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Photo-Plasticity in Thiol-ene Network Polymers – A Review

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Summary: In this paper we briefly overview the area of stimuli responsive polymers and the subset of photo-plastic polymers which change shape or undergo stress relaxation during irradiation. The chemistry, mechanism and properties of a new class of photo-plastic polymers is presented in detail – these tetrathiol-diene networks contain an allylic dithioether (also termed allylic disulphide) unit in the network strands and when this moiety is attacked by a photogenerated radical, the allylic dithioether undergoes β-cleavage which breaks one network bond and reforms another. Two different methods of integration of the allylic dithioether unit into the backbone are investigated – the use of a cyclic allylic dithioether which copolymerizes with a thiol-ene system or the incorporation of the allylic dithioether moiety in a divinyl ether monomer which can directly copolymerize with the thiol. The photo-plasticity effect of these thiol-ene networks is revealed in both creep and stress relaxation experiments, however, the extent of photo-plasticity is less extensive than expected. The polymerization kinetics and evolution of the rheological properties during photocuring are studied and the slower copolymerization of the monomer containing the allylic dithioether is discussed. The photo-rheology and dynamic mechanical properties of the thiol-ene networks are interpreted in terms of the network structure.

Keywords: photo-induced creep; photo-induced stress relaxation; photo-plasticity; photopolymerization; photo-rheology; thiol-ene network polymers

Introduction

There has been considerable interest during the last 25 years in the area of stimuli responsive polymers [1–4] which can swell or change their shape in response to an external stimuli, and also in the related area of self-healing polymers which respond to damage.[5–8] Both the fundamental and engineering aspects of stimuli responsive polymers have been investigated and some of them are presently commercial materials. In particular, some stimuli responsive polymers can be easily fabricated into thin films,[9] fibers [10] or wires, particles[4] and even porous bulk materials,[11] enabling them to be incorporated with other materials to form hybrid composites.[12]

Self healing polymeric materials have the built-in capability to substantially recover their load transferring ability after damage without change in shape or dimensions[6,13] autonomously[5] or via activation after an application of an external stimulus such as heat[14] or light.[15] As such, these

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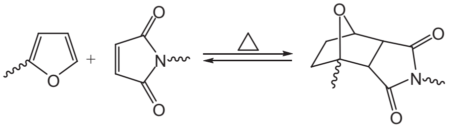
materials are expected to contribute greatly to the safety and durability of polymeric components without the high costs of active monitoring or external repair. One of the pioneers in this field is White and *co*-workers[16], whose approach involved mixing microcapsules containing healing monomers into an epoxy polymer matrix that contains a catalyst. When a crack develops in the matrix, the microcapsules are destroyed, releasing the monomers into the crack. These monomers come into contact with the catalyst, thus triggering a polymerization reaction that swells the healing materials until the crack is closed. Chen *et al.* [8] developed another strategy in which polymers were modified with moieties that undergo thermoreversible Diels-Alder reactions (see Scheme 1) - these polymers are able to repair themselves after mechanical damage by reformation of the network strands in an unstressed state, however, this reaction must be performed at elevated temperatures. Most recently, Cordier *et al.* [5] reported the use of a supramolecular assembly of small molecules to create a material that not only has the properties of rubber, but is also self-healing. The resulting supramolecular network exhibits partial cross-linking, through hydrogen bonds. When a break in the material occurs, the active ends of the hydrogen-bond network are exposed but can be recombined by simply bringing the two surfaces into intimate contact.

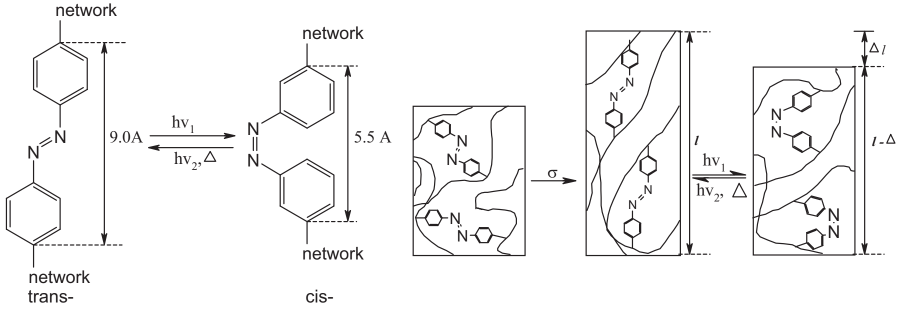
Shape memory polymers (SMPs) represent another class of stimuli responsive polymers. One method of achieving a once-off shape change of a polymer is used in shrink-wrapping and usually employs a special thermoplastic polymer where the chains are physically entangled or connected by crystallites.[17] When this material is heated (usually heated above the glass transition temperature, T_g) to increase the chain mobility and so soften it, the polymer can be stretched up to several hundred percent. If the material is then rapidly cooled under strain, it retains the stressed state. If this material is subsequently heated above its transition temperature, the polymer chains are able to move to relieve the residual stresses and so the sample changes its shape towards its original form.[17] A related phenomenon which uses the crystallizability of polyurethanes has been discussed by Koerner *et al.*[12] Alternatively, lightly crosslinked polymers can be made into SMPs by deforming the material above the glass transition temperature followed by quenching to retain the deformed state.[18] SMPs have many advantages over their non-polymer shape memory metal or ceramic counterparts in their easy processing, low manufacturing cost, low density, low modulus, high shape recovery and high recoverable strain. In particular, the recoverable strain in SMPs is of an order of 700%,[9] while shape memory metals or ceramics can recover only about 10% or 1%, respectively.[19,20] The ability of shape memory polymers to spontaneously recover large strains in restricted environments has been exploited in many applications ranging from shrink-wrap packaging, biomedical devices[21,22], to aerospace (e.g. solar cell paddle).[23]



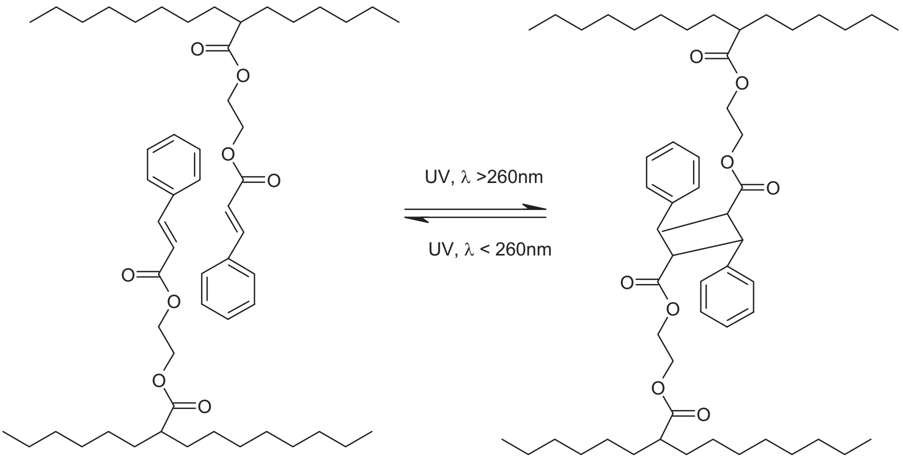
Scheme 1.
Thermoreversible Diels-Alder cycloaddition of a diene and a dienophile. A highly cross-linked network can be formed and its thermal reversibility can be accomplished by the retro Diels-Alder reaction.[8]

In addition to the use of heat as an external stimulus (as discussed above), stimuli responsive materials have also used magnetic,[24,25] electric fields,[26] pH changes/ionization,[11,27] and irradiation[7,28,29] as methods of activation. The use of irradiation as an external stimulus is interesting because it can be controlled rapidly, precisely and remotely in a range of different environments. The combination of radiation as the stimulus with photoresponsive crosslinked polymers is of further interest because of their potential for the development of reversible shape-changing systems. Additionally, such materials may solve a major problem with crosslinking systems in which the polymerization shrinkage causes the development of internal stresses - if radiation can be used to allow shape change then it can also be used to reduce these internal stresses.

Photo-induced actuation has been demonstrated *via* the *trans-cis* photo-isomerization of azobenzene chromophores,[30–33] (Scheme 2) and the spiro-merocyanine photo-isomerization of spiropyrans[34] to effect changes in the shape of elastomers. Recently, Lendlein *et al.* [7] described a method for photoinduced shape memory involving the photodimerization and photocleavage of cinnamic groups crosslinking the polymer backbone (Scheme 3). These polymers can be deformed and fixed into more complicated shapes, such as elongated films and tubes, arches or spirals, by irradiation with UV light, and can recover their original shape at ambient temperatures when exposed to UV light of a different wavelength.[7] Most recently, Kobatake *et al.* [35] reported that molecular crystals based on diarylethene chromophores and with the size ranging from 10 to 100 μm exhibit rapid and



Scheme 2.
Azobenzene photo-plasticity. The isomerization process from the *trans-* to the *cis*-form involves a decrease in the distance between the *para* carbon atoms in the azobenzene derivative from about 9.0 to 5.5 Å.[30] Thus when the specimen is stressed and the azobenzene moieties are oriented, irradiation can cause changes in the shape of the network.



Scheme 3.
Mechanism of photoreversible crosslinks via cinnamic acid type molecules of photoresponsive shape-memory polymers. Cinnamic acid type units are grafted onto a polymer and these molecular switches are photoreversible crosslinks, fixing the deformed temporary shape when irradiated with UV light of $\lambda > 260$ nm, and recovering the original shape when exposed to UV light of $\lambda < 260$ nm.[7]

reversible macroscopic changes in shape and size induced by UV and visible light (Scheme 4). The main limitations of these methods are their need of specific UV radiation to cause the photo-plastic effect, the long irradiation periods required and the low quantum yield (i.e. ≤ one chain scission per photon) observed.

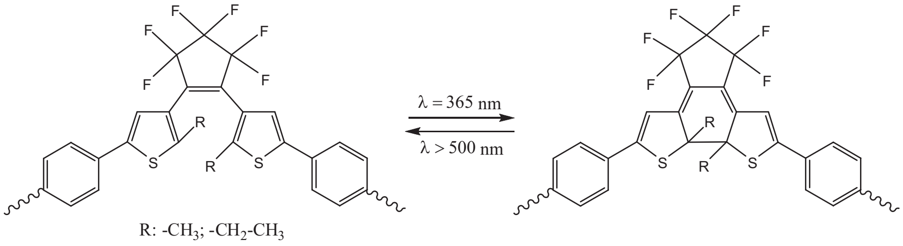
Recently, thiol-ene polymer networks containing a free radical photoinitiator and allylic dithioether (previously termed[15,36,37] "allylic disulphide") groups in the network strands were shown to undergo creep and stress relaxation behavior during irradiation.[15,36,37] The mechanism for this process is the attack by a thiol radical on the allylic dithioether followed by its β-cleavage and reformation of a new network strand with a regenerated allylic dithioether group. This review focuses on the photo-plasticity of these thiol-ene network polymers, as an alternative system to those previously reported and discusses their advantages, potential for development and their shortcomings.

Experimental Part

Materials

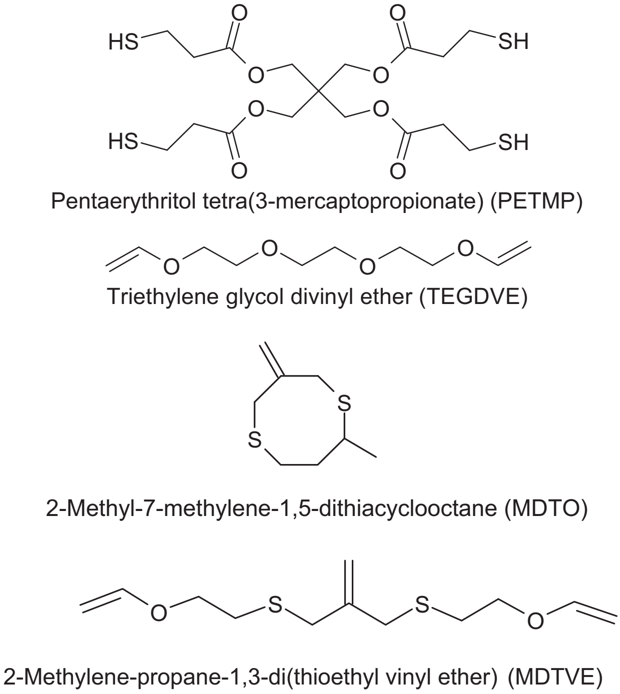
Pentaerythritol tetra(3-mercaptopropionate) (PETMP, Aldrich), triethylene glycol divinyl ether (TEGDVE, Aldrich), 2-methylene-propane-1,3-di(thioethyl vinyl ether) (MDTVE), and 2-methyl-7-methylene-1,5-dithiacyclooctane (MDTO) were used as monomers (see Scheme 5). The MDTO was synthesized[15] in a manner analogous to that described in the literature[38]. The MDTVE was synthesized by Scott *et al.* [37] from 3-mercapto-2-(mercaptomethyl)-1-propene and 2-chloroethyl vinyl ether. Thiol-ene networks were prepared from stoichiometric ratios of vinyl ether (but not allylic) groups and thiol groups. For the systems with MDTO, four systems were studied with PETMP/TEGDVE system modified by the addition of 0, 25, 50, 75 wt % of the ring-opening monomer MDTO. For the systems with TEGDVE, three systems were studied with PETMP:TEGDVE:MDTVE molar ratios of 1:2:0, 1:1:1 and 1:0:2.

The photopolymerization and dark reaction polymerization of PETMP with TEGDVE was undertaken with camphorquinone (CQ supplied by Aldrich) and tetramethylaniline (TMA supplied by Aldrich) as an initiator system. For the PETMP/TEGDVE/MDTO system, two photoinitiators were used: a cyclopentadiene titanate, bis(η,5,2,4-cyclopentadien-1-yl) bis-(2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl)-titanium (CPDTiAr, supplied by Ciba Specialty Chemicals as Irgacure 784) and a phosphine oxide, bis(2,4,6-trimethylbenzoyl)phenyl-phosphineoxide (BAPO, supplied as Irgacure 819 by Ciba). For the PETMP/TEGDVE/MDTVE system, the two photoinitiators were BAPO, and benzoin ethyl ether (BEE, supplied by Aldrich). Due to the relative thermal



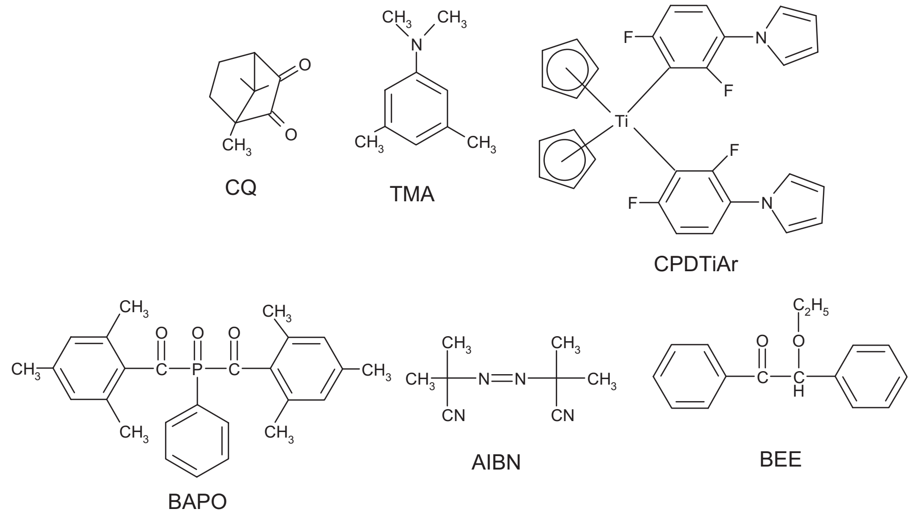
Scheme 4.

Molecular structure of the open- and closed- ring isomers of the diarylethene compounds. The structural units and single-crystal change shape on alternate irradiation with UV of $\lambda = 365$ nm and visible light of $\lambda > 500$ nm. Irradiation with UV transforms the open-ring isomers into closed-ring isomers, reversibly changing the 88° and 92° corner angles of the crystals of 82° and 98°, causing a change in shape from a square to a lozenge. On the irradiation with visible light, the crystals switch back to their original state.[35]



Scheme 5.
Structures of the monomers used.

instability of mixtures of PETMP and TEGDVE,[39] the photoinitiators were dissolved in one of the monomers before the monomers were mixed and the resin systems were used within 10 min. Thermal polymerization studies were also undertaken with 1 wt% azobisisobutyronitrile (AIBN, supplied by Aldrich) as a thermal initiator. Scheme 6 shows the structure of the initiator systems.



Scheme 6.
Structures of the photo and thermal initiators.

Photo-Differential Scanning Calorimetry

Isothermal photopolymerization studies were performed under a N_2 flow at 50 °C with the Perkin Elmer DSC-7 (USA) equipped with an Intracooler and modified[40] to allow irradiation of both the sample and reference DSC pans, minimizing the thermal imbalance created by the radiation source. For the photopolymerization and dark cure studies of PETMP/TEGDVE/0.25 wt% CQ/0.3 wt% TMA, a broad band dental curing light (Visilux by 3 M) with a maximum emittance at 470 nm was used. For photocuring studies of PETMP/TEGDVE/MDTVE, narrow band radiation from a Polilight PL400 (Rofin, Australia) was used to polymerize the resins using 415 nm radiation (390 to 440 nm). Sample masses of approximately 3 mg were used, producing samples approximately 0.2 mm thick. The calorimeter was calibrated for temperature and enthalpy using high purity zinc and indium standards. The photo-DSC data was converted into fractional photopolymerization rate (the heat flux divided by the heat of polymerization, assumed to be 60 kJ/mol which is close to that expected[41]) versus vinyl (not allyl) group conversion.

Photo-Rheometry

Photo-rheometry was performed at a frequency of 0.3 Hz with a Bohlin (UK) CS-50 constant stress rheometer in parallel plate mode using a 25 mm diameter plate, a 0.5 mm gap, a dynamic strain of 0.05 and controlled to 80 °C, as described elsewhere.[36] The 415 nm radiation intensity from the Polilight PL400 at the specimen was measured as 1.2 mW/cm^2 using the USB2000 fiber optic spectroradiometer.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical properties were measured using a Rheometrics Scientific (USA) DMTA IV in dual cantilever mode at 1 Hz scanning at 2 °C/min and a maximum strain of 0.1%. Temperature ramp tests were performed on 2 mm × 6 mm × 30 mm specimens of PETMP/TEGDVE and PETMP/MDTVE with 1 wt% AIBN cured for 4 hours at 80 °C then 2 hours at 150 °C. The T_g was taken as the temperature at the peak of the tanδ curve in the glass transition region.

Photo-Induced Creep and Stress-Relaxation

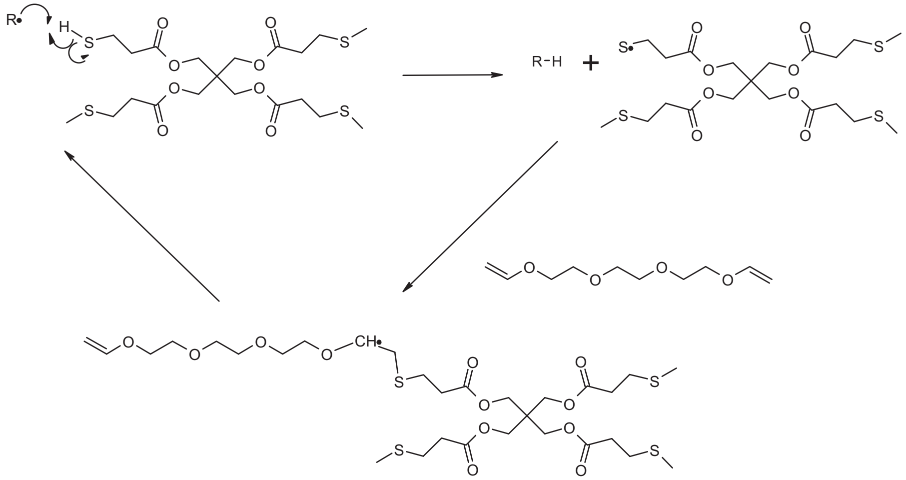
For the creep and creep recovery experiments, specimens were prepared from the resin mixtures containing 0.25 wt% BAPO and 0.1 wt% CPDTiAr for PETMP/TEGDMA/MDTO and 1 wt% of both BEE and BAPO for PETMP/TEGDMA/MDTVE. The specimens were irradiated at a wavelength which caused photoinitiation and thus polymerization by one of the initiators, but left the second photoinitiator intact as a source of radicals for the photoplasticity studies.

For the creep experiments, the cured specimens were mounted in a tensile testing machine and a stress of 0.1 MPa was applied during irradiation with ca. 320–500 nm radiation with an intensity of 30 mW/cm^2 for PETMP/TEGDMA/MDTO or ca. 360 nm with an intensity of 9 mW cm^{-2} for PETMP/TEGDMA/MDTVE at room temperature.

Stress relaxation studies were performed in a similar fashion on cured specimens of PETMP/TEGDVE/MDTVE using a strain of 0.1 and a ca. 360 nm light intensity of 9 mW cm^{-2} at room temperature.

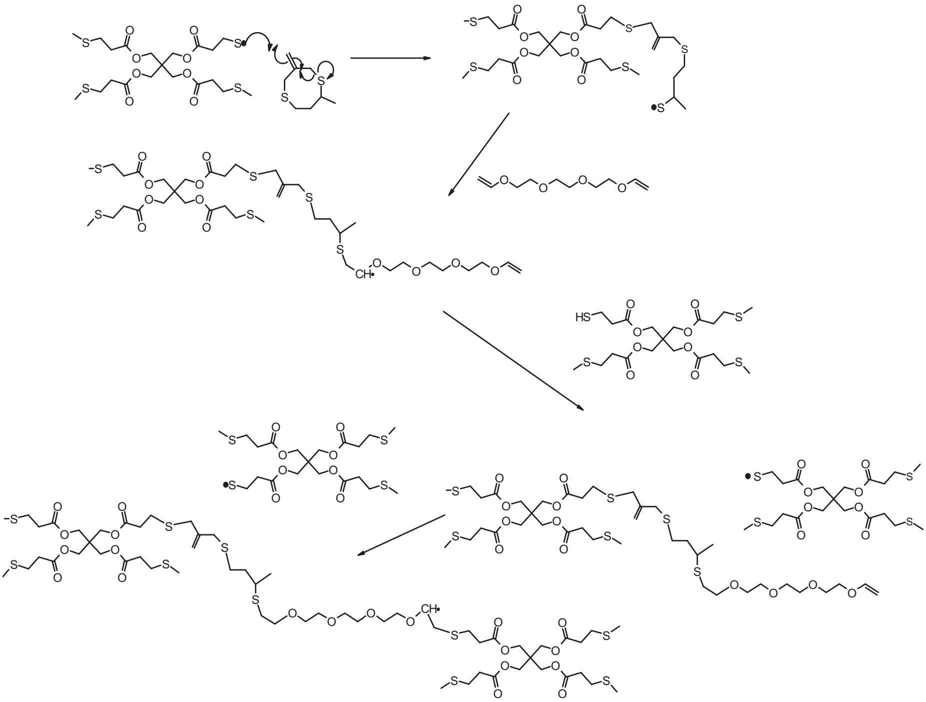
Results and Discussion

The free radical homopolymerization of vinyl ethers is relatively slow at room temperature[42] and so the main reaction in the free-radical initiated reaction of a thiol and a vinyl ether is primarily that of alternating copolymerization via addition and chain transfer[43,44] as shown in Scheme 7. This mechanism is only slightly modified when a monomer containing an allylic dithioether, for example MDTO, is added to the polymerizing mixture. Allylic monomers homopolymerize slowly at room temperature[45] and do not readily copolymerize with vinyl ethers.[46] As shown in Scheme 8, the ring opening of MDTO



Scheme 7.
Reaction of a tetrathiol (PETMP) with a divinyl ether (TEGDVE) to form a network.

inserts an allylic dithioether unit into the network backbone but the thiol radical formed in this reaction is only able either to react with another MDTO unit or with a vinyl ether, thus extending the network strand. The alternative reaction of a thiol radical with the allylic dithioether only causes β-scission and the reformation of another allylic dithioether unit and thiol radical, while H-abstraction by the thiol radical of the opened MDTO unit from the tetrathiol only regenerates another thiol

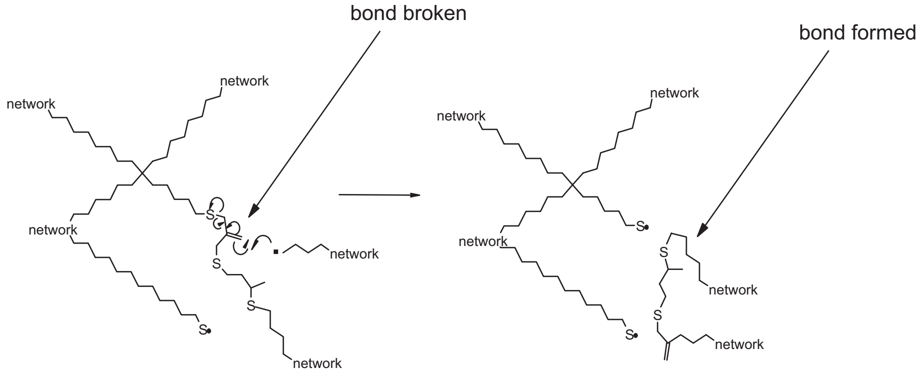


Scheme 8.
Copolymerization of MDTO with the tetrathiol (PETMP) with a divinyl ether (TEGDVE).

radical. Thus, these latter reactions do not affect the final network structure.

Allylic dithioethers have been often used as efficient addition-fragmentation chain transfer agents.[38,47] Therefore, during, and most significantly, after formation of a thiol-ene network containing the allylic thioether moiety, any radicals formed either thermally or photochemically should add to the vinyl group of an allylic thioether in a network chain and cause β-scission, thus breaking the chain and producing a new allylic group and another thiol radical.[47–51] In turn, this thiol radical can attack a neighbouring allylic thioether group, also causing β-scission, and this process will continue until the thiol radicals terminate. The relevance of this mechanism is that the reaction between a relatively mobile thiol radical and a stressed network segment containing an allylic unit causes bond rearrangement (also termed "bond-interchange reaction" by Tobolsky[52,53] who worked on chemically induced stress relaxation and creep in disulphide-cross-linked Thiokol rubbers) which changes the stress distribution on the network chains as shown in Scheme 9. If this process occurs a number of times, the molecular rearrangement of the network strands will translate into macroscopic strain in a specimen under a load, or stress relaxation of a specimen under a strain. It is also worth noting that the process of thiol radical addition, allylic thioether β-scission and strand rearrangement followed by reformation of a thiol radical can occur many times for every photon initiating this series of processes. As such, this mechanism of photo-plasticity is much more efficient than those discovered previously.[7,17,30–33,31,34]

Physical evidence for photo-induced plasticity[15] is given in Figure 1, which shows the photo-induced deformation response of a PETMP/TEGDVE thiol-ene network polymer modified by varying levels of the cyclic allylic-dithioether, MDTO. The amount of time-dependent creep is minimal when the stress is applied without concomitant irradiation however when the MDTO-containing networks are irradiated under stress, the material shows substantial levels of creep. Most of this creep is permanent because removal of the stress (without irradiation) does not lead to significant creep recovery. Figure 1 also shows that the extent of creep under irradiation and load also depends on the amount of MDTO added to the monomer mixture because the allylic thioether unit is the source of the bond-interchange reaction. This photo-responsive behaviour much faster than that exhibited in previously reported systems[7,17,30–33] because the latter can only be activated by UV radiation for several hours, whereas the response in the present system takes seconds to minutes.



Scheme 9.
Mechanism of shape change or stress relaxation in a thiol-ene network as a result of β-scission of an allylic thioether unit.

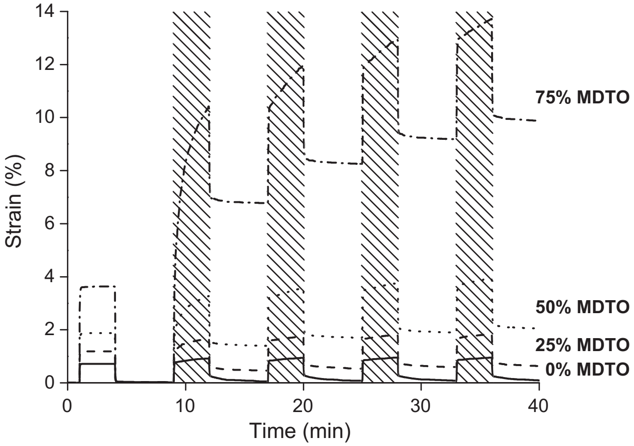
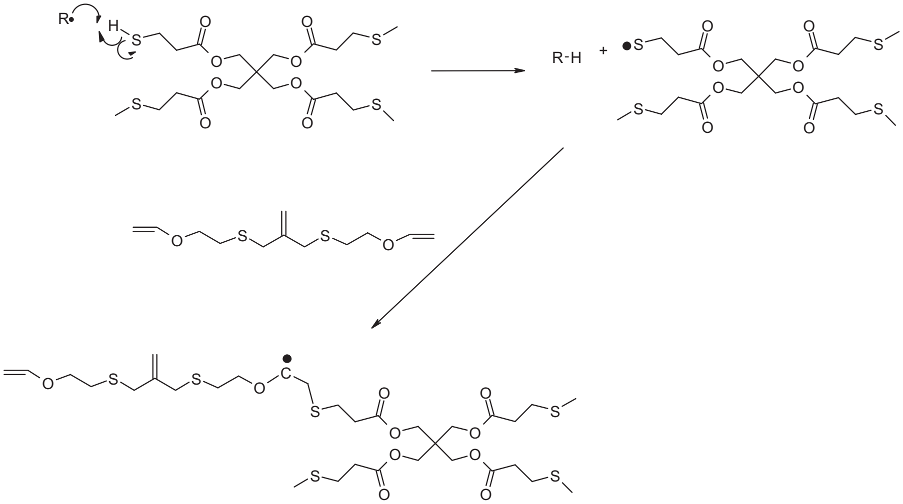


Figure 1.

Creep/creep recovery profiles of PETMP/TEGDVE specimens with varying concentrations of MDTO. The stress was alternated between 0 and 10^5 Pa. The specimen was exposed to near-UV radiation to photolyse the free radical source (BAPO) during stress application after the first load cycle (irradiation is indicated by the shaded areas).

One disadvantage with the photo-plastic thiol-ene system PETMP/TEGDVE/MDTO is that the cyclic monomer (MDTO) makes the network strands longer and so reduces the crosslink density - in fact it is not possible to form a network where all of the strands contain the photo-plastic groups using this system. To counter this problem, we have recently used an allylic dithioether divinyl ether (MDTVE) to copolymerize with the tetrathiol (PETMP),[36,37] as shown in Scheme 10. In contrast to MDTO, the two vinyl ether units of MDTVE can copolymerize with two thiol groups of PETMP molecules thus forming a network strand with a β-cleavable allylic dithioether unit whereas if TEGDVE reacts with the two thiol groups, the strand formed is not cleavable by radicals. Thus theoretically the level of photo-plasticity of the network can be varied from zero to an infinite amount depending on the ratio of TEGDVE to MTDVE.



Scheme 10.

Copolymerization of PETMP with MDTVE or TEGDVE.

Creep experiments during irradiation of specimens prepared from PETMP/TEGDVE, PETMP/TEGDVE/MDTVE and PETMP/MDTVE and containing a UV-sensitive radical source are shown in Figure 2. A small amount of strain occurs immediately on application of the stress (10^5 Pa) to all of the thiol-ene networks but the strain increases with time when the samples containing MDTVE are irradiated and specimens with more MDTVE show greater levels of photo-plasticity.[36] As with the networks containing MDTO (see Figure 1), this photo-induced deformation is permanent because it remains when the radiation is terminated. It is important to note that the amount of photo-induced creep should be proportional to the stress and so photo-induced creep of more than 100% should be readily achievable. This behaviour is consistent with the bond interchange mechanism shown in Scheme 9.

In Figure 2, it can be observed that the amount of creep is reduced during each successive radiation period and appears to be approaching a plateau after the third irradiation period. Two possible causes for this observation may be considered. The first possibility is that the source of the photo-generated radicals (BEE) is depleted during irradiation and after an extended period there is no radical source or radicals remaining. A second possibility is that a small fraction of the carbon-based radicals (vinyl radicals or initiator radicals) formed during the polymerization and photo-plasticity experiments attack the allylic group, leading to a cessation of photo-plastic activity due to loss of allylic dithioether units (see the left side of Scheme 11) – note that attack by thiol radicals on the allylic group has no effect on the concentration of these groups (see the right side of Scheme 11).

Figure 3 shows the effect of UV radiation during stress relaxation studies of PETMP/TEGDVE/MDTVE networks containing a free radical generator (BEE). In agreement with the creep behaviour, stress relaxation only occurs with MDTVE-containing networks and the stress relaxation rate increases with the concentration of MDTVE in the network. As found with the creep studies, the extent of radiation-induced stress relaxation is not complete for the PETMP/MDTVE system even though it theoretically has the potential to fully stress relax. The reason for this may be due to BEE depletion by photolysis or due to loss of allylic dithioether units as discussed above.

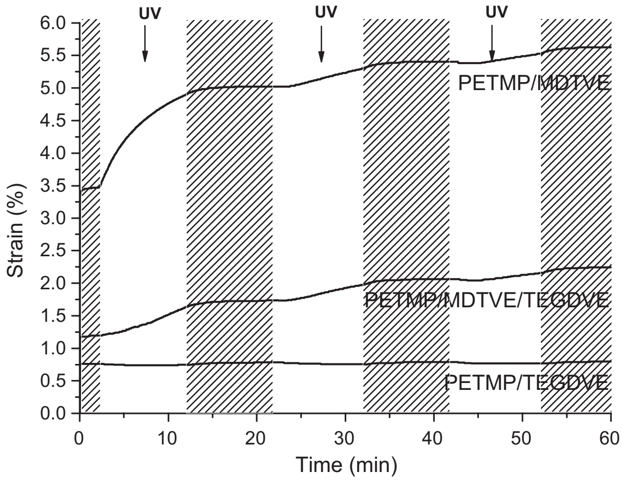
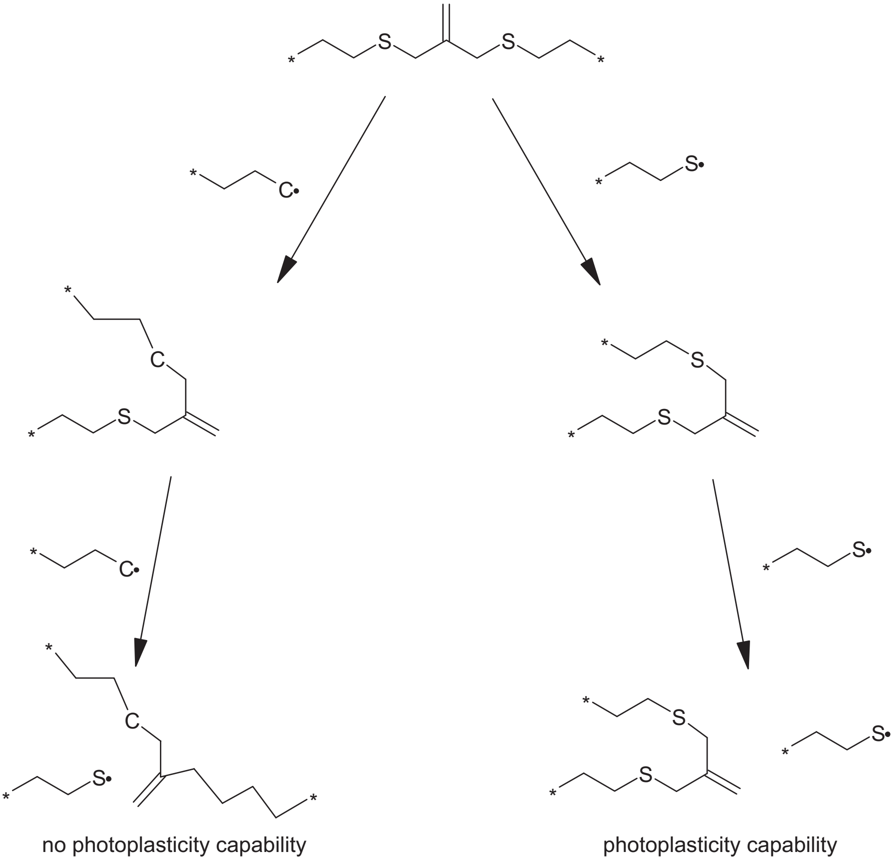


Figure 2.

Photo-plastic creep response under a tensile stress of 10^5 Pa of PETMP/TEGDVE, PETMP/TEGDVE/MDTVE and PETMP/MDTVE networks containing UV photoinitiator (BEE) as radical source during exposure to 360 nm UV radiation. The shaded regions correspond to the periods when the radiation was turned off.



Scheme 11.
Effect of the reaction of either a carbon or thiol radical with the allylic group.

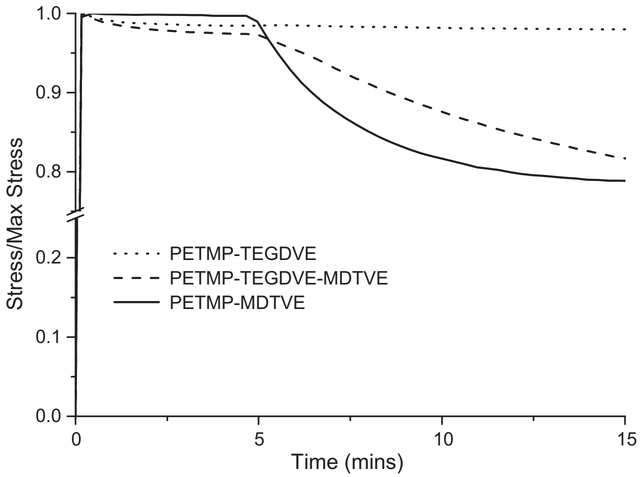


Figure 3.
Normalized stress relaxation of PETMP/TEGDVE/MDTVE networks under a constant strain of 10%. Irradiation of the specimens with 360 nm UV light started at 5 mins.

The polymerization kinetics of these thiol-ene networks is also of interest because of the information it can provide regarding the termination rate of radicals. The photopolymerization of PETMP with varying ratios of TEGDVE and MDTVE and photo-initiated by 1 wt% BAPO using >400 nm radiation was studied by photo-DSC (see Figure 4).[36] The maximum rate of polymerization occurs much closer to the start of the polymerization (approximately 15% conversion) compared with the radical photopolymerization of other systems such as dimethacrylates[54] (maxima between 20 to 50% conversion) and vinyl ester resins[55] (10 to 60% conversion). In addition, the rate is almost linear with conversion (and thus monomer concentration). In contrast, most photopolymerization studies[54,55] show that the rate of free radical photopolymerization is decidedly non-linear because the termination rate constant, and to a limited extent the propagation rate constant, are both dependent on conversion which suggests that in the thol-ene systems both rate constants are much less dependent on conversion than is usually observed. There are two reasons for these observations. The propagation rate constant should be relatively constant because the polymerization is occurring above the T_g of the cured polymer (as shown below). In addition, the topology of the thiol-ene network is relatively open and the reactive thiol and vinyl groups and radicals are either at the ends of a dangling chain or are mid chain whereas in conventional divinyl polymerization, these groups are in the vicinity of other crosslink points. Thus the termination rate constant should be much more constant for the thiol-ene systems because the terminating radicals have considerable segmental mobility and are able to terminate relatively easily irrespective of the degree of conversion.

Further information of the termination rate of radicals in the thiol-ene systems is given by the dark cure studies in Figure 5. During full irradiation the polymerization rate rises to a maximum and then decreases as monomer is consumed. If the radiation is turned on and off over a number of periods it can be seen that the rate rises rapidly when the radiation is on but the rate also drops very rapidly when the radiation is turned off, due to a rapid drop in the rate of polymerization due to loss of radicals to bimolecular termination.

Figure 4 also shows that the polymerization rate decreases as the amount of MDTVE is raised[36]. This may be due to several factors. The simplest explanation is

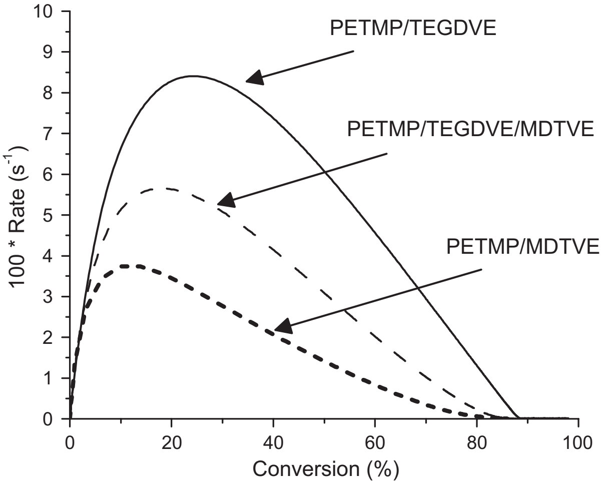


Figure 4.
Fractional conversion rate versus conversion for PETMP with TEGDVE and/or MDTVE at 50 °C with 1 wt% BAPO and 415 nm radiation.[36]

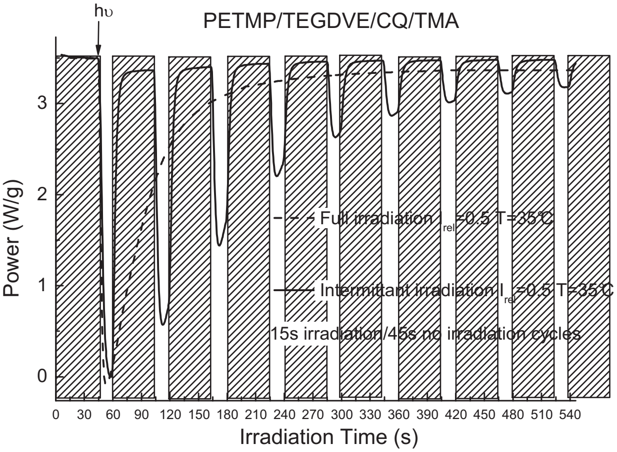
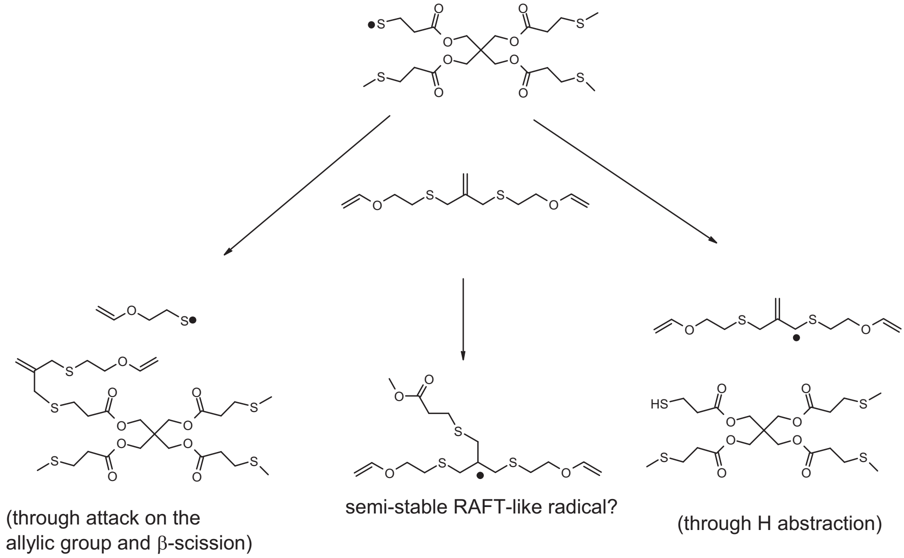


Figure 5.
Heat flux of PETMP/TEGDVE with camphorquinone and tetramethylaniniline initiator versus time during full and intermittent irradiation with 470 nm light at 35 °C.

that the vinyl groups in MDTVE are less reactive than those in TEGDVE due to the presence of the allylic thioether group. This seems unlikely because the electrophilic character of a thioether link is low and it is four atoms removed from the vinyl group. Another possibility is that the thiol radicals may attack the allylic double bond (followed by β-scission) thus producing an ethyl ether-based thiol radical which may have lower reactivity to vinyl groups (see Scheme 12). Alternatively the thiol radicals may abstract a hydrogen atom from the allylic group and the resulting species may not react as readily with thiol or vinyl ether groups, thus slowing the overall rate of reaction (see Scheme 12). A last possibility is that addition of the thiol radical on the allylic dithioether forms a relatively stable radical somewhat analogously to the



Scheme 12.
Possible causes for reduced reactivity of MDTVE.

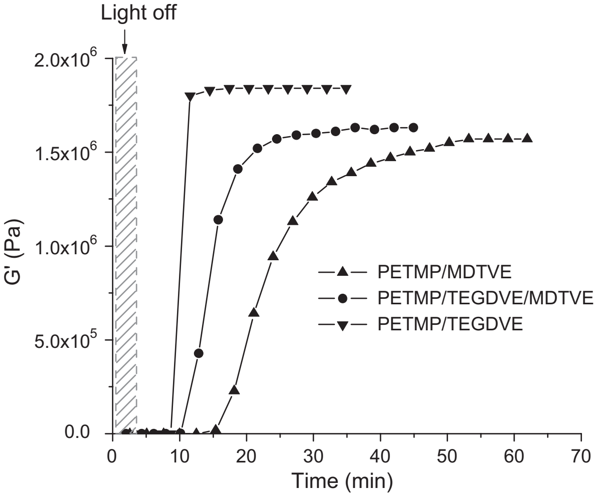


Figure 6.
Photo-rheology of PETMP/TEGDVE, PETMP/TEGDVE/MDTVE and PETMP/MDTVE with 1 wt% BAPO irradiated with 415 nm radiation at 50 °C.[36] The radiation intensity was 1.15 mW/cm^2 and irradiation commenced at 4 min.

hypothesized stable tri-arm radical in RAFT polymerization[56] as shown in Scheme 12.

Figure 6 compares the evolution of the shear modulus during the photopolymerization of PETMP with TEGDVE and/or MDTVE using 1 wt% BAPO.[36] The substitution of TEGDVE with MDTVE slows the reaction in agreement with the DSC (Fig 4) studies. The final rubbery modulus also decreases as the amount of MDTVE is raised and this is mainly due to the fact that the latter has a higher molecular weight than TEGDVE and this reduces the concentration of network strands in the network in accordance with the theory of rubber elasticity.

Figure 7 shows that the DMTA of cured PETMP/TEGDVE and PETMP/MDTVE. The glass transition temperatures for PETMP/TEGDVE and PETMP/MDTVE were –27 °C and –13 °C, respectively, so

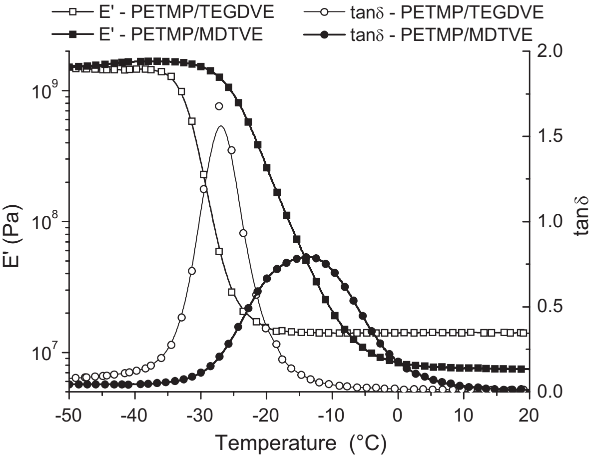


Figure 7.
DMTA behavior at 1 Hz for PETMP/TEGDVE and PETMP/MDTVE cured with AIBN.[36]

these materials are rubbery at room temperature. As noted with the rheology data, the rubbery elastic modulus of PETMP/TEGDVE is the higher, because its network strand density (2.24×10^{-3} mol/g, theoretically) is higher than that for PETMP/MDTVE (1.98×10^{-3} mol/g).

Conclusion

There have been many important developments in the field of stimuli responsive polymers in the last 25 years and particularly more recently in the sub-field of photo-plasticity of crosslinked materials. Ordinarily, the network structure that provides the excellent mechanical properties of crosslinked polymers also results in the polymer shape and properties being fixed upon polymerization, requiring degradation of the crosslinks to make them reshapeable. However the introduction of photo-responsive crosslinked polymers provides the possibility of shape change and stress relaxation, and importantly the reduction of stress inhomogeneities formed as a result of shrinkage during the polymerization process.

In this paper we have illustrated that the incorporation of radical-cleavable and reformable moieties in the network strands - in the present case, β-cleavable allylic thioether units - have a much greater potential for the development of fast and fully photo-plastic crosslinked polymers because a single photon may cause many bond interchanges and because the concentration of photo-plastic moieties can be varied by selection of the monomer composition. In addition, the mechanism of photo-plasticity illustrated here is theoretically unconstrained to thiol-ene networks, because the thiol and vinyl ether groups only serve to form the network. Thus, it should be possible to incorporate radical-cleavable allylic thioether units and similar units in a range of different networks such as anhydride-cured epoxies and cationically polymerized vinyl ethers which we are currently investigating. However there still remains the challenge of determining why the extent of photo-plasticity is not as large as expected.

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