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Stress Reduction and T_g Enhancement in Ternary Thiol-Yne-Methacrylate Systems via Addition-fragmentation Chain Transfer

Hee Young Park¹, Christopher J. Kloxin², Mark F. Fordney¹, and Christopher N. Bowman^{1,3,4,*}

¹Department of Chemical and Biological Engineering, Jennie Smolly Caruthers Biotechnology Building, University of Colorado, Boulder, CO 80309-0596, USA

²Department of Materials Science and Engineering and Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

³Department of Restorative Dentistry, School of Dentistry, University of Colorado at Denver, Aurora, CO 80045, USA

⁴BioFrontiers Institute, University of Colorado at Boulder, Boulder, CO 80309-0596

Abstract

Since polymerization-induced shrinkage stress is detrimental in many applications, additionfragmentation chain transfer (AFCT) was employed to induce network relaxation and adaptation that mitigate the shrinkage stress. Here, to form high glass transition temperature, high modulus polymers while still minimizing stress, multifunctional methacrylate monomers were incorporated into allyl sulfide-containing thiol-yne resins to provide simultaneously high glass transition temperatures and a facile mechanism for AFCT throughout the network. As a negative control, in an attempt to isolate just the effects of AFCT in the polymerization, a propyl sulfide-based divne, which has a nearly identical chemical structure though absent any AFCT-capable functional group, was synthesized and implemented in place of the allyl sulfide-based diyne. The glass transition temperature of the ternary systems increased from 39°C to 79°C as the methacrylate content increased while the shrinkage stress of the optimal ternary resin was lower than either the binary thiol-yne resin or the pure methacrylate resin. The stress relaxation benefit associated with AFCT increased with increasing allyl sulfide concentration as shown by a decrease in the relative stress from 0.98 to 0.53. The allyl sulfide-based thiol-yne-methacrylate system exhibits stress relaxation up to 55% and increased T_g up to 40°C compared with the control, AFCT-incapable thiol-yne. This ternary system has less than 1/3 of the stress of conventional dimethacrylate monomer resins while possessing similarly outstanding mechanical behavior.

INTRODUCTION

Shrinkage stress represents one of the most detrimental characteristics of photopolymerizations and other thermosetting polymerization reactions where it ultimately leads to device failure by initiating microcracks, causing shape distortion, and leading to various mechanisms of delamination. As a methodology for reducing polymerization-induced volume shrinkage and the corresponding shrinkage stress, many approaches have been proposed such as the implementation of thiol-ene polymerization reactions with delayed gelation as the implementation of thiol-ene polymerization reactions with delayed gelation polymerization-induced phase separation. Recently, we have explored inclusion of reversible covalent bond structures into monomers and the resulting crosslinked

^{*}Corresponding author, christopher.bowman@colorado.edu.

polymer networks. These structures incorporate moieties that undergo addition-fragmentation chain transfer (AFCT) in the presence of radicals. Thus, this AFCT reaction occurs simultaneously with polymerization (or in the already formed polymer networks), promoting molecular rearrangement throughout the polymer network. Hence, AFCT relaxes the shrinkage stress while preserving the crosslink density, mechanical properties and molecular structure of otherwise identical networks that do not contain the AFCT-capable moiety (Scheme 1(A)) Ultimately, in this approach the network architecture remains unchanged while promoting stress relaxation. The allyl sulfide functional group has been shown to enhance the stress reduction in both thiol-ene 10 and thiol-yne 11 binary polymerizations. The allyl sulfide group was ideally suited for these polymerizations because it undergoes reversible AFCT in the presence of the thiyl radical, enabling each allyl sulfide to react repeatedly to promote network rearrangement and relaxation throughout, and even after, the polymerization reaction.

Thiol-ene¹ and thiol-yne reactions^{12,13,14} have a number of advantages over conventional radically polymerized monomers undergoing chain-growth polymerization including delayed gelation, low stress evolution, and oxygen inhibition as well as their overall click reaction nature.¹⁴ However, the crosslink density and resulting mechanical properties of the polymer networks are insufficient for many applications since they have relatively low elastic moduli and sub-ambient or limited super-ambient glass transition temperatures.^{1,10,11,13}

Incorporation of methacrylate monomers into the allyl sulfide-containing thiol-ene polymerization improved the glass transition temperature as well as the stress relaxation effect. However, since the T_g of the thiol-ene binary system was relatively low (\sim –20°C), a large amount of methacrylate was required to form a polymer with a super-ambient T_g . In contrast, here, an allyl sulfide-containing diyne is synthesized and utilized to promote stress relaxation in ternary thiol-yne-methacrylate formulations. We hypothesized that this thiol-yne-methacrylate combination, which undergoes AFCT, will exhibit the desired high glass transition temperature and modulus while simultaneously being able to undergo AFCT. The material properties, shrinkage stress, and functional group conversion are all investigated while increasing the methacrylate content in these ternary resins.

EXPERIMENTAL

Materials

Materials used in this study are shown in Figure 1. Pentaerythritol tetrakis(3-mercaptopropionate (PETMP, Evans Chemetics), ethoxylated bisphenol A dimethacrylate (EBPADMA, Esstech), and 1-hydroxycyclohexylphenylketone (HCPK, BASF, formerly Ciba Specialty Chemicals) were used as received without further purification.

Synthesis of 2-methylene-propane-1,3-di(thiobut-1-yne) (DYAS, diyne allyl sulfide)

The desired molecular precursor, 3-mercapto-2-(mercaptomethyl)-1-propene, was synthesized according to a previously reported method. \$11,16,17\$ Briefly, a 50% v/v solution of 8 g (66.7 mmol) of 3-mercapto-2-(mercaptomethyl)-1-propene and 20 g (150.4 mmol) of 4-bromo-1-butyne (Sigma Aldrich) in methanol was prepared and added to a refluxing solution of sodium (4g, Sigma Aldrich) in methanol under argon protection. The reaction was allowed to react for 3 h, and then a mixture of methanol (240 ml) and hydrochloric acid (40 ml) was added to quench the reaction. The solution was then purified using a liquid-liquid water-ether solution and dried over calcium chloride. The ether was evaporated, and the product was vacuum distilled (140°C, 0.7 mmHg) to give 10.5 g (70%) of a slightly yellow, clear oil. To remove residual disulfides, which may reduce the polymerization rate,

the monomers were further purified by being treated with a strong reducing agent. The distilled DYAS was dissolved in a mixture of methanol, water, and tetrahydrofuran (1 to 1 to 1.3 in volumetric ratio, respectively). 1.5 grams of sodium borohydride were added to the solution and stirred for 2 hours at ambient temperature. The solvents were evaporated, residual dissolved in ethyl ether, and the ether phase was washed with strong aqueous sodium hydroxide. The ether extracts were dried with calcium chloride, evaporated, and redistilled to yield a clear, colorless liquid. The structure was confirmed by 1H NMR spectroscopy (Varian INOVA 500) (see Supporting Information).

Synthesis of 2-methyl-propane-1,3-di(thiobut-1-yne) (DYPS, diyne propyl sulfide)

2-methyl-propane-1,3-di(thiobut-1-yne) (DYPS, diyne propyl sulfide) was synthesized from 1,3-dimercapto-2-methylpropane (synthesized^{11,16,17}) in the same manner as with the synthesis of DYAS. After purification procedures were performed, 12 g (80 %) of a clear, colorless liquid was given. The structure was confirmed by 1H NMR spectroscopy (Varian INOVA 500) (see Supporting Information).

Preparation of the resin mixture

Unless otherwise noted, resins were comprised of a stoichiometric mixture of DYAS (313.6 mg, allyl sulfide-based diethynyl monomer) and PETMP (684.1 mg, tetrathiol) at a 1:2 ethynyl/thiol ratio since each ethynyl group is capable of reacting with two thiol groups, and this mixture was then formulated with EBPADMA in various relative amounts. All components were added in a vial then mixed using a Vortex mixer. As a negative control, DYPS, was used in place of DYAS. Additionally, an off-stoichiometric mixture of DYAS (132.2 mg) and PETMP (432.5 mg) at a 1:3 ethynyl/thiol ratio was formulated with various amounts of EBPADMA to enhance the AFCT mechanism by increasing the relative thiol mole fraction. Similar to the stoichiometric thiol-yne mixture, AFCT-incapable DYPS was used in place of DYAS to isolate the stress relaxation effect associated with the allyl sulfide functionality. Detailed formulations of each resin such as the ratio of functional groups and weight percent of EBPADMA are presented in Table 1. For all resins, HCPK was utilized at 3 wt% as a UV-activated photoinitiator.

Methods and Equipment

Shrinkage stress and functional group conversion were monitored simultaneously using tensometry (Paffenbarger Research Center, American Dental Association Health Foundation) coupled with Fourier transform infrared (FTIR) spectroscopy (Nicolet 670) during the photopolymerization of each resin (see Supporting Information for detailed spectra and conversion measurement examples). For the yne functional group, only its initial disappearance is measured. This initial disappearance corresponds to the addition of the first thiol to the yne which results in the formation of a vinyl sulfide that eventually reacts with a second thiol to form the disubstituted product. No evidence of any significant build-up of vinyl sulfide was found in these polymerizations, and it is known that the vinyl sulfide in these ynes is more reactive than the initial yne functional group 13. Thus, we have assumed as an approximation that the measurement of the yne disappearance correlates with the total amount of disubstituted yne that has been formed.

The tensometer utilizes the cantilever beam deflection approach and theory to evaluate the stress level based on beam deflection. Since the compliance and length of the cantilever beam affect the obtained stress value, it is optimal if the same experimental settings are used to compare the stress of each sample. Here, all resin formulations were evaluated with a single set of compliance conditions (stainless steel beam) except the DYPS-PETMP resin for which the polymerization-induced stress is higher than ultimate strength of the material. In this case, the stress of the thiol-yne resins (DYPS-PETMP and DYAS-PETMP) was

measured under more compliant conditions (aluminum beam). Here, all resin formulations were evaluated with a single set of compliance conditions (stainless steel beam) except the DYPS-PETMP resin for which the stress level is higher than can be accurately measured at this compliance. Ultimately, the stress of the thiol-yne resins (DYPS-PETMP and DYAS-PETMP) was measured under different compliance conditions (aluminum beam). The relative stress (see the notation in Figure 5) under these conditions was utilized to estimate what the stress level of the DYPS-PETMP resin would have been if it could accurately be measured at the initial compliance conditions. This approach provides a basis for comparing the stress levels of all samples on a relative basis.

The tensometer experiment was performed by loading resins (sample size: 6 mm in diameter and 1 mm thick) between two glass rods and irradiating for 10 minutes at 10 mW/cm² intensity with a UV lamp (Acticure, EXFO) equipped with a 365 nm bandpass filter. The evolution of the yne, methacrylate, and allyl sulfide double bond conversions was determined by monitoring the infrared absorption peaks centered at 6483 cm⁻¹ (C≡C-H stretching, overtone), 6166 cm⁻¹ (C=C-H stretching, overtone), and 6121 cm⁻¹ (C=C-H stretching, overtone), respectively (see Supporting Information for more detail and examples). Gaussian fitting was used to deconvolute the peak areas as the methacrylate peak is overlapped with the allyl sulfide peak. ^{10,11}

To measure the mechanical properties of the materials, the elastic moduli (E') and glass transition temperatures of polymerized samples were determined by dynamic mechanical analysis (DMA) (TA Instruments Q800). Samples were prepared by sandwiching the material between two glass slides with a 1 mm thickness spacer such that the final sample size was 8mm*5mm*1mm (length*width*thickness, sample size was varied slightly for each experiment) with DMA samples irradiated under the same conditions as those used in the tensometer experiments. DMA experiments were performed at a strain and frequency of 0.1% and 1 Hz, respectively, scanning the temperature twice at 1 °C/minute with one cooling cycle in between the two heating cycles. To eliminate any residual cure issues associated with the first heating cycle, the T_g was assigned as the temperature of the tan delta maximum^{19,20} in the second heating cycle. For rubbery modulus measurements used in determining the relative stress values reported in Table 1, moduli at identical temperatures were used with the moduli determined at the higher T_g (of the allyl and propyl comparisons) plus $40^{\circ}C$.

RESULTS AND DISCUSSIONS

The overall focus of this work is on implementing AFCT-capable monomers and resins in a manner that simultaneously improves both the ultimate mechanical performance of the final polymer network and the shrinkage stress that results from the polymerization reaction. Here, that outcome is achieved by incorporating stiff dimethacrylate monomers into an allyl sulfide containing thiol-yne system that itself is known to lead to increased mechanical performance and lower stress.

The elastic moduli of the thiol-yne and thiol-yne-methacrylate ternary resins as a function of temperature are shown in Figure 2, and characteristic values are summarized in Table 1. As the methacrylate content increases from 0 wt% to 78 wt%, the behavior qualitatively remains similar yet becomes shifted to higher temperatures with increasing methacrylate content. Overall, the primary effect of adding the dimethacrylate to this resin is that the polymer networks become more glassy due to the presence of the stiff bisphenol A structure present within EBPADMA.

The rubbery elastic modulus, which is proportional to the network's crosslink density²¹, increases slightly with increasing EBPADMA content; however, the binary thiol-yne networks are found to have the highest elastic modulus. Generally, in mixed-mode polymerizations replacing functional groups that primarily undergo step growth, such as the thiol and ene, with those that proceed through a chain growth mechanism, such as methacrylates and acrylates, will lead to an increase in the crosslink density. Here, however, by using a tetrathiol, a diyne (where each yne may react with two thiols) and a dimethacrylate, all of the monomers that were selected are capable of forming up to four bonds to other monomers (i.e., they have a functionality of four). Thus, as the thiol-yne portion of the resin is replaced with the dimethacrylate, the average functionality of the network, and to a first approximation the crosslinking potential at full conversion, does not change. The higher rubbery elastic modulus in the thiol-yne polymer results from the higher functional group conversion that is achieved in that polymerization reaction. There are limited effects of vitrification on the relatively low T_g thiol-yne system, and the reaction proceeds to near completion (see Table 1 for the conversion values). The yne conversion drops as more methacrylate is added due to the formation of a more glassy network that limits the extent of reaction due to vitrification. The crosslink density increases as the methacrylate content increases since more of the methacrylates participate in chain growth homopolymerization reactions, which forms two bonds per methacrylate, rather than undergoing chain transfer reactions, which leads to formation of only a single network connecting bond per methacrylate. While significant, these effects are relatively minimal in this overall comparison and lead to no more than a factor of two difference in the crosslink density in any of the networks formed here.

To determine whether DYPS-PETMP-EBPADMA is an appropriate control system which isolates the effect of AFCT, the elastic modulus of DYPS-PETMP-EBPADMA formulations is also presented in Figure 2 and Table 1. Since the stress evolution is a function of the modulus evolution at the curing temperature and the final network crosslinking density, an appropriate control system should have a similar modulus when compared with the AFCT-capable allyl sulfide-containing ternary system. The allyl and propyl sulfide resins have almost identical elastic moduli throughout the entire temperature range which implies that the allyl sulfide moiety and the AFCT reaction do not alter the polymer network significantly. Thus, the propyl sulfide resins do serve as appropriate controls, isolating the impact of AFCT on the stress relaxation.

The shrinkage stress that arises in the DYPS-PETMP-EBPADMA (AFCT-incapable) polymerizations is presented in Figure 3. By incorporating methacrylate into a stoichiometrically balanced thiol-yne resin (thiol to yne = 2 to 1), the stress of the resins is reduced compared with the binary thiol-yne resin (Figure 3(A)) whether AFCT occurs or not. The reduced stress is caused by the decreased crosslink density due to the lower yne and methacrylate conversions (Table 1) as well as the potential increase in the gel point conversion that arises with the addition of a small initial amount of methacrylate. As the methacrylate content increases from 58 wt% to 78 wt%, the stress increases since the polymerization-induced stress mainly develops in the post-gelation region especially after vitrification. Here, the increasing amount of chain-growth polymerization of the methacrylate results in early gelation as compared with the step-growth polymerization of the thiol-yne. Excitingly, the shrinkage stress of the ternary resin was even lower than the binary thiol-yne resin though the ternary resins all form polymers that have higher glass transition temperatures.

In addition to the lower stress that occurs in ternary systems relative to binary thiol-yne reactions, stress relaxation was also found to depend strongly on the presence of AFCT-capable allyl sulfides in the yne monomer structure. In Figure 2, it was demonstrated that the

allyl sulfide-containing DYAS-PETMP-EBPADMA has a nearly identical polymer network as compared with the AFCT-incapable control DYPS-PETMP-EBPADMA. In Figure 4, the shrinkage stress of the allyl sulfide containing resins is compared with the stress of the propyl sulfide resins. As the allyl sulfide concentration is increased, the stress of the thiolyne-methacrylate decreased (Figure 4(A)). Note that propyl sulfide-based resin (DYPS-PETMP-EBPADMA) does not include an allyl sulfide functionality but comparative formulations which have the same amount of the thiolyne/methacrylate are plotted using the corresponding allyl sulfide concentration. While the stress level for both the propyl and allyl sulfide-containing resins decreases as the propyl or the allyl sulfide content increases, owing to the decreasing methacrylate content, the difference between the stress of DYAS-PETMP-EBPADMA and DYPS-PETMP-EBPADMA becomes larger. Here, the stress differences between these systems arise almost exclusively because of the AFCT mechanism.

To quantify the stress relaxation associated with AFCT and eliminate the effect of slightly different crosslinking densities between the model and control resin, the final stresses for the allyl and propyl sulfide-containing resins were divided by the rubbery elastic modulus, which is directly related to the crosslink density through rubbery elasticity theory. The ratio of dimensionless stresses in allyl to propyl sulfide-containing resins is denoted as the relative shrinkage stress (Figure 5). The relative stress decreases with increasing allyl sulfide concentration (Figure 5(A)) and decreasing T_g of the material (Figure 5(B)). This result indicates that AFCT reduced the stress effectively even in the glassy ternary system through the mechanism shown in Scheme 1. Also, the glass transition temperature was improved compared with the binary system while preserving the stress relaxation behavior. A ternary resin consisting of an off-stoichiometric thiol-yne mixture with an excess of thiol functional groups relative to the yne (3 to 1 thiol to yne) exhibited slightly lower (i.e., better) relative stress when compared with those of the stoichiometric thiol-yne-methacrylate mixture since the increased thiol content promoted the AFCT reaction and the resulting stress relaxation (Figure 5).

CONCLUSIONS

Methacrylate monomer was incorporated into propyl and allyl sulfide-based thiol-yne resins to increase the polymer glass transition temperature and reduce the stress in addition to investigating stress relaxation associated with AFCT of the allyl sulfide functional group. The glass transition temperature of the ternary systems increased as the methacrylate content increased. One unique outcome was that the shrinkage stress of the ternary resin was even lower than the binary thiol-yne resin until the methacrylate content was 68 wt.% because of the reduced crosslinking density. The stress relaxation effect associated with AFCT, which is interpreted as the non-dimensionalized relative stress, was improved with increasing allyl sulfide concentration in the ternary resin. In this study, the allyl sulfide-based thiol-ynemethacrylate system demonstrates stress relaxation up to 55% and a T_g increase of up to 40°C compared with the control AFCT-incapable thiol-yne. This ternary system exhibits a polymerization induced shrinkage stress level that is less than 1/3 the stress level of conventional dimethacrylate monomers (2.9MPa)\(^1\) while possessing excellent mechanical properties that make it appropriate for use in a variety of applications where it would replace the conventional di(meth)acrylate monomers.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Monomers and photoinitiator used: (1) DYAS, (2) DYPS, (3) PETMP, (4) EBPADMA, and (5) HCPK.

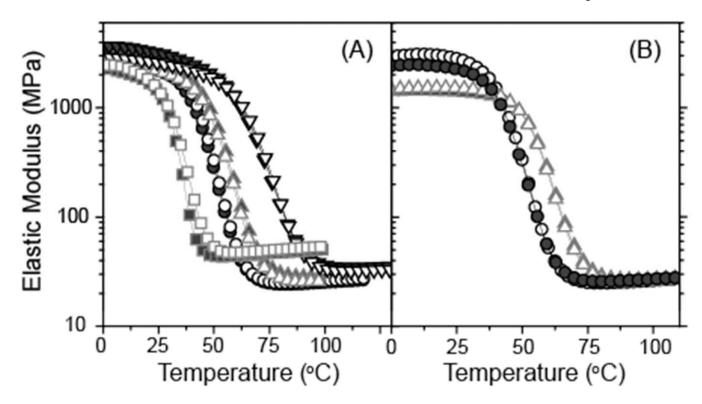


Figure 2. (A) Elastic moduli of the thiol-yne-methacrylate ternary resins. Stoichiometrically balanced thiol-yne (functional group ratio thiol: yne = 2:1) mixtures were used for the ternary resins. Allyl sulfide-containing resins are represented by an open symbol and propyl sulfide-based resins by a closed symbol. The thiol:yne:methacrylate ratios are 2:1:0 (\blacksquare , 0 wt% methacrylate), 2:1:2 (\blacksquare , 58 wt% methacrylate), 2:1:3 (\triangle , 68 wt% methacrylate), and 2:1:5 (\blacktriangledown , 78 wt% methacrylate). (B) Elastic modulus of the off-stoichiometric thiol-yne-methacrylate ternary resins. An off-stoichiometric thiol-yne ratio (functional group ratio thiol: yne = 3:1) was used for these ternary resins. Allyl sulfide-based resins are represented by an open symbol and propyl sulfide-based resins by a closed symbol. The thiol:yne:methacrylate ratios are 3:1:2.7 (\blacksquare , 58 wt% methacrylate) and 3:1:4 (\triangle , 68 wt% methacrylate).

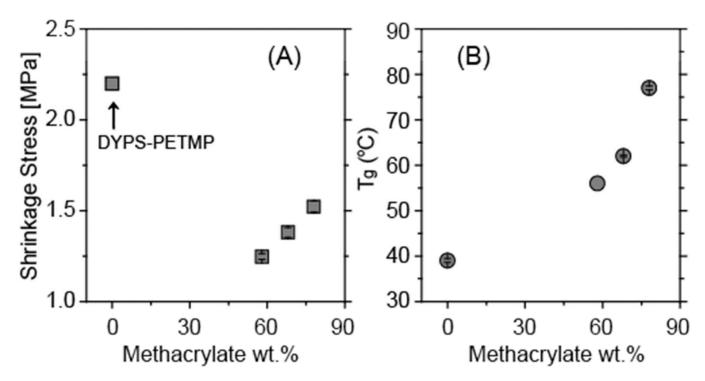


Figure 3.(A) Polymerization shrinkage stress and (B) glass transition temperature versus EBPADMA (methacrylate) weight fraction in DYPS-PETMP-EBPADMA ternary resins. The thiol:yne:methacrylate ratio varies from 2:1:0 (0 wt% methacrylate) to 2:1:5 (78 wt% methacrylate). The thiol:yne ratio was stoichiometrically balanced for all formulations (thiol:yne = 2:1). Samples contain 3 wt% HCPK and are irradiated at 10 mW/cm² using 365 nm light. The stress of DYPS-PETMP was estimated according to the relative stress (see the methods and equipment section and Table 1).

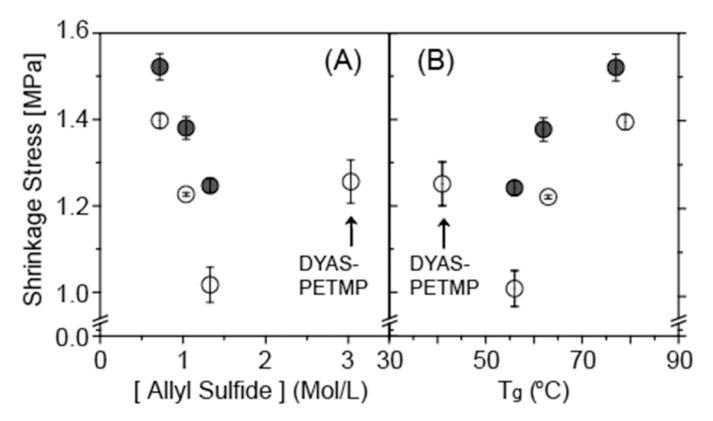


Figure 4.

(A) Polymerization shrinkage stress versus allyl sulfide concentration and (B) versus glass transition temperature for DYAS-PETMP-EBPADMA (○) and DYPS-PETMP-EBPADMA (●) resins. The ratio of the thiol:yne:methacrylate resin varies from 2:1:0 to 2:1:5. The thiolyne mixture was stoichiometrically balanced at all conditions (thiol:yne = 2:1). Samples contain 3 wt% HCPK and are irradiated at 10 mW/cm² using 365 nm light.

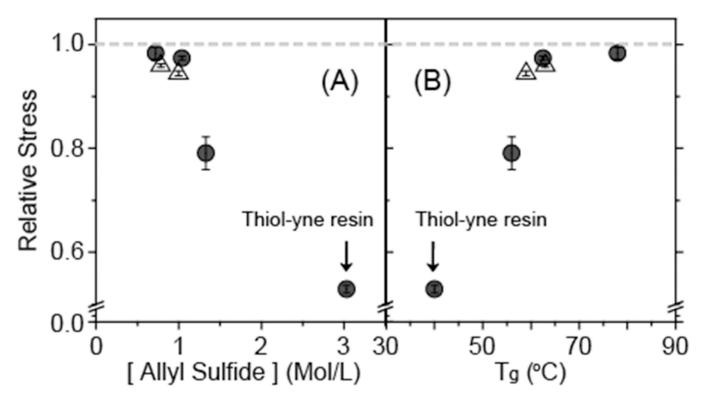


Figure 5.

(A) Relative polymerization shrinkage stress versus allyl sulfide concentration and (B) versus glass transition temperature for stoichiometric thiol-yne-methacrylate (♠, thiol to yne ratio was maintained as 2:1 and methacrylate ratio varies from 0 to 5, thiol:yne:methacrylate = 2:1:0 ~ 2:1:5) and off-stoichiometric thiol-yne-methacrylate (△, thiol to yne ratio was maintained as 3:1 and methacrylate ratio varies from 2.7 to 4, thiol:yne:methacrylate = 3:1:2.7 ~ 3:1:4). Relative stress = (The stress of the allyl sulfide-based resin/the rubbery elastic modulus)/ (The stress of the propyl sulfide-based resin/the rubbery elastic modulus). The rubbery elastic moduli were taken at the same temperature for the allyl and propyl sulfide-based resins. Samples contain 3 wt% HCPK and are irradiated at 10 mW/cm² using 365 nm light.

$$(A) \quad R_1 \stackrel{S_*}{\longrightarrow} \\ R_1 \stackrel{$$

$$(B) \longrightarrow R_1 \xrightarrow{R_1 \xrightarrow{C}} R_1 \xrightarrow{C} R_1 \xrightarrow{C} R_1 \xrightarrow{C} R_1 \xrightarrow{C}} R_1 \xrightarrow{C} R_1 \xrightarrow{C} R_1 \xrightarrow{C} R_1 \xrightarrow{C} R_1 \xrightarrow{C} R_1$$

Scheme 1.

(A) Reversible AFCT mediated by reactions with the thiyl radical, (B) irreversible allyl sulfide AFCT mediated by reactions with a carbon-centered radical, and (C) consumption of the allyl sulfide moiety by abstraction of a hydrogen from a thiol.

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Table 1

Summary of the final conversion, Tg, elastic moduli, and shrinkage stress for various resin formulations. Rubbery moduli are measured at the same temperature for both the allyl sulfide-based resin and its analogous non-allyl sulfide containing resin.

Yne monomer used in the ternary system			Final fur conve	Final functional group conversion [%]	đn			
(thiol:yne: methacrylate ratio)	Methacrylate content (wt %)	Allyl sulfide concentration (mol/L)	Methacrylate	Yne	Allyl sulfide	$T_{\rm g}(^{\circ}{ m C})$	Rubbery E' at $T = T_g + 40^{\circ}C$ (MPa)	Shrinkage stress (MPa)
DYAS (2:1:0)	0	3.03	1	97 ± 0.5	42 ± 2	41 ± 0.4	50.3 ± 0.1	$1.25 \pm 0.05 (0.4 \pm 0.005)^*$
DYPS (2:1:0)	0		1	99 ± 0.2		39 ± 0.2	47.5 ± 0.1	$2.2^{\dagger} (0.7 \pm 0.006)^*$
DYAS (2:1:2)	58	1.33	100 ± 0.4	85 ± 4	67 ± 5	56 ± 0.1	25.8 ± 0.1	1.02 ± 0.04
DYPS (2:1:2)	58		98 ± 0.2	89 ± 1		56 ± 0.1	25 ± 0.1	1.25 ± 0.02
DYAS (2:1:3)	89	1.04	98 ± 0.2	76 ± 3	66 ± 4	63 ± 0.2	26.1 ± 0.1	1.23 ± 0.01
DYPS (2:1:3)	89		97 ± 0.4	81 ± 2		62 ± 0.3	28.6 ± 0.6	1.38 ± 0.03
DYAS (2:1:5)	78	0.72	95 ± 0.3	68 ± 3	74 ± 0.2	79 ± 0.4	32.5 ± 0.1	1.40 ± 0.02
DYPS (2:1:5)	78		94 ± 0.3	73 ± 1	-	77 ± 1	34.8 ± 0.1	1.52 ± 0.03
DYAS (3:1:2.7)	58	1.00	99 ± 0.2	90 ± 1	73 ± 4	54 ± 0.1	26.5 ± 0.2	1.15 ± 0.01
DYPS (3:1:2.7)	58		99 ± 0.4	94 ± 0.7		54 ± 0.5	27.1 ± 0.2	1.24 ± 0.03
DYAS (3:1:4)	<i>L</i> 9	0.78	98 ± 0.1	80 ± 0.2	76 ± 0.2	63 ± 2	26 ± 0.1	1.2 ± 0.01
DYPS (3:1:4)	29		98 ± 0.2	90 ± 2	1	63 ± 1	27.1 ± 0.2	1.31 ± 0.04

Shrinkage stress of the thiol-yne binary systems is measured at two different tensometer settings (see the experimental method section). The stress in parenthesis represents the stress value at a different