ADHESIVE COATINGS USING ADDITION-FRAGMENTATION CHAIN TRANSFER

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Introduction

Photopolymerization is industrially useful in a wide range of applications, including optical lenses, coatings, lithographically defined systems, and adhesives [1-9]. Advantages associated with photopolymerizations include the ability to control the reaction, both spatially and temporally, through control of the reaction initiating light [1-9]. More specifically, the unique photo-controlled properties of Covalent Adaptable Networks (CANs) offer additional benefits over conventional thermosets and other photopolymerized systems. CANs are polymer networks that are covalently crosslinked, but contain specific functionalities either in the network backbone or at linkage points that allow the bonded structure of the network to rearrange in response to a specific stimulus. There are two classes of CANs, thermal and photochemical, depending on the stimulus implemented to induce network rearrangement. Thermal CANs utilize reversible Diels-Alder adducts that form covalent bonds at low temperature and reversibly de-bond at high temperatures [10]. Photochemical CANs, on the other hand, use light triggered radical reactions to undergo rearrangement.

There are a number of important applications and benefits for the type of network rearrangement implemented in photochemical CANs. These materials can be designed to reduce the shrinkage stress that arises during polymerization due to the reduction that occurs in the space between monomers as weak intermolecular interactions are replaced by covalent bonds [11-16]. Network rearrangement can also lead to reduction in external stresses applied post-polymerization via photo-induced creep [17]. Materials have also been designed that exhibit self-healing characteristics, where fractured pieces of material reform upon irradiation [18]. When photo-induced CAN materials are stretched and irradiated in a patterned manner, changes can be made to both the 3D shape and surface topography of materials [19]. Other possible applications for photo-induced CANs include irradiation triggerable adhesion and photochemically defined lithographic features formed on materials.

In addition to CANs, there are other molecular systems that result in networks with dynamic properties. One recent and exciting approach taken by Montarnal and co-workers [20] uses epoxy networks that are constantly rearranging via transesterification exchange reactions. At ambient temperature, the kinetics of this reaction is such that the overall network structure appears to be essentially static; however, at elevated temperatures the exchange reactions occur much more rapidly, allowing the material to flow, undergo repair, and be easily molded. Another method used by Deng and co-workers [21] implements networks crosslinked with acyl-hydrazone bonds. These bonds form and break reversibly depending on the pH of their environment. By controlling pH the material can be made to transition between a soft solid and a liquid and exhibit self-healing properties. While both of these systems exhibit exciting capabilities, they also require changes to the bulk environment of the material. This approach can make them less suited for certain applications, such as dental materials, where it would be unsuitable to elevate temperature or change pH of the surrounding environment. Photo-induced network rearrangement, in contrast, allows specific, patterned, well-controlled "hands free" initialization.

The photochemically-initiated mechanism that gives rise to the network rearrangement in photo-induced CANs is known as addition-fragmentation chain transfer (AFCT) or reversible addition-fragmentation chain transfer (RAFT) [22, 23], as illustrated in Figure 1.
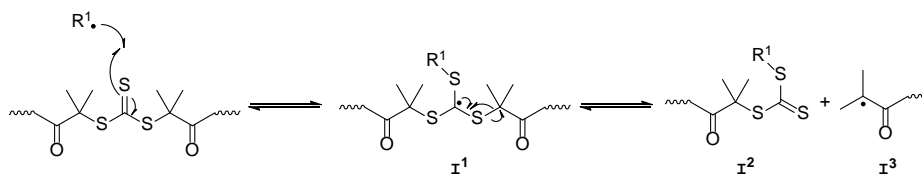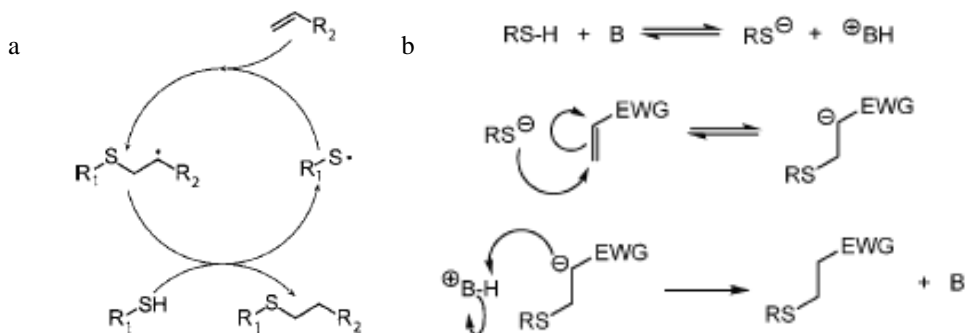

Figure 1: RAFT Polymerization

The RAFT process involves a radical, here initially generated by light exposure, attacking a double bond to form a tri-centered radical intermediate (I^1). This intermediate then cleaves in one of three possible manners, leaving a newly formed double bond (I^2) and another radical species to further the RAFT process (I^3).

Traditionally, RAFT synthons have had disadvantages such as being hard to synthesize, requiring harsh reaction conditions, and the foul odor of sulfur containing compounds. Due to advances in synthetic organic chemistry, the synthesis of RAFT monomers is possible with facile, high yielding, and efficient reaction processes. Furthermore, the RAFT moieties can be used orthogonally with –ene systems. When RAFT agents are reacted with these –ene systems CAN type materials are formed with the ability to rearrange the topology of the network without affecting the overall network connectivity under appropriate equilibrium conditions [24].

The two main classes of synthons used in CANs that contain RAFT moieties are the allyl sulfides and the trithiocarbonates (TTC). The most interesting RAFT monomers are the allylic and methacrylic containing allyl sulfide and trithiocarbonates. By taking advantage of the reactivity of the acrylate and methacrylate functionalized RAFT synthons, a polymer network can be formed by a photo-catalyzed radical thiol-ene reaction (Scheme 1a) or by a base catalyzed thiol-ene Michael addition reaction (Scheme 1b).
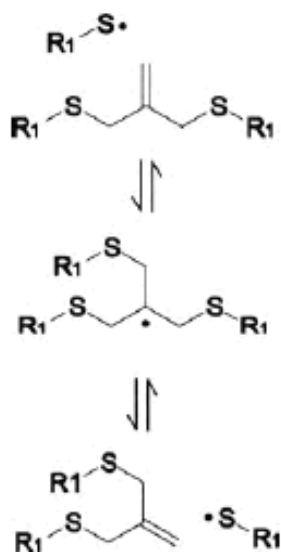
Scheme 1: (a) Thiol-ene radical reaction [25] (b) Thiol-ene Michael addition reaction [25]

When the network is formed by a radical-mediated thiol-ene reaction, RAFT can occur concurrently with and subsequent to polymerization, while when the thiol-ene Michael addition reaction is used, the RAFT mechanism occurs only during post-polymerization rearrangement of the network. The differences in when the RAFT rearrangement of the network occurs relative to polymerization, as well as differences in network structure, optical characteristics of the material, and other physical properties of the material can be adjusted to give the variety of behaviors described below.

Molecular Systems

Allyl Sulfide

Allyl sulfide containing molecules allow network rearrangement to occur by the mechanism shown in Scheme 2. A radical attacks the double bond, forming a tri-centered radical intermediate. This intermediate then cleaves, forming a new cross-link and another radical to continue the AFCT process. Because the AFCT radical intermediate is not symmetrical, the process is not reversible unless it occurs with a sulfur radical adding to the double bond. This outcome means that in a conventional radical polymerization of species such as (meth)acrylates, the formed network containing allyl sulfide AFCT agents will rearrange and relax only until all of the allyl sulfide has been consumed. This behavior is unlike a RAFT system where the RAFT agent concentration remains constant within the network, as would be the case for an allyl sulfide in a thiol-ene reaction where thiyl radicals are the primary species participating in the AFCT process. However, there are advantages presented by allyl sulfide monomers compared to trithiocarbonates, such as their lack of color and odor, and their ease of synthetic formulation. Various allyl sulfide agents, including allyl sulfide containing divinyl ethers, diethynyl molecules, and diacrylates have been used by our group to facilitate AFCT network rearrangement.

Scheme 2: Allyl sulfide AFCT radical rearrangement mechanism [13]

Allyl sulfide containing divinyl ethers and diethynyl molecules have been used to reduce polymerization shrinkage stress in thiol-ene networks [13]. The shrinkage stress in networks made from pentaerythritol tetrakis(3-mercaptoproionate), ethoxylated bisphenol A dimethacrylate (EBPADMA), and the AFCT agent 2-methylene-propane-1,3-di(thioethyl vinyl ether) (MDTVE) was compared to that in networks where MDTVE was replaced by an equivalent molecule, 2-methyl-propane-1,3-di(thioethyl einyl ether) (MeDTVE), that is not an AFCT agent (Figure 2).
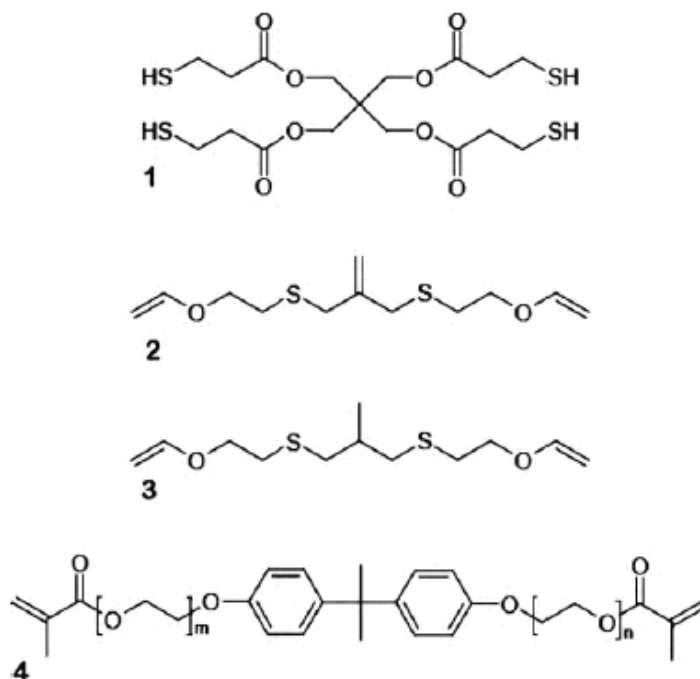
Figure 2: (1) PETMP (2) MDTVE (3) MeDTVE (4) EBPADMA [13]

The two different networks had similar kinetic and conversion profiles. The MDTVE-containing network had slightly lower conversion of the methacrylate and vinyl ether functional groups compared to the MeDTVE network, due to reaction of the allyl sulfide double bond. The MDTVE-containing networks displayed decreased shrinkage stress compared to the MeDTVE networks during polymerization, due to the network rearrangement via the AFCT mechanism. Furthermore, the amount of shrinkage stress relaxation could be modified by changing the amount of MDTVE in the network. This change was also accompanied by a change in the T_g of the network, with increasing MDTVE concentration giving more stress relaxation and also a lower T_g.

   A similar approach was taken to show that AFCT agents could reduce shrinkage stress in the more highly crosslinked networks that form from thiol-yne polymerizations [14]. The shrinkage stress during polymerization was compared for two similar ynes, 2-methylenepropane-1,3-di(thiobut-1-yne) (MDTBY) and 2-methylpropane-1,3-di(thiobut-1-yne) (MeDTBY), where MDTBY is AFCT-capable and MeDTBY is not (Figure 3).
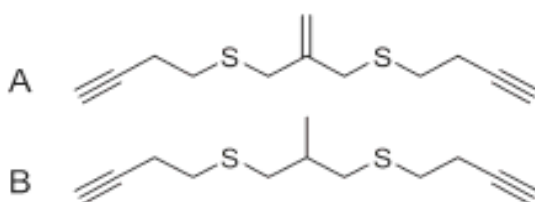

Figure 3: (A) MDTBY (B) MeDTBY [14]

Each of these monomers were polymerized with PETMP in a 1:2 yne:thiol ratio. In the MeDTBY/PETMP networks, the ethynl was almost completely consumed, while in the

MDTBY/PETMP network the ethynl conversion was lower due to reaction of the thiol with the allyl sulfide. However, both materials had similar elastic moduli and cross-link densities. The AFCT-capable network containing MDTBY showed decreased shrinkage stress during polymerization when compared to the MeDTBY network. This result indicated that the allyl sulfide mediated AFCT could alleviate shrinkage stress in a glassy as well as in a rubbery material.

Additionally, acrylic allyl sulfide monomers have been used to induce stress relaxation and give 3D shape control through network rearrangement [19]; however, in this instance the networks were formed via a base catalyzed Michael reaction between a thiol, PETMP or ethylene glycol bis(3-mercaptopropionate) (EGBMP), and 2-methylene-propane-1,3-bis(thioethyl acrylate) (MBTA), an allyl sulfide containing diacrylate (Figure 4).
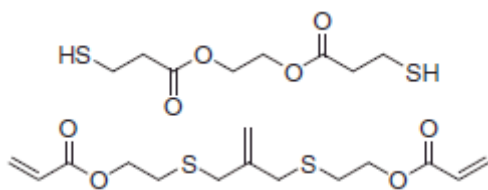

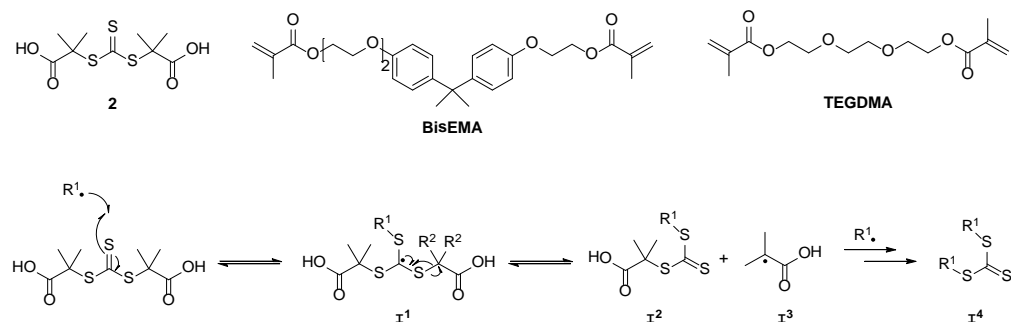**Figure 4:** (top) EGBMP (bottom) MBTA [19]

Photoinitiator was incorporated into the material, so that irradiation subsequent to the material synthesis could initiate AFCT rearrangement. After formation, stress applied to the material was relaxed by irradiating the stressed sample and activating the AFCT process. Furthermore, if only select areas of a stressed sample were irradiated, AFCT mediated stress relaxation in those areas led to changes in the 3D shape of the material. By including multiple photoinitiators and absorbers tuned to different wavelengths, multiple shape modifications could be made on the sample, altering both bulk shape and surface topography.

Trithiocarbonate

Trithiocarbonates have been used often as efficient RAFT agents. They have an advantage over the allyl sulfides in that the trithiocarbonates have the ability to undergo radical B-scission at all three sulfur centers. The allyl sulfides only have the capability of inducing B-scission at two of its radical centers. This unique feature allows the trithiocarbonates to undergo stress relaxation and photo-induced creep more efficiently than its allyl sulfide counterpart. Further, the TTC moiety is capable of reacting reversibly with carbon-centered radicals to promote network adaptation throughout and following polymerization. The major disadvantage of the trithiocarbonates is the unpleasant odor and color of the materials.

One of the shortcomings of the RAFT agents is that they must contain a good leaving group adjacent to the RAFT center. Lai and coworkers were able to overcome this downfall by the synthesis of S,S'-bis (α,α'-dimethyl-α''-acetic acid) trithiocarbonate, which contains a tertiary centered radical with carbonyl stabilization [26]. Lai showed that these were very active RAFT agents that showed highly controlled radical polymerization with predictable MW and narrow MW distributions in monovinyl polymerizations. When Lai's trithiocarbonate was added directly to multimethacrylate monomer resins, a significant reduction in shrinkage stress was observed, indicative of the fact that its addition, without necessitating any monomer modifications, was promoting reversible network

rearrangement [16]. Another method to incorporate the trithiocarbonate into the backbone of the network was through the addition of an additive that contains the trithiocarbonate functionality without the presence of polymerizable moieties, e.g., trithiocarbonate 2 (Scheme 3).

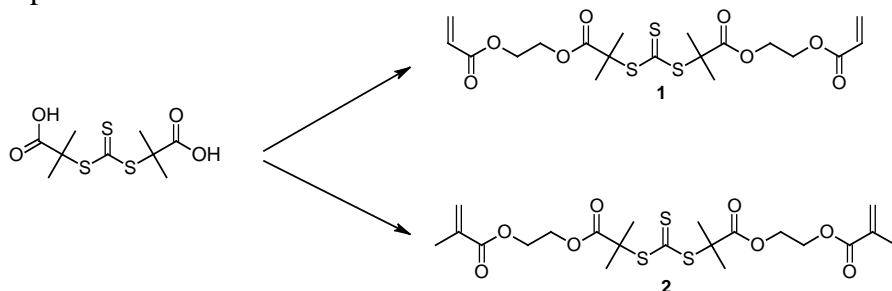**Scheme 3:** The method by which TTC can be incorporated into a polymer network

This approach can be applied broadly to almost any kind of radically polymerized monomer resin, without any synthetic modification of the monomer unit though it has significant limitations as well.
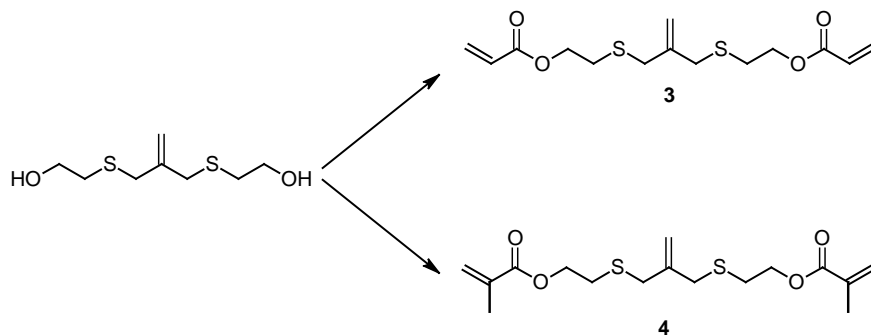
Matyjaszewski was able to functionalize Lai's trithiocarbonate by coupling HEMA to the trithiocarbonate through a Misunobu coupling. Matyjaszewski was able to form a polymer network with the TTC and a crosslinking agent (EDGMA) and MMA with AIBN as a thermal radical intiator. The newly formed gels could be placed in contact in the presence of CuBr/PMDETA at 60 °C and the gels were found to heal. This methacrylate-functionalized trithiocarbonate was not only able to undergo RAFT, but through its ability to form dynamic covalent polymers, this material was able to alternate cleavage and reformation reactions to self-heal [18].

Current Work

Synthesis

The current work in our group is based on the formation of dynamic covalent polymer networks by utilizing a thiol-ene Michael addition of a sulfur containing cross-linker to a RAFT containing synthon. The following RAFT functionalized monomer has been synthesized for our initial studies. The two TTC's (1, 2 in Scheme 4) were synthesized by Mitsunobu coupling from the carboxylic acid precursor. The two allyl sulfides (3, 4 in Scheme 4) were synthesized from acid chloride ester coupling from the thio-ether precursor.

Scheme 4: Reaction Diagrams for the synthesis of the acrylate tethered Trithiocarbonates and Allyl Sulfides

Allyl Sulfide

We are continuing to work with CANs that utilize the allyl sulfide functionality. Networks are formed from PETMP, EGBMP, and MBTA in a 1:1 thiol:acrylate functional group ratio via a base catalyzed Michael reaction (Scheme 1b). Including the linear thiol EGBMP in the network gives a more rubbery, less crosslinked network that can more easily undergo rearrangement. Varying the amount of EGBMP in the network is an additional parameter that can be used to control the material's physical properties. Reaction profiles were obtained from FTIR. The thiol conversion was monitored via the SH stretch at ~2600 cm^{-1}, and the acrylate conversion was monitored via the CH stretch at ~1600 cm^{-1}.
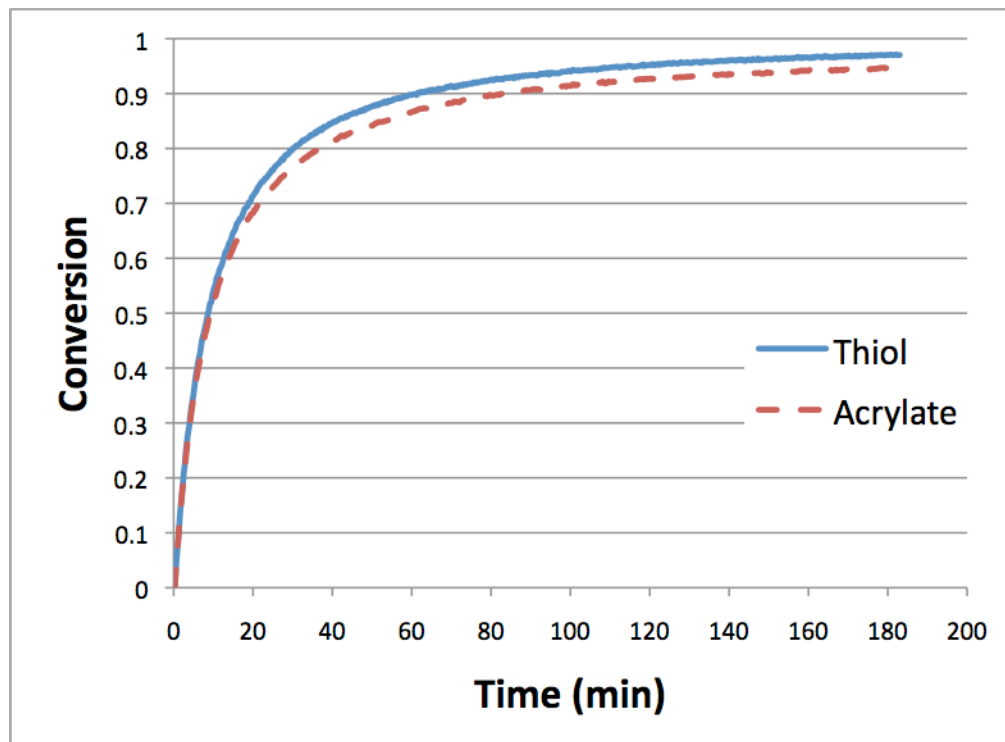

Figure 5: Kinetic Profile of Michael addition reaction between PETMP and MBTA

The reaction in Figure 5 of PETMP with MBTA proceeds via the Michael thiol-ene reaction. This is clear since the thiol functional groups in the PETMP and the acrylate functional groups from the MBTA are consumed at nearly the same rate. Both components are nearly 100% consumed after a reaction time of three hours as has been previously observed for these click-type reactions.

The mechanical properties of these materials are being characterized as well. Dynamic Mechanical Analysis (DMA) is done to measure the T_g of the material. The T_g is taken to be the maximum of the tan(delta) versus temperature curve, which occurs at about -23°C for a 1:2:4 molar ratio of PETMP:EGBMP:MBTA (Figure 6) and varies depending on the composition, crosslink density and stiffness of the monomer systems.
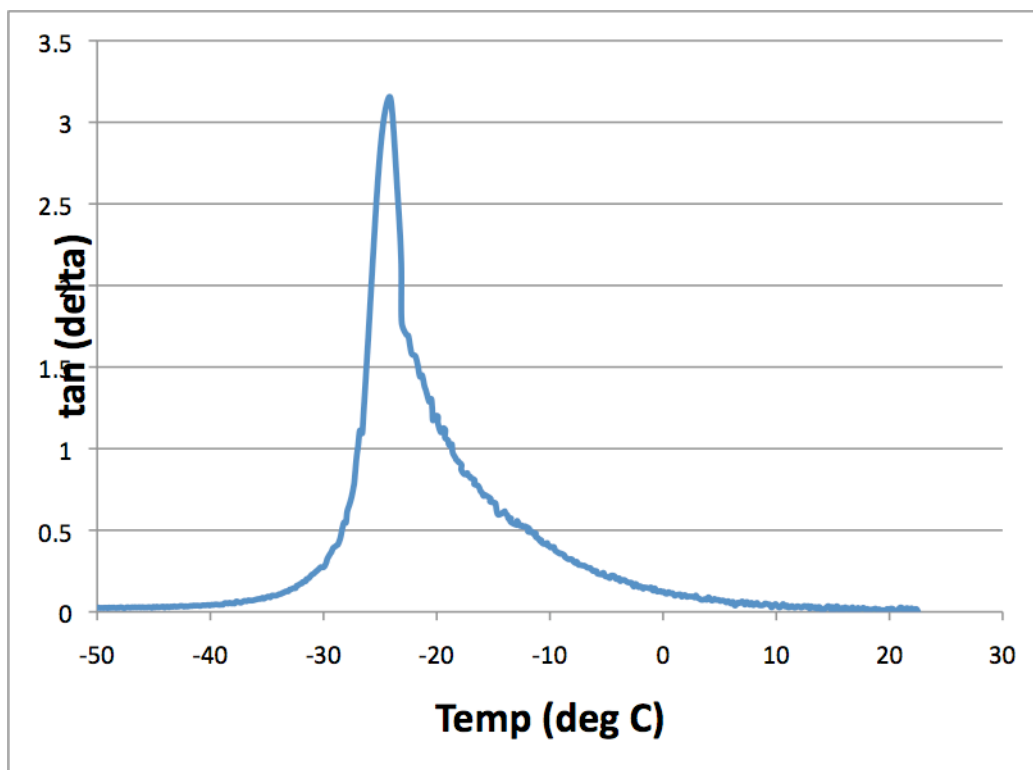

Figure 6: tan(delta) v. temperature data for a 1:2:4 molar ratio of PETMP:EGBMP:MBTA

Trithiocarbonate

The formation of the CAN polymer network is achieved by a Thiol-Michael Conjugate Addition using PETMP, TEGDMA or TEGDA, the respective trithiocarbonate, DMSO, and a phosphine catalyst. The functional group ratio for the thiol:acrylate is 1:1 to form ideal networks. The thin films exhibit a low Young's modulus and are very elastic and rubbery. The films are yellow in color and exhibit low T_g's due to the reduced crosslink density. Reaction profiles of the Michael addition were monitored by FTIR. The thiol conversion was monitored via the SH stretch at ~2600 cm^{-1}, and the acrylate conversion was monitored via the CH stretch at ~1600 cm^{-1}.
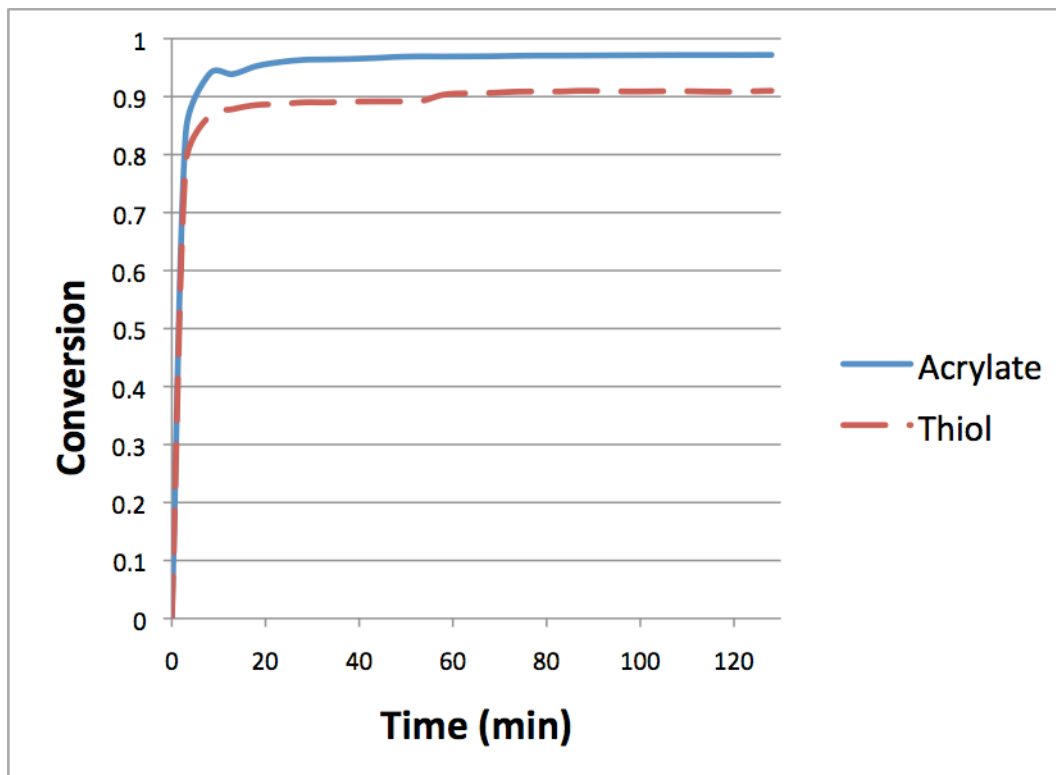
Figure 7: Kinetic Profile of Michael addition reaction between PETMP and TTCDMA

The reaction of PETMP with trithiocarbonate proceeds via the thiol-Michael addition reaction. This conclusion results from the observed equal consumption of the thiol functional groups in the PETMP and the acrylate functional groups from the TTC. Both components are consumed quantitatively.

The mechanical properties of these materials are being characterized as well. Dynamic Mechanical Analysis (DMA) is done to measure the T_g of the material. The T_g is taken to be the maximum of the tan(delta) versus temperature curve, which occurs at about -10°C for a 1:1:1 molar ratio of PETMP:TTCDMA:TEGDMA (Figure 8) and varies depending on the composition, crosslink density and stiffness of the monomer systems.
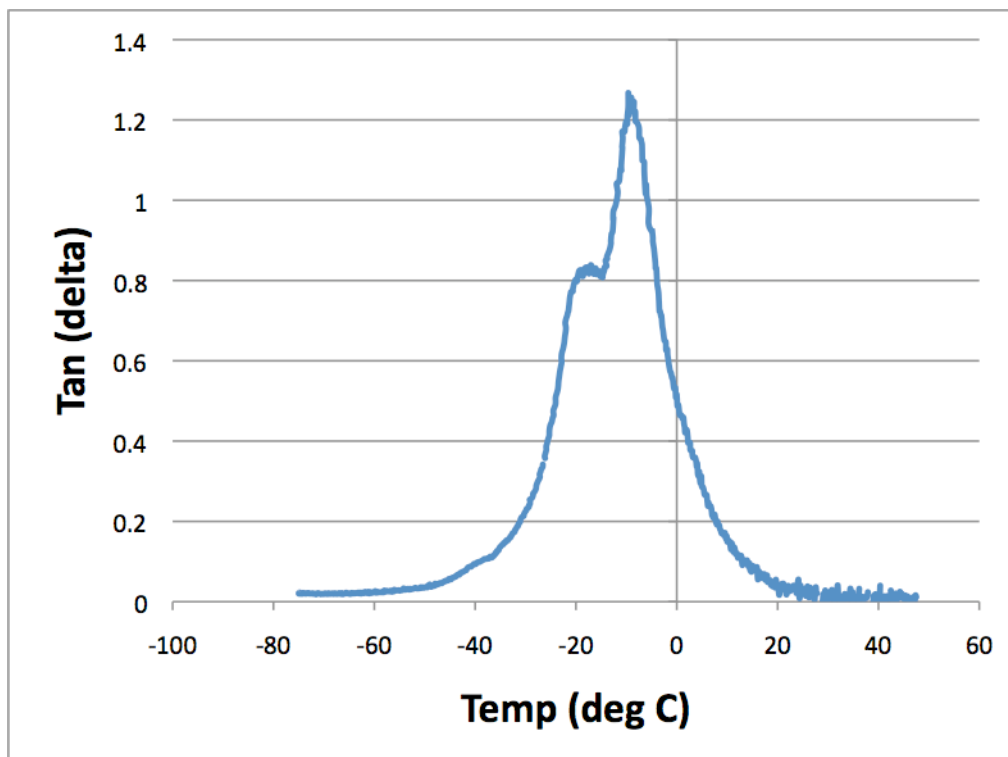
Figure 8: tan(delta) v. temperature data for a 1:1:1 molar ratio of PETMP:TTCDMA:TEGDMA

Ultimately, these CAN materials with AFCT-capable moieties can be synthesized readily as described herein and implemented in a wide range of materials' applications including adhesion, coatings, self-healing materials and others.

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