemical reactions capable of undergoing reversible addition are the basic constituents of CANs. While there are several reversible condensation reactions that make up dynamic covalent chemistry,[11] the evolution and subsequent loss of a small molecular species eliminates the material's capacity to reversibly form a network. CANs are fabricated from monomers with reversible linkages (e.g., the Diels–Alder adduct shown in Figure 1, panel A) that are formed as part of the network fabrication process (e.g., Figure 1, panel B) or flanked by network forming functional groups (e.g., Figure 1, panel C). In this former process, the network formation mechanism is inherently step growth and forms a structure having at least one reversible linkage per cross-link (e.g., panel B inset has two reversible linkages per cross-link). In contrast, the network structure for the latter monomer type is entirely defined by the polymerization reaction of the flanking polymerizable functional groups. The example shown in panel C of Figure 1 consists of a Diels–Alder adduct flanked by acrylate groups that are capable of undergoing a radical-initiated, chain-growth polymerization or a base-catalyzed step-growth copolymerization with a multifunction thiol monomer. The network topology, resulting from the differing mechanisms, is vastly different where the chain-growth polymerization consists of ideally linear polymers cross-linked by DA adducts (inset i of panel C, Figure 1) while the step-growth copolymerization consists of monomeric-sized units each linked via a DA adduct (inset ii of panel C, Figure 1). The addition of chain transfer agents will decrease the contiguous polymer length not containing a reversible linkage. When this nonreversible contiguous polymer length approaches that of the monomer, the network structure approaches that of a step-growth mechanism.

2.1. Chemistries for Thermoreversible CANs.

All bimolecular addition reactions are, to some extent, reversible as dictated by the temperature dependence of the equilibrium constant. Nevertheless, most reactions can essentially be considered irreversible as there are several temperature constraints that exclude the majority of these reactions from being a thermoreversible CAN building block, including consideration of a practical temperature range, high temperature induced side reactions, and chemical decomposition temperatures. Moreover, the forward and reverse reaction rates (i.e., the kinetics) must allow for bond rearrangement on an application appropriate time scale such that the network is able to adapt to an environmental stimulus. Therefore, both thermodynamic and kinetic elements of a given thermoreversible reaction must be taken into account while also considering the application and its time scale.

There are several thermoreversible cross-linking reactions that have been used to fabricate thermoreversible networks, such as those shown in Figure 2. Several of these reactions have been summarized in Engle and Wagner's 1993 review of thermoreversible polymers.[16] However, many thermoreversible reactions have practical limitations, such as limited reversibility owing to side reactions, precluding them from CANs applications. Here, we will note a few of the more recent utilizations of thermoreversible cross-links, with a particular emphasis on reactions that proceed at practical rates without the use of a catalyst.

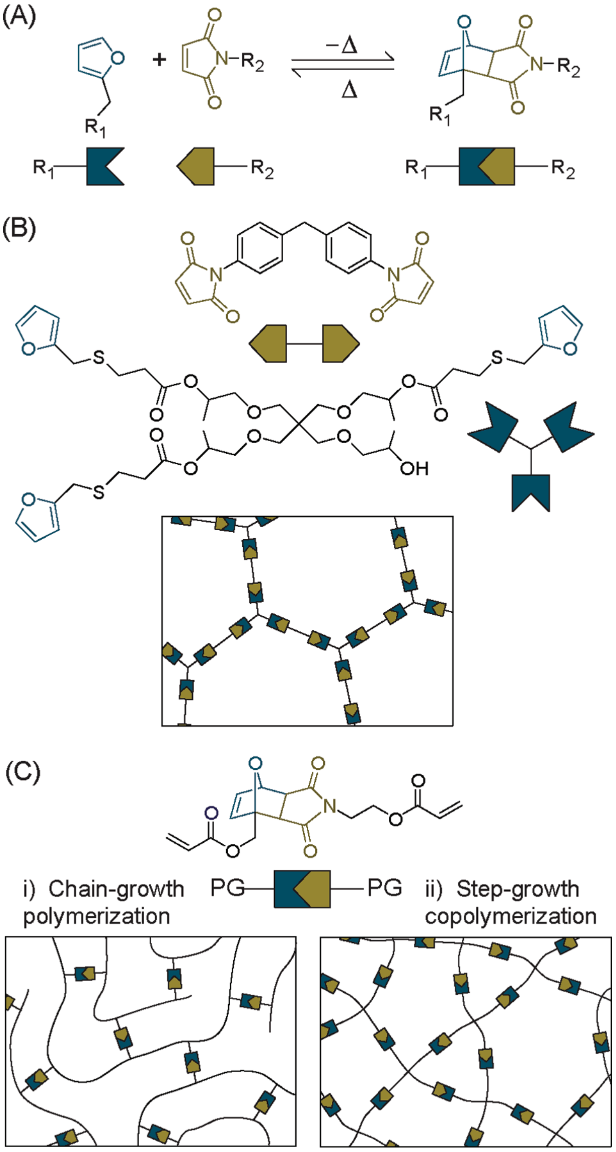


Figure 1. Thermoreversible Diels–Alder (DA) reaction between furan and maleimide (panel A) is used to demonstrate CAN fabricated by formation of the reversible linkage (panel B) or by polymerizable functionality flanking the reversible linkage (panel C). In each of the panels, the reactions between maleimide and furan are represented as complementary geometric shapes. In panel A, the DA cycloaddition between furan (left) and maleimide (middle), which forms the bicyclic compound (right) at low temperatures, is shown. This model thermoreversible reaction undergoes the retro-Diels–Alder reaction at elevated temperatures. In panel B, the network is formed by bismaleimide and trisfuran monomers[12] that undergo a step-growth polymerization via the reversible linkage. In panel C, the reversible CAN linkage is flanked by two polymerizable groups (PG) which, as an example, are given as acrylate functional groups. These acrylate functional groups can be either (i) polymerized via a radical-mediated chain-growth mechanism[13,14] or (ii) copolymerized with a multifunctional thiol monomer (e.g., pentaerythritol tetrakis(3-mercaptopropionate)) via base-catalyzed Michael addition.[15] The insets of B and C represent the formed network structure, which contains reversible linkages that enable reversible depolymerization. It should be noted that although a thermoreversible CAN was used as an example, this demonstration of polymerization types is equally applicable for photoreversible CANs.

Nucleophilic addition reactions are well-suited as thermoreversible reactions as they do not produce a condensate; however, the nucleophile must also be a good leaving group in order to be reversible over a reasonable temperature range. For example, the reaction of an isocyanate with a

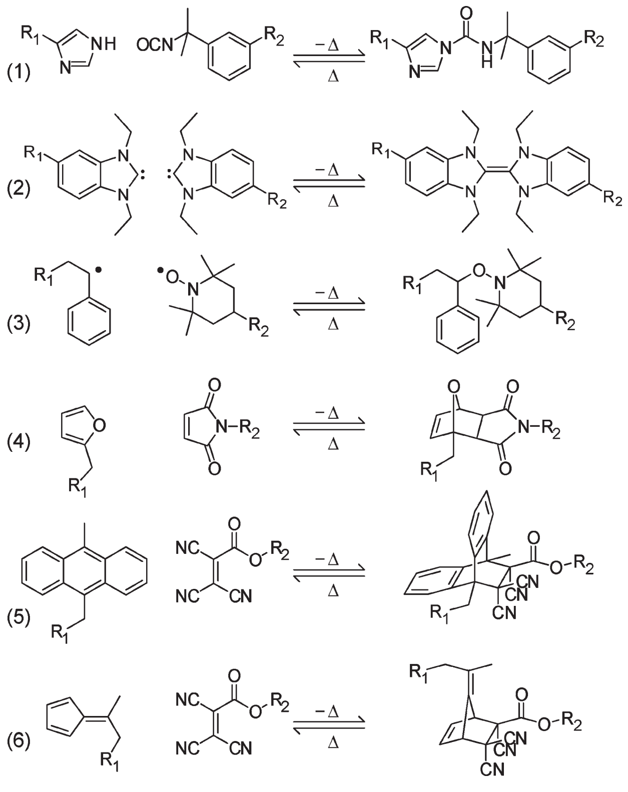


Figure 2. A selection of thermoreversible cross-linking addition reactions. Here, we show the thermoreversible (1) nucleophilic addition between isocyanate and imidazole,[17] (2) carbene dimerization,[18] (3) reversible radical coupling between TEMPO and a styryl radical,[19] and the DA cycloaddition between (4) furan and maleimide,[20] (5) anthracene and tricyanoacrylate,[21] and (6) fulvene and tricyanoacrylate[22] (only the exo product is shown).

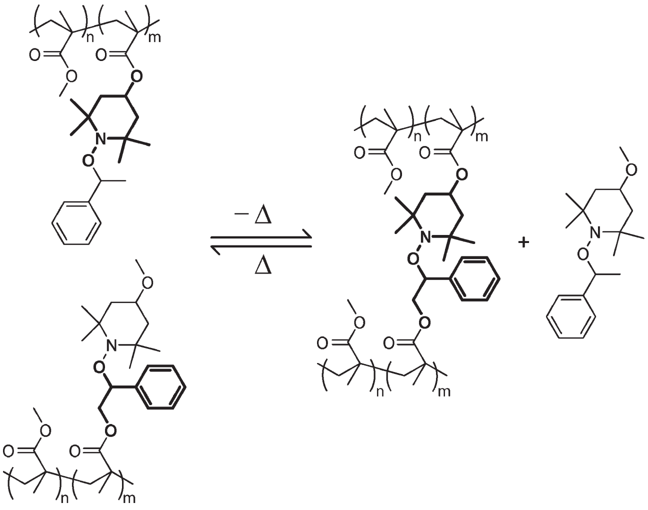


Figure 3. Thermoreversible homolytic cleavage of alkoxyamine producing linear chains with pendant styryl and TEMPO radicals.[19] In this radical crossover reaction, heating causes the capping styryl and TEMPO functional groups to dissociate from their respective linear chain, revealing a pendant TEMPO radical from one chain and a pendant styryl radical from another chain that are capable of forming a thermoreversible cross-link. The small molecular styryl and TEMPO capping species are also able to thermoreversibly combine.

nucleophile such as an alcohol or amine is thermoreversible but inadequate for CANs applications. Whereas the reaction of isocyanate with imidazole has been successfully demonstrated as able to form a thermal CAN under inert conditions (reaction 1 in Figure 2),[17] the intolerance of isocyanates to moisture significantly limits its implementation. Nucleophilic addition reaction involving ring-opening has also received attention as thermal CANs. Linear polymers with either pendant maleate[23] or azlactone[25] functional groups cross-linked by a bis-alcohol have been shown as a viable thermoreversible cross-linking reaction; however, these materials have limited reversibility owing to various side reactions.[26] Carbene dimerization is another candidate reaction for the basis of a thermal CAN (reaction 2 in Figure 2). Hitherto, this reaction has been used to fabricate linear polymers;[18] however, a network could be fabricated by flanked polymerizable functionalities (similar to shown in Figure 1, panel C). Nevertheless, carbenes tend to be highly reactive species; the exposure of carbene species shown in Figure 2 to oxygen results in the irreversible formation of a cyclic urea.[18]

The thermoreversible homolytic cleavage of the alkoxyamine bond (reaction 3 in Figure 2), producing both a stable, nonpropagating radical [e.g., 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)] and an active radical (e.g., a styryl radical), has been utilized extensively in nitroxide-mediated living/controlled radical polymerizations as well as in the formation of CANs (see Figure 3). With respect to CAN formation, the production of the active radical often limits the reversibility of the material since it is capable of undergoing biomolecular termination. Nevertheless, this active radical has been utilized to incorporate other functionality into the network by swelling the network with monomer, followed by heating the material.[27] Higaki et al.[19] utilized this reaction to cross-link linear polymers having pendant TEMPO and styryl radicals that were capped with the corresponding styryl and TEMPO radical species, respectively, to facilitate the initial network fabrication. Although the cross-linking reaction produces a small molecular weight species, the absence of this species does not prevent cross-link thermoreversibility. One prospect for thermoreversible homolytic cleavage-type linkages for CANs is use of a disulfide-based TEMPO analogue, such as bis(2,2,6,6-tetramethylpiperidyl-1) disulfide (TEMPS). This compound exhibits both photo- and thermolytic cleavage, producing a stable, nonpropagating sulfur radical and, in principle, would produce a CAN that does not undergo irreversible termination.[28,29]

While each of these synthetic methodologies has its own unique advantages, the cyclical reversion potential of the [4 + 2] cycloaddition, known as the Diels−Alder (DA) reaction, in polymer networks is unmatched. This owes to the fact that the DA reaction exhibits many of the attributes of a click-type reaction[30] which is reasonably tolerant of typical environmental species such as water and oxygen and can be tuned to be responsive over a wide range of temperatures through changes in the reactive functionalities. The DA reaction has been used extensively to create thermoreversible polymer networks between a conjugated diene and, typically, an electronically activated double bond (i.e., a dienophile).[31] Several researchers have utilized the ability of cyclopentadiene to act as both a diene and dienophile, forming a cross-linking dimer.[32,33] In a 1969 patent, Craven describes a material that is reshaped upon heating but forms an insoluble network upon cooling.[20] This material was synthesized by the cross-linking of linear polymers having pendant furan moieties with (bis)maleimide and (tris)maleimide moieties via a DA reaction (reaction 4 in Figure 2). Several researchers have adopted this strategy;[34−43] however, the common use of functionalized linear chains, which essentially act as a macromonomer with a high degree of functionality, significantly reduces the gel's ability to undergo a gel-to-sol transition. Thus, other researchers have utilized low molecular weight, low functionality diene and dienophile monomers, e.g., a trifuran with a bismaleimide, to increase dramatically the gel-point conversion and significantly improve the ability of these systems to revert to liquids at reasonable temperatures.[12,44−49]

Furan and maleimide have been the predominant functional groups used to create thermoreversible CANs. Their selection is attributed to the convenient temperature range in which this reaction shifts from products to reactants. Unfortunately, many networks that utilize diene and dienophile pairs require excessive heating to undergo the retro-DA reaction, which can also trigger irreversible side reactions. Despite the attention that furan−maleimide networks have received, there is still a need to characterize these novel materials. In particular, the kinetics of the forward and reverse reactions as a function of temperature (i.e., pre-exponential factor and activation energy), which determines the adaptation time scale, is largely absent from the thermoreversible network literature.

Recently, there has been an emergence of interest in finding alternative diene and dienophile candidates to be used as thermoreversible linkages. Lehn and co-workers have explored diene and dienophile functional groups as dynamic covalent linkages in supramolecular chemistry (reactions 5 and 6 in Figure 2).[21,22] They extended these novel linkages in a network and observed self-healing properties.[50] In this regard, CANs represent the convergence of smart covalent networks with supramolecular science.

2.2. Chemistries for Photochemically Reversible CANs. In addition to thermoreversible CANs, two distinct approaches to photochemically triggered CANs have also been developed. These processes, which utilize light to reversibly break and re-form bonds, include photoinduced cyclization reactions and photochemical radical-mediated addition−fragmentation approaches. Unlike thermoreversible CANs, photoreversible networks only undergo bond rearrangement upon irradiation, otherwise exhibiting little to no creep or adaptation in the absence of irradiation. Photochemical approaches have the clear advantage of enabling the 3D spatial control of the reversion as well as the ability to remotely trigger a process on and off. The cyclization reactions are limited in their relative response rate, as at most a single cross-link is reversibly broken for each absorbed photon. Conversely, the addition−fragmentation reactions undergo a network rearrangement cascade, where multiple reversible bond breaking and re-forming reactions occur for each absorbed photon. However, the addition−fragmentation reactions are limited by never having a large fraction of the bonds cleaved at a given time, thus restricting such materials from any applications where a gel-to-sol transition is required.

Photoinduced cyclization reactions, hereafter referred to as photodimerizations, occur when two functionalities incorporating carbon−carbon double bonds undergo a photoinduced cycloaddition reaction. The corresponding photoscission reaction is achieved simply by exposure of the sample to a different irradiating wavelength. This process, with its associated ability to spatially pattern material processes and network structures, has been utilized extensively for reversible polymer network connectivity rearrangement. Several functionalities, including coumarins,[51−55] cinnamates,[56−60] anthracenes,[61−63] and thymines,[64] have been investigated to effect this polymer network rearrangement. With the exception of anthracenes, which undergo a [4 + 4] cycloaddition (Figure 4), photodimerization typically proceeds via a [2 + 2] cycloaddition of ethylenic bonds (Figure 4). Near-ultraviolet irradiation of materials incorporating photodimerizable functionalities effects the forward, cycloaddition reaction while irradiation at shorter wavelengths favors the reverse, scission reaction. Thus, these reactions are analogous to the thermally controlled Diels−Alder forward and retro reactions where the light intensity, controlling the rates of the forward and reverse reactions, and the wavelength, controlling the equilibrium extent of the cyclization and scission reactions, are analogous to the temperature control that is exerted over Diels−Alder and other thermoreversible systems. In keeping with that analogy, the photoinduced cyclization systems are unique among the photochemical CANs in that, with sufficient light exposure at the appropriate wavelength, they are capable of reverting to a liquid state with the assorted benefits of crack healing and mending available to materials in that state.

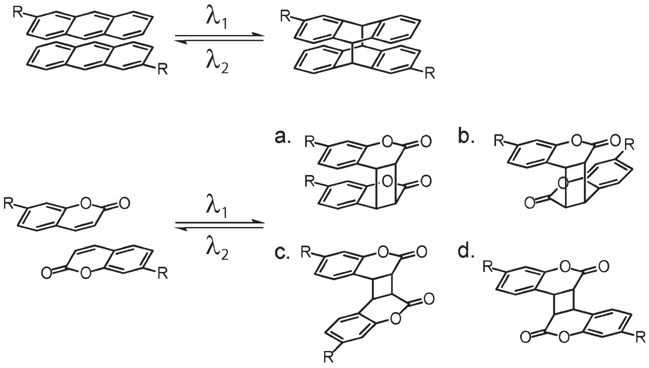


Figure 4. Photodimerization of coumarin and anthracene as controlled by irradiation wavelenth. The four potential isomers resulting from the [2 + 2] coumarin dimerization include (a) head-to-head, syn; (b) head-to-head, anti; (c) head-to-tail, syn; and (d) head-to-tail, anti. For clarity, one of the four potential isomers resulting from the [4 + 4] anthracene dimerization is shown.

In addition to the photoinduced cycloaddition, photoinduced, radical-mediated addition−fragmentation approaches have recently been exploited in the formation of photoresponsive CANs (e.g., Figure 5). This technique exhibits all the advantages of photoinduced reactions whereby the network exists in a permanent, nonadaptable state in the absence of light, the network adaptation response is photopatternable, and the adaptation process can be commenced and ceased on demand. Moreover, addition−fragmentation chain transfer functional groups are readily incorporated into the backbone of monomers (and subsequently polymer networks) possessing a wide variety of polymerizable functionalities. Since this process employs a radical reaction, the opportunity exists for each absorbed photon to induce a chain process whereby each radical causes multiple reactions. This form of adaptability in cross-linked networks takes advantage of mechanisms that have traditionally been employed in small molecule chemistry. Here, radicals are known to react with allyl sulfides to effect homolytic substitution displacement of the thiyl group (i.e., S_H2').[65,66] The recognition that this mechanism could be utilized for chain transfer during radical polymerizations of styrene and methyl methacrylate led to controlled molecular weight linear polymers possessing terminal vinyl groups.[67,68] The same mechanism was subsequently used in radical ring-opening polymerizations whereby cyclic monomers consisting of 7- and 8-membered rings incorporating an allyl sulfide functionality underwent radical-mediated ring-opening and continued propagation.[69−75]

A unique, photoinduced, nondestructive scission approach was recently developed for rearranging network connectivity by utilizing allyl sulfide functionalities incorporated in the backbone of cross-linked polymers.[76−78] These polymer networks were fabricated such that a significant

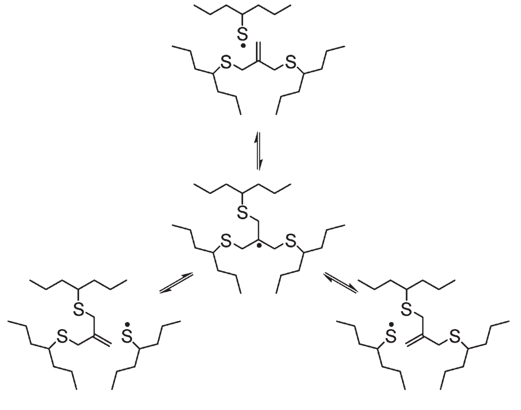


Figure 5. Radical-mediated addition−fragmentation chain transfer allows for rearrangement of polymer connectivity. The thiyl radical and the allyl sulfide units in the polymer are in a dynamic pseudoequilibrium relation where the thiyl radical catalyzes the cleavage and re-formation of the allyl sulfide linkages in the polymer network.

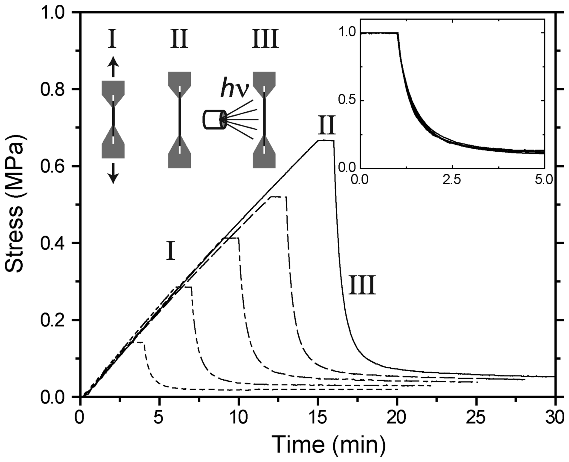


Figure 6. Photoinduced stress relaxation (i.e., permanent set) of an allyl sulfide thiol−ene network.[76] The sample is (I) uniaxially stretched to 1.5 (dot), 3.0 (dot-dot-dash), 4.5 (dot-dash), 6.0 (dash), and 7.5% (solid) strain, (II) held at constant strain for 1 min, and (III) irradiated with 365 nm light at an intensity of 40 mW/cm^2. The inset shows the time shifted (to the beginning of phase II) and normalized stress, which demonstrates 90% stress reduction for all the samples presented here. Adapted from ref 83.

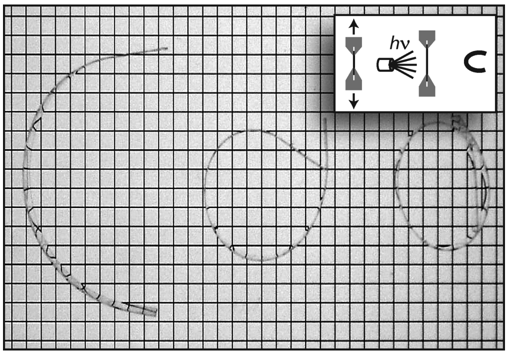


Figure 7. Samples containing allyl sulfide deforming in response to stress gradient "written" via light attenuation through the sample.[77] As shown in the inset, the samples are uniaxially stretched and irradiated (365 nm light at 40 mW/cm^2 for 30, 60, and 90 s—left to right), triggering bond rearrangement via addition−fragmentation of allyl sulfide functional groups in the network backbone. Since the samples are optically thick (using ultraviolet light absorber), the light is attenuated, producing a gradient of active bond rearrangement and thus a gradient in stress. After irradiation, the samples deform by warping to equilibrate the internal stresses.

residual amount of a radical generating photoinitiator remained after polymerization. Thus, upon irradiation subsequent to fabrication, cleavage of the residual photoinitiator introduces radicals into these materials, initiating the addition−fragmentation chain transfer reaction (shown in Figure 5) and ultimately effecting network adaptation. In postpolymerization studies, allyl sulfide-containing networks demonstrated the utility of this phenomenon via photoinduced creep, stress relaxation, and photoinduced actuation. In a similar manner to the vulcanized rubbers studied by Tobolsky,[79,80] irradiating these samples while a tensile stress is applied, network rearrangement due to the reversible addition−fragmentation chain transfer process allows for either stress relaxation or creep, depending on the mode of the applied stress, and the equilibrium shape and state of the material are altered (i.e., permanent set, Figure 6). Unlike its photodimerization/photoscission counterpart, this approach does not effect a concomitant variation in the cross-link density since, although individual bonds are being broken and re-formed, the overall cross-link density remains essentially constant before, during, and after exposure. Moreover, photodimerization/photoscission systems exhibit a photon to reaction event ratio no greater than one, where one photon at most causes either one addition or one scission event. Conversely, while a single photon absorbed in the addition-fragmentation chain transfer system leads to at most a single cleavage event of a photoinitiator molecule, each radical formed as a result of the initiator cleavage can lead to a cascade of many chain transfer events, i.e., cross-link breakage and reformation. It should also be noted that the introduction of radicals is not limited to photoactivation; other stimuli such as heat to induce decomposition of thermal initiators or exposure to chemical species able to induce redox reactions[81,82] are capable of effecting radical production and network adaptation.

Photoactivation of network rearrangement allows for spatial definition of stress relaxation, whether defined by masking the incident light or by controlling the absorption or focus of light throughout the thickness of the sample. For example, by irradiating optically thick samples under tension, a stress gradient is readily induced through the sample thickness with stresses rapidly relieved on the incident surface and much more slowly relieved at the bottom of the sample, i.e., the nonincident surface. Upon release from the externally applied stress, such a sample deforms by curling to equilibrate the internal stress (see Figure 7). Ultimately, such samples exhibited photoinduced actuation which was realized by subsequent irradiation of the previously unirradiated side, resulting in straightening of the sample, with the sample progressing back toward its original shape.[77]

3. Mechanical Properties and Gelation of CANs

Inherent to a polymer network is the transition from a mixture of small molecular species to a material having at least one sample-spanning molecule, which defines the incipient gel. The gel-point conversion is the precise point in the progression of a polymerization where the incipient gel is formed. In addition to providing a functional mathematical definition (i.e., where M_w diverges), it typically coincides with the experimentally observed transition of a completely soluble mixture to one having a fraction of insoluble gel (i.e., a sol-to-gel transition). To this extent, the formation and definition of a polymer network are well developed and generally accepted among the greater polymer science community. Here, we use a similar definition of the network structure while noting that for CANs the gel point now depends on the time scale on which one evaluates the formation of a sample-spanning molecule.

The main characteristic imparting CANs with their unique material behavior owes to the capability of the cross-links to reversibly break and re-form. Since CANs are chemical networks that exhibit weak gel characteristics at appropriate time scales in thermoreversible systems, at appropriate light intensities in photocyclization systems, or at appropriate radical concentrations in photoinduced addition—fragmentation systems, the mechanical properties can be similar to those observed in physical gels, such as gelatin.[84] Specifically, consider for thermoreversible CANs that given enough time and under appropriate reversibility conditions, the polymer network will demonstrate plasticity or flow. As recognized by de Gennes, such behavior precludes weak gels from possessing a gel point as traditionally defined in chemical gels by the divergence in the viscosity and the emergence of a finite zero-frequency elastic modulus (i.e., Young's modulus).[9] However, CANs must possess a gel point, as it is a prerequisite for network formation.

Dynamic mechanical analysis (DMA) is perhaps the best method for gel-point determination, since it allows for the direct measurement of elastic and viscous moduli and their temporal scaling. Winter and Chambon experimentally demonstrated that chemical gels exhibit similar frequency scaling at the gel point (i.e., $G' \sim G'' \sim \omega^{\Delta}$), which is now referred to as the Winter−Chambon criterion.[85−88] Since the incipient gel is characteristically fractal, it possesses the same ensemble averaged similarity on all but the smallest length scales; thus, the temporal−spatial interpretation dictates that the elastic and viscous moduli should scale similarly with frequency.[89,90] In practice, the Winter−Chambon criterion is not applicable to the entire frequency range. As previously alluded to, the Winter−Chambon criterion fails at high frequencies, owing to the onset of glassy dynamics. The type of the gel also affects the applicability of the Winter−Chambon criterion. For example, the gel point of a cross-linked, entangled polymer exhibits similar scaling only in the terminal region of the spectrum, and the plateau and high-frequency region are relatively unaffected by the cross-linking.[91] Additionally, weak gels depart from the similar scaling behavior in the low-frequency, terminal region, owing to bond breaking and re-forming.[12,92] Thus, one can determine the gel point of a CAN using the Winter−Chambon criterion provided that the time scale of bond breaking and re-forming is sufficiently long to observe the elastic and viscous moduli scaling identically with frequency. Furthermore, the Winter−Chambon criterion must be used with caution as, although similar scaling does occur at the gel point, self-similarity by itself does not necessitate the existence of a gel.

Remarkably, the DMA of most thermoreversible CANs near the gel-point temperature has not been rigorously examined. DMA measurements are available for several systems[40,42,93,94] but are performed while ramping temperature that may not allow the system to obtain thermodynamic equilibrium. Additionally, these experiments are often limited to single frequency scans, which only reveal the crossover of the storage and loss moduli rather than establishing the gel point by the Winter−Chambon criteria. Networks formed by the DA reaction between a trifunctional furan and a difunctional maleimide (structures shown in Figure 1, panel C) were recently examined,[12] which have a Flory−Stockmayer predicted gel-point conversion of 0.71 and yield a gel-point temperature of 92.5 ± 0.5 °C as determined using FTIR spectroscopy. Figure 8 shows the complex stress relaxation moduli for three frequency sweeps above (95 °C), near (91 °C), and below (87 °C) the gel-point temperature. The material near the gel point exhibits the Winter−Chambon expected similar scaling at higher frequencies, while demonstrating the terminal relaxation scaling of a viscoelastic liquid at lower frequencies (i.e., $G' \sim \omega^2$ and $G'' \sim \omega^1$) due to bond rearrangement at longer time scales.

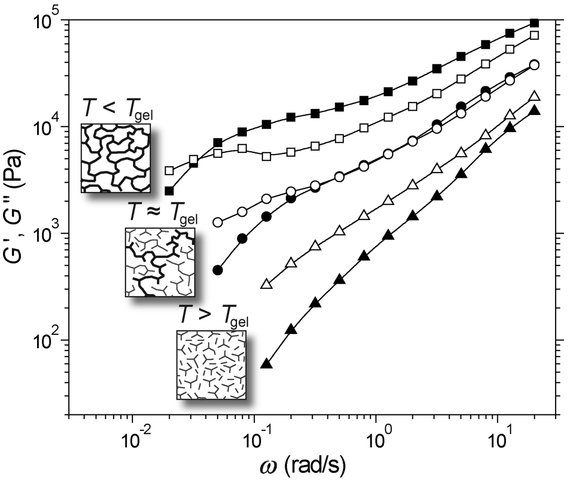
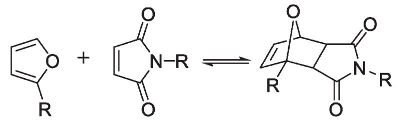


Figure 8. Elastic (closed symbols) and viscous (open symbols) moduli as a function of angular frequency for a stoichiometric bismaleimide and trisfuran monomer mixture above (triangles, 95 °C), near (circles, 91 °C), and below (squares, 87 °C) the gel-point temperature. For all temperatures, the terminal behavior (i.e., $\omega \rightarrow 0$) approaches that of a viscoelastic liquid ($G' \sim \omega^2$ and $G'' \sim \omega^1$). The moduli exhibit similar frequency scaling ($G' \sim G'' \sim \omega^{0.56}$) at the gel-point temperature, corresponding well to that determined by the Flory−Stockmayer gel-point conversion determined by FTIR (92.5 ± 0.5 °C). Adapted from ref 12.

At elevated temperatures the material exists as a liquid, with a loss modulus that is greater than the storage modulus (triangles in Figure 8). As the network is cooled below the gel-point temperature, the cross-linking increases and the elastic modulus dominates the viscous modulus for intermediate time scales (squares in Figure 8). The bond rearrangement rate of the networks slows as indicated by a terminal relaxation shift to lower frequencies. Further cooling shifts the crossover point to longer and longer times until it can no longer be observed with DMA ($\sim 10^{-2}$ rad/s).

In the absence of kinetic limitations, such as vitrification[12] or crystallization,[95] bond formation in thermoreversible CANS is dictated by thermodynamic equilibrium, and thus the equilibrium functional group conversion is dictated by the temperature. Uniquely in these thermoreversible CANs, the equilibrium constant, K, provides a direct relationship between the gel-point temperature and the gel-point conversion (see Figure 9). Given the monomer functionality, f, and functional group stoichiometric ratio, r, the gel-point conversion is determined for a step-growth polymerization via the Flory−Stockmayer equation, $p_{gel} = [r(f_a - 1)(f_b - 1)]^{-1/2}$.[96,97] Thus, the gel-point temperature is manipulated through monomer functionality, concentration, and stoichiometry as well as the thermodynamics and energetics of the specific thermoreversible coupling reaction. In contrast to the relatively simple reversion of low molecular weight, lower functionality system that is readily shown, higher molecular weight linear polymers with pendant functional groups have a relatively low gel-point conversion, owing to their high functionality. These types of thermoreversible networks generally necessitate very high and generally impractical temperatures if they are to revert to an ungelled state.

While the thermodynamics predicts the gel-point temperature, the kinetics of the bond rearrangement dictates the characteristic



$$\ln K = \frac{-\Delta H_{rxn}}{RT} + \frac{\Delta S_{rxn}}{R}$$

$$K = \frac{rp_E}{c_0\left(1-p_E\right)\left(1-rp_E\right)}$$

$$T_{gel} = \frac{\Delta H_{rxn}}{\Delta S_{rxn} - \ln \dfrac{rp_{E,gel}}{c_0\left(1-p_{E,gel}\right)\left(1-rp_{E,gel}\right)}}$$

Figure 9. Relationship between the gel-point temperature, T_{gel}, and conversion, $p_{\text{E,gel}}$, for the reaction between diene and dienophile (shown as furan and maleimide functional groups, respectively, where R is the connectivity to the remainder of the monomer structure) is related through the initial functional group concentration, c_0, equilibrium conversion, p_{E}, heat of reaction, ΔH_{rxn}, and entropy of reaction, ΔS_{rxn}. For the case that the diene and dienophile are not stoichiometric, r is the stoichiometric ratio defined as the limiting functional group concentration divided by the functional group concentration in excess, and where c_0 and $p_{\text{E,gel}}$ are the limiting functional group concentration and conversion, respectively.

mechanical properties of the network, specifically, the terminal relaxation. The forward reaction between the diene and dienophile is pseudo-second-order and the retro reaction is first-order with respect to the adduct.[12,37,94,98] Utilizing a kinetic model, the forward and reverse reaction rate constants of a network cross-link are determined from unsteady-state conversion vs time data.[12] The half-life of a cross-link, i.e., the adduct, is calculated from the reverse reaction rate constant, k_{r}, via $t_{1/2} = \ln 2/k_{\text{r}}$. For the system shown in Figure 8, this half-life is on the same order of magnitude as the inverse of the crossover frequency, confirming that the crossover in storage and loss moduli is owing to network rearrangement. By measuring k_{r} as a function of temperature, one finds that the cross-link half-life increases from seconds to years, and the material behaves as a solid on most relevant time scales (graduate student and postdoc half-lives!).[12]

4. Applications of CANs

4.1. Thermoreversible Covalent Networks. The applications of CANs are those that require the mechanical properties of a covalent network but simultaneously benefit from a lack of permanence in the structure as would be typical of a conventional thermoset. An associated potential disadvantage of these materials that must be considered is their long-term creep behavior that, depending on the specific chemical nature of the CAN, may lead to long-term changes in the material shape, particularly for those materials held under stress during their implementation. The creation of an easily recyclable material that possesses the characteristics of a thermoset has been a motivating idea since the inception of thermally controlled CANs,[20] and a number of systems have been synthesized that are readily manipulated postpolymerization.[12,19,20,33,39] Thermal CANs have also been employed in so-called hot-melt applications, such as hot-melt inks[99] and hot-melt adhesives,[6,94] where the material is manipulated in a heated liquid state and then cooled to produce a cross-linked solid.

Electronic components are often protected from the environment in a thermoset encapsulate. If the component is found to be faulty after encapsulation, rework of the circuit requires shearing off the component and the thermoset encapsulate. Accordingly, the use of thermoreversible materials that can be easily removed has been explored as alternative encapsulates[3−6] and anisotropic conductive adhesives.[100] Interestingly, in such applications the reverse reaction can be driven far from equilibrium by flushing sol fraction away with solvent. As a consequence, it is no longer necessary to drive the material past the conversion required for reverse gelation; rather, only a sufficient rate of the reverse reaction is required. This strategy enables the use of polymers that are highly functionalized with cross-linking groups.

Thermoreversible cross-links have been used to align dendritic nonlinear optical chromophores to achieve high electrical optical coefficients.[7,8] Cross-linking of the dendrimers reduces the free volume, improving the long-term stability of the material. Furthermore, the reversible nature of the Diels−Alder reaction permits the materials to be cured until alignment is achieved. It is also possible to incorporate a second chromophore, without inducing phase separation that improves the poling efficiency.[101] Thermoreversible materials have also been employed as the cladding material in light guides and other electro-optic devices.[102]

More recent work has been directed at the use of thermoreversible bonds for creating healing materials.[33,42,44,45,103] Healing materials possess the ability to recover their initial mechanical properties after damage. On small size scales healing is nearly universal in polymers due to reptation of polymer chains though this behavior is limited in cross-linked polymer networks;[104] however, macroscopic crack healing is always a significantly more difficult challenge. Autonomic healing schemes, where monomer is encapsulated in spheres, fibers, or channels and is released upon fracture to flow and subsequently polymerizes in the crack, have been shown to be successful but suffer from a limited number of healing cycles as the monomer is depleted.[105] While polymers incorporating reversible bonds do not permit macroscale autonomous healing, they do offer a more simple approach to healing. For cracks where two surfaces are in close contact, bond rearrangement alone permits material self-healing. Chen et al.[44,45] synthesized multifunctional furan and maleimide monomers and demonstrated, for a material above its gel point, 50% fracture toughness recovery after initial fracturing and 41% after a second fracture.[44] Second generation materials by the same group recovered 80% and 78% of their initial fracture toughness after two subsequent sample fracture and healing cycles.[45] Since reverse gelation in thermal CANs results in material flow, full mechanical strength recovery is possible provided that irreversible side reactions, particularly common at elevated temperatures, are suppressed. Unfortunately, reverse gelation also results in slump or deformation in the overall material shape; thus, for many structural applications, near gel reversion is desirable.

4.2. Photoreversible Covalent Networks. In one particular application of photoreversible CANs, photodimerization and photoscission have been exploited to alter the mechanical properties of hydrogels reversibly.[51,60] Hydrogels are commonly used as encapsulating and substrate media for cells;[106,107] thus, many experiments utilizing adaptable networks to examine the effect of dynamic variation of mechanical properties on the local cell environment can be envisaged where the intimate and reversible control of the network structure enables studies not possible with other covalent or physical network structures. Although the irradiation wavelengths typically used for the dimerization and scission reactions extend well into the ultraviolet and are incompatible with cell viability, sensitization of both forward[108−111] and reverse[112−114] reactions using

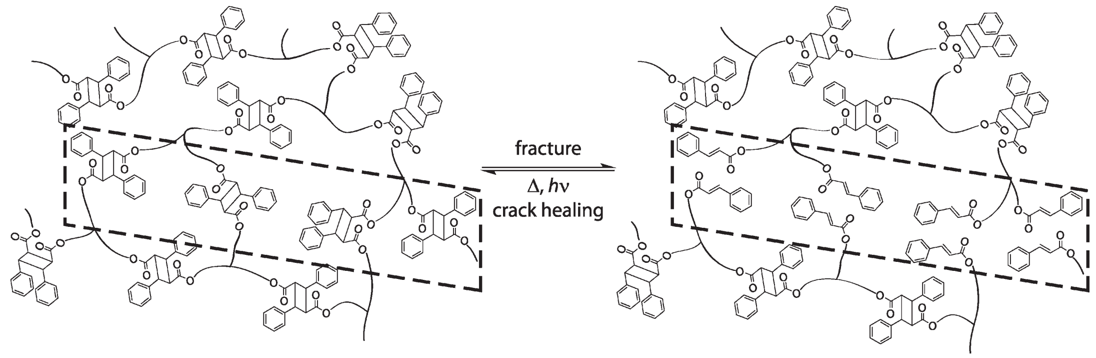


Figure 10. Schematic of photoinduced cinnamate crack healing.[115] Crack propagation in a cinnamate cross-linked network promotes the retro-[2 + 2] cycloaddition as evidenced by the appearance of a C=C absorption monitored by infrared spectroscopy. The subsequent photoinduced healing of the crack resulted in an increase in flexural strength as well as a reduction of the C=C absorption. Adapted from ref 115.

visible-light absorbing compounds would be a facile path to cell compatibility.

Applications for network rearrangement via photodimerization and photoscission are not limited to complete network reverse gelation. Lendlein et al. utilized the reversible photodimerization of cinnamates to great effect in their implementation of photoinduced shape memory in permanently cross-linked polymers.[56,57] Here, permanently cross-linked, elastomeric, (meth)acrylate polymers incorporating cinnamate functionalities were fabricated, strained, and subjected to irradiation at $\lambda > 260$ nm. The incorporated cinnamate functionalities were dimerized during this irradiation step, increasing the cross-link density and fixing the material into a new shape. Subsequent cleavage of the dimers by irradiation at $\lambda < 260$ nm resulted in nearly complete recovery of the original shape of the material.

Another recently investigated application for photodimerization is light-induced crack healing. Chung et al.[115] found that the cyclobutane cross-links in a material incorporating dimerized cinnamate groups were cleaved when the material was cracked, yielding the original, undimerized cinnamate groups. Subsequent heating, necessary to increase molecular mobility and allow for intimate contact between the two fracture surfaces, accompanied by concurrent irradiation of the cracked samples led to re-photodimerization of the surface cinnamate groups and a partial recovery of the flexural strength (see Figure 10).[115]

The combination of polymerization and adaptation is of particular relevance for applications where cross-linked networks are polymerized *in situ*, as shrinkage stress generally has a deleterious effect on the interface between the polymer network and the substrate and potentially on the substrate itself.[116−118] Recently, we utilized addition−fragmentation chain transfer concurrently with the polymerization reactions, allowing network adaptivity via bond shuffling and reducing the polymerization shrinkage stress.[78] Monomers incorporating the allyl sulfide functionality were employed in a radical mediated, step-growth thiol−ene polymerization. To demonstrate conclusively that the polymerization stress reduction resulted from the addition−fragmentation reaction, analogous, nearly identical monomers (see Figure 11, panel A) and networks were formed: one containing allyl sulfide and a second containing propyl sulfide functionalities. The propyl sulfide-containing networks are essentially identical structurally although the elimination of the allyl sulfide renders them incapable of addition−fragmentation chain transfer. Upon polymerization, the shrinkage stress was >75% lower in the allyl sulfide-containing network as compared to the shrinkage stress developed in the propyl sulfide-containing network due to the addition−fragmentation chain transfer reaction leading to adaptation of the polymer network. This reduction in shrinkage stress in the allyl sulfide-containing networks was particularly apparent toward the end of the polymerization (see Figure 11, panel B) where even the qualitative behavior is different with the allyl sulfide CAN exhibiting stress reduction and the propyl sulfide exhibiting a continued stress increase.[78]

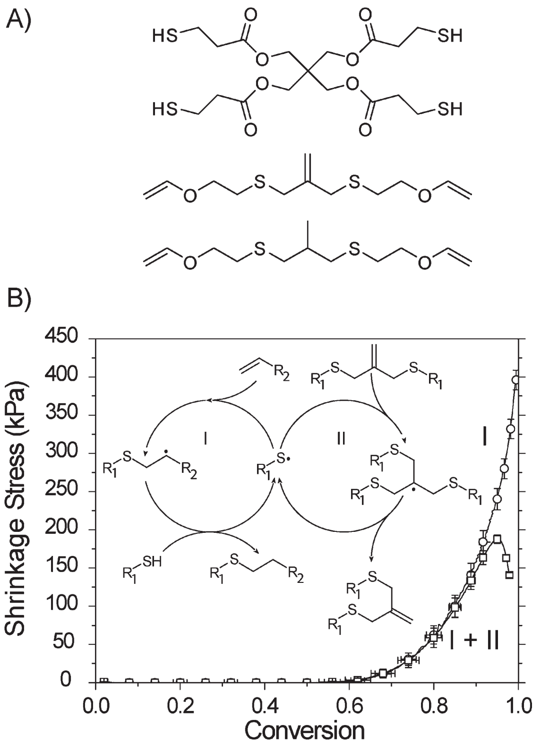


Figure 11. Using a model thiol−ene photopolymerization of a tetrathiol (panel A, top) and an allyl sulfide divinyl ether (panel A, middle), a reduction in polymerization stress (panel B) was achieved when compared to the analogue tetrathiol and propyl sulfide divinyl ether (panel A, bottom) thiol−ene photopolymerization. In panel B the polymerization stress is measured as a function of conversion, where the propyl sulfide-based material exhibits an increase in stress at the gel point (∼58% conversion) that continues until achieving full conversion. The propyl sulfide monomer is incapable of undergoing addition−fragmentation and thus only follows the step-growth mechanism shown as cycle I (inset). While the allyl sulfide-based material also exhibits an increase in stress at the gel point, the evolution in stress reaches a maximum followed by a decrease that is roughly one-third the stress of analogue. The allyl sulfide monomer is capable of both the step-growth mechanism (cycle I, inset) and the addition−fragmentation mechanism (cycle II, inset), which is responsible for the observed decrease in stress. Adapted from ref 78.

5. Summary and Outlook

The utilization of reversible covalent chemistry in polymer networks yields a novel class of materials possessing network adaptability and yielding properties such as recyclability, healability, tunability, and low polymerization stress. Each of these attributes is complementary to the trend of polymeric materials becoming more tuned to specific applications. Ultimately, CANs constitute an emerging thrust for rational fabrication of smart materials capable of adapting to a predetermined stimulus.

Although much progress has been made in developing fabrication methodologies for novel thermo- and photoreversible CANs, there still remains significant room for improvement, specifically in the continued incorporation of novel thermo- and photoreversible moieties into covalent networks. Ideally, thermoreversible covalent linkages would revert at a specific application-relevant temperature, have rapid reaction kinetics, and have low susceptibility to side reactions. New photoreversible linkages would target application relevant wavelengths, have enhanced photocleavage efficiencies, and have low susceptibility to irreversible chain transfer and termination. Moreover, rational design of CANs requires an expansion in the characterization of mechanical properties, thermodynamics, and polymerization and reversion kinetics of these materials. As demonstrated above for the case of the trisfuran with bismalemide, each of these areas is inherently related; however, this finding needs to be further explored in combination with theoretical developments.

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