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Stress Relaxation by Addition–Fragmentation Chain Transfer in Highly Cross-Linked Thiol–Yne Networks

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Polymerization of multifunctional monomers yields cross-linked polymeric networks (i.e., thermosets) that are extensively utilized in applications ranging from coatings and adhesives to dental materials and microelectronics.[1−3] Unfortunately, these polymerizations are typically accompanied by a significant amount of volumetric shrinkage,[4] where the associated stress that arises leads to a wide range of deleterious effects, such as material warping and cracking. Mitigation of this polymerization-induced shrinkage and/or the associated stress has been the focus of extensive research efforts over the past several decades[5,6] and has been explored using an array of approaches, including ring-opening polymerization,[7] thiol-ene polymerizations,[8] and polymerization-induced phase separation.[9]

One approach to mitigate shrinkage stress was recently conceived where the minimization of polymerization *shrinkage* itself is not directly addressed. Rather, the network connectivity continuously rearranges during the polymerization, thus promoting network relaxation and alleviating polymerization *shrinkage stress*, establishing these materials as covalent adaptable networks.[10,11] This network connectivity rearrangement approach is realized via radical-mediated, addition—fragmentation chain transfer (i.e., AFCT) that occurs through the cross-linking strands. Thus, the network is rearranged without a concomitant change in network chemistry or cross-link density, while simultaneously being compatible with radical-mediated polymerizations. Although our approach was capable of dramatically reducing the polymerization shrinkage-induced stress in elastomeric networks,[10] demonstrating its effectiveness in glassy materials would vastly broaden its utility.

Our previous work exploiting AFCT mechanisms to reduce polymerization stress utilized thiol–ene networks, whereby multifunctional thiol and vinyl monomers were copolymerized via a radical-mediated step-growth reaction mechanism to incorporate an allyl sulfide functionality[12,13] in the cross-linking strands.[10] Thiol–ene polymerizations possess many desirable attributes, such as extraordinary resistance to oxygen inhibition (owing to the facile abstractability of the thiol hydrogen)[14,15] and rapid polymerization kinetics; moreover, their step-growth nature produces a homogeneous, cross-linked material with uniformly distributed allyl sulfide functional groups throughout the network. Unfortunately, thiol–ene polymerizations often yield elastomeric materials with low glass transition temperatures (T_gs) that are ill-suited for structural applications. Utilization of the thiol–yne polymerization mechanism (i.e., replacing the vinyl-based monomer with an ethynyl-based monomer) preserves the desirable characteristics of the thiol–ene mechanism while effectively doubling the cross-link density, yielding a concomitant increase in the T_g.[16−19] Here, we incorporate allyl sulfide functional groups into thiol–yne networks to effect stress relaxation in superambient T_g materials.

The allyl sulfide AFCT functionality was incorporated in a thiol–yne system via the formulation of an allyl sulfide-based diethynyl monomer (2-methylenepropane-1,3-di(thiobut-1-yne), MDTBY; Figure 1A) with a tetrathiol (pentaerythritol tetrakis-(3-mercaptopropionate), PETMP; Figure 1C) at a 1:2 ethynyl/thiol stoichiometric ratio, as each ethynyl group is capable of reacting with two thiol groups. For comparison, an analogous thiol–yne network was fabricated utilizing a propyl sulfide-based diethynyl monomer (2-methylpropane-1,3-di(thiobut-1-yne), MeDTBY; Figure 1B), where the propenyl sulfide is incapable of undergoing the AFCT-mediated relaxation mechanism, in place of MDTBY. These resins were additionally formulated with 3 wt % UV photoinitiator (1-hydroxycyclohexyl phenyl ketone, HCPK; Figure 1D) to initiate the thiol–yne polymerization upon UV irradiation. Shrinkage stress and functional group conversion were monitored simultaneously using tensometry[8,20] and Fourier transform infrared (FTIR) spectroscopy during the photopolymerization of each resin (see Supporting Information).

The thiol–ene reaction follows an elegant mechanism of sequential propagation and chain transfer events, whereby addition of a thiyl radical to a vinyl functional group yields a carbon-centered radical that subsequently abstracts a thiol hydrogen, regenerating the thiyl radical and producing a thioether (Figure 2, cycle B). Utilization of an ethynyl-based monomer (i.e., thiol–yne) increases the polymerization reaction complexity as the mechanism proceeds via two sequential thiol addition reactions (Figure 2, cycles A and B). Incorporation of the allyl sulfide further increases the reaction complexity and provides a route for network connectivity rearrangement via the AFCT reaction, whereby a thiyl radical adds to an allyl sulfide functional group to yield an unstable carbon-centered radical intermediate, the fragmentation of which regenerates both the allyl sulfide functional group and the thiyl radical (Figure 2, cycle C). Whereas MeDTBY participates exclusively in the thiol–yne polymerization reaction (i.e., Figure 2, cycles A and B), MDTBY participates in both the thiol–yne polymerization and AFCT network connectivity rearrangement reactions concurrently (i.e., Figure 2, cycles A–C). Thus, MeDTBY acts as a negative control monomer possessing similar chemical structure and molecular weight.

The stress that accumulates during a polymerization is typically attributed to the extent of postgelation shrinkage and the modulus of the polymerized material. A comparison of the thermomechanical properties of the fully cured allyl and propyl sulfide-based materials demonstrates excellent similarity between the two network structures with respect to their cross-link density and glass transition behavior, as expected given their similar molecular structures (Figure 3). More specifically, the onset of the thermal transition from a glassy to elastomeric material occurs at approximately the same temperature, and the rubbery moduli, which are proportional to the cross-link density, are similar. The temperature at the tan δ maximum (assigned here as the T_g)[22,23] demonstrates that both allyl and propyl sulfide-based materials exhibit superambient T_gs (allyl sulfide-based system: 41 ± 1 °C; propyl sulfide-based system: 39 ± 1 °C). Overall, the mechanical property similarity between the two materials indicates that the propyl sulfide-based network serves as an excellent control, where any differences are attributed to the simultaneous AFCT polymerization mechanism rather than differences in the network structure.

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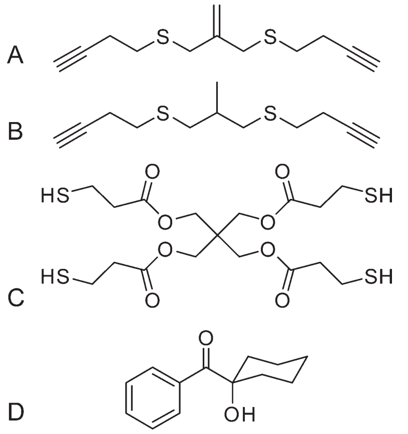

Figure 1. Materials used: (A) MDTBY, (B) MeDTBY, (C) PETMP, and (D) HCPK.

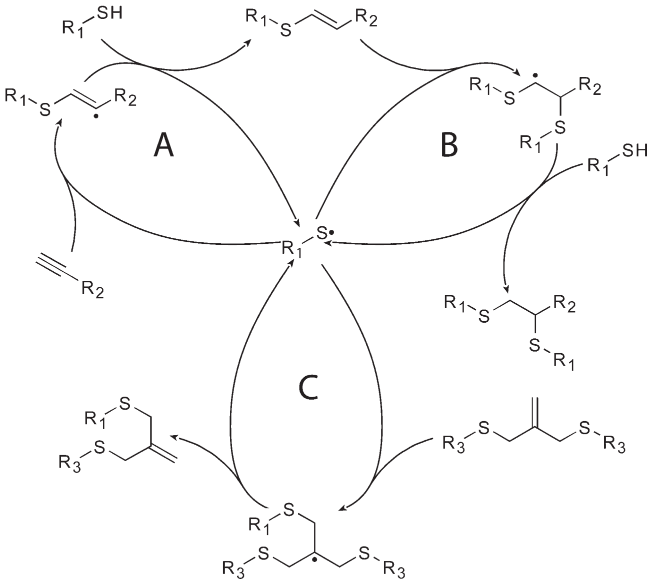

Figure 2. Schematic of concurrent thiol−yne (cycles A and B) and allyl sulfide AFCT (cycle C) mechanisms. The thiol−yne mechanism is comprised of two sequential addition events, whereby addition of a thiyl radical to an ethynyl functional group yields a vinyl sulfide functional group (cycle A); subsequent thiyl radical addition across this vinyl completes the thiol−yne polymerization mechanism (cycle B).[18] Thiyl radical addition to and subsequent fragmentation of the allyl sulfide functional group conserves the concentrations of both the thiyl radical and allyl sulfide functional group (cycle C).[10,21]

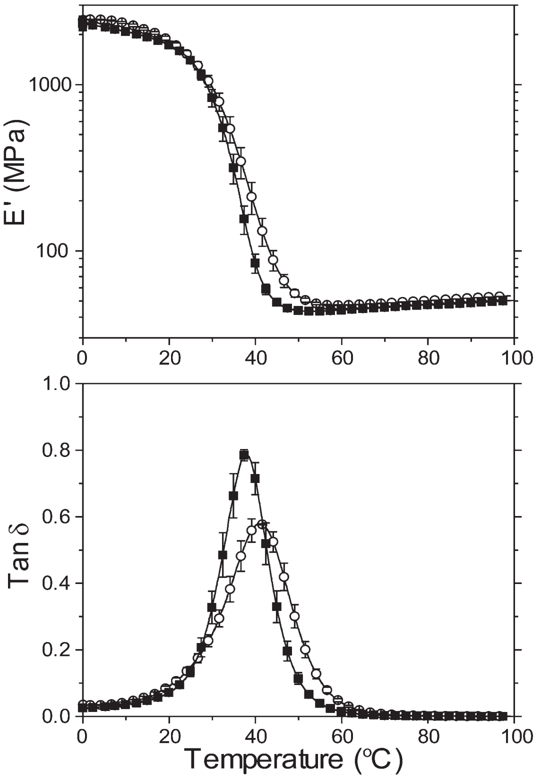

Figure 3. (A) Elastic modulus and (B) tan δ versus temperature for stoichiometrically balanced mixtures of PETMP−MDTBY (○) and PETMP−MeDTBY (■). Samples were formulated with 3 wt % HCPK and irradiated at 365 nm, 10 mW/cm^2, for 30 min.

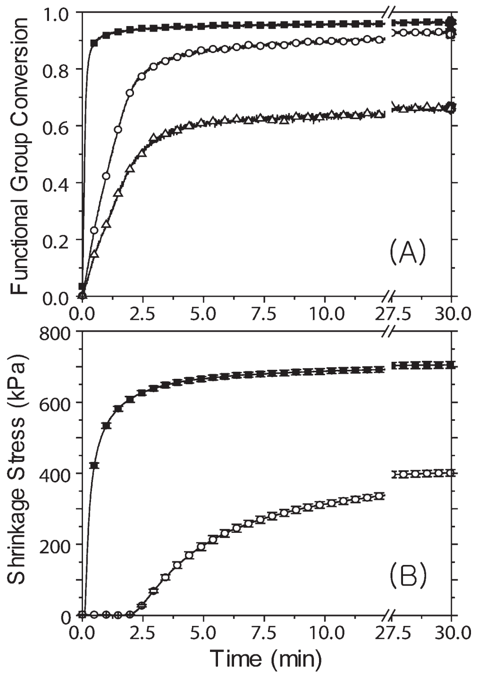

Figure 4. (A) Functional group conversion (ethynyl conversion of PETMP−MDTBY (○), ethynyl conversion of PETMP−MeDTBY (■), and allyl sulfide of PETMP−MDTBY (△)) and (B) polymerization shrinkage stress evolution (PETMP−MDTBY (○) and PETMP−MeDTBY (■)) versus time for a 2:1 stoichiometric mixture of thiol:yne. Samples contain 3 wt % HCPK and were irradiated at 10 mW/cm^2 using 365 nm light.

The IR spectroscopy of PETMP−MeDTBY indicates rapid consumption of the ethynyl functional group; however, the ethynyl consumption does not proceed to complete conversion, presumably owing to severely reduced molecular mobility resulting from vitrification (Figure 4A).[24] Conversely, the ethynyl consumption during the PETMP−MDTBY photopolymerization (i.e., the allyl sulfide-containing system) proceeds at a slower rate, attributable to the sequestration of radicals participating in the AFCT mechanism.[10] Moreover, consumption of the allyl sulfide is observed during the PETMP−MDTBY photopolymerization (Figure 4A), in contrast to the idealized reaction mechanism detailed in Figure 2 (i.e., cycle C). Previous work in thiol−ene systems demonstrated a minor side reaction whereby the AFCT carbon-centered radical intermediate abstracts a thiol hydrogen, thus consuming a small fraction of both allyl sulfide and thiol.[10] In the current thiol−yne system (i.e., PETMP−MDTBY), a large fraction of the allyl sulfide is consumed during the polymerization (Figure 4A), presumably reacting with an equivalent amount of thiol and thus producing an ethynyl/thiol stoichiometric imbalance. This ethynyl/thiol imbalance results in a limited amount of ethynyl homopolymerization, effecting a mixed-mode step- and chain-growth polymerization mechanism[18] that would be expected, in the absence of any other differences, to increase both the cross-linking density and the corresponding stress. Furthermore, homopolymerization results in a lower gel-point conversion, which would reduce the stress dissipated by pregelation viscous flow, further heightening the stress level expected in such a system. Thus, in the absence of any network relaxation associated with the AFCT-mediated relaxation mechanism, the photopolymerization of PETMP−MDTBY is expected to exhibit a much higher polymerization stress level as compared to PETMP−MeDTBY. In contrast, Figure 4B demonstrates the dramatic effect of the AFCT-mediated relaxation mechanism as the PETMP−MDTBY resin exhibits significantly reduced polymerization stress (43%) as compared to the PETMP−MeDTBY control, attributable to the allyl sulfide AFCT mechanism facilitating network connectivity rearrangement during the polymerization. This relaxation behavior is observed despite the glassy nature of the polymer networks that are formed.

In this study, we found that the incorporation of allyl sulfide functional groups in the polymer backbone of a material possessing a superambient T_g reduces polymerization-induced shrinkage stress, owing to network connectivity rearrangement via a AFCT mechanism. To our knowledge, this observation is the first successful demonstration of AFCT-mediated network rearrangement during the polymerization of a glassy polymer network to induce stress relaxation. As this approach is well-suited for incorporation in free radical polymerizations, or indeed any other thermosetting polymerization where radicals can be generated, the mitigation of polymerization stress can be achieved even in high-performance materials.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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