

THIOL-ENE/YNE PHOTOPOLYMERIZATIONS

A Thesis Submitted to the Faculty of the Graduate School of
the University of Colorado at Boulder

by

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B.S., Tongji University, 2003

M.S., Tongji University, 2006

In partial fulfillment of the requirement for

the degree of Doctor of Philosophy

Department of Chemical and Biological Engineering

2011

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Thiol-Ene/Yne Photopolymerization
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THIOL-ENE/YNE PHOTOPOLYMERIZATIONS

Thesis directed by Professor Christopher Bowman

To address challenges related to developing photocurable resin and composite systems combining high modulus and low shrinkage stress, this thesis was focused on understanding and investigating the interrelationships between monomer formulations, curing conditions, and material properties in photopolymerizable thiol-ene/yne formulations.

By evaluating various radical photocuring systems including chain-growth, step-growth and mixed chain-step-growth systems, a relationship between glass transition temperature (T_g) and curing conditions was developed. T_g was quantified as a function of the network mobility which is related to the cure temperature (T_{cure}), the maximum achievable glass transition temperature ($T_{g\text{max}}$), and the network heterogeneity ($T_{g1/2\text{width}}$). Deviations between the theory and experiments were found to be approximately 10%.

The ternary thiol-yne-(meth)acrylate systems were evaluated for their potential to achieve simultaneously outstanding T_g and modulus and low shrinkage stress. The crosslinking density and the amount of volumetric shrinkage that occurs prior to gelation relative to the total shrinkage were determined as the two dominant factors that control the final shrinkage stress of the ternary systems which was reduced by more than 40% in the ternary system as compared to either pure monomer formulation. To increase the modulus further, silica nanoparticles functionalized by a 16-functional hyperbranched alkene were incorporated into this ternary resin, which demonstrated 30% reduced shrinkage stress without sacrificing the modulus (3200 ± 200 MPa) or T_g (62 ± 3 °C). Moreover, it was observed that the shrinkage stress of the composite builds up at much later stages of the polymerization.

Finally, an induction polymerization method was developed as an alternative to UV curing to address challenges associated with the restriction of light accessibility in highly filled composite

systems. This method was able to cure completely samples up to 1 cm thick in as little as 2 minutes. The reaction kinetics of thiol-ene and thiol-acrylate systems were studied and a model of heat transfer profiles combined with reaction kinetics was developed and utilized to predict reaction temperatures and kinetics for systems with varying thermal initiator concentration, initiator half-life, monomer molecular weight and temperature gradients in samples with varying thickness; thereby demonstrating that induction curing represents a designable and tunable polymerization method.

This thesis is dedicated to my family and especially my parents, Yanjie Ye and Yuanmin Dan, who supported me immensely throughout this work.

Acknowledgements

I would like to thank all the organizations and people in this research and this thesis. First, I would like to acknowledge the National Science Foundation and the National Institutes of Health for their funding this project. Next, I would like to thank my advisor Chris Bowman for his great advice, encouragement and patience during my graduate study and research; and my committee members Kristi Anseth, Robert Sani, Jeffrey Stansbury and John Woods for the suggestions and help on my project, reviewing my thesis and attending my defense. Next, I would like to thank Bowman research group and Stansbury research group for the support and contribution to my work. Finally, I would like to thank Blake Stevens, Ian Smith, Katerina Voigt and Setareh Azarnoush for experimental work in this thesis.

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Chapter 1

Introduction and Background

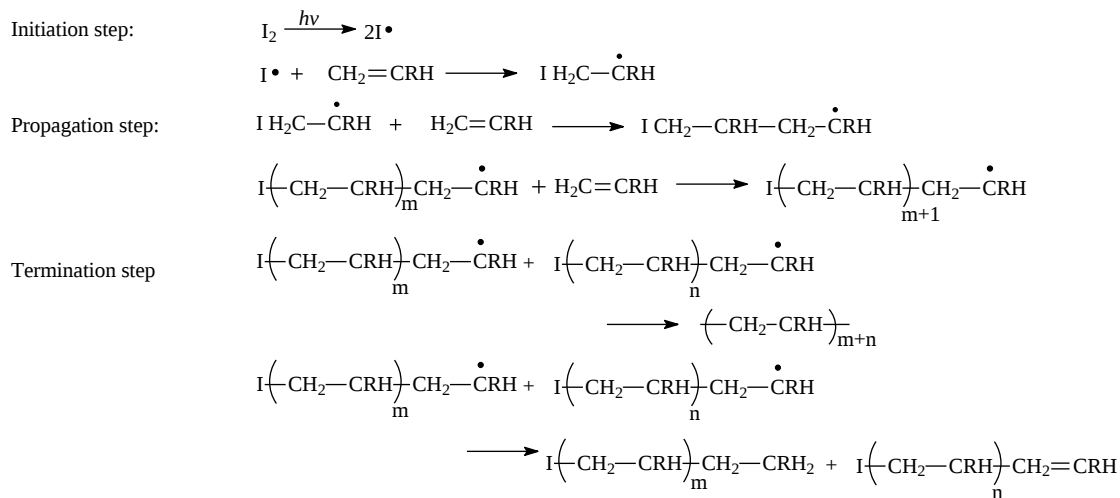
Photopolymerization is often a desirable way to produce polymers due to the advantages of ambient cure, cure on command, high energy efficiency, no solvent usage, and spatial and temporal control of the polymerization. Both large scale applications such as automobile and floor coatings and small scale applications such as adhesives for attachment of microchips are widely used in industry.¹ Photopolymerizations are also used in human health for numerous applications such as dental materials and contact lenses.² The most common photocuring systems are radical mediated polymerizations of acrylates and methacrylates. (Meth)acrylates are able to achieve high glass transition temperature and modulus, which is desirable for many applications, but attain these properties with the associated problem of high shrinkage stress which limits the types of applications and their geometry.¹ (Meth)acrylate systems are also strongly inhibited by oxygen, often requiring the use of high initiator concentrations and irradiation intensities and/or nitrogen to promote curing at surfaces exposed to ambient oxygen.³

Although the technology is well developed, photocuring still has many challenges to overcome to expand the range of applications in which it is used. From the methodology perspective, photocuring is limited by the restriction of light accessibility in highly filled systems that are needed for high strength composites or pigmented systems. In the material area, there is a large focus to design resin systems with high mechanical properties and low shrinkage stress. In recent years, thiol-ene and thiol-yne systems have attracted more attention because of their low shrinkage stress and insensitivity to oxygen inhibition.^{4,5} The overarching goal of this research is to investigate and understand the complex interrelationships between monomer formulations, curing conditions, and material properties of thiol-ene and thiol-yne photopolymerizations and to develop systems that eliminate the restriction of light accessibility in highly filled systems.

1.1 Reaction mechanisms and properties of radical photocuring polymers

1.1.1 Chain-growth mechanism: Acrylate and methacrylate networks

Acrylate or methacrylate systems polymerize via a chain-growth reaction mechanism. The reactions are initiated by photoinitiator systems, which generate radicals by one of a variety of methods when irradiated with UV or visible light. The radicals rapidly react with the (meth)acrylate carbon-carbon double bond to generate a primary radical that then starts the propagation. Radical termination occurs either via radical-radical combination or by disproportionation (Scheme 1.1).^{6,7} During the network formation process, the propagation reactions first primarily occurs near the initiation sites, forming microgel regions that have restricted mobility of all species; while the rest of the resin experiences less polymerization and contains far more mobile microenvironments. The microgels are subsequently aggregated by intermolecular crosslinking reactions to create macrogel structures and eventually form the final polymer networks (Scheme 1.2).^{8,9} Based on this chain growth reaction mechanism of multi(meth)acrylate monomers, heterogeneous networks are formed with a very broad distribution of relaxation times and chain mobilities.

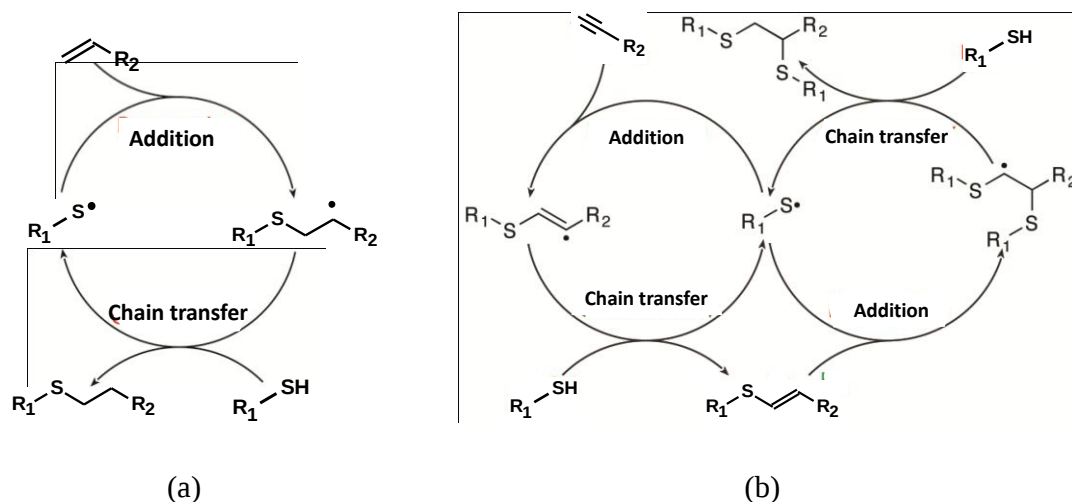


Scheme 1.1 Chain-growth radical polymerization mechanism⁶

1.1.2 Step-growth mechanism: Thiol-ene and thiol-yne networks

Thiol-ene reactions follow a step-growth radical polymerization mechanism with respect to their structural evolution. The primary initiator radical either abstracts a hydrogen from the thiol monomer to form a thiyl radical, which further reacts with an ene monomer to form a carbon-centered radical by an addition reaction, or the primary radical reacts directly with carbon-carbon double bond to form a carbon-centered radical. In either case, the thiyl radical is (re)generated by a subsequent chain transfer step (Scheme 1.2 (a)).¹⁰ The alternating addition and chain transfer reactions result in step growth network structure development that ultimately leads to the formation of a relatively homogeneous polymer network. This radical mediated step-growth thiol-ene mechanism, which is one type of click reaction mechanism,¹¹ exhibits several unique, and often advantageous, properties including high selectivity, high yield or conversion, delayed gelation, reduced oxygen inhibition, and low shrinkage stress as compared to chain growth methacrylate or acrylate polymerizations.⁵

Recently, thiol-yne reactions have also been demonstrated to follow a radical step growth polymerization mechanism.¹² The alkyne group first reacts with a thiyl radical to generate a carbon-centered radical, which abstracts a hydrogen from a thiol monomer to generate a reactive vinyl sulfide functional group. The double bond on the vinyl sulfide moiety is capable of subsequent reaction with a second thiyl radical to form another carbon-centered radical which abstracts a hydrogen from another thiol (Scheme 1.2 (b)).¹³ In this ideal reaction mechanism, each alkyne group reacts twice with thiyl radicals, thereby achieving a higher crosslink density and increased mechanical properties relative to other comparable thiol-ene systems.¹⁴



Scheme 1.2 Radical mediated step-growth polymerization mechanism for both the (a) thiol-ene and (b) thiol-yne reactions.¹⁴

1.1.3 The mixed-mode mechanism: Thiol-(meth)acrylate and thiol-ene-(meth)acrylate ternary networks

Thiol-(meth)acrylate systems follow a mixed-mode mechanism exhibiting characteristics of both radical step-growth polymerization between thiols and (meth)acrylates and homopolymerization of (meth)acrylates.¹⁵ As previously reported, acrylates exhibit higher rates of chain transfer to thiol compared to methacrylates.¹⁶ The mixed-mode mechanism largely maintains the advantages of the thiol-ene systems while providing the ability to achieve higher glass transition temperatures resultant from the homopolymerization portion of the (meth)acrylates.¹⁷

Thiol-ene-(meth)acrylate ternary systems are a type of mixed-mode radical polymerization mechanism. When a methacrylate or acrylate is added to thiol-ene systems, the methacrylate or acrylate homopolymerization is accompanied with chain transfer to thiol and thiol-ene step-growth polymerization.^{16, 18} Ternary polymerization systems enable tailoring of the polymerization and network properties because of the unique competitive reaction kinetics and network formation processes. The glass transition temperature (T_g),¹⁹ the heterogeneity of the ternary networks²⁰ and

the shrinkage stress²¹ were able to be controlled by varying the amount and nature of each of the monomers used in these ternary blends.

1.2 Polymerization induced shrinkage and shrinkage stress

1.2.1 Shrinkage and shrinkage stress in resin systems

Polymerization induced shrinkage and shrinkage stress results in a variety of limitations for photocuring systems that can in some cases result in the formation of cracks between the polymer and substrates of the coatings and poor adhesion, or micro-leakage in the case of dental restoratives.²¹ The shrinkage is caused by the reduction of free volume as covalent bonds bring monomer units more closely together in the crosslinked networks. The volumetric shrinkage of the resin systems is theoretically calculated based on the conversion of carbon-carbon double bond by equation (1.1)²².

$$VS = [C = C]_0 \cdot X \cdot SF \quad 1.1$$

in which, VS is the total volumetric shrinkage, $[C=C]_0$ is the initial concentration of double bonds, X is the double bond conversion, SF is the shrinkage factor. The SF of (meth)acrylate systems is 22.6 mL/mol and the SF of thiol-ene systems is around 12 – 14 mL/mol, depending on the particular ene functional group structure.²²

Once the resin is covalently connected to the substrate and gelled, it cannot shrink to the ideal volume during curing and shrinkage stress accumulates.²³ Shrinkage stress is primarily built up after gelation due to the restricted mobility of the gel. Subsequent vitrification raises the glass transition and modulus, also leading to higher stress levels. Prior to gelation and given sufficient time, the liquid resin is able to accommodate the equilibrium shrinkage via flow and therefore builds up minimal stress.²¹ For example, it has been demonstrated that thiol-ene systems following the step-growth mechanism delay the gelation and thus reduce shrinkage stress as compared to (meth)acrylate systems.²²

Various methods have been studied to reduce the shrinkage stress of the resin systems. Cationic ring opening polymerizations, such as oxiranes,²⁴ siloranes²⁵ or epoxides,²⁶ reduce shrinkage stress due to their low molar volume shrinkage values. Low shrinkage additives (pre-polymers)²⁷; reactive nanogels,²⁸ phase separating systems,²⁹ hyper-branched polymers³⁰ and dendrimers³¹ have also been added to resins to reduce both the shrinkage and shrinkage stress without compromising mechanical properties. Stress reductions have also been achieved by photo-induced addition-fragmentation-chain transfer reactions that conserve the network connectivity and properties while promoting stress relaxation.^{32,33} Ternary systems have been demonstrated as another method to reduce shrinkage stress.²¹ Due to the large amount of methacrylate homopolymerization, a pseudo two-stage hybrid polymerization was reported in thiol-ene-methacrylate systems that also resulted in the reduction of shrinkage stress.^{34,35}

1.2.2 Shrinkage and shrinkage stress in filled systems

Polymer mechanical properties, especially modulus and hardness, are increased significantly when inorganic fillers are added to resin formulations. These inorganic fillers are often functionalized with reactive organic groups to achieve enhanced compatibility and covalent coupling between the filler and the polymer matrix.³⁶ For example, methacrylate siloxane functionalized glass particles are added to dental restorative resin formulations to achieve mechanical properties that mimic the mechanical properties of teeth.³⁷ In filled systems, shrinkage is ideally reduced by reducing the resin volume fraction; however, in some cases the overall shrinkage stress might increase due to the increased modulus of the composite, according to Hooke's law.³⁸ Here, stress is generated in the resin and at the interface between the resin and the filler. Heightened stress is often accumulated at the resin/filler interface because filler is the lower compliance portion in the composites.³⁹ Moreover, during the exothermic radical polymerization, a significant difference of thermal expansion between the polymer matrix and inorganic filler also results in the stress

accumulating at the interface.⁴⁰ There have been very few studies related to modifying the filler/resin interfacial layer to reduce shrinkage stress. Stansbury *et al.* reported that the shrinkage stress is reduced by functionalizing glass filler with polymer brushes as an interfacial buffer layer.^{41,42} In this thesis Chapter 5, we demonstrated utilizing a hyperbranched molecule to functionalize glass filler as an interfacial layer between the polymer matrix and the inorganic filler to reduce shrinkage stress.

1.3 Utilizing ‘click’ reactions to synthesize dendrimers

Dendrimers, described as well-defined three dimensional molecular structures, have unique properties such as highly available, terminal reactive functional groups and low viscosity compared to other similar molecular weight molecules.⁴³ Due to these properties, dendrimers have numerous potential applications in biomedical systems, diagnostics, catalysts, coatings and many others.⁴⁴ In the past decades, condensation, addition and ring-opening reactions have been the most common chemical routes to synthesize dendrimers, often via AB₂ structural monomers.^{45,46} However, these multistep reactions result in complicated purification steps, low yield and relatively small amounts of product, which limit most applications of dendrimers.

To simplify the synthesis route and increase the yield, ‘click reactions’ have more recently been utilized to synthesize dendrimers due to their high selectivity, high yield, no by-products and insensitivity to water and air.⁴⁷ Diels-Alder (DA) [4+2] cycloadditions were used to synthesize polyphenylene dendrimers and functionalize the diene or dienophile dendrimer as well.⁴⁸ The temperature sensitive reversible behavior of this DA click reaction enables this type of dendrimer to have unique encapsulation and release behavior.⁴⁹ Cu(I)-catalyzed alkyne-azide cycloadditions (CuAAC) are another type of ‘click reaction’ that has been utilized to synthesize triazole dendrimers and various symmetric and asymmetric dendrimers with different functional groups have been reported.⁵⁰ Very recently, thiol-ene reactions were utilized as a new dendrimer synthesis route because of the advantages of high conversion, solvent free formulation, UV initiated reaction and

limited oxygen inhibition. Different types of thioether⁵¹ and double bond terminated dendrimers⁵² were synthesized via thiol-ene click reactions. Moreover, it has been reported that a combination of two click reactions, the CuAAC and thiol-ene reactions, was utilized to synthesize a 6-generation dendrimer in a single day, which significantly improves the efficiency of dendrimer synthesis.⁵³ Thiol-yne reactions are another type of click reaction that is similar to the thiol-ene reaction but each alkyne functional group is capable of reacting with thiol twice so that the functionality of the product can be doubled as compared with more conventional thiol-ene click reactions.⁵⁴ By this route, a sixteen-functional alcohol or acid functionalized molecule was synthesized from a tetrayne and an AB₂ molecule via a one-step reaction.⁵⁵ Moreover, a UV curable resin with allyl ether terminated dendrimers and thiol monomers was investigated.⁵⁶

1.4 Induction heating as another radiation curing method

1.4.1 Mechanism of induction heating

Induction heating is the process whereby a ferromagnetic material is exposed to an alternating magnetic field with the subsequent generation of heat resulting from that interaction. In this case, heat is generated by magnetization/demagnetization reversal losses (core loss), hysteresis loss and/or excess eddy current loss (sometimes referred to as anomalous or dynamic losses).⁵⁷ Eddy current loss occurs as a direct consequence of joule heating associated with electric currents induced in the material by the changing magnetization while the hysteresis loss results from distortion of the crystalline structure. The excess eddy current loss results from the magnetic domain-wall dynamics.⁵⁸ When the ferromagnetic particles are micro- or nanoscale, eddy current and excess eddy current losses are dramatically diminished; therefore, hysteresis loss becomes the primary heat generation mechanism, and the induction heating is often referred to as hysteresis heating under these circumstances.⁵⁹ Uniquely and of significant benefit here, hysteresis heating associated with

different ferromagnetic materials is limited by the particular material's Curie temperature, above which hysteresis heating no longer occurs.⁵⁸

1.4.2 Current applications of induction heating

Induction heating represents a simple method for increasing temperature that has been widely utilized in the metal industry because of its advantages of rapid heating, controlled local heating, no radiant heating of the environment, and relatively high efficiency as compared with conventional heating methodologies.⁶⁰ More recently, induction heating has been implemented by embedding ferromagnetic particles in thermoplastic or thermosetting polymer matrices to achieve induction-heating induced melting, welding,⁶¹ coating,⁶² shape memory actuation,^{63,64} and adhesion^{65,66}. Suwanwatana and co-workers also developed a heat transfer model relating different nickel particle size, loading, magnetic field and frequency to the temperature change in cured polymer substrates.^{59,66} Induction heating has not previously been utilized to induce an *in situ* radical polymerization. In this thesis Chapter 6, we demonstrated induction heating as an alternative method to UV curing for *in situ* curing of composite resins.

1.5 References

1. Fouassier, J.-P.; Rabek, J. F., *Radiation curing in polymer science and technology, volume 1. Fundamentals and methods*. Elsevier Applied Science: London; New York, 1993.
2. Anseth, K. S.; Newman, S. M.; Bowman, C. N., Polymeric dental composites: Properties and reaction behavior of multimethacrylate dental restorations. *Adv Polym Sci* **1995**, *122*, 177-217.
3. O'Brien, A. K.; Bowman, C. N., Impact of oxygen on photopolymerization kinetics and polymer structure. *Macromolecules* **2006**, *39* (7), 2501-2506.
4. Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol-enes: Chemistry of the past with promise for the future. *J Polym Sci Part a-Poly Chem* **2004**, *42* (21), 5301-5338.

5. Bowman, C. N.; Kloxin, C. J., Toward an enhanced understanding and implementation of photopolymerization reactions. *AIChE J* **2008**, *54* (11), 2775-2795.
6. Odian, G. G., *Principles of polymerization*. 4th ed.; Wiley-Interscience: Hoboken, N.J., 2004; p xxiv, 812 p.
7. Kloosterboer, J. G., Network formation by chain crosslinking photopolymerization and its applications in electronics. *Adv Polym Sci* **1988**, *84*, 1-61.
8. Chiu, Y. Y.; Lee, L. J., Microgel formation in the free-radical cross-linking polymerization of ethylene-glycol dimethacrylate (EGDMA) .1. Experimental. *J Polym Sci Part a-Poly Chem* **1995**, *33* (2), 257-267.
9. Funke, W.; Okay, O.; Joos-Muller, B., Microgels - Intramolecularly crosslinked macromolecules with a globular structure. *Microencapsulation - Microgels - Iniferters* **1998**, *136*, 139-234.
10. Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. N., Mechanism and modeling of a thiol-ene photopolymerization. *Macromolecules* **2003**, *36* (12), 4631-4636.
11. Hoyle, C. E.; Bowman, C. N., Thiol-ene click chemistry. *Angew Chem Int Edit* **2010**, *49* (9), 1540-1573.
12. Hoyle, C. E.; Lowe, A. B.; Bowman, C. N., Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem Soc Rev* **2010**, *39* (4), 1355.
13. Fairbanks, B. D.; Sims, E. A.; Anseth, K. S.; Bowman, C. N., Reaction rates and mechanisms for radical, photoinitiated addition of thiols to alkynes, and implications for thiol-yne photopolymerizations and click reactions. *Macromolecules* **2010** *43* (9), 4113-4119.
14. Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N., Thiol-yne photopolymerizations: Novel mechanism, kinetics, and step-growth formation of highly cross-linked networks. *Macromolecules* **2009**, *42* (1), 211-217.
15. Cramer, N. B.; Reddy, S. K.; O'Brien, A. K.; Bowman, C. N., Thiol-ene photopolymerization mechanism and rate limiting step changes for various vinyl functional group chemistries. *Macromolecules* **2003**, *36* (21), 7964-7969.
16. Reddy, S. K.; Cramer, N. B.; Bowman, C. N., Thiol-vinyl mechanisms. 2. Kinetic modeling of ternary thiol-vinyl photopolymerizations. *Macromolecules* **2006**, *39* (10), 3681-3687.

17. Cramer, N. B.; Bowman, C. N., Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared. *J Polym Sci Part a-Poly Chem* **2001**, 39 (19), 3311-3319.
18. Lee, T. Y.; Smith, Z.; Reddy, S. K.; Cramer, N. B.; Bowman, C. N., Thiol-allyl ether-methacrylate ternary systems. Polymerization mechanism. *Macromolecules* **2007**, 40 (5), 1466-1472.
19. Wei, H. Y.; Senyurt, A. F.; Jonsson, S.; Hoyle, C. E., Photopolymerization of ternary thiol-ene/acrylate systems: Film and network properties. *J Polym Sci Part a-Poly Chem* **2007**, 45 (5), 822-829.
20. Senyurt, A. F.; Wei, H. Y.; Hoyle, C. E.; Piland, S. G.; Gould, T. E., Ternary thiol-ene/acrylate photopolymers: Effect of acrylate structure on mechanical properties. *Macromolecules* **2007**, 40 (14), 4901-4909.
21. Lee, T. Y.; Carioscia, J.; Smith, Z.; Bowman, C. N., Thiol-allyl ether-methacrylate ternary systems. Evolution mechanism of polymerization-induced shrinkage stress and mechanical properties. *Macromolecules* **2007**, 40 (5), 1473-1479.
22. Lu, H.; Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N., Investigations of step-growth thiol-ene polymerizations for novel dental restoratives. *Dent Mater* **2005**, 21 (12), 1129-1136.
23. Feng, L.; Suh, B. I.; Shortall, A. C., Formation of gaps at the filler-resin interface induced by polymerization contraction stress gaps at the interface. *Dent Mater* **2010**, 26 (8), 719-729.
24. Eick, J. D.; Kostoryz, E. L.; Rozzi, S. M.; Jacobs, D. W.; Oxman, J. D.; Chappelow, C. C.; Glaros, A. G.; Yourtee, D. M., In vitro biocompatibility of oxirane/polyol dental composites with promising physical properties. *Dent Mater* **2002**, 18 (5), 413-421.
25. Van Ende, A.; De Munck, J.; Mine, A.; Lambrechts, P.; Van Meerbeek, B., Does a low-shrinking composite induce less stress at the adhesive interface *Dent Mater* **2010**, 26 (3), 215-222.
26. Oxman, J. D.; Jacobs, D. W. Ternary photoinitiator system for curing of epoxy resins. 1998-US4029
27. Cao, X.; Lee, L. J., Control of shrinkage and final conversion of vinyl ester resins cured in low-temperature molding processes. *J Appl Polym Sci* **2003**, 90 (6), 1486-1496.
28. Moraes, R. R.; Garcia, J. W.; Barros, M. D.; Lewis, S. H.; Pfeifer, C. S.; Liu, J. C.; Stansbury, J. W., Control of polymerization shrinkage and stress in nanogel-modified monomer and composite materials. *Dent Mater* **2011**, 27 (6), 509-519.

29. Cramer, N. B.; Stansbury, J. W.; Bowman, C. N., Recent Advances and Developments in Composite Dental Restorative Materials. *J Dent Res* **2011**, *90* (4), 402-416.
30. Dodiuk-Kenig, H.; Lizenboim, K.; Eppelbaum, I.; Zalsman, B.; Kenig, S., The effect of hyper-branched polymers on the properties of dental composites and adhesives. *J Adh Sci Tech* **2004**, *18* (15-16), 1723-1737.
31. Mezzenga, R.; Boogh, L.; Manson, J. A. E., A review of dendritic hyperbranched polymer as modifiers in epoxy composites. *Compos Sci Tech* **2001**, *61* (5), 787-795.
32. Scott, T. F.; Draughon, R. B.; Bowman, C. N., Actuation in crosslinked polymers via photoinduced stress relaxation. *Adv Mater* **2006**, *18* (16), 2128-2132.
33. Park, H. Y.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N., Covalent adaptable networks as dental restorative resins: Stress relaxation by addition–fragmentation chain transfer in allyl sulfide-containing resins. *Dent Mater* **2010**, *26* (10), 1010-1016.
34. Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Carioscia, J. A.; Boulden, J. E.; Stansbury, J. W.; Bowman, C. N., Investigation of thiol-ene and thiol-ene–methacrylate based resins as dental restorative materials. *Dent Mater* **2010**, *26* (1), 21-28.
35. Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Boulden, J. E.; Wydra, R.; Stansbury, J. W.; Bowman, C. N., Properties of methacrylate–thiol–ene formulations as dental restorative materials. *Dent Mater* **2010**, *26* (8), 799-806.
36. Fortin, D.; Vargas, M. A., The spectrum of composites: New technologies and materials. *J Am Dent Assoc* **1999**, *131*, 26S-30S.
37. Sideridou, I. D.; Karabela, M. M., Effect of the amount of 3-methacyloxypropyltrimethoxysilane coupling agent on physical properties of dental resin nanocomposites. *Dent Mater* **2009**, *25* (11), 1315-1324.
38. Braga, R.; Ballester, R.; Ferracane, J., Factors involved in the development of polymerization shrinkage stress in resin-composites: A systematic review. *Dent Mater* **2005**, *21* (10), 962-970.
39. Davidson, C. L.; Feilzer, A. J., Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. *J Dent* **1997**, *25* (6), 435-440.
40. Ferracane, J., Developing a more complete understanding of stresses produced in dental composites during polymerization. *Dent Mater* **2005**, *21* (1), 36-42.

41. Shah, P. K.; Stansbury, J. W., Polymer-brush modified fillers for dental composites. *Abstracts of Papers Am Chem Soc* **2006**, 231.
42. Shah, P. K.; Stansbury, J. W., Modified filler-matrix interfaces in polymeric composites used as dental restoratives. *Abstracts of Papers Am Chem Soc* **2007**, 233.
43. Mishra, M. K.; Kobayashi, S., *Star and hyperbranched polymers*. Marcel Dekker: New York, 1999; p ix, 350 p.
44. Inoue, K., Functional dendrimers, hyperbranched and star polymers. *Prog Polym Sci* **2000**, 25 (4), 453-571.
45. Newkome, G. R.; Moorefield, C. N.; Vögtle, F., *Dendrimers and dendrons : concepts, syntheses, applications*. Wiley-VCH: Weinheim ; New York, 2001; p xii, 623 p.
46. Yates, C. R.; Hayes, W., Synthesis and applications of hyperbranched polymers. *Euro Polym J* **2004**, 40 (7), 1257-1281.
47. Franc, G.; Kakkar, A. K., "Click" methodologies: efficient, simple and greener routes to design dendrimers. *Chem Soc Rev* **2010**, 39 (5), 1536.
48. Morgenroth, F.; Mullen, K., Dendritic and hyperbranched polyphenylenes via a simple Diels-Alder route. *Tetrahedron* **1997**, 53 (45), 15349-15366.
49. Chen, X. X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H. B.; Nutt, S. R.; Sheran, K.; Wudl, F., A thermally re-mendable cross-linked polymeric material. *Science* **2002**, 295 (5560), 1698-1702.
50. Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless, K. B.; Fokin, V. V., Efficiency and fidelity in a click-chemistry route to triazole dendrimers by the copper(I)-catalyzed ligation of azides and alkynes. *Angew Chem Int Edit* **2004**, 43 (30), 3928-3932.
51. Rissing, C.; Son, D. Y., Application of thiol-ene chemistry to the preparation of carbosilane-thioether dendrimers. *Organometallics* **2009**, 28 (11), 3167-3172.
52. Killops, K. L.; Campos, L. M.; Hawker, C. J., Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene "Click" chemistry. *J Am Chem Soc* **2008**, 130 (15), 5062-5064.
53. Antoni, P.; Robb, M. J.; Campos, L.; Montanez, M.; Hult, A.; Malmström, E.; Malkoch, M.; Hawker, C. J., Pushing the limits for thiol-ene and CuAAC reactions: Synthesis of a 6th generation dendrimer in a Single Day. *Macromolecules* **2010**, 43 (16), 6625-6631.

54. Hoogenboom, R., Thiol-yne chemistry: A powerful tool for creating highly functional materials. *Angew Chem Int Edit* **2010**, 49 (20), 3415-3417.
55. Chan, J. W.; Hoyle, C. E.; Lowe, A. B., Sequential phosphine-catalyzed, nucleophilic thiol-ene/radical-mediated thiol-yne reactions and the facile orthogonal synthesis of polyfunctional materials. *J Am Chem Soc* **2009**, 131 (16), 5751-5756.
56. Nilsson, C.; Simpson, N.; Malkoch, M.; Johansson, M.; Malmstrom, E., Synthesis and thiol-ene photopolymerization of allyl-ether functionalized dendrimers. *J Polym Sci Part a-Poly Chem* **2008**, 46 (4), 1339-1348.
57. Rapoport, E.; Pleshivtseva, Y., *Optimal control of induction heating processes*. CRC/Taylor & Francis: Boca Raton, FL, 2007.
58. Willard, M. A.; Francavilla, T.; Harris, V. G., Core-loss analysis of an (Fe, Co, Ni)-based nanocrystalline soft magnetic alloy. *J Appl Phys* **2005**, 97 (10).
59. Suwanwatana, W.; Yarlagadda, S.; Gillespie, J. W., Influence of particle size on hysteresis heating behavior of nickel particulate polymer films. *Composites Science and Technology* **2006**, 66 (15), 2825-2836.
60. Lozinski*, M. G., *Industrial applications of induction heating*. [1st English ed.; Pergamon Press: Oxford, New York, 1969; p xviii, 672 p.
61. Zinn, S.; Semiatin, S. L.; Electric Power Research Institute.; Battelle Memorial Institute. Columbus Laboratories., *Elements of induction heating : design, control, and applications*. ASM International: Metals Park, Ohio, 1988; p xv, 335 p.
62. Martinazzo, F. Induction cured power coatings for temperature sensitive substrates. 2004-983115, 20050123743.
63. Schmidt, A. M. S. A. M., Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. *Macromol Rapid Comm* **2006**, 27 (14), 1168-1172.
64. Yakacki, C. M.; Satarkar, N. S.; Gall, K.; Likos, R.; Hilt, J. Z., Shape-memory polymer networks with Fe(3)O(4) nanoparticles for remote activation. *J Appl Polym Sci* **2009**, 112 (5), 3166-3176.
65. Tay, T. E.; Fink, B. K.; McKnight, S. H.; Yarlagadda, S.; Gillespie, J. W., Accelerated curing of adhesives in bonded joints by induction heating. *J Compos Mater* **1999**, 33 (17), 1643-1664.

66. Suwanwatana, W.; Yarlalagadda, S.; Gillespie, J. W., Hysteresis heating based induction bonding of thermoplastic composites. *Compos Sci Tech* **2006**, 66 (11-12), 1713-1723.

Chapter 2

Objectives

Photopolymerization has been widely used in various areas due to the advantages of ambient cure, cure on command, energy efficiency and no solvents. Acrylates and methacrylates dominate the photocuring market because of their fast reaction rates, high glass transition temperature and modulus, and the wide commercial availability of monomers.¹ However, these systems also encounter problems associated with high shrinkage stress that limits further applications. Recently, thiol-ene systems have attracted more attention because of the low shrinkage stress resulting from the step growth radical polymerization mechanism.² Thiol-ene reactions also generate uniform networks and have very limited oxygen inhibition and side reactions. Moreover, thiol-yne reactions follow the same radical step growth polymerization mechanism and maintain the advantages of thiol-ene systems but achieve higher mechanical properties due to higher crosslinking density.³ Thus, the overarching goal of this thesis was to investigate and understand relationships between monomer formulations, curing conditions, and material properties of thiol-ene and thiol-yne photopolymerizations. Four specific aims were investigated. In particular, we aim to:

Specific Aim 1: Develop a relationship to quantify the interrelationships between the curing conditions (T_{cure}), monomer structure, and heterogeneity on the ultimate polymer properties achieved, specifically the glass transition temperature (T_g);

Specific Aim 2: Evaluate the behavior and performance of ternary thiol-yne-(meth)acrylate systems with the goal of tailoring materials to achieve high mechanical properties (T_g and modulus) while minimizing the shrinkage stress;

Specific Aim 3: Utilize the thiol-ene and thiol-yne click reactions to synthesize hyperbranched molecules to functionalize glass fillers and create composite thiol-yne-methacrylate systems with low shrinkage stress; and

Specific Aim 4: Create composite resin systems cured by induction heating and develop and understand the induction-heating mediated polymerization behavior through modeling and experimental characterization.

In Specific Aim 1, to obtain an overall understanding of the material properties relating curing conditions of photocuring, the final conversions and mechanical properties (T_g and heterogeneity) of various radical photocuring systems including chain-growth (acrylates), step-growth (thiol-ene and thiol-norbornene) and mixed chain-step-growth (thiol-acrylates) systems were evaluated at different curing temperatures. The relationship between glass transition temperature and curing temperature was quantified as dependent on the monomer structure (flexible vs. rigid) and polymer network heterogeneity.

After evaluating different kinds of photocuring radical polymerization systems, in Specific Aim 2, thiol-yne-methacrylate and thiol-yne-acrylate ternary systems were designed as model resin systems to achieve high mechanical properties (T_g and modulus) and low shrinkage stress. The competitive reaction kinetics of this mixed chain-step-growth polymerization, mechanical properties and shrinkage stress were evaluated. Moreover, the mechanism for the reduction of shrinkage stress in this ternary system was studied.

To further increase the modulus, glass filler composites with the thiol-yne-methacrylate resin matrix were studied in Specific Aim 3. Usually, shrinkage stress increases with increasing modulus. Here, a flexible hyperbranched molecule was synthesized by thiol-ene and thiol-yne click reactions. This hyperbranched molecule was covalently bonded to glass nanoparticles as an interfacial layer between the inorganic filler and polymer matrix. By adding this type of particles, the high modulus filler composite system was demonstrated to reduce the shrinkage stress without sacrificing the mechanical properties.

The studies in Specific Aims 1 – 3 are focused on addressing challenges in the materials area relating to how to design a resin or composite system with high mechanical properties and low

shrinkage stress. In Specific Aim 4, induction polymerization was implemented as an alternative method of UV curing to address challenges associated with the restriction of light accessibility in highly filled composite systems. A heat transfer model combined reaction kinetics was developed to further understand the induction curing behavior.

Reference

1. Fouassier, J.-P.; Rabek, J. F., *Radiation curing in polymer science and technology, volume 1. Fundamentals and methods*. Elsevier Applied Science: London; New York, 1993.
2. Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol-enes: Chemistry of the past with promise for the future. *J Polym Sci Part a-Poly Chem* **2004**, 42 (21), 5301-5338.
3. Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N., Thiol-yne photopolymerizations: Novel mechanism, kinetics, and step-growth formation of highly cross-linked networks. *Macromolecules* **2009**, 42 (1), 211-217.

Chapter 3

Relationship between Glass Transition Temperature and Polymerization

Temperature for Cross-Linked Photopolymers*

Monomeric resins are frequently polymerized at a temperature that is far below the desired glass transition temperature for the final polymer network. This work quantitatively investigates the relationship between the glass transition temperature (T_g), the cure temperature (T_{cure}), the maximum achievable glass transition temperature for a particular monomer formulation (T_{gmax}), and the network heterogeneity as indicated by the half-width of the glass transition region ($T_{\text{g1/2width}}$) for both chain growth and step growth polymerization systems. Various monomer resins were systematically photopolymerized at 25, 50, 75, and 100 °C to the maximum achievable double bond conversion with living radical photo-polymerizations employed as necessary to eliminate issues associated with postcuring during heating of the samples for dynamic mechanical analysis. For polymer samples that have the potential for much higher glass transition temperatures than the curing temperature (i.e., where $T_{\text{cure}} < T_{\text{gmax}} - T_{\text{g1/2width}}$), mass transfer limitations and the network heterogeneity combine to control T_g such that $T_g \approx T_{\text{cure}} + T_{\text{g1/2width}}$. For systems polymerized at temperatures closer to their maximum glass transition temperature, i.e., where $T_{\text{cure}} \geq T_{\text{gmax}} - T_{\text{g1/2width}}$, the polymer structure becomes the dominant factor and $T_g \approx T_{\text{gmax}}$. These relationships were broadly and successfully applied to cross-linked networks formed from both chain growth and step growth polymerizations, incorporating networks of vastly different heterogeneity, with T_g 's ranging from 35 to 205 °C with approximately 10% error found between predicted and experimental glass transition temperatures.

3.1 Introduction

* This chapter is from the publication S. Ye, N.B. Cramer, C.N. Bowman, *Macromolecules* **2010**,44,490-494

The glass transition temperature (T_g) of a polymer network is often times of singular importance in determining the performance and potential implementation of polymer networks. For applications requiring a high T_g , the polymerization temperature is often far below the final polymer T_g , even including the often significant polymerization-induced exotherm. Consequently, significant polymerization must occur after the transition to the glassy state if the T_g is to be sufficiently greater than the curing temperature. The decrease in free volume and the significant mobility restriction of polymer segments post-vitrification typically reduce the reaction rate by orders of magnitude, making it difficult to achieve increased glass transition temperatures without significantly increasing the polymerization temperature.¹ For photopolymerization reactions in particular, where the initial reaction temperature is often ambient or near-ambient, these restrictions may be quite pronounced. Specifically, autodeceleration, reaction-diffusion-controlled termination, trapped radicals and limited double bond conversion have all been found to be controlling factors in polymerization kinetics of polymer network forming systems.^{2,3,4,5} These phenomena are strongly influenced by both the chemical structure of the monomers, the crosslink density of the resulting polymer, the heterogeneity of the material, the polymerization mechanism and the curing conditions.^{2,3,6,7} The understanding of these complex interrelationships that impact the ultimate glass transition temperature is thus an important factor for many practical applications such as coatings, dental restorative materials, and optical fiber coatings.

Due to the complex nature and importance of the relationship between T_g , curing conditions and network formation, extensive evaluation has been performed on the relationship between T_g and T_{cure} . Studies evaluating crosslinked epoxy-amines, cyanate esters, polyimides and others have been performed.^{8,9,10,11,12,13} Numerous studies focused on time-temperature-transition (TTT) diagrams for thermosetting systems, particularly those cured by step growth polymerizations.^{8,9,10,11} Gillham and co-workers studied different epoxy systems and reported that the cure path did not affect the relationship between T_g and conversion.¹² Rozenburg reported that the reaction kinetics of epoxy

systems were strongly affected by the network structure and properties in the glassy state rather than rubbery state.¹³ Oleinik reported that in epoxy-aromatic amine systems, $T_g \approx T_{cure} + 0.5\Delta T_g$ and further derived T_g was not above T_{cure} by more than 15-30 °C.¹⁴ This work led to a long-established rule of thumb that the T_g cannot exceed T_{cure} by more than 25°C. Far less work has been conducted on the T_g vs. T_{cure} relationship for polymers formed from chain growth photopolymerizations as these systems have several inherent complications. One primary difficulty is that the trapped radicals become mobile upon heating and result in significant post-cure that made it traditionally difficult to evaluate the T_g of the as-cured polymer, which is necessary to determine the $T_g - T_{cure}$ relationship. Sample heating is necessary to determine T_g and the resultant post-cure affects (causes an increase in) the T_g during measurement of the same.^{15,16} Additionally, chain growth polymerizations are also traditionally highly exothermic, leading to significant temperature rises during the reaction that alter the relationship between cure and glass transition temperature.

Here, two common polymerization mechanisms are evaluated, chain growth and step growth polymerizations.¹⁷ Radical polymerizations that proceed via a chain growth mechanism result in networks that are very heterogeneous in nature.^{18,19} Heterogeneous networks contain broad distributions of chain mobilities and relaxation times, resulting in a broad glass transition region,²⁰ as is often described by the half width of the tan delta curve at half its maximum value ($T_{g1/2width}$).²¹ In contrast to chain growth polymerizations, step growth polymerizations are step-wise reactions between the functional groups of the monomers leading initially to the formation of dimers, trimers, tetramers, etc. and resulting in slow and uniform molecular weight and network development during the early stages of the reaction.¹⁷ The step growth reaction mechanism results in the formation of ideal, homogeneous polymer networks.

Thiol-ene reactions are the examples of radical polymerizations that also exhibit a step growth polymerization mechanism.²² The primary initiator radical abstracts a hydrogen from the

thiol monomer to form a thiyl radical, which further reacts with an ene monomer to form a carbon-centered radical by an addition reaction. The thiyl radical is regenerated by a subsequent chain transfer step.^{23,24} The alternating addition and chain transfer reactions result in step growth network development that ultimately leads to the formation of a homogenous polymer network.^{22, 25}

Radical photopolymerizations are both rapid and strongly exothermic, making it difficult to maintain isothermal reaction conditions during polymerization, and the non-isothermal reaction conditions convolute the evaluation of the T_g vs. T_{cure} relationship. Thus, it is critical to determine the maximum temperature achieved during the polymerization, which becomes the effective curing temperature, or to have the polymerization proceed slowly enough that heat transfer renders the polymer sample nearly isothermal.

To eliminate post-cure effects associated with additional polymerization that occurs during the T_g measurement, living radical photopolymerizations initiated by p-xylylene bis(N,N-diethyl dithiocarbamate) (XDT)²⁶ have been employed and demonstrated to successfully eliminate post-curing effect from trapped radicals.^{27,28} XDT photocleaves upon absorption of ultraviolet light into a carbon-based initiating radical that will propagate with both carbon-carbon double bond and thiol functional groups. The other cleavage product is a sulfur-based dithiocarbamate radical that acts to terminate propagating radicals. The pseudo living radical polymerization also results in a slower polymerization rate, thus decreasing the heat generated by the exothermic reaction.²⁹ The relationship presented here is similar in nature to the equation previously developed by Olienik.¹⁴ In this work, the T_g ranges for the equation validity are defined and the equation is demonstrated to be valid for a wide range of polymerization mechanisms. Moreover, our relationship provides for a quantitative relationship describing the T_g range of the resulting polymer as it depends on both the polymerization mechanism and the polymer properties. This work proposes to develop a broadly applicable semiquantitative relationship between T_g and T_{cure} as a means for understanding the network evolution and as a means for controlling the polymer behavior.

To determine how different reaction mechanisms affect the T_g vs. T_{cure} relationship, we evaluated radical-mediated chain growth polymerization systems (acrylates), step growth polymerization systems (thiol-enes), and mixed step-chain growth polymerization systems (thiol-acrylates) as well as analyzing previous data from step growth systems that are not radically mediated such as epoxy-amines systems. These polymerization systems represent a wide range of reaction mechanisms used throughout thermosetting systems and they result in significantly different network development and ultimate heterogeneity. Additionally, both aliphatic monomers with relatively flexible core structures and cyclic monomers with rigid core structures were utilized to ascertain the effect of monomer structure on these relationships.

3.2 Experimental

Materials. The monomers 1,6-hexanediol diacrylate (HDDA), tricyclodecane dimethanol diacrylate (TCDDA), and triallyl-1,3,5-triazine-2,4,6-trione (TATATO) were purchased from Sigma-Aldrich Co. (Milwaukee, WI). Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Evans Chemetics, and trimethylolpropane tri-(norborn-2-ene-5-carboxylate) (TMPTN) was synthesized in our lab by a previously reported procedure.³⁰ 2,2-dimethoxyphenyl acetophenone (Irgacure 651, DMPA, Ciba-Geigy Co., Hawthorne, NY) and p-xylylene bis(N,N-diethyl dithiocarbamate) (XDT, 3M Corp., Minneapolis, MN) were used as photoinitiators.

FTIR. Fourier transform infrared spectroscopy (FTIR) was used to monitor conversion. Samples were cured inside a custom built FTIR chamber³¹ (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) with a UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) with primary output at 365 nm. A horizontal-mounting unit, which redirects the IR light beam vertically, was used in combination with a temperature cell (0-120 °C) to allow for real-time kinetic characterization. The sample temperature was allowed to stabilize for 10 minutes prior to irradiation.

Mid-IR was utilized to monitor the cure of monomer samples placed between NaCl crystals ($\sim 10\ \mu\text{m}$ thickness) and initiated by 0.5 wt% DMPA. Thiol conversion was monitored by the S-H stretching peak at $2570\ \text{cm}^{-1}$ while the acrylate, allyl ether, and norbornene conversions were monitored by the C=C vibration at $1636\ \text{cm}^{-1}$, C-H stretch at $1640\ \text{cm}^{-1}$ and C-H bending at $711\ \text{cm}^{-1}$, respectively. Near-IR was utilized to monitor the cure of monomer samples placed between glass slides (1 mm thickness) and initiated by 0.25% XDT. Conversion was monitored by the C=C vibration at $6020\ \text{cm}^{-1}$.

Mechanical Measurements. Dynamic mechanical analysis (DMA) was performed with a DMA Q800 dynamic mechanical analyzer (TA Instruments). The samples were rectangular films with dimensions of 1 x 5 x 10 mm. Multi frequency strain mode was used to measure moduli and loss tangent as a function of temperature by applying a sinusoidal stress of frequency 1 Hz over a temperature range of -40 to $100\ ^\circ\text{C}$ with a ramping rate of $3\ ^\circ\text{C}/\text{minute}$. The T_g was taken to be the maximum of the tan delta curve, which is the ratio of the loss modulus to the storage modulus. $T_{g1/2\text{width}}$ was taken to be the width of the tan delta curve at half the maximum value. Sample conversions were checked by FTIR after DMA testing to ensure that only a minimal amount of additional cure occurred during the heating. In no case was the increase in glass transition temperature observed from the first heating to the second heating cycle more than $10\ ^\circ\text{C}$.

3.3 Results and Discussion

Due to the complications associated with post-cure effects, it is not feasible to determine the T_g versus T_{cure} relationship from a single experiment. Here, our method was to first cure samples at $100\ ^\circ\text{C}$ initiated by XDT to various conversions. With the elimination of post-curing upon heating, it is then possible to determine accurately the glass transition temperature as a function of the conversion, verifying that limited additional reaction occurs during the measurement. Critically,

when cured to the same conversion, networks initiated by XDT have been demonstrated to exhibit similar network structures to those initiated by other traditional photoinitiators such as dimethoxy phenyl acetophenone (DMPA).²⁹ For the analysis, DMPA is then utilized as a traditional photoinitiator to determine how the conversion (and hence the glass transition temperature as determined from the XDT initiated samples) varies with the T_{cure} . Conversion versus T_{cure} is determined from isothermally cured 10 μm thick samples initiated by DMPA to reach the maximum conversions at 25, 50, 75 and 100 $^{\circ}\text{C}$, and the T_g vs. T_{cure} relationship is then determined from the T_g values at the corresponding conversion.

Five model systems were studied in this work. HDDA and TCDDA are traditional chain growth acrylate systems that form heterogeneous polymer networks. TCDDA has a rigid monomer structure for comparison with the more flexible, aliphatic core structure of HDDA. PETMP/TATATO and PETMP/TMPTN are traditional radical-mediated step growth thiol-ene systems that lead to more homogeneous polymer networks while PETMP/TCDDA is a mixed mode step-chain growth thiol-acrylate system. These systems result in polymer networks with a wide range of glass transition temperatures and network heterogeneities as shown in the loss tangent curves in Figure 1.1 and the data in Table 3.1. The maximum achievable conversion and glass transition temperature achieved by reacting for long times at elevated temperatures are presented in Table 3.2.

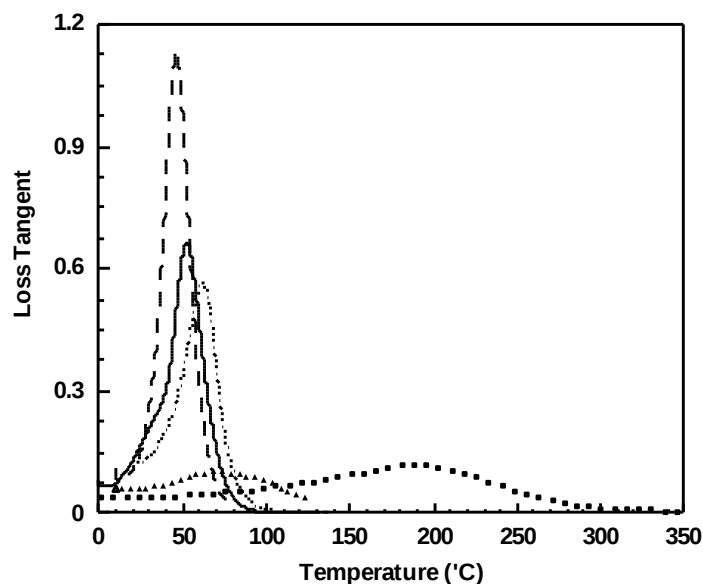


Figure 3.1. Loss tangent versus temperature for PETMP-TATATO (---), PETMP-TCDDA (—), PETMP-TMPTN (...), HDDA (▲) and TCDDA (○) cured to 85% ($\pm 1\%$) double bond conversion. Systems contain 0.25wt% XDT and are irradiated at 15 mW/cm² and 100°C until the sample achieves the desired conversion.

Table 3.1. T_g and $T_{g1/2width}$ values for samples cured to 85% ($\pm 1\%$) double bond conversion. Systems contain 0.25wt% XDT and are irradiated at 15 mW/cm² and 100°C until the sample achieves the desired conversion.

	T_g (°C)	$T_{g1/2width}$ (°C)
PETMP-TCDDA	52	20
PETMP-TATATO	46	17
PETMP-TMPTN	62	21
HDDA	69	50
TCDDA	189	103

Table 3.2. Conversion_{max} and T_{gmax} for samples cured to their ultimate conversion. All samples were laminated between NaCl plates, cured at 100 °C with 0.5 wt% DMPA, and irradiated with 2.5 mW/cm² UV light to reach Conversion_{max}. The T_{gmax} values at these conversions were calculated from the glass transition-conversion relationships presented in Figure 3.2.

	Conversion _{max} (%)	T _{gmax} (°C)
PETMP-TCDDA	100 ± 0	94
PETMP-TATATO	100 ± 0	60
PETMP-TMPTN	98 ± 1	93
HDDA	93 ± 1	87
TCDDA	88 ± 2	n/a

To determine the T_g as a continuous function of conversion, the T_g vs. conversion data were fit using free volume theory assuming that the free volume increases linearly with increasing temperature below or above the glass transition temperature, that at the glass transition temperature polymers have a universal free volume 0.025, and that the fractional free volumes of the monomer and polymer are added ideally.^{32,33,34} Other methodologies result in similar interpolation of the relationship between glass transition temperature and conversion. The polymer volume fraction is calculated from monomer conversion³³ and the volumetric shrinkage factor³⁵ such that glass transition temperature (T_g) as a function of conversion (X) is obtained and is represented by Equation 3.1²⁹:

$$T_g = \frac{\alpha_m \cdot v_m \cdot T_{gm} + (\alpha_p \cdot v_p \cdot T_{gp} - \alpha_m \cdot v_m \cdot T_{gm}) \cdot X}{\alpha_m \cdot v_m + (\alpha_p \cdot v_p - \alpha_m \cdot v_m) \cdot X} \quad (3.1)$$

in which α_m and α_p are expansion coefficients of the monomer and polymer (taken to be 0.0005 and 0.000075 1/°C, respectively³⁴); v_m and v_p are specific volumes of the monomer and polymer; T_{gm} is the glass transition temperature of the monomer taken to be the extrapolated glass transition

temperature at $X = 0$; and T_{gp} is the extrapolated glass transition temperature of the polymer at 100% double bond conversion. For each system, the glass transition temperature was determined at a number of different conversions and the data was fit with Equation 1 with the results presented in Figure 3.2.

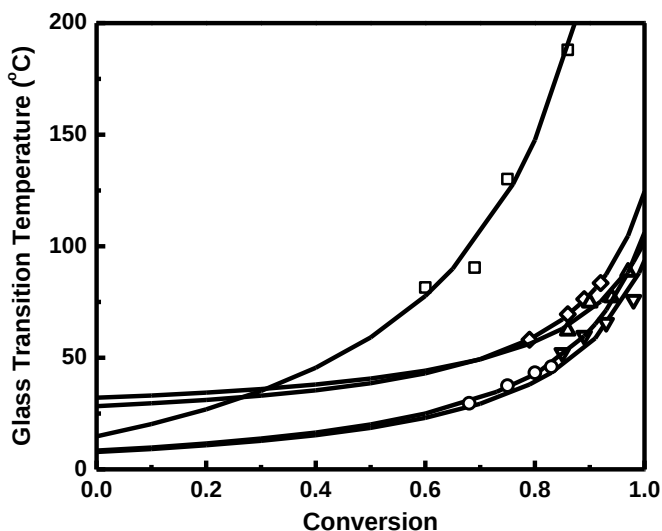


Figure 3.2. Glass transition temperature (T_g) as a function of double bond conversion for TCDDA ($\square$), HDDA ($\diamond$), PETMP-TMPTN (Δ), PETMP-TCDDA (∇), and PETMP-TATATO ($\circ$). Curves were fit with the T_g vs. conversion relationship as determined from Equation. 1. Systems contained 0.25 wt% XDT and were irradiated at 15 mW/cm² and 100 °C until they achieved the desired conversion.

To determine the conversion achieved at each cure temperature and obtain the conversion vs. T_{cure} relationship, thin samples (10 μ m) were cured at 25, 50, 75 and 100 °C. Since the samples are thin and heat transfer is extremely rapid to the salt crystals that act as effective heat sinks, the reactions are assumed to be isothermal. Heat transfer modeling³⁶ of similar systems predicts temperature changes of less than 0.3 °C during the reaction, verifying this assumption. Conversion versus T_{cure} data is shown in Table 3.3, and the T_g values are obtained from the T_g vs. Conversion relationships presented in Figure 3.2. Finally, the determined T_g vs. T_{cure} data is shown in Figure 3.3.

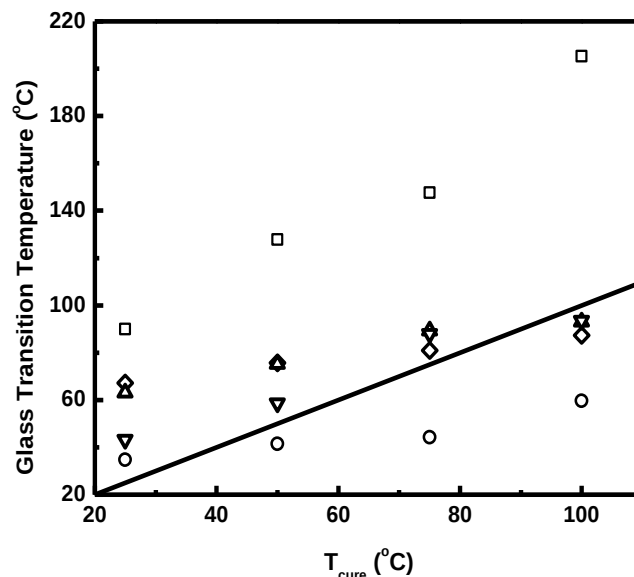


Figure 3.3. Glass transition temperature vs. cure temperature for TCDDA (□), HDDA (◇), PETMP-TMPTN (Δ), PETMP-TCDDA (▽), PETMP-TATATO (○). For reference $T_g = T_{cure}$ (—) is also plotted. All samples were laminated between NaCl plates and cured at 25, 50, 75 or 100 °C with 0.5 wt% DMPA and were irradiated with 2.5 mW/cm² UV light. The T_g values were obtained from the glass transition-conversion relationships presented in Figure 3.2.

Previous work on chain growth methacrylate systems indicated that the heterogeneity of polymer networks is an important factor in T_g vs. T_{cure} relationship, i.e. the more heterogeneous the sample, the larger the maximum difference between T_g and T_{cure} .¹ Another important factor in the T_g vs. T_{cure} relationship is the maximum T_g (T_{gmax}). The data in Figure 3.3 helps to illustrate this point by indicating that HDDA and PETMP/TMPTN have very similar T_g vs. T_{cure} trends though they have different network heterogeneities associated with the different formation mechanisms. HDDA has a $T_{g1/2width}$ of 50 °C and PETMP/TMPTN has a $T_{g1/2width}$ of 21 °C. The similarity in T_g vs. T_{cure} behavior is primarily a result of these two systems exhibiting a similar maximum T_g (T_{gmax}). This result implies that both network heterogeneity and monomer structure, as evidenced by the maximum possible glass transition temperature, contribute to the T_g vs. T_{cure} behavior. Summarizing, our hypothesis is that polymerizations continue as long as there are regions with sufficient mobility,

independent of the specific type of polymerization reaction that is occurring. Mobility (and hence T_g) is a function of cure temperature, network heterogeneity and molecular structure. These three factors can be further related to T_{cure} , $T_{g1/2width}$ and T_{gmax} (see Figure 3.1, Table 3.1 and Table 3.2). Therefore, the following relationship is proposed:

For polymerizing systems cured well below their maximum glass transition temperature, i.e., where

$$T_{cure} < T_{gmax} - T_{g1/2width} \quad (3.2)$$

we propose

$$T_g \approx T_{cure} + T_{g1/2width} \quad (3.3)$$

In contrast, for systems polymerized near or above their maximum possible glass transition temperature, i.e., for polymerizations where

$$T_{cure} \geq T_{gmax} - T_{g1/2width} \quad (3.4)$$

we propose

$$T_g \approx T_{gmax} \quad (3.5)$$

Thus, the relationship between the cure temperature and $T_{gmax} - T_{g1/2width}$ is utilized as a criterion to divide the polymerizing systems into two distinct regions; diffusion controlled and topologically controlled. For systems where $T_{gmax} - T_{g1/2width} > T_{cure}$, the samples are expected to be diffusion controlled, and for systems where $T_{gmax} - T_{g1/2width} < T_{cure}$, the samples are considered to be topologically controlled with limitations associated with the molecular structure and ultimate glass transition temperature of the material dominating.

In the diffusion controlled region, the cure temperature and network heterogeneity strongly affect the T_g vs. T_{cure} behavior. As T_{cure} is increased, the free volume at a given conversion increases and diffusional limitations do not arise until later in the polymerization, ultimately resulting in the

reaction proceeding to higher conversions. This result is evidenced in the shaded data of Table 3.3 where the conversions of the systems increase with increasing T_{cure} . For PETMP/TCDDA and PETMP/TMPTN systems, the conversions increase 8% and 7%, respectively, when increasing T_{cure} from 25 to 50 °C. In contrast, in the topologically controlled region, the conversions increase only 1% when T_{cure} is increased from 75 to 100 °C. Heterogeneity also strongly affects the T_g vs. T_{cure} behavior. The more heterogeneous networks maintain regions of higher mobility, even when the overall glass transition temperature exceeds the cure temperature by a wide margin, resulting in greater differences between T_g and T_{cure} .¹

In the topologically controlled region ($T_{\text{cure}} > T_{g\text{max}} - T_{g1/2\text{width}}$), the unshaded data in Table 3.3, there is more free volume in the network which increases the mobility of the polymer segments and reduces diffusional limitations such that the polymers essentially achieve their maximum conversion. Thus, topological restrictions become the dominant factor controlling T_g . This phenomenon is illustrated in Figure 3.3 where the HDDA, PETMP/TMPTN, and PETMP/TCDDA systems achieve a maximum T_g that does not increase further with increasing cure temperature from 75 to 100 °C. For most of the systems that have been evaluated, there is minimal change in T_g when T_{cure} is increased from 75 to 100 °C. Therefore, $T_{g\text{max}}$ is taken to be the T_g when $T_{\text{cure}} = 100$ °C (see Table 3.2). TCDDA has a T_g of 205 °C at $T_{\text{cure}} = 100$ °C, which is significantly greater than the T_g at 75 °C. However, 205 °C is still approximated as the $T_{g\text{max}}$ for TCDDA.

Table 3.3. Double bond conversion at different cure temperatures for various monomer systems. The shaded values represent the samples cured under the condition where $T_{\text{cure}} < T_{\text{gmax}} - T_{\text{g1/2width}}$ and diffusion control dominates. The unshaded values represent the samples cured where $T_{\text{cure}} \geq T_{\text{gmax}} - T_{\text{g1/2width}}$ where topological control limits the polymerization. All samples were laminated between NaCl plates and cured at 25, 50, 75 or 100 °C with 0.5 wt% DMPA and were irradiated with 2.5 mW/cm² UV light.

T_{cure} (°C)	C=C Conversion					
	TCDDA	PETMP /TCDDA	PETMP /TMPTN	HDDA	PETMP /TATATO	
25	0.65	0.83	0.85	0.85	0.92	$T_{\text{cure}} < T_{\text{gmax}} - T_{\text{g1/2width}}$
50	0.76	0.91	0.92	0.89	0.96	$T_{\text{g1/2width}}$
75	0.80	0.99	0.97	0.91	0.97	$T_{\text{cure}} \geq T_{\text{gmax}} - T_{\text{g1/2width}}$
100	0.88	1.00	0.98	0.93	1.00	$T_{\text{g1/2width}}$

To demonstrate the validity of the proposed relationships, the experimental data and the predictions from Equations 3.3 and 3.5 are plotted in Figure 3.4. The same relationships are also applied to traditional step growth epoxy-amine thermoset systems studied by Cook *et al*,²¹ (diglycidyl ether of bisphenol-A (DGEBA) and diaminodiphenyl methane (DDM)) and Gillham *et al*, (DGEBA and trimethylene glycol di-p-aminobenzoate (TGAB)).¹⁰ Figure 3.4 depicts the predicted T_g vs. the experimental T_g for the step growth radical polymerization systems, the chain growth systems and the epoxy-amine polymerization systems with the average errors of 7, 7, and 13 °C, respectively. Given the simplistic nature of the proposed relationship, the broad range of glass transition temperatures and reaction mechanisms, and the very different heterogeneity and molecular structures of the polymer products; this relatively limited error represents significant agreement between the proposed relationships and the experimental data. Moreover, we analyzed the $T_{\text{g1/2width}}$ of Gillham's DGEBA-TGAB system.¹⁰ Here, the $T_{\text{g1/2width}}$ for these thermosets ranges from 26 - 32 °C for the four T_g curves presented in the original work, which indicates that the originally proposed

empirical rule of thumb that $T_g = T_{cure} + (15 \sim 30K)$ for these polymerizations is consistent with our proposed relationship for all systems that under these circumstances $T_g \approx T_{cure} + T_{g1/2width}$.

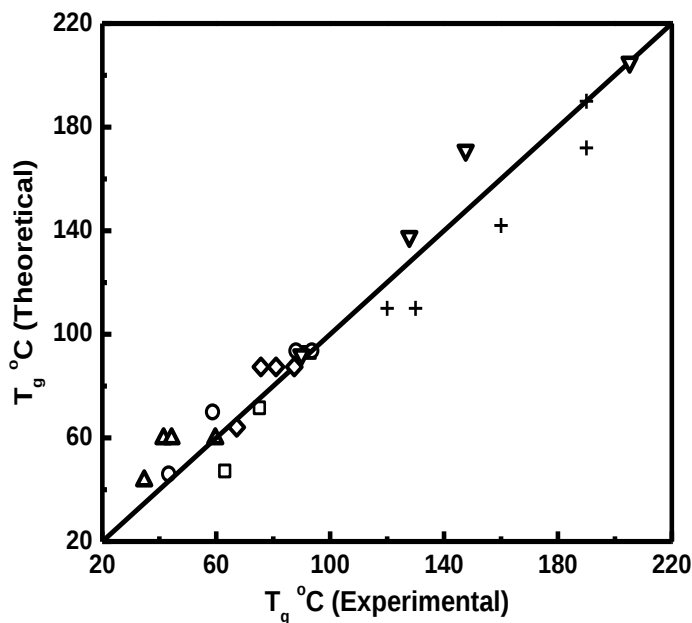


Figure 3.4. The predicted T_g (from equations 3 and 5) as a function of the experimentally determined T_g for PETMP-TMPTN ($\square$), PETMP-TCDDA ($\circ$), PETMP-TATATO ($\diamond$), HDDA (Δ), TCDDA (∇), and DGEBA-DDM (+) which were obtained from Figures 3.1 and 3.3 in Cook's paper.²¹

3.4 Conclusions

Here, the polymer T_g is determined to be a function of the cure temperature, network heterogeneity, and molecular structure. A quantitative relationship for glass transition temperature (T_g) as a function of T_{cure} , $T_{g1/2width}$ and T_{gmax} was successfully applied to a range of polymerization systems with minimal error found between experimental and predicted data for both condensation and radical-mediated step and chain growth polymerizations. For the polymerizations performed well below the maximum possible glass transition temperature, where $T_{cure} < T_{gmax} - T_{g1/2width}$, the reaction is diffusion controlled and the network heterogeneity dictates T_g such that $T_g \approx T_{cure} + T_{g1/2width}$. For other polymerizations where $T_{cure} \geq T_{gmax} - T_{g1/2width}$, the monomer structure becomes the

dominant factor and $T_g \approx T_{gmax}$. The relationships between glass transition temperature and cure temperature describe well a range of polymerization systems covering chain growth, radical step growth and condensation step growth systems.

3.5 Acknowledgements

The authors gratefully acknowledge the National Science Foundation Grant CBET 0626023 for funding this work.

3.6 References

1. Lu, H.; Lovell, L. G.; Bowman, C. N., Exploiting the heterogeneity of cross-linked photopolymers to create high- T_g polymers from polymerizations performed at ambient conditions. *Macromolecules* **2001**, 34 (23), 8021-8025.
2. Kloosterboer, J. G., Network formation by chain crosslinking photopolymerization and its applications in electronics. *Adv Polym Sci* **1988**, 84, 1-61.
3. Anseth, K. S.; Newman, S. M.; Bowman, C. N., Polymeric dental composites: Properties and reaction behavior of multimethacrylate dental restorations. *Adv Polym Sci* **1995**, 122, 177-217.
4. Anseth, K. S.; Wang, C. M.; Bowman, C. N., Kinetics evidence of reaction-diffusion during the polymerization of multi(meth)acrylate monomers. *Macromolecules* **1994**, 27 (3), 650-655.
5. Anseth, K. S.; Wang, C. M.; Bowman, C. N., Reaction behavior and kinetics constants for photopolymerizations of multi(meth)acrylate monomers. *Polymer* **1994**, 35 (15), 3243-3250.
6. Bowman, C. N.; Kloxin, C. J., Toward an enhanced understanding and implementation of photopolymerization reactions. *AIChE J* **2008**, 54 (11), 2775-2795.
7. Cook, W. D.; Forsythe, J. S.; Irawati, N.; Scott, T. F.; Xia, W. Z., Cure kinetics and thermomechanical properties of thermally stable photopolymerized dimethacrylates. *J Appl Polym Sci* **2003**, 90 (14), 3753-3766.
8. Enns, J. B.; Gillham, J. K., Time temperature transformation (TTT) cure diagram – modeling the cure behavior of thermosets. *J Appl Polym Sci* **1983**, 28 (8), 2567-2591.

9. Aronhime, M. T.; Gillham, J. K., Time temperature transformation (TTT) cure diagram of thermosetting polymeric systems. *Adv Polym Sci* **1986**, 78, 83-113.
10. Wang, X. R.; Gillham, J. K., TG-temperature property (TGTP) diagram for thermosetting systems – Anomalous behavior of physical properties vs extent of cure. *J Appl Polym Sci* **1993**, 47 (3), 425-446.
11. Venditti, R. A.; Gillham, J. K., Relationship between the glass transition temperature (T-g) and fractional conversion for thermosetting systems. *J Appl Polym Sci* **1997**, 64 (1), 3-14.
12. Wang, X. R.; Gillham, J. K., Analysis of cross-linking in amine-cured epoxy systems – the one-to-one relationship between T(G) and conversion. *J Appl Polym Sci* **1992**, 45 (12), 2127-2143.
13. Rozenberg, B. A., Kinetics, Thermodynamics and mechanism of reactions of epoxy oligomers with amines. *Adv Polym Sci* **1986**, 75, 113-165.
14. Oleinik, E. F., Epoxy-aromatic amine networks in the glassy state structure and properties. *Adv Polym Sci* **1986**, 80, 49-99.
15. Cook, W. D.; Simon, G. P.; Burchill, P. J.; Lau, M.; Fitch, T. J., Curing kinetics and thermal properties of vinyl ester resins. *J Appl Polym Sci* **1997**, 64 (4), 769-781.
16. Kloosterboer, J. G.; Lijten, G., Photopolymers exhibiting a Large difference between glass-transition and curing temperature. *Polymer* **1990**, 31 (1), 95-101.
17. Odian, G. G., *Principles of polymerization*. 4th ed.; Wiley-Interscience: Hoboken, N.J., 2004; p xxiv, 812 p.
18. Funke, W.; Okay, O.; Joos-Muller, B., Microgels - Intramolecularly crosslinked macromolecules with a globular structure. *Microencapsulation - Microgels - Iniferters* **1998**, 136, 139-234.
19. Chiu, Y. Y.; Lee, L. J., Microgel formation in the free-radical cross-linking polymerization of ethylene-glycol dimethacrylate (EGDMA) .1. Experimental. *J Polym Sci Part a-Poly Chem* **1995**, 33 (2), 257-267.
20. Sandler, S. R., *Polymer synthesis and characterization : a laboratory manual*. Academic Press: San Diego, 1998.
21. Cook, W. D.; Scott, T. F.; Quay-Thevenon, S.; Forsythe, J. S., Dynamic mechanical thermal analysis of thermally stable and thermally reactive network polymers. *J Appl Polym Sci* **2004**, 93 (3), 1348-1359.

22. Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol-enes: Chemistry of the past with promise for the future. *J Polym Sci Part a-Poly Chem* **2004**, 42 (21), 5301-5338.
23. Cramer, N. B.; Bowman, C. N., Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared. *J Polym Sci Part a-Poly Chem* **2001**, 39 (19), 3311-3319.
24. Hoyle, C. E.; Lowe, A. B.; Bowman, C. N., Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem Soc Rev* **2010**, 39 (4), 1355.
25. Hoyle, C. E.; Bowman, C. N., Thiol-ene click chemistry. *Angew Chem Int Edit* **2010**, 49 (9), 1540-1573.
26. Otsu, T.; Yoshida, M.; Tazaki, T., A model for living radical polymerization. *Makromol Chem-Rapid Comm* **1982**, 3 (2), 133-140.
27. Kannurpatti, A. R.; Lu, S.; Bunker, G. M.; Bowman, C. N., Kinetic and mechanistic studies of iniferter photopolymerizations. *Macromolecules* **1996**, 29 (23), 7310-7315.
28. Lovell, L. G.; Lu, H.; Elliott, J. E.; Stansbury, J. W.; Bowman, C. N., The effect of cure rate on the mechanical properties of dental resins. *Dent Mater* **2001**, 17 (6), 504-511.
29. Kannurpatti, A. R.; Anderson, K. J.; Anseth, J. W.; Bowman, C. N., Use of "living" radical polymerizations to study the structural evolution and properties of highly crosslinked polymer networks. *J Polym Sci Part b-Poly phys* **1997**, 35 (14), 2297-2307.
30. Carioscia, J. A.; Schneidewind, L.; O'Brien, C.; Ely, R.; Feeser, C.; Cramer, N.; Bowman, C. N., Thiol-norbornene materials: Approaches to develop highTg thiol-ene polymers. *J Polym Sci Part a-Poly Chem* **2007**, 45 (23), 5686-5696.
31. Lovell, L. G.; Berchtold, K. A.; Elliott, J. E.; Lu, H.; Bowman, C. N., Understanding the kinetics and network formation of dimethacrylate dental resins. *Polym Adv Tech* **2001**, 12 (6), 335-345.
32. Bueche, F., *Physical properties of polymers*. Interscience Publishers: New York, 1962.
33. Scheirs, J.; Priddy, D. Modern styrenic polymers polystyrenes and styrenic copolymers. John Wiley & Sons, Inc.: West Sussex, U.K., 2003.
34. Anseth, K. S.; Bowman, C. N., Reaction diffusion enhanced termination in polymerizations of multifunctional monomers. *Polym Reac Eng* **1993**, 1 (4), 499-520.

35. Lu, H.; Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N., Investigations of step-growth thiol-ene polymerizations for novel dental restoratives. *Dent Mater* **2005**, *21* (12), 1129-1136.
36. O'Brien, A. K.; Bowman, C. N., Modeling thermal and optical effects on photopolymerization systems. *Macromolecules* **2003**, *36* (20), 7777-7782.

Chapter 4

Reaction Kinetics and Reduced Shrinkage Stress of Thiol-Yne-Methacrylate and Thiol-Yne-Acrylate Ternary Systems*

Thiol-yne-methacrylate and thiol-yne-acrylate ternary systems were investigated for polymerization kinetics and material properties and compared to the analogous pure thiol-yne and (meth)acrylate systems. Both thiol-yne-methacrylate and thiol-yne-acrylate systems were demonstrated to reduce polymerization induced shrinkage stress while simultaneously achieving high glass transition temperatures (T_g) and moduli. Formulations with 70 wt% methacrylate increased the T_g from 51 ± 2 to 75 ± 1 °C and the storage modulus at ambient temperature from 1800 ± 100 to 3200 ± 200 MPa over the pure thiol-yne system. Additionally, the shrinkage stress was 1.2 ± 0.2 MPa, which is lower than that of the pure methacrylate, binary thiol-yne and thiol-ene-methacrylate control systems which are all > 2 MPa. Interestingly, with increasing methacrylate or acrylate concentration, a decrease and subsequent increase in the shrinkage stress values were observed. A minimum shrinkage stress value (1.0 ± 0.2 MPa) was observed in the 50 wt% methacrylate and 70 wt% acrylate systems. This tunable behavior results from the competitive reaction kinetics of the methacrylate or acrylate homopolymerization versus chain transfer to thiol and the accompanying thiol-yne step-growth polymerization. The crosslinking density of the networks and the amount of volumetric shrinkage that occurs prior to gelation relative to the total volumetric shrinkage were determined as two key factors that control the final shrinkage stress of the ternary systems.

4.1 Introduction

Methacrylate and acrylate resins make up the majority of photocuring systems and exhibit numerous desirable properties that include ambient cure, cure on demand, high energy efficiency and

* This chapter is from the publication S. Ye, N.B Cramer, I.R. Smith, K.R. Voigt, C.N. Bowman, accepted by *Macromolecules*

require minimal or no solvents. These systems also have limitations such as oxygen inhibition and high shrinkage stress.¹ The polymerization induced shrinkage and shrinkage stress are caused by the reduction of free volume during the formation of covalent bonds in the crosslinking networks. Shrinkage and shrinkage stress result in a variety of limitations for these systems that often result in the formation of cracks and/or delamination at the interface between the polymer and substrate.² Various methods have been used to reduce the shrinkage stress of these resin systems. Cationic ring opening polymerizations, such as oxiranes,³ siloranes⁴ or epoxides,⁵ are alternative systems that reduce shrinkage stress due to their relatively low shrinkage per mole of functional groups that react. Low shrinkage additives (pre-polymers);⁶ reactive nanogels,⁷ phase separating systems,⁸ hyper-branched polymers⁹ and dendrimers¹⁰ have all been added to resins to reduce both the shrinkage and shrinkage stress without compromising mechanical properties. Stress reductions have also been achieved by photo-induced addition fragmentation reactions that conserve the same network connectivity and properties.¹¹

Thiol-ene polymerization reactions, which proceed via a radical mediated step-growth polymerization mechanism, have also been demonstrated to maintain lower shrinkage stress due to the chain transfer step delaying gelation during the polymerization.¹² The step-growth polymerization mechanism proceeds by thiyl radical addition across a carbon-carbon double bond to form a carbon-centered radical. The carbon-centered radical subsequently abstracts a hydrogen from another thiol functional group, regenerating the thiyl radical.¹³ These alternating addition and chain transfer reactions form the basis for the step growth polymerization which results in slow and uniform network formation that leads to delayed gelation and reduced shrinkage stress as compared to chain growth methacrylate or acrylate polymerizations. Thiol-ene reactions, which are one type of click reaction, have the advantages of high selectivity and high yield with minimal side reactions while also exhibiting little sensitivity to oxygen or moisture.¹⁴ Recently, thiol-yne reactions have also been demonstrated to follow a radical step growth polymerization mechanism. The alkyne group first

reacts with a thiyl radical to generate a carbon-centered radical, which abstracts a hydrogen from a thiol monomer to generate a vinyl sulfide moiety. The double bond on the vinyl sulfide moiety reacts with another thiyl radical to generate another carbon-centered radical followed again by chain transfer to thiol. In this reaction, each alkyne group reacts twice with thiyl radicals thereby achieving a higher crosslink density and increased mechanical properties relative to other comparable thiol-ene systems.¹⁵

Ternary polymerization systems enable a way to directly tailor the network material properties because of the unique competitive reaction kinetics and network formation process. A range of previous studies has evaluated the polymerization mechanism, kinetics, and ensuing material properties of ternary (meth)acrylate-thiol-ene systems. When a methacrylate or acrylate is added to thiol-ene systems, the methacrylate or acrylate homopolymerization is accompanied with chain transfer to thiol and thiol-ene step-growth polymerization.¹⁶ A model for the reaction kinetics of thiol-ene-methacrylate ternary systems was built and evaluated the ratio of homopolymerization and chain transfer kinetic parameters.¹⁷ Due to the high amount of methacrylate homopolymerization, a pseudo two-stage hybrid polymerization was reported in thiol-ene-methacrylate systems that also resulted in the reduction of shrinkage stress.² Moreover, it has also been reported that by adding methacrylates with a bis-phenyl structure and varying the stoichiometric ratio of thiol to ene, the shrinkage stress was further reduced while maintaining modulus and strength at values close to the bulk methacrylate systems.^{18,19} The glass transition temperature (T_g) and the heterogeneity of thiol-ene-acrylate networks were able to be controlled by varying the amount and chemical structure of the acrylate monomers.²⁰ The use of addition-fragmentation reactions has also been combined with thiol-ene-methacrylate ternary systems to achieve reduced shrinkage stress.²¹

Due to the higher modulus and T_g of thiol-yne systems as compared with thiol-enes and the tunable ternary system properties, thiol-yne-methacrylate systems have significant potential to reduce shrinkage stress while maintaining or improving further the mechanical properties. Moreover, it is

interesting to investigate the mechanism of the reduction of shrinkage stress in this complex system. This work evaluated a thiol-yne model system which also incorporated methacrylate or acrylate monomers with rigid bis-phenol A core structures. The pure methacrylate, binary thiol-yne and thiol-ene-methacrylate systems were also studied for comparison. The reaction kinetics, gel point, and mechanical properties (crosslinking density, T_g , modulus) along with shrinkage and shrinkage stress were studied, and the relationship between the mechanism of shrinkage stress reduction and unique network formation was evaluated.

4.2 Experimental

Materials. 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184), pentaerythritol tetra(3-mercaptopropionate) (PETMP), and ethoxylated bisphenol A dimethacrylate (EO/phenol 1.5) (EBPADMA) were donated by BASF Corp., Evans Chemetics and Esstech Inc., respectively. 1,6-heptadiyne (HDY), 1,6-heptadiene (HDE) and ethoxylated bisphenol A diacrylate (EO/phenol 1.5) (EBPADA) were purchased from Aldrich.

FTIR Fourier transform infrared spectroscopy (FTIR) (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) combined with a vertical UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) was utilized to measure the real time conversion during curing.²² The samples were cured with 365 nm light at 10 mW/cm² in the FTIR chamber. Mid-IR was employed to study the reaction kinetics with ~10 μ m thick samples between NaCl plates. The conversion of alkyne functional groups was determined by the C-H stretch at 3288 cm⁻¹, conversion of thiol functional groups was determined by the S-H stretching at 2570 cm⁻¹, and (meth)acrylate functional group conversion was determined by the C=C vibration at 1637 cm⁻¹. To couple with various mechanical property measurements, near-IR was utilized to evaluate functional group conversions in polymerizations of 1 mm thick samples polymerized between glass slides. The alkyne and

(meth)acrylate conversions were monitored by the C-H vibration peak at 6505 cm^{-1} and the C=C vibration peak at 6163 cm^{-1} , respectively.

Mechanical Measurements. A dynamic mechanical analyzer DMA Q800 (TA Instruments) was utilized to measure the glass transition temperatures and the storage moduli of samples with $1 \times 5 \times 10\text{ mm}$ rectangular dimensions. Multi-frequency strain tension mode was utilized by applying a sinusoidal stress of 1 Hz frequency with the temperature ramping from -40 to $160\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C}/\text{minute}$. The T_g was determined as the maximum of the tan delta curve. The modulus values at ambient temperature and well into the rubbery state were measured at $25\text{ }^{\circ}\text{C}$ and at $T_g + 50\text{ }^{\circ}\text{C}$, respectively. For the pure methacrylate or acrylate systems, the modulus values for the rubbery state were read at $T_g + 100\text{ }^{\circ}\text{C}$ due to the breadth of the tan delta peak. $T_{g1/2\text{width}}$ was taken as the half width of tan delta peak at half maximum value.

Shrinkage Stress Measurement. A cantilever mode tensometer (American Dental Association Health Foundation) combined with a vertical UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) and the horizontal remote FTIR optical fibers (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) was utilized to simultaneously measure the shrinkage stress and conversion during polymerization.²³ The samples were disk shapes with 6 mm diameter and 1 mm thickness. An aluminum beam with $4.76\text{ }\mu\text{m}/\text{N}$ compliance was chosen to enable both the sensitive measurement of the low shrinkage stress values achieved in many of the ternary systems while simultaneously enabling accurate evaluation of stress values up to 2 MPa. Under these conditions, stress values greater than 2.0 MPa cannot be accurately measured and are indicated throughout the text as simply being $> 2\text{ MPa}$.

Gelation Measurement. A rheometer (ARES 4400, TA Instruments) combined with a vertical UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) and FTIR measurement achieved via optical fibers (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) was utilized to measure

the conversion at gelation during the polymerization.²⁴ Parallel plate geometry with 22 mm diameter plates and 0.3 mm thickness and dynamic stress with 20% strain was utilized. The gel point was determined as the conversion at the crossover point of the storage and loss moduli.

4.3 Results and Discussion

Figure 4.1 shows the T_g , modulus and shrinkage stress values of a polymerizing system with stoichiometric thiol-yne mixture (i.e., two thiol functional groups for each yne functional group) and varying amounts of methacrylate. These results demonstrate the feasibility of adding a methacrylate component to the thiol-yne system, and that this approach is able to increase the T_g and modulus while maintaining relatively low shrinkage stress. With increasing methacrylate ratio in this ternary system, the T_g and modulus are increased from 51 ± 2 to 75 ± 1 °C and from 1800 ± 100 to 3200 ± 400 MPa, respectively. The increase in mechanical properties is resultant from the increased amount of methacrylate homopolymerization and incorporation of the rigid bis-phenol structure into the polymer network. Due to the chain transfer to thiol that results in the mixed mode step-chain growth polymerization mechanism, the $T_{g2/1width}$, which is related to the network heterogeneity, is reduced from 75 ± 2 °C for the pure methacrylate to 34 ± 1 °C for the ternary system that still contains 70% methacrylate. At the same time, the shrinkage stress is reduced from >2 MPa to 1.2 ± 0.2 MPa. If the chain transfer step were the primary factor that results in reduced shrinkage stress, the pure thiol-yne system, which has the greatest amount of chain transfer, would be expected to have the lowest shrinkage stress. However, the shrinkage stress of the ternary systems is much lower than either the pure methacrylate or binary thiol-yne systems. This result implies that additional factors, besides chain transfer, also contribute to the overall shrinkage stress in the thiol-yne-methacrylate ternary systems. We hypothesize that a combination of the competitive reaction kinetics and the unique

network formation results in the reduction of shrinkage stress in the thiol-yne-methacrylate ternary systems.

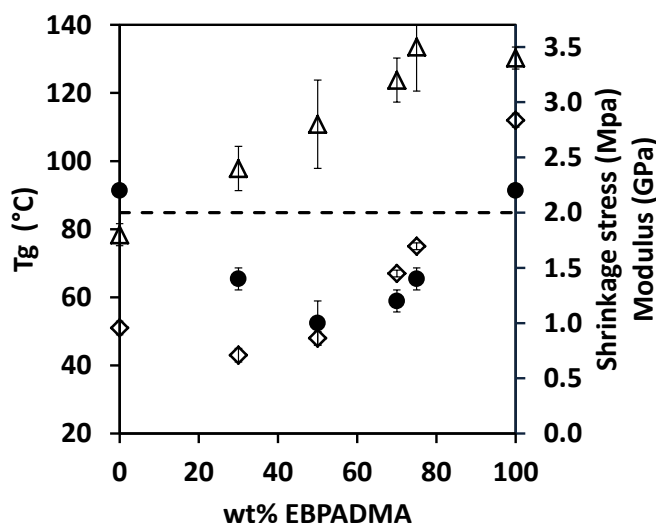
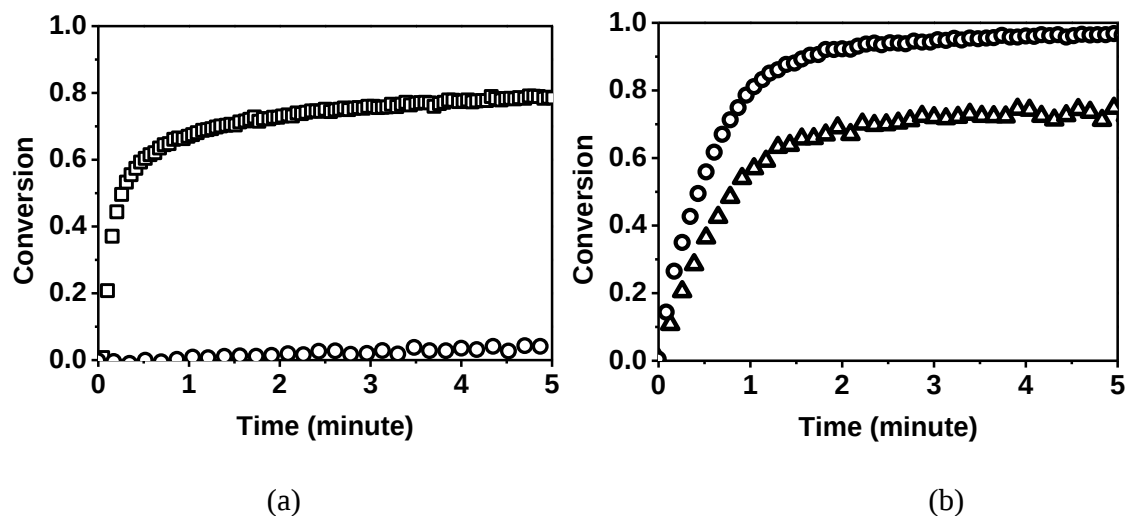
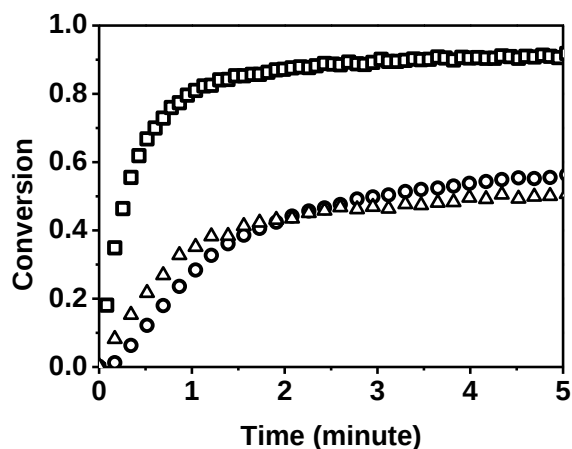


Figure 4.1. Glass transition temperature (◇), modulus (Δ) and shrinkage stress (●) of PETMP-HDY-EBPADMA (2:1:x) initiated with 1 wt% Irgacure 184 and cured by 365 nm light at 10 mW/cm². Note: 2 MPa is the maximum stress accurately measured by the tensometer under these conditions. Stress values greater than this threshold are indicative of greater than 2 MPa stress rather than exact values.

For the heptadiyne monomer, the reactivity of the thiyl radicals towards vinylsulfides is much higher than the reactivity towards alkynes, thus the concentration of vinylsulfide moieties remains low and the polymerizations are effectively monitored by following only the yne conversion.²⁵ When added to a thiol-yne reaction, the methacrylate simultaneously participates in both homopolymerization of the double bond and chain transfer to thiol. Figure 4.2(a) indicates that in the HDY-EBPADMA control system in the absence of any thiol, the alkyne group is effectively unreactive, achieving only 4% conversion, while the methacrylate functional groups achieve 80% conversion due to the homopolymerization of EBPADMA. In the pure thiol-yne control system (PETMP-HDY, Figure 4.2(b)), the thiol conversion is slightly lower than the yne conversion during the reaction because not all of the vinyl sulfide groups have reacted. For the PETMP-HDY-

EBPADMA ternary system (Figure 4.2c), there are multiple competitive reactions including the methacrylate homopolymerization, chain transfer to the thiol from the various radicals and propagation through the yne/vinyl sulfide by the thiyl radical. Initially, the thiol conversion exceeds that of the alkyne due to chain transfer from the methacrylic radical. At the latter stages of the polymerization, when the methacrylate has reached higher conversions, the thiol-yne reaction becomes the primary reaction and the yne conversion exceeds that of the thiol as in the pure thiol-yne system. The final conversions of both thiol and yne are reduced, relative to the binary system, due to vitrification that occurs at the latter stages of the polymerization. Moreover, Figure 4.3(c) also indicates the total reaction rate of methacrylate including both homopolymerization and chain transfer is higher than the thiol-yne step-growth reaction rate. However, the difference in the reaction rates is not as significant as observed in thiol-ene-methacrylate systems.^{2,19} Due to the reduced conversion of the yne functional groups in the stoichiometric thiol-yne ternary systems, off stoichiometric ratios of thiol-yne in the PETMP-YNE-EBPADMA resins were also studied (Table 4.1). Increasing the thiol ratio while keeping the amount of methacrylate constant serves to increase the amount of methacrylate chain transfer to thiol and further reduces the shrinkage stress. The overall shrinkage stress was reduced from 1.2 ± 0.1 MPa for the 2:1 thiol:yne stoichiometric system to 1.0 ± 0.1 for the 2.5:0.5 thiol:yne off stoichiometric system with the same methacrylate content.





(c)

Figure 4.2. Functional group conversion (methacrylate (□), thiol (Δ) and yne (○)) as a function of time for (a) HDY-EBPADMA (1:2.7), (b) PETMP-HDY (2:1) and (c) PETMP-HDY-EBPADMA (2:1:2.7) resins initiated with 1.0 wt% Irgacure 184, and cured by 365nm light at 10mW/cm².

Table 4.1. Shrinkage stress values for PETMP-HDY-EBPADMA cured resins with off stoichiometric thiol-yne ratios. The systems were initiated with 1.0 wt% Irgacure 184, and cured by 365nm light at 10mW/cm²

Functional group ratio Thiol: Yne: Methacrylate	Shrinkage stress (MPa)
1.5: 1: 2.7	1.4 ± 0.1
2: 1: 2.7	1.2 ± 0.1
2.5: 1: 2.7	1.1 ± 0.1
1.5: 1.5: 2.7	1.3 ± 0.1
2: 1: 2.7	1.2 ± 0.1
2.5: 0.5: 2.7	1.0 ± 0.1

Thiol-yne-acrylate systems (PETMP-HDY-EBPADMA) follow a similar reaction mechanism to the thiol-yne-methacrylate systems; however, the chain transfer reaction to the thiol is more

competitive and of comparable rate to the acrylate homopolymerization, even at relatively low acrylate conversions. To compare the extent of chain transfer to thiol between the thiol-yne-methacrylate and the thiol-yne-acrylate systems, double bond consumption per thiol was calculated in the first ten seconds of the reaction. In this regime which represents relatively low conversions, it is assumed that the reaction kinetics are not affected by any diffusional limitations associated with vitrification. The double bond consumption per thiol normalized by the initial ratio of (meth)acrylate to thiol is shown in Figure 4.3 where the slope approximately represents the kinetic parameter ratio of (meth)acrylate homopolymerization to chain transfer.¹⁶ The ratio for the thiol-yne-acrylate systems is 1.8 compared to 4.9 in the thiol-yne-methacrylate systems, indicating that the chain transfer reaction is more competitive with homopolymerization in the acrylate system. In this case, if reductions in shrinkage stress were primarily resultant from chain transfer, the shrinkage stress of the thiol-yne-acrylate systems would be expected to be lower than that of the thiol-yne-methacrylate systems. However, the shrinkage values of these two systems are very similar and are in the range of 1.0 – 1.5 MPa as shown in Figure 4.4. To evaluate further this interesting phenomenon, the polymerization kinetics of each component were studied. As seen in Figure 4.5, at early stages of the polymerization, there is a greater difference between methacrylate and yne conversion than there is between acrylate and yne conversion. This difference allows the thiol-yne component to act as a solvent in the early stages of the polymerization and results in reduced shrinkage stress development. In the thiol-yne-acrylate systems, a reduced solvation effect appears to counter balance the increased chain transfer, thereby resulting in similar overall behavior. This outcome is further evidence that the reduction of shrinkage stress in the ternary resins is resultant from a combination of both reaction kinetics and the complex network evolution. Figure 4.6 shows the final conversions of each component in the ternary systems; the final conversion of both methacrylate and acrylate double bonds (Figure 4.6 (a)) are above 0.9 and do not significantly change with increasing methacrylate or acrylate content. In contrast, the final conversions of both the alkyne (Figure 4.6 (b)) and thiol

(Figure 4.6 (c)) decrease with increasing methacrylate or acrylate content due to earlier vitrification of the networks with higher (meth)acrylic compositions. Moreover, in the thiol-yne-acrylate systems, both the thiol and yne achieve higher final conversion than those in the thiol-yne-methacrylate systems due to the general reduction in glass transition temperatures found in acrylic polymers as compared to methacrylic polymers.

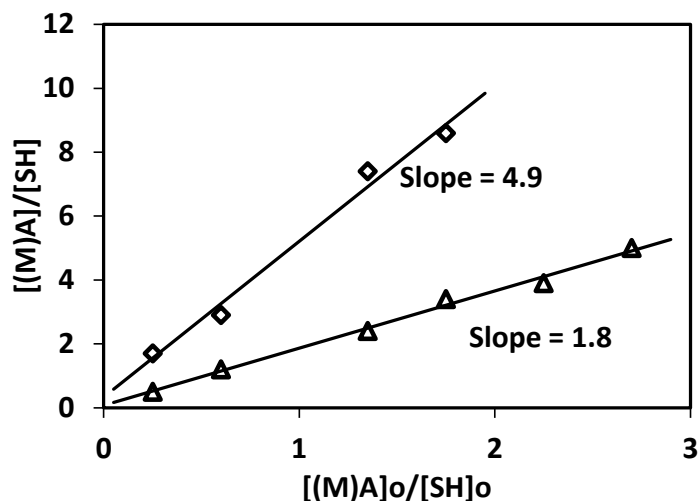


Figure 4.3. (Meth)acrylate functional group consumption per thiol functional group versus the initial ratio of (meth)acrylate to thiol functional group concentrations. PETMP-HDY-EBPADMA (2:1:x) (◇) and PETMP-HDY-EBPADA (2:1:x) (Δ) systems initiated with 1 wt% Irgacure 184 and cured by 365nm at 10mW/cm²

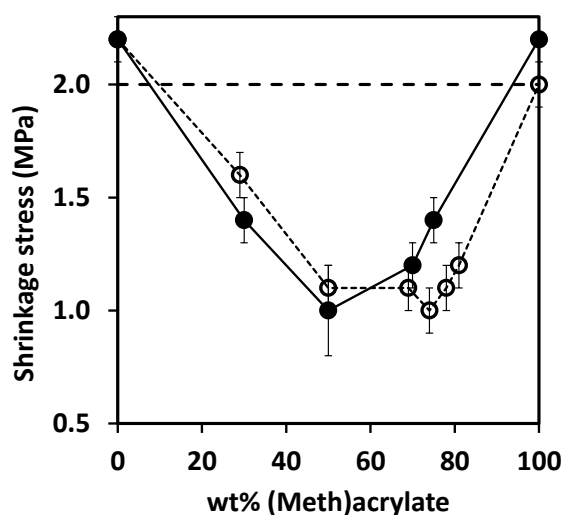


Figure 4.4. Shrinkage stress of PETMP-HDY-EBPADMA (filled symbols) and PETMP-HDY-EBPADA (open symbols) with stoichiometric thiol:yne and changing (meth)acrylate content. The

systems were initiated with 1.0 wt% Irgacure 184, and cured by 365nm light at 10mW/cm². Note: 2 MPa is the maximum range of the tensometer measurement. The stress values above this line indicate higher than 2 MPa rather than the exact values.

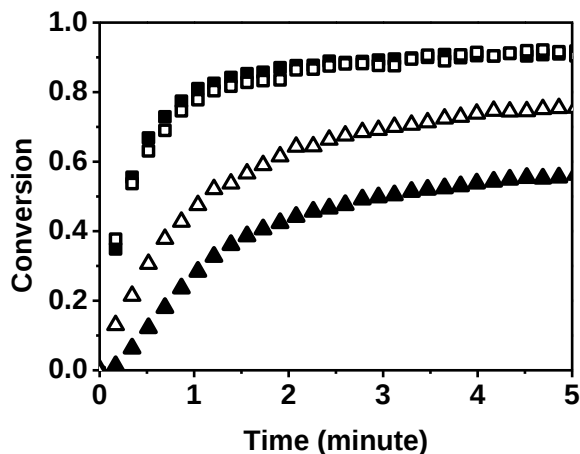
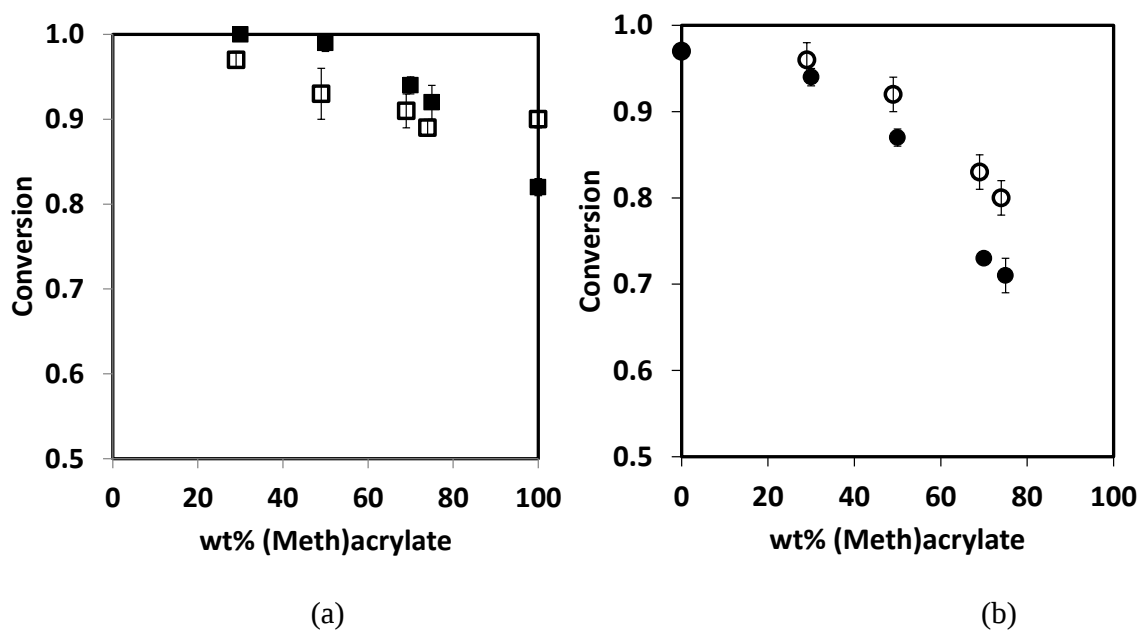
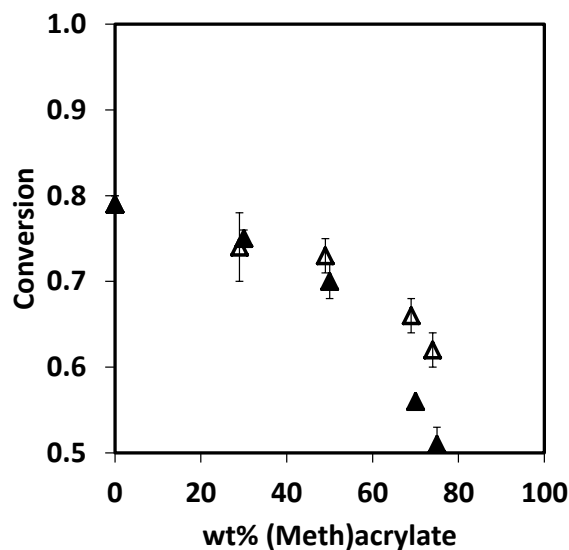


Figure 4.5. Real time conversions of 2:1:2.7 PETMP-HDY-EBPADMA (filled symbols) and 2:1:2.7 PETMP-HDY-EBPADA (open symbols) ((meth)acrylate (□) and thiol (Δ)). The systems were initiated with 1.0 wt% Irgacure 184, and cured by 365nm light at 10mW/cm².





(c)

Figure 4.6. PETMP-HDY-EBPADMA (filled symbols) and PETMP-HDY-EBPADA (open symbols) with stoichiometric thiol:yne and changing (meth)acrylate content (a) (Meth)acrylate, (b) yne, and (c) thiol conversion. The systems were initiated with 1.0 wt% Irgacure 184, and cured by 365nm light at 10mW/cm².

The crosslinking density (ρ_x) was determined at the end of the polymerization for the range of ternary systems studied from rubber elasticity theory (Equation 4.1)

$$\rho_x = \frac{E}{2(1+\gamma)RT} \quad \text{Equation 4.1}$$

in which, E is the storage modulus in the rubbery state, R is the gas constant, T is the absolute temperature, and γ is the Poisson's ratio which is assumed to be 0.5 for incompressible networks. The shrinkage stress as a function of the crosslinking density for stoichiometric thiol:yne:(meth)acrylates, off stoichiometric thiol:yne:methacrylate and thiol-ene-methacrylate control systems is plotted in Figure 4.7. The linear relationship between shrinkage stress and crosslinking density indicates that the crosslinking density plays an important role in controlling the final shrinkage stress of the ternary systems. This plot also indicates that the shrinkage stress of the pure (meth)acrylate and thiol-yne polymer networks are much higher than the ternary systems

because of the higher crosslinking density of the systems. EBPADMA ($\blacklozenge$), EBPADA ($\blacktriangle$) and PETMP-HDY ($\times$) systems achieve crosslinking densities of 6.2 ± 0.3 , 5.1 ± 0.2 and 7.0 ± 0.1 M, respectively; while the crosslinking density of the ternary systems ($\diamond$, Δ) are in the range of 2 – 4 M. Moreover, to demonstrate the importance of the increased yne functionality relative to the ene, thiol-ene-methacrylate systems with a stoichiometric ratio of thiol to ene and excess methacrylate (PETMP-HDE-DBPADMA 1.5:1.5:2.7) with similar molecular structure were studied as a control system in Figure 4.7. At the same crosslinking density value (2.7 M), the thiol-ene-methacrylate system ($\circ$) has a much higher shrinkage stress value (> 2 MPa) as compared with the thiol-yne-(meth)acrylate systems (~ 1.1 MPa) demonstrating the advantages of the thiol-yne-(meth)acrylate systems to reduce shrinkage stress.

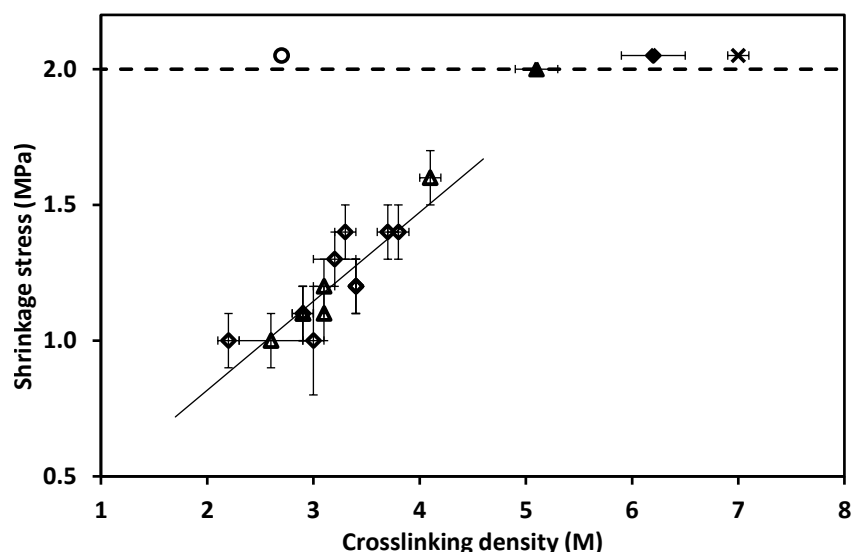


Figure 4.7. Shrinkage stress versus crosslinking density of PETMP-HDY-EBPADMA systems. PETMP-HDY-EBPADMA (2:1:x and x:y:2.7) ($\diamond$), PETMP-HDY-EBPADA (2:1:x) (Δ), EBPADMA ($\blacklozenge$), EBPADA ($\blacktriangle$), PETMP-HDY (2:1) ($\times$) and PETMT-HDE-EBPADMA (1.5:1.5:2.7) ($\circ$). All resins were initiated with 1 wt% Irgacure 184 and were cured by 365nm light at 10mW/cm². Note: 2 MPa is the maximum stress accurately measured by the tensometer under these conditions. Stress values greater than this threshold are indicative of greater than 2 MPa stress rather than exact values.

The competitive reaction kinetics in thiol-yne-(meth)acrylate ternary systems leads to a unique network formation process. The radical mediated step-growth mechanism of the thiol-yne reaction and the (meth)acrylate chain transfer to thiol delay gelation during the polymerization. Figure 4.8 shows how the shrinkage stress develops with conversion for different reaction mechanisms. The pure dimethacrylate system (1) builds up the stress at a very low conversion and reaches a high final stress value (> 2 MPa) due to the early gelation and subsequent vitrification associated with this homopolymerization. Prior to gelation, the resin systems are able to accommodate for the polymerization induced shrinkage through material flow, thus generating minimal stress. The shrinkage stress is primarily built up after gelation due to the restricted mobility and relaxation of the gel accompanied by the subsequent vitrification of the network.² However, this theory does not fully account for the behavior of the thiol-yne binary system as evidenced in Figure 4.8. The thiol-yne binary system (2) follows the step-growth polymerization mechanism and the gelation is significantly delayed, but this polymerization still reaches a high final stress (> 2 MPa) resulting from the high final crosslinking density (7.0 ± 0.1 M). The 2PETMP-1HDY-2.7EBPADMA thiol-yne-methacrylate system (3) builds up the stress later resulting from the mixed mode step-chain growth polymerization; and obtains a relatively lower crosslinking density (3.4 ± 0.1 M) and final stress (1.2 ± 0.1 MPa). As a control system, the thiol-ene-methacrylate (1.5PETMP-1.5HDE-2.7EBPADMA) (4) builds up stress slightly earlier than thiol-yne-methacrylate system, since each alkene reacts with only a single thiol. Also the shrinkage stress of the thiol-ene-methacrylate builds up faster than the thiol-yne-methacrylate system due to the faster reaction rate at the same curing condition. Therefore, this behavior indicates that delaying gelation contributes to, but is not the dominant factor controlling the reduction of shrinkage stress. Moreover, the shape of these curves relating to the network formation and stress development was investigated. The shrinkage stress value for the pure methacrylate system increases gradually with increasing conversion because the chain growth mechanism creates a very heterogeneous network with a broad glass transition region ($T_{g1/2width} \sim 75$

± 1 °C) enabling a greater amount of polymerization to occur after vitrification. In contrast, the step-growth mechanism of the thiol-yne binary system leads to a more homogeneous network with a narrow $T_{g1/2width}$ (17 ± 1 °C) so that less polymerization occurs after vitrification, and the stress builds up rapidly after 50% conversion of the alkyne groups. The $T_{g1/2width}$ of the thiol-yne-methacrylate (2:1:2.7) is 34 ± 1 °C indicating that the heterogeneity of the network is between that of the pure methacrylate and thiol-yne systems. Thus, the shape of the stress curve is a combination of these behaviors as well.

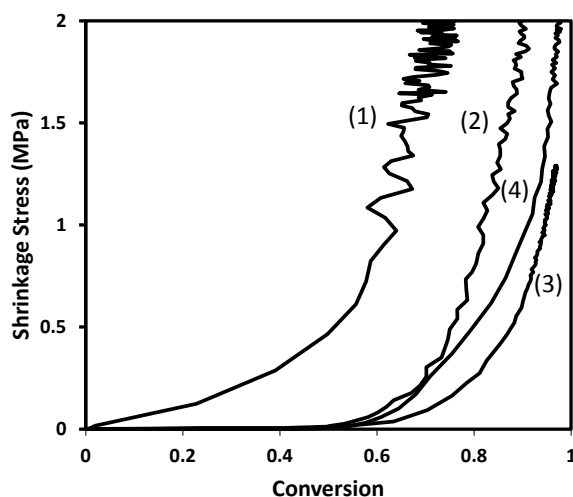


Figure 4.8. Shrinkage stress versus conversion of EBPADMA (1), PETMP-HDY 2:1 (2), PETMP-HDY-EBPADMA 2:1:2.7 (3) and PETMP-HDE-EBPADMA 1.5:1.5:2.7 (4). The systems were initiated with 1 wt% Irgacure 184, and cured by 365nm light at 10mW/cm².

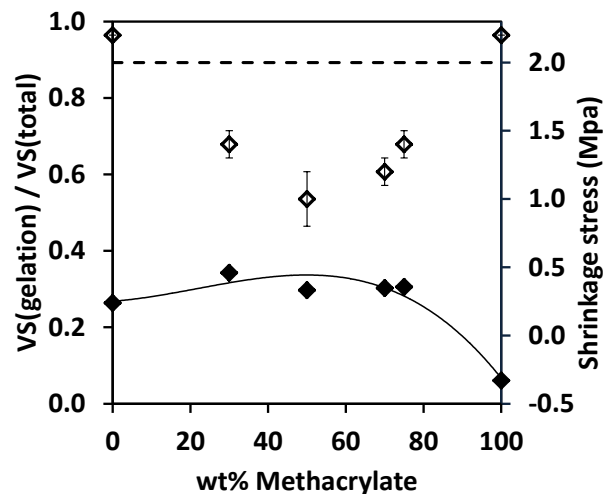
Here, we introduce a new parameter, the ratio of the volumetric shrinkage at gelation to the final volumetric shrinkage. This parameter is representative of the network formation and correlates to shrinkage stress. The polymerization induced shrinkage stress is related to the volumetric shrinkage of the resin during network formation. Shrinkage stress primarily results from volume shrinkage that occurs post gelation. The volumetric shrinkage of the resin systems before gelation is theoretically calculated based on the conversion of each component at the gel point and the total volumetric shrinkage is calculated based on the final conversion of each component by equation (4.2).²⁶

$$VS = \sum_i (C_{0i} \cdot X_i \cdot SF_i) \quad \text{Equation 4.2}$$

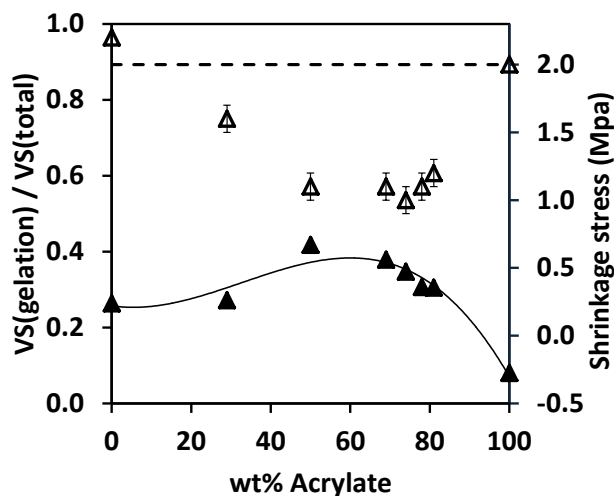
VS is volumetric shrinkage, C_0 is the initial concentration of the functional group, X is conversion, SF is the shrinkage factor (listed in Table 4.2) and i represents each functional group in the resin system. The assumption is 1) alkyne and vinylsulfide only react with thiol, and 2) the proportion consumptions of thiol reacting with alkyne and vinylsulfide in both binary and ternary systems are the same if the alkyne conversions are the same. The percentage of volumetric shrinkage before gelation relative to the total shrinkage was calculated and plotted versus (meth)acrylate content in Figure 4.9. The shrinkage ratio of both thiol-yne-methacrylate and thiol-yne-acrylate systems are seen to increase and then decrease with increasing methacrylate or acrylate content, which inversely correlates to the final shrinkage stress. The lowest shrinkage stress was observed in the systems containing 50 wt% methacrylate or 70 wt% acrylate (Figure 4.9), which indicates that at these double bond concentrations, the competitive reaction kinetics result in a maximum volumetric shrinkage that occurs before gelation relative to the total volumetric shrinkage.

Table 4.2. Shrinkage factors of thiol-yne-methacrylate systems

Mixed reaction mechanisms in the ternary systems	Shrinkage factor (mL/mol)	Notes
Methacrylate homopolymerization	22.6	Reference ²⁶
Methacrylate chain transfer to thiol	12.6	Estimated as a thiol-ene reaction ²⁶
Yne reacting with thiol once	12.6	Estimated as a thiol-ene reaction ²⁶
Yne reacting with thiol twice	21.0	Measured by butyl 3-mercaptopropionate with 1-octyne



(a)



(b)

Figure 4.9. The fraction of volumetric shrinkage that occurs prior to gelation relative to the total volume shrinkage (filled symbols) and shrinkage stress (open symbols) versus (meth)acrylate content. (a) PETMP-HDY-EBPADMA 2:1:x and (b) PETMP-HDY-EBPADA 2:1:x. The systems were initiated with 1.0 wt% Irgacure 184, and cured by 365nm light at 10mW/cm². Note: 2 MPa is the maximum stress accurately measured by the tensometer under these conditions. Stress values greater than this threshold are indicative of greater than 2 MPa stress rather than exact values.

4.4 Conclusions

Thiol-yne-methacrylate and thiol-yne-acrylate ternary systems are demonstrated as resin systems that achieve high glass transition temperatures and moduli while maintaining low shrinkage stress. The crosslinking density and the percentage of volumetric shrinkage before gelation relative to the total shrinkage were investigated as factors that control the final shrinkage stress. The shrinkage stress of the ternary systems is lower than both the pure (meth)acrylate and pure thiol-yne resins; and the lowest shrinkage stress was observed in the ternary system with 50 wt% methacrylate or 70 wt% acrylate. This tunable behavior is resultant from the competitive reaction kinetics and unique network formation process. When (meth)acrylate is added to the thiol-yne step growth system, gelation is delayed causing more volumetric shrinkage to occur before gelation relative to the total volumetric shrinkage; thereby reducing the shrinkage stress.

4.5 Acknowledgements

The authors gratefully acknowledge the National Science Foundation CBET 0626023 and National Institutes of Health NIH/NIDCR Grants DE10959 and DE018233-0142 for funding this work.

4.6 References

1. Fouassier, J.-P.; Rabek, J. F., *Radiation curing in polymer science and technology, volume 1. Fundamentals and methods*. Elsevier Applied Science: London; New York, 1993.
2. Lee, T. Y.; Carioscia, J.; Smith, Z.; Bowman, C. N., Thiol-allyl ether-methacrylate ternary systems. Evolution mechanism of polymerization-induced shrinkage stress and mechanical properties. *Macromolecules* **2007**, *40* (5), 1473-1479.
3. Eick, J. D.; Kostoryz, E. L.; Rozzi, S. M.; Jacobs, D. W.; Oxman, J. D.; Chappelow, C. C.; Glaros, A. G.; Yourtee, D. M., In vitro biocompatibility of oxirane/polyol dental composites with promising physical properties. *Dent Mater* **2002**, *18* (5), 413-421.

4. Van Ende, A.; De Munck, J.; Mine, A.; Lambrechts, P.; Van Meerbeek, B., Does a low-shrinking composite induce less stress at the adhesive interface? *Dent Mater* **2010**, 26 (3), 215-222.
5. Bretscher, K. R.; Rusin, R. P.; Craig, B. D.; Mitra, S. B.; Oxman, J. D.; Gust, J. R.; Hayne, C. A.; Westberg, J. W.; Trom, M. C.; Kolb, B. U.; Jacobs, D. W.; Kaisaki, D. A.; Baker, J. A. Radiopaque cationically polymerizable compositions comprising a radiopacifying filler. 1999-US5717; 2000020494, 19990316., 2000.
6. Cao, X.; Lee, L. J., Control of shrinkage and final conversion of vinyl ester resins cured in low-temperature molding processes. *J Appl Polym Sci* **2003**, 90 (6), 1486-1496.
7. Moraes, R. R.; Garcia, J. W.; Barros, M. D.; Lewis, S. H.; Pfeifer, C. S.; Liu, J.; Stansbury, J. W., Control of polymerization shrinkage and stress in nanogel-modified monomer and composite materials. *Dent Mater* **2011**, 27 (6), 509-519.
8. Cramer, N. B.; Stansbury, J. W.; Bowman, C. N., Recent Advances and Developments in Composite Dental Restorative Materials. *J Dent Res* **2011**, 90 (4), 402-416.
9. Dodiuk-Kenig, H.; Lizenboim, K.; Eppelbaum, I.; Zalsman, B.; Kenig, S., The effect of hyper-branched polymers on the properties of dental composites and adhesives. *J Adh SciTech* **2004**, 18 (15-16), 1723-1737.
10. Mezzenga, R.; Boogh, L.; Manson, J. A. E., A review of dendritic hyperbranched polymer as modifiers in epoxy composites. *Compo Sci Tech* **2001**, 61 (5), 787-795.
11. Scott, T. F.; Draughon, R. B.; Bowman, C. N., Actuation in crosslinked polymers via photoinduced stress relaxation. *Adv Mater* **2006**, 18 (16), 2128-2132.
12. Bowman, C. N.; Kloxin, C. J., Toward an enhanced understanding and implementation of photopolymerization reactions. *AIChE J* **2008**, 54 (11), 2775-2795.
13. Cramer, N. B.; Bowman, C. N., Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared. *J Polym Sci Part a-Poly Chem* **2001**, 39 (19), 3311-3319.
14. Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol-enes: Chemistry of the past with promise for the future. *J Polym Sci Part a-Poly Chem* **2004**, 42 (21), 5301-5338.
15. Fairbanks, B. D.; Sims, E. A.; Anseth, K. S.; Bowman, C. N., Reaction rates and mechanisms for radical, photoinitiated addition of thiols to alkynes, and implications for thiol-yne photopolymerizations and click reactions. *Macromolecules* **2010**, 43 (9), 4113-4119.

16. Reddy, S. K.; Cramer, N. B.; Bowman, C. N., Thiol-vinyl mechanisms. 2. Kinetic modeling of ternary thiol-vinyl photopolymerizations. *Macromolecules* **2006**, 39 (10), 3681-3687.
17. Reddy, S. K.; Cramer, N. B.; Kalvaitas, M.; Lee, T. Y.; Bowman, C. N., Mechanistic modelling and network properties of ternary thiol-vinyl photopolymerizations. *Aust J Chem* **2006**, 59 (8), 586-593.
18. Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Boulden, J. E.; Wydra, R.; Stansbury, J. W.; Bowman, C. N., Properties of methacrylate–thiol–ene formulations as dental restorative materials. *Dent Mater* **2010**, 26 (8), 799-806.
19. Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Carioscia, J. A.; Boulden, J. E.; Stansbury, J. W.; Bowman, C. N., Investigation of thiol-ene and thiol-ene–methacrylate based resins as dental restorative materials. *Dent Mater* **2010**, 26 (1), 21-28.
20. Senyurt, A. F.; Wei, H. Y.; Hoyle, C. E.; Piland, S. G.; Gould, T. E., Ternary thiol-ene/acrylate photopolymers: Effect of acrylate structure on mechanical properties. *Macromolecules* **2007**, 40 (14), 4901-4909.
21. Park, H. Y.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N., Covalent adaptable networks as dental restorative resins: Stress relaxation by addition–fragmentation chain transfer in allyl sulfide-containing resins. *Dent Mater* **2010**, 26 (10), 1010-1016.
22. Lovell, L. G.; Berchtold, K. A.; Elliott, J. E.; Lu, H.; Bowman, C. N., Understanding the kinetics and network formation of dimethacrylate dental resins. *Polym Adv Tech* **2001**, 12 (6), 335-345.
23. Lu, H.; Stansbury, J. W.; Dickens, S. H.; Eichmiller, F. C.; Bowman, C. N., Probing the origins and control of shrinkage stress in dental resin-composites: I. Shrinkage stress characterization technique. *J Mater Sci-Mater Med* **2004**, 15 (10), 1097-1103.
24. Pfeifer, C. S.; Wilson, N. D.; Shelton, Z. R.; Stansbury, J. W., Delayed gelation through chain-transfer reactions: Mechanism for stress reduction In methacrylate networks. *Polymer* **2011**, 52 (15), 3295-3303.
25. Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N., Thiol-yne photopolymerizations: Novel mechanism, kinetics, and step-growth formation of highly cross-linked networks. *Macromolecules* **2009**, 42 (1), 211-217.
26. Lu, H.; Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N., Investigations of step-growth thiol-ene polymerizations for novel dental restoratives. *Dent Mater* **2005**, 21 (12), 1129-1136.

Chapter 5

Using Hyperbranched oligomer Functionalized Glass Fillers in Ternary Resin Composites to Reduce Shrinkage Stress*

Fillers are widely utilized to enhance the mechanical properties of polymer resins. However, at the same time the polymerization induced shrinkage stress also has the potential to increase due to the increasing modulus. Here, we demonstrate a new type of composite system which is able to reduce the shrinkage stress without sacrificing mechanical properties. Silica nanoparticles are functionalized with a flexible 16-functional alkene-terminated hyperbranched oligomer which is synthesized by multistage thiol-ene/yne reactions. 93% of the particle surface was covered by this oligomer and an interfacial layer ranging from 0.8 – 4.5 nm thickness is generated. A composite system with these functionalized silica nanoparticles incorporated into the thiol-yne-methacrylate demonstrates 30% reduction of shrinkage stress (from 0.9 MPa to 0.6 MPa) without sacrificing the modulus (3200 ± 200 MPa) or glass transition temperature (62 ± 3 °C). Moreover, the shrinkage stress of the composite system builds up at much later stages of the polymerization as compared to the control system.

5.1 Introduction

Inorganic fillers are widely incorporated into photocurable resins to increase the mechanical properties, especially the modulus and hardness. These inorganic fillers are often functionalized with reactive organic groups so that the filler and the polymer matrix are integrated by covalent bonds between the phases to achieve enhanced reinforcement.¹ Shrinkage and shrinkage stress are unavoidably generated during polymerization due to the accompanying volume shrinkage and the gelation of the polymer network. In filled systems, the shrinkage is reduced by reducing the volume

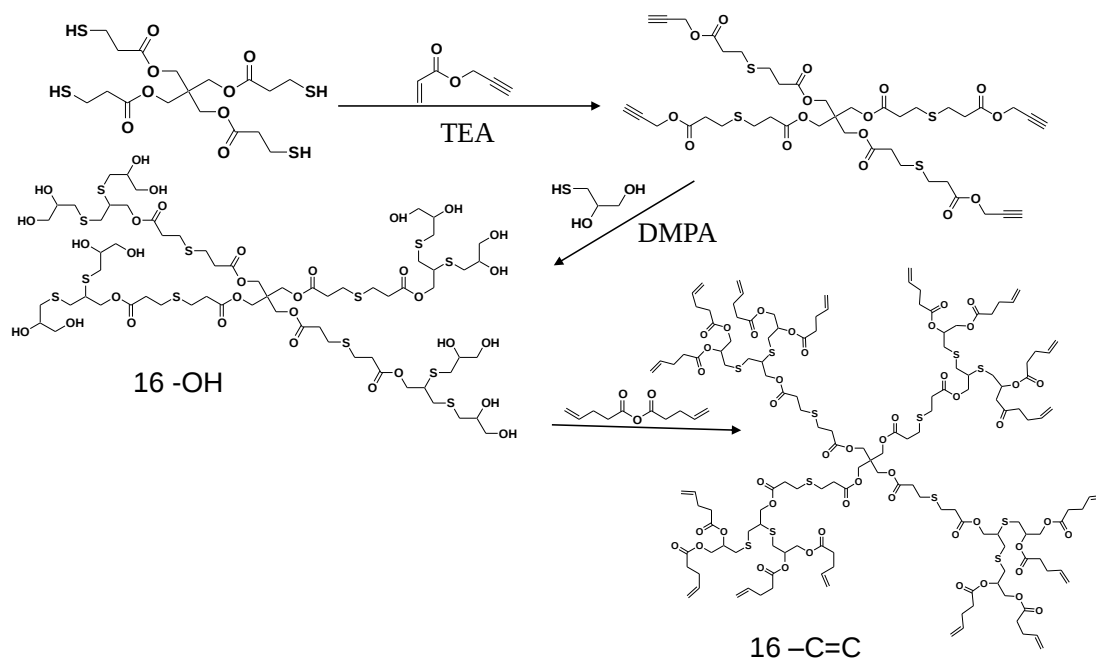
* This chapter is from the publication S. Ye, N.B. Cramer, S. Azarnoush, I.R. Smith, C.N. Bowman, submitted to *Dental Materials*.

fraction of the resin;² however, the overall shrinkage stress in some cases may increase due to the increased modulus of the composites, and this general behavior is predicted according to Hooke's law³. Under these conditions, stress is generated throughout the resin and is often concentrated at the resin-filler interface. The stress accumulates at the resin/filler interface because the filler is the lowest compliance portion of the composites.⁴ Moreover, during the exothermic radical polymerization, a significant difference in the temperature and thermal expansion arises between the polymer matrix and the inorganic filler, resulting in further stress accumulation at the resin/filler interface.⁵ As discussed in section 1.2.1, many studies have focused on modifying the resin systems as a means to reduce shrinkage stress. In contrast, there are far fewer methods that have been investigated for modifying the filler/resin interface as a means to reduce the shrinkage stress. In one collection of work, Stansbury and coworkers reported that shrinkage stress is reduced when glass filler is functionalized with polymer brushes that serve as an interfacial layer to mitigate stress development.^{6,7}

In recent years, dendrimers and hyperbranched polymers have been reported as an additional component in polymer resin systems that reduce shrinkage or shrinkage stress as compared with other similar molecular weight molecules. It has been reported that mixtures of dendrimers and epoxy composites reduced polymerization shrinkage stress based on the different reactivities of the dendrimer and the resin systems;⁸ and that the mixture of the hyper-branched polymers and dental resin systems reduces the volumetric shrinkage.⁹ With this potential to reduce shrinkage or shrinkage stress, it will be interesting to explore the use of a hyperbranched polymer as an interfacial layer between the filler and resin in the composite system. In this chapter, a flexible hyperbranched molecular structure is designed and immobilized on the glass filler (i.e. the glass filler is functionalized with the hyperbranched oligomer rather than just mixing them into the formulation). Using the hyperbranched oligomer as an interfacial layer provides lower compliance and enough mobility between the polymer matrix and the inorganic fillers to reduce the shrinkage stress.

Moreover, the highly available functional groups on the surface of the hyperbranched oligomer may also improve the efficiency of the covalent bounding between the glass filler and the resin.

The benefits of utilizing click reactions to synthesize dendrimers were described in Chapter 1. In particular, thiol-ene reactions have been utilized to control molecular architecture in polymer systems as synthetic routes for dendrimer synthesis have been developed implementing thiol-X click reactions of various types^{10,11} because of the advantages of high conversion, solvent free formulation, UV initiated reaction and limited oxygen inhibition.¹² Different types of thioether¹³ and double bond terminated dendrimers¹⁴ have been synthesized, and it has been reported that a combination of two click reactions, the CuAAC and thiol-ene reactions, was utilized to synthesize a 6-generation dendrimer in a single day.¹⁵ Thiol-yne reactions have also been employed in dendrimer synthesis,¹⁶ and a sixteen-functional alcohol or acid functionalized oligomer was synthesized from a tetrayne and an AB₂ molecule via a one-step reaction.¹⁷ Based on those methods, here, a 16-alkene-terminated hyperbranched oligomer was synthesized via a combination of thiol/acrylate and thiol-yne reactions as shown in Scheme 5.1. First, a tetrathiol core was reacted with propargyl acrylate via a thiol/acrylate Michael addition using triethylamine as the catalyst to obtain a tetrayne molecule,¹⁸ which was further reacted with thioglycerol via a thiol-yne click reaction initiated by a UV photoinitiator Irgacure 651.¹⁷ Subsequently, a condensation reaction of alcohol and anhydride was carried out to obtain a 16 alkene functional hyperbranched oligomer.¹⁴ Then this hyperbranched alkene oligomer is immobilized to the thiol functionalized glass filler via a UV photoinitiated thiol-ene reaction. The reaction kinetics, mechanical properties and shrinkage stress of the ternary resin systems incorporated with the hyperbranched oligomer functionalized glass filler were studied.



Scheme 5.1 Synthesis route for making the 16 functional alkene-terminated hyperbranched oligomer.

5.2 Experimental

5.2.1 Materials

Propargyl acrylate, triethylamine (TEA), thioglycerol, *N,N*-dimethylformamide (DMF), 4-pentenoic anhydride, anhydrous tetrahydrofuran (THF), pyridine, 4-(dimethylamino)pyridine (DMPA), trans-indole acrylic acid (IAA), and sodium citrate monobasic were purchased from Sigma-Aldrich. Dichloromethane (DCM), ethyl ether, hexane, ethyl acetate, sodium bicarbonate, sodium chloride and anhydrous sodium sulfate were purchased from Fisher. 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651) and 1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184) was donated by BASF Co. Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Evans Chemetics.

5.2.2 Experimental details

5.2.2.1 Synthesis of 4-functional alkyne molecule

PETMP (4.88 g, 10 mmol) was dissolved in 120 mL DCM in a one-neck round flask and TEA (0.28 mL, 2 mmol) was added. 4.4 equivalents (to PETMP) of propargyl acrylate (4.84 g, 44 mmol) was dissolved in 60 mL DCM and added dropwise to the flask by an addition funnel. The reaction was left overnight with stirring. Then, the reaction mixture was washed by saturated sodium citrate monobasic, saturated sodium bicarbonate and brine (3 × 200 mL each). The organic layer was dried over anhydrous sodium sulfate, filtered and then concentrated. A clear viscous liquid (14 g, 15 mmol, 75% yield) was obtained. ^1H NMR (300 MHz, CDCl_3 , δ (ppm)): δ 4.67 (8H), δ 4.12 (8H), δ 2.80 – 2.73 (16H), δ 2.65 – 2.57 (16H), δ 2.48 (4H).

5.2.2.2 Synthesis of 16 functional alcohol-terminated oligomer

The 4-functional alkyne (14 g, 15 mmol) was dissolved in 40 mL DMF in a one-neck round flask and mixed with thioglycerol (13.7 g, 127 mmol, 5% excess) and Irgacure 651 (1.35 g, 5 mmol, 5 wt%). The flask was vacuumed and purged by nitrogen with stirring. The sample was irradiated by a UV light source (Acticure, EFOS, Mississauga, Ontario, Canada) passing through a 320~500 nm filter at 10 mW/cm^2 for 4 hours. After rotavapping the DMF, the viscous material was precipitated by ethyl ether five times and dried overnight. A yellow viscous liquid (17 g, 9.5 mmol, 63% yield) was obtained. ^1H NMR (300 MHz, $\text{DMSO-}d_6$, δ (ppm)): δ 4.84 – 4.75 (8H), δ 4.60 – 4.54 (8H), δ 4.31 – 4.05 (16H), δ 3.60 – 3.51 (8H), δ 3.21 – 3.13 (4H).

5.2.2.3 Synthesis of 16 hyperbranched alkene-terminated oligomer

The 16-functionanl alcohol (4.73 g, 2.6 mmol) was dissolved in 150 mL anhydrous THF in a one-neck round flask and purged with argon. This liquid was transferred to a three-neck flask with molecular sieves. 0.15 equivalents (to alcohol group) of DMAP (0.77 g, 6 mmol), 3 equivalents of anhydrous pyridine (10 g, 126 mmol) and 3 equivalents of 4-pentenoic anhydride (23 g, 126 mmol)

added to the flask with stirring. The reaction was left overnight, quenched by water, and then diluted by DCM and filtered. The reaction mixture was then washed by water (5 × 300 mL), saturated sodium bicarbonate and brine (3 × 200 mL each). The organic layer was dried over anhydrous sodium sulfate, filtered and then concentrated. A clear viscous liquid (4.7 g, 1.5 mmol, 57% yield) was obtained. ¹H NMR (300 MHz, CDCl₃, δ (ppm)): δ 5.90 – 5.72 (16.5H), δ 5.20 – 4.95 (41.8H), δ 4.46 – 4.05 (32H), δ 3.19 – 3.03 (3.7H), δ 2.95 – 2.49 (55.4H), δ 2.49 – 2.28 (67.6H).

5.2.2.4 Synthesis of thiol functionalized glass filler

Silica nanoparticles OX50 (5 g) were added to 100 mL cyclohexane with stirring until well dispersed in a one-neck round flask. n-propylamine (0.1 g) was added to the mixture with stirring for 15 minutes. (3-mercaptopropyl)trimethoxysilane (0.5 g) was added to the mixture and reacted for 30 minutes at room temperature followed by increasing the temperature to 60 °C to react for another 30 minutes. The solvent was removed at 60 °C and the powder was heated 90 °C for 1 hour by a rotary evaporator. The powder was then dried at 80 °C in a vacuum oven overnight.¹⁹

5.2.2.5 Reactive immobilization of the hyperbranched oligomer to the glass filler

The 16 alkene-terminated hyperbranched oligomer (0.5 g) and Irgacure 651 (0.05 g) were dissolved in 10 mL DMC in a one-neck round flask. Silica nanoparticles OX50 (1 g) were added to the mixture with stirring until well dispersed. Then, the mixture was reacted under 320 – 500 nm UV light at 15 mW/cm² for 2 hours. The particles were isolated by centrifuge and washed by DCM 3 times, then finally dried in a vacuum oven at 35 °C overnight.

5.2.3 Characterizations

5.2.3.1 Characterizations of the hyperbranched oligomer

300 MHz NMR spectrometer (Bruker 300 UltraShield) was used to obtain ¹H spectra. The chemical shifts are referenced to CHCl₃ 7.25 ppm and DMSO 2.5 ppm. MALDI-TOF (positive

mode) was used to determine the molecular weight of the product. 200mg product was dissolved in 1:1 methanol/DCM and IAA was used as the matrix. Gel permeation chromatography (GPC) (Viscotek 3580) was performed in tetrahydrofuran (THF) with a differential refractive index detector.

5.2.3.2 Characterizations of the particles

Thermogravimetric analysis (TGA) (Pyris 7, Perkin Elmer) was utilized to determine the weight loss from functionalized silica particles. The weight change of a 10 mg sample as a function of temperature was evaluated with temperature ramping from 50 - 850 °C at 10 °C/min under nitrogen flow at 20 mL/min.

5.2.3.3 Characterizations of the filler composites

Fourier transform infrared spectroscopy (FTIR) (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) combined with a UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) was utilized to measure the real time conversion during curing. The samples were cured with 365 nm light at 10 mW/cm² in the FTIR chamber. Mid-IR was employed to study the reaction kinetics with ~10 µm thick samples between NaCl plates. The conversion of the alkyne functional groups was determined by the C-H stretch at 3288 cm⁻¹, conversion of the thiol functional groups was determined by the S-H stretch at 2570 cm⁻¹, and the methacrylate functional group conversion was determined by the C=C vibration at 1637 cm⁻¹. To couple with various mechanical property measurements, near-IR was utilized to evaluate functional group conversions in polymerizations of 1 mm thick samples polymerized between glass slides. The alkyne and methacrylate conversions were monitored by the C-H vibration peak at 6505 cm⁻¹ and the C=C vibration peak at 6163 cm⁻¹, respectively.

A dynamic mechanical analyzer DMA Q800 (TA Instruments) was utilized to measure the glass transition temperatures and moduli of samples with 1 x 2 x 10 mm rectangular dimensions. Multi-frequency strain mode was utilized by applying a sinusoidal stress of 1 Hz frequency with the

temperature ramping from -40 to 160 °C at 3 °C/minute. The T_g was determined as the maximum of the tan delta curve. The modulus values at ambient temperature and well into the rubbery state were measured at 25 °C and at $T_g + 50$ °C, respectively.

A cantilever mode tensometer (American Dental Association Health Foundation) combined with a UV-light source (Acticure, EFOS, Mississauga, Ontario, Canada) and the simultaneous implementation of FTIR via optical fibers (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) was utilized to measure the shrinkage stress and conversion during polymerization. The samples were disk shapes with 6 mm diameter and 1 mm thickness. An aluminum beam with 3.6 $\mu\text{m}/\text{N}$ compliance was chosen to enable the stress measurement of all the test and control formulations.

5.3 Results and discussion

The first step product tetra-yne was synthesized via the thiol-acrylate Michael addition reaction between propargyl acrylate and PETMP in DCM catalyzed by triethylamine. The peaks in the range of 6.5 – 5.7 ppm (1 and 2) shown in Figure 5.1(a) and the peak from 1.7 -1.5 ppm (3) shown in Figure 5.1(b) correspond to alkene protons on the acrylate and the thiol proton on PETMP, respectively. These peaks disappear in the spectrum of the product (Figure 5.1c) clearly indicating the reaction completion. After liquid-liquid extraction to remove the catalyst, a clear viscous liquid product with 75% yield was obtained.

The second step product is a 16 hydroxyl-terminated oligomer synthesized by the thiol-yne click reaction. The initial tetrayne product was reacted with thioglycerol (Figure 5.2 a) under 320 – 500 nm UV light irradiation with Irgacure 651 as the photoinitiator in DMF. The peaks in the range of 4.8 – 4.5 ppm (4 and 5) and near 2 ppm (6) correspond to the protons on the hydroxyl and thiol, respectively. Comparing with Figure 5.2 (a) and (b), peak (6) was significantly reduced and peak 4 and 5 showed around 16 hydrogens on the hydroxyl groups, indicating the reaction reaches high

conversion, which was also supported by IR evaluation. Figure 5.3(a) shows the IR spectrum before and after reaction of the thiol (2675 cm^{-1}) and alkyne (2130 cm^{-1}). The disappearance of these two peaks indicates the high conversion achieved in the thiol-yne click reaction. Here, the IR study was conducted with a $\sim 50\text{ }\mu\text{m}$ thin resin layer reacted between two salt plates which is much different from starting with $\sim 14\text{ g}$ of reactants in a round bottom flask. Therefore, even though Figure 5.3 (b) shows the reaction between the salt plates almost reached full conversion in less than a half minute, the large scale reaction was still run for 4 hours to achieve maximum conversion. After precipitation in ethyl ether to remove the unreacted thioglycerol, a yellowish clear viscous liquid product with 63% yield was obtained. The relatively low yield is due to the material lost during the precipitation process though the reaction achieves high conversion.

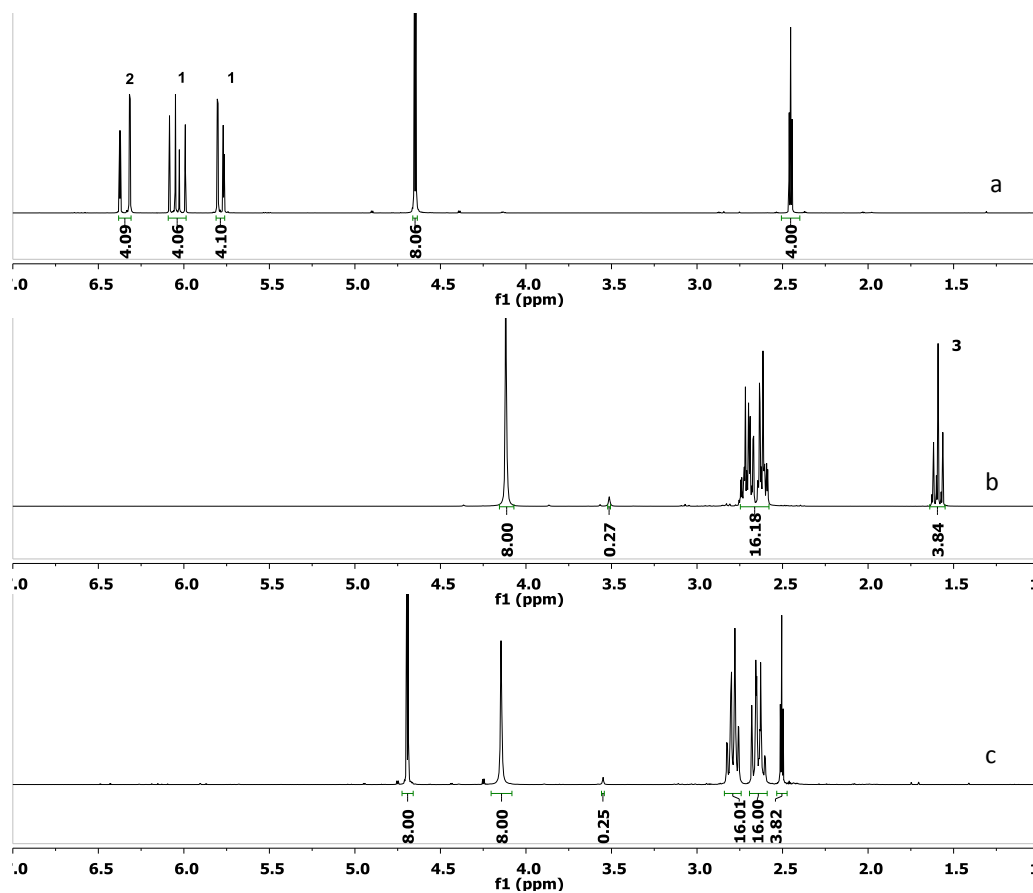


Figure 5.1 ^1H -NMR spectrum of (a) propargyl acrylate, (b) PETMP and (c) the 1st step product tetrayne synthesized from reaction of (a) and (b) with TEA catalyst in DCM.

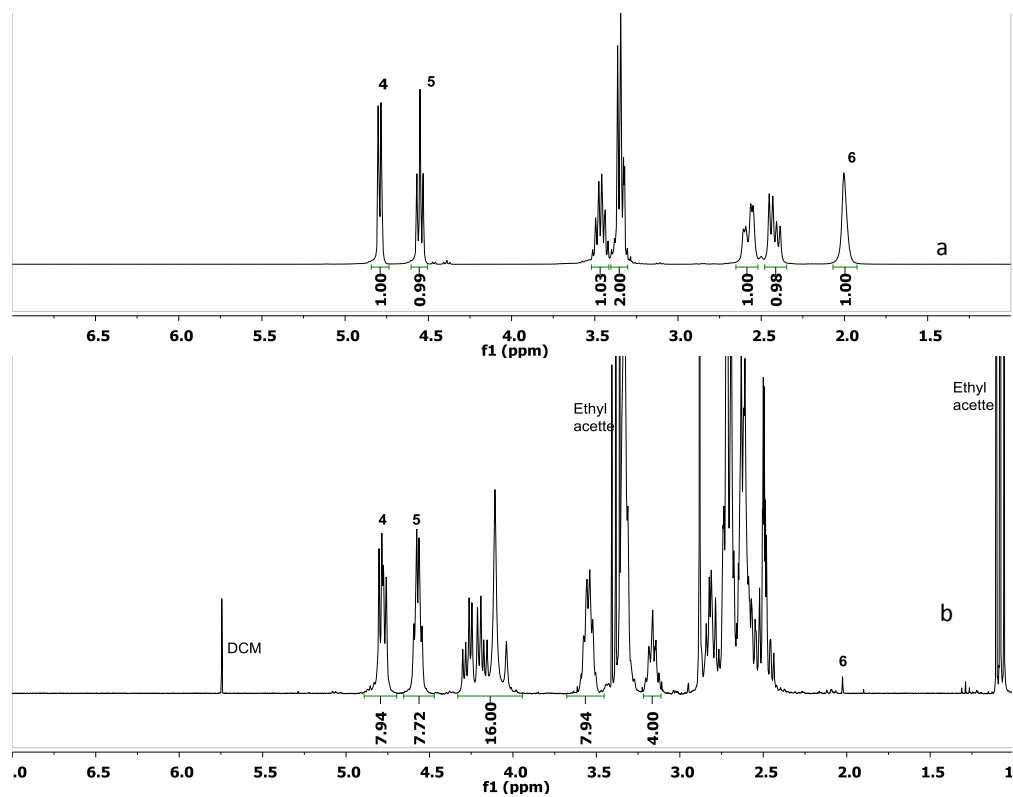
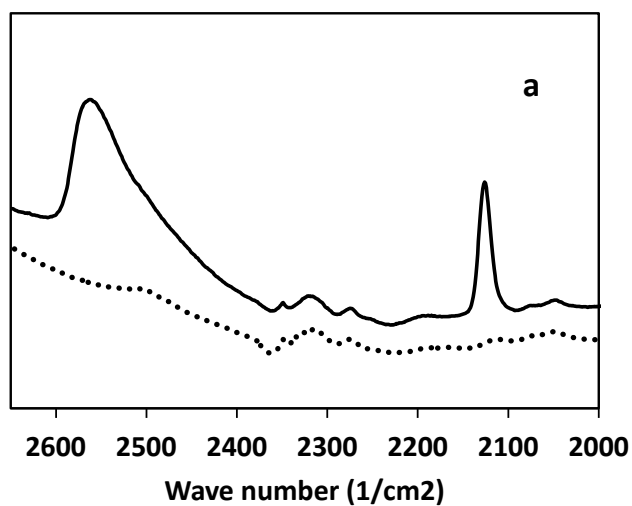


Figure 5.2 ^1H -NMR spectrum of (a) thioglycerol and (b) the 2nd step product 16 hydroxyl-terminated oligomer synthesized from a reaction of (a) and tetrayne irradiated with 10 mW/cm^2 of 320 – 500 nm UV light with 5 wt% Irgacure 651 in DMF.



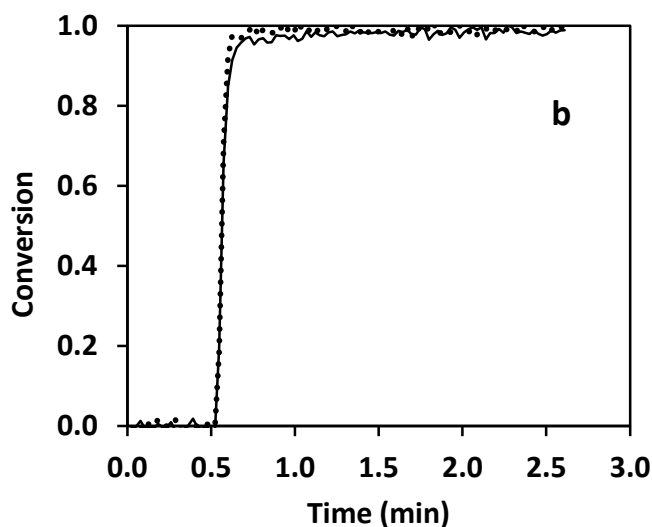


Figure 5.3 (a) FTIR spectrum before (—) and after (...) and (b) thiol (—) and alkyne (...) conversion vs. time. The sample was irradiated with 10 mW/cm^2 of 320 – 500 nm UV light with 5 wt% Irgacure 651 in DMF.

The third step product, 16 functional alkene-terminated oligomer, was synthesized via the alcohol-anhydride reaction. The 16 functional hydroxyl-terminated oligomer from the previous step was reacted with 4-pentenoic anhydride in dry THF catalyzed by DMAP. The disappearance of the hydroxyl peaks (4 and 5) ranging between 4.8 – 4.5 ppm from the second step product (Figure 5.2 b) and the appearance of the peaks (7 and 8) ranging between 5 – 6 ppm corresponding to the protons on the double bond of 4-pentenoic anhydride (Figure 5.4 b) indicate the successful completion of this reaction. GPC was used to determine the molecular weight of the major product peak (b) as Mn 3200 which is close to the MALDI result $[M+\text{Na}^+] m/z = 3130$ (Fig. 5.6 a), HPLC/MS result $[M+(\text{NH}_4^+)_2] m/z = 1571$ (Fig. 5.6 b) and the theoretical molecular weight of 3108. GPC also identified a shoulder peak (a) with Mn 6600 which appears to result from two of the targeted oligomers coupling together; and a peak (c) with Mn 360 corresponding to 3-alkene-terminated oligomer from the 2nd step residual thioglycerol reacting with anhydride (theoretical Mn 370.5) which matches the HPLC/MS result $[M+\text{H}^+] m/z = 372$. By deconvoluting and integrating the GPC peak areas, the final product contains 70% 16-alkene terminated hyperbranched oligomer,

19% coupling by-products and 11% small molecule impurities. The GPC results further explain the NMR in Figure 5.4 (b). The alkene peaks 7 and 8 show 16.54 and 41.86 protons, which are slightly more than the 16 and 40 theoretical values. This result is because the small amount of 3-alkene-terminated oligomer from thioglycerol reacting with anhydride would increase the peak areas (larger than 16 and 40) and the product molecules coupling would reduce the peak areas (smaller than 16 and 40). Thus, balancing these two factors, NMR finally shows a very slightly higher peak area compared with theoretical values. Moreover, MALDI (Figure 6.5) also shows 8 functional alkene-terminated oligomer $[M+Na^+]$ $m/z = 2468$. The other peaks around 600 might be the fragmentation products since these molecular weights are not apparent in the GPC measurement. Therefore, we consider the product to be the targeted 16 functional alkene-terminated hyperbranched oligomer with coupling byproduct estimated as three 16-functional alkene-terminated oligomers coupling and 11% 3-alkene-terminated small molecules.

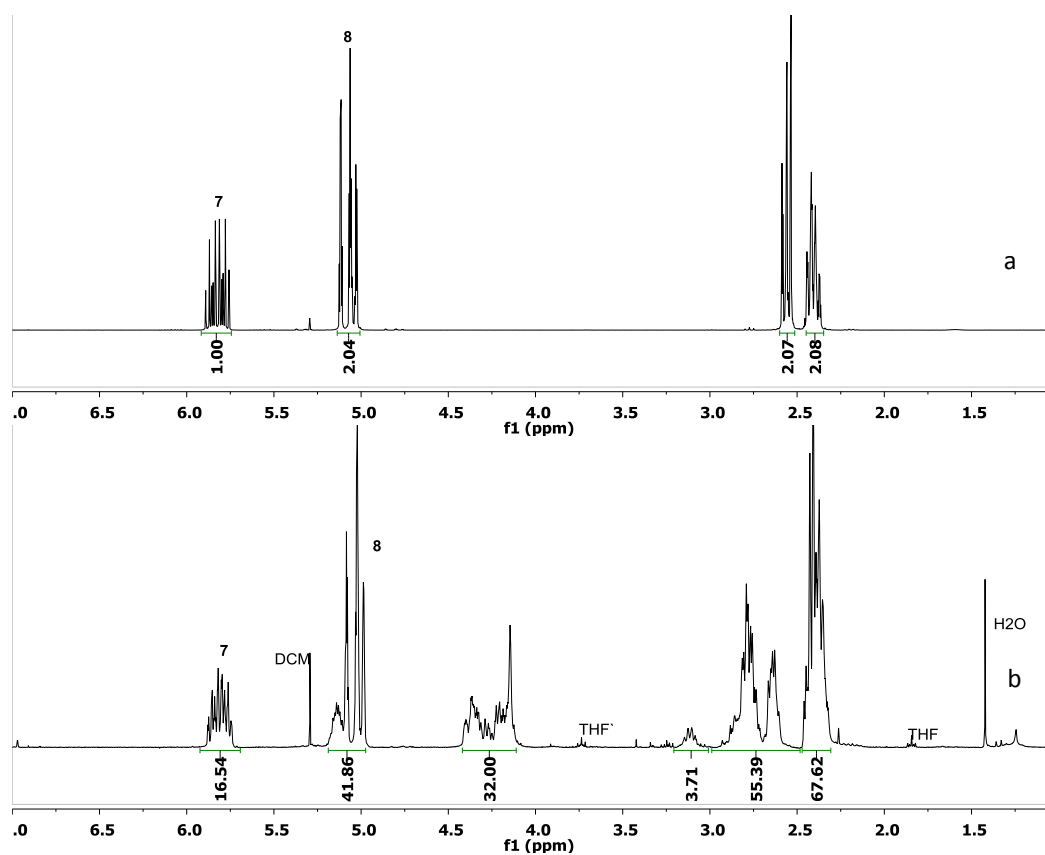


Figure 5.4 ^1H -NMR spectrum of (a) 4-pentenoic anhydride and (b) the 3rd step product 16-alkene-terminated oligomer synthesized by (a) and 16-hydroxyl-terminated oligomer with DMAP catalyst in THF.

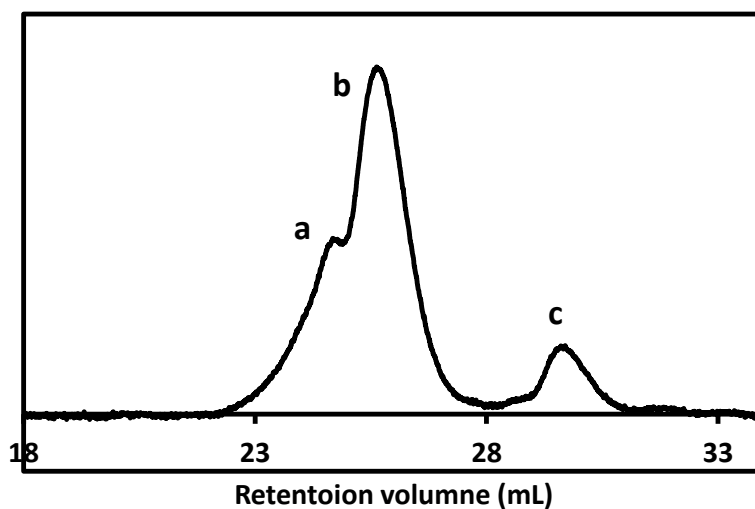


Figure 5.5 GPC trace of the 3rd step product 16 alkene-terminated oligomer with Mn and PDI (a) 6600, 1.17, (b) 3200, 1.08, and (c) 360, 1.67

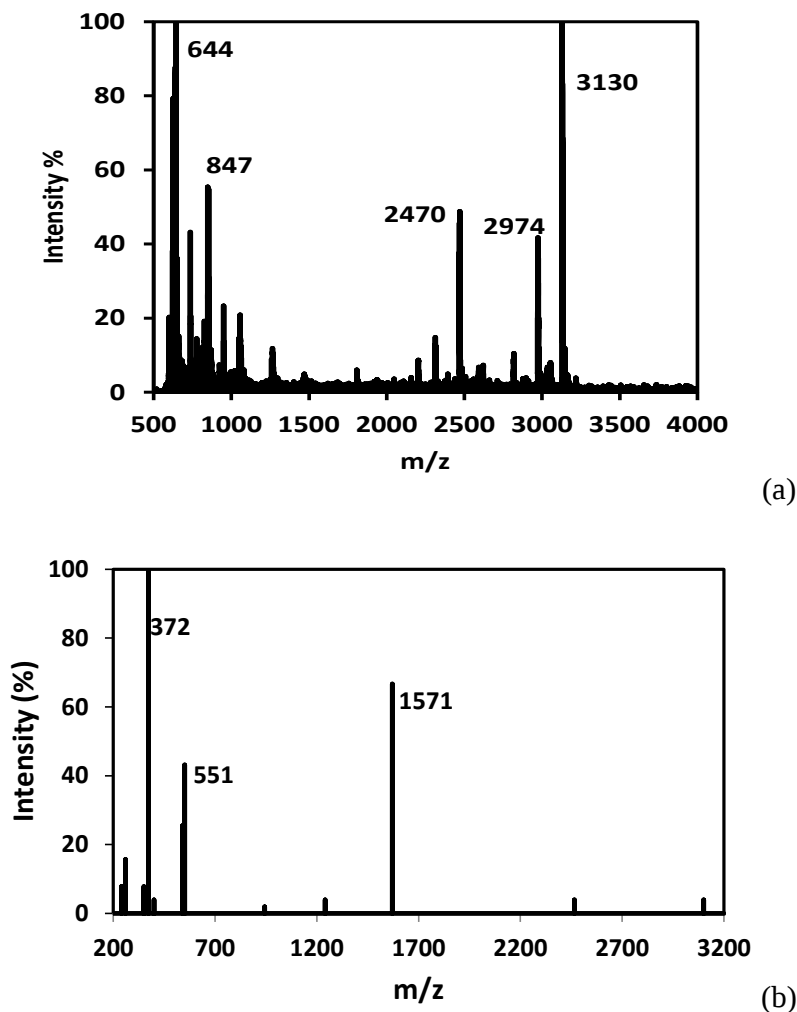
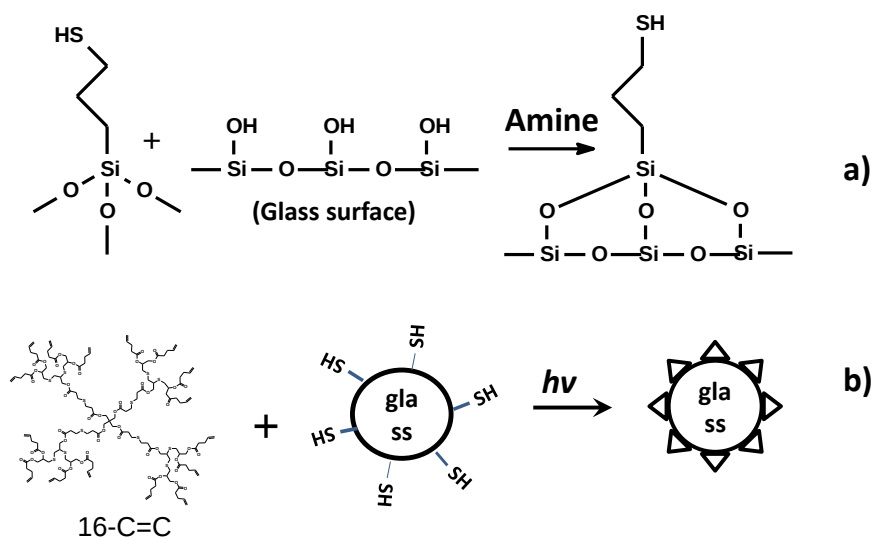


Figure 5.6 Mass spectrum of the 3rd step product 16 alkene-terminated oligomer with target molecule (a) $[M+Na^+]$ $m/z = 3130$ from MALDI and (b) $[M+(NH_4^+)_2]$ $m/z = 1571$ from HPLC/MS on an Agilent-TOF.

This 16 functional alkene-terminated hyperbranched oligomer was covalently immobilized to the thiol functionalized OX50 silica nanoparticles by the thiol-ene click reaction initiated by 320 – 500 nm UV light irradiation and the photoinitiator Irgacure 651 (Scheme 5.2). The TGA result in Figure 5.7 shows that 1.7 and 5.3 % initial weight loss was found from thiol and oligomer-functionalized particles, respectively. Based on the weight loss, there are 1.3 thiols per nm^2 , which is estimated as approximately a monolayer; and there are 0.14 hyperbranched oligomer per nm^2 indicating that each hyperbranched oligomer reacts with approximately 9 thiol groups, leaving

approximately 0.8 free alkene functional groups per nm^2 on the interfacial layer. Moreover, Chemdraw 3D predicts a tetrahedral shape with the cross-sectional area of approximately 6.5 nm^2 for the hyperbranched oligomer at its lowest energy (Scheme 5.3). Compared with a spherical OX50 particle having a diameter of 40 nm, if the surface of the particles is fully packed with tetrahedral molecules, theoretically there is approximately 0.15 oligomeric molecules per nm^2 , and the experimental result of 0.14 molecules per nm^2 would represent 93% coverage. Furthermore, when attaching on the particle surface, the tetrahedral molecules are likely to assume a different, non-equilibrium shape. So the maximum thickness of the interfacial layer would be $\sim 4.5 \text{ nm}$ for the tetrahedral shape and the minimum thickness of $\sim 0.7 \text{ nm}$ is estimated for dense packing, assuming the density of the grafted organic layer is 1.1 g/mol . The thickness of the interfacial layer may also change during polymerization of the composite resin in response to the shrinkage and interfacial stress.



Scheme 5.2 Synthesis route of a) thiol functionalized silica particle and b) hyperbranched oligomer functionalized silica particle

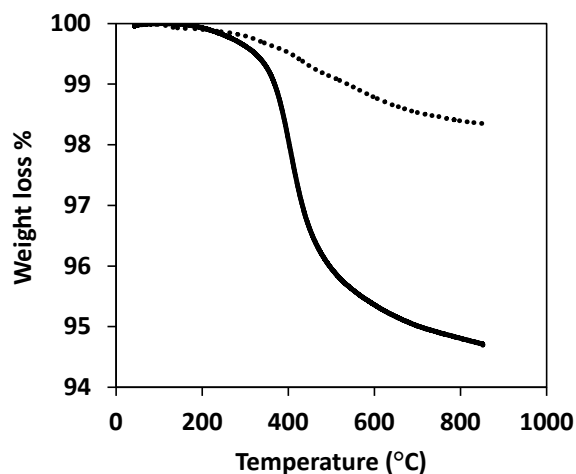
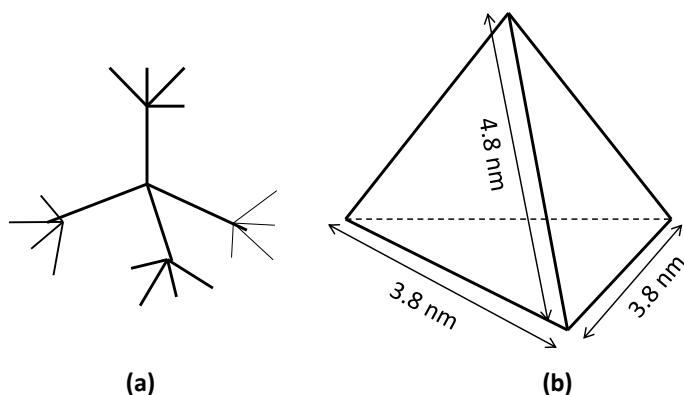


Figure 5.7 Weight loss of thiol functionalized OX50 silica particle (...) and 16 alkene-terminated hyperbranched oligomer functionalized OX50 silica particle (—) with increasing temperature



Scheme 5.3 Predicted (a) the shape and (b) geometry size of 16 alkene-terminated hyperbranched oligomer at lowest energy

This functionalized filler was incorporated into the thiol-yne-methacrylate ternary resin which was developed in chapter 4. In Figure 5.8, the reaction kinetics were evaluated for four different samples: (1) resin without filler, (2) with 20% thiol functionalized filler, (3) 20% hyperbranched oligomer functionalized filler and (4) 20% thiol functionalized filler with additional hyperbranched oligomers added to the bulk resin. That is, in sample 3 the oligomers are immobilized on the filler by covalent bonding while in sample 4 a similar amount of functional oligomer is added into the bulk resin by physically mixing. The reaction rates of the samples with fillers (Δ , ∇ and $\circ$) are all slightly faster than the control resin without filler ($\square$) due to the increasing viscosity of the

filled systems. The termination rate is reduced by increasing viscosity resulting in a faster overall reaction rate in the filled systems. Moreover, the reaction rates of the composites with thiol functionalized particles (∇) are slightly higher than that of the system with the hyperbranched oligomer functionalized particles ($\circ$) due to the different functional group concentration and mobility in the interfacial layer. However, since the amount of the functional group on the particle surface is very small comparing with the functionality in the bulk, only minor differences are observed. Though having different reaction rates at early stage, these four systems all reach similar final methacrylate and thiol conversions after 15 minutes of irradiation. (MA = 90 ± 2 % and thiol = 54 ± 1 %) The final conversion of the alkyne group in all three filler systems is 73 ± 2 %, and in the control resin system it is 64 ± 4 %.

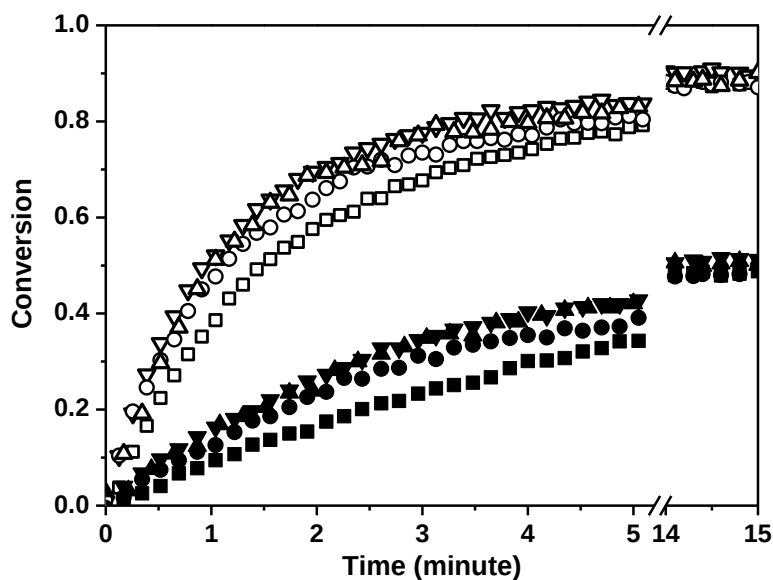
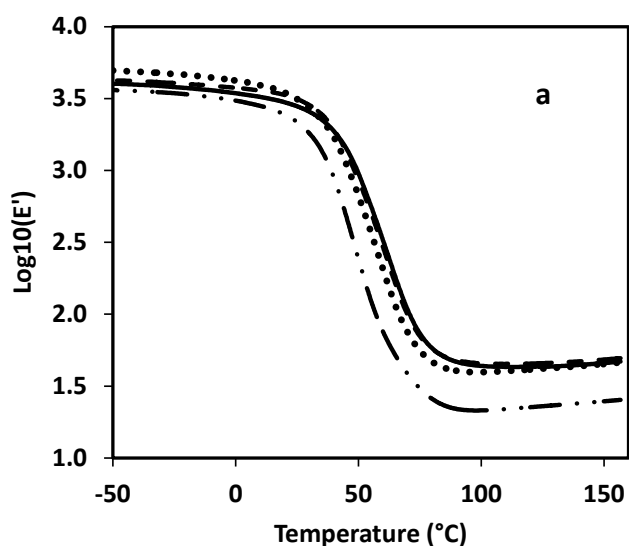


Figure 5.8 Methacrylate (open symbols) and thiol (filled symbols) real time conversions of resin without filler ($\square$), resin with 20 wt% thiol functionalized filler (∇), hyperbranched oligomer functionalized filler ($\circ$) and thiol functionalized filler with physically mixed hyperbranched oligomer (Δ). The systems were initiated with 1.0 wt% Irgacure 184 and cured by 365nm light at 10mW/cm².

The moduli of all three filled systems are obviously higher than the control resin at both ambient temperature and in the rubbery state as shown in Figure 5.9 (a). Compared with the glassy modulus of the control resin (system 1) (2200 ± 200 MPa) at ambient temperature, those of the thiol

functionalized filler (system 2), hyperbranched oligomer functionalized filler (system 3), and the thiol functionalized filler with additional hyperbranched oligomer (system 4) are 3100 ± 300 , 3100 ± 200 and 2800 ± 200 MPa, respectively, resulting from the reinforcement of the inorganic filler. Clearly, for the same oligomers bound to surfaces multiple times as compared to those free in solution, the geometry of these molecular species is expected to be much different. The free oligomers in the resin (system 4) causes slightly reduction of modulus (2800 ± 200 MPa) compared with the composite resin (system 3) with immobilized oligomer (3200 ± 200 MPa). The rubbery moduli of all three filled systems reach around 40 MPa, significantly higher than the control resin in the absence of filler (22 ± 1 MPa). The T_g of the thiol functionalized filler, hyperbranched oligomer functionalized filler, and the thiol functionalized filler with additional hyperbranched oligomer are 64 ± 4 , 62 ± 3 and 66 ± 1 °C, respectively, and slightly higher than the non-filled system (58 ± 3 °C), which also shows a slightly broader glass transition window.



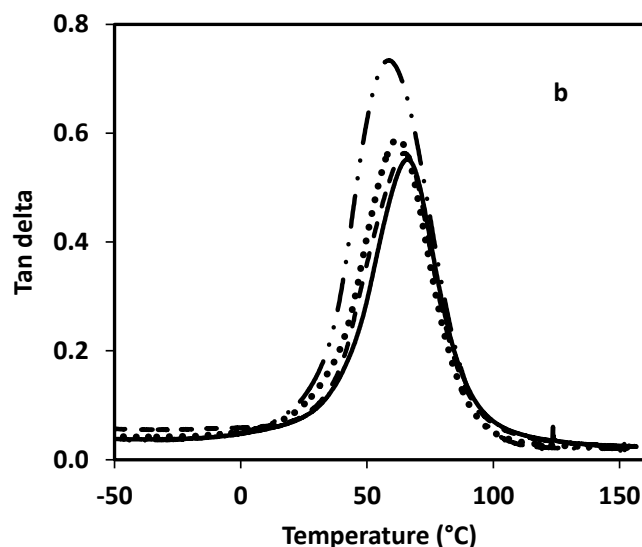


Figure 5.9 (a) Modulus and (b) $\tan \delta$ vs. temperature for the resin without filler (-...-), resin with 20 wt% thiol functionalized filler (- - -), hyperbranched oligomer functionalized filler (...) and thiol functionalized filler with additional hyperbranched oligomer (—). The systems were initiated with 1.0 wt% Irgacure 184 and cured by 365nm light at 10mW/cm². The curves are the average of triplet replicates.

In the filled systems, the volumetric shrinkage is reduced due to the reduction of the resin fraction which, by itself, would reduce the shrinkage stress. However, the higher modulus of the filled system is expected to lead to an increase in the shrinkage stress. Demonstrating a balance of these two factors, Figure 5.10 shows similar shrinkage stress values (0.9 ± 0.1 MPa) for the resin without filler (-...-) and the resin containing only 20 wt% thiol functionalized filler (- - -). Interestingly, both hyperbranched oligomer functionalized filler (...) and thiol functionalized filler with additional hyperbranched oligomer (—) show a much lower shrinkage stress (0.6 ± 0.1 MPa) indicating that the incorporation of a functional hyperbranched oligomer into filled systems is able to reduce the shrinkage stress. This function of the hyperbranched oligomer might be caused by the extension of the hyperbranched chains during the polymerization to provide extra mobility to release the shrinkage stress. Figure 5.11 demonstrates that the shrinkage stress builds up with the methacrylate conversion. The resin without filler (1), resin with thiol functionalized filler (2), and hyperbranched oligomer functionalized filler (3) all reach nearly the same methacrylate conversion

(92%) and the thiol functionalized filler with additional hyperbranched oligomer (4) reaches a slightly higher 95% conversion, indicating the shrinkage stress of the systems with hyperbranched oligomer (3 and 4) are reduced by 30% without sacrificing conversion and mechanical properties. Moreover, these two systems (3 and 4) develop the stress at a very late curing stage ($\sim 70\%$ MA conversion).

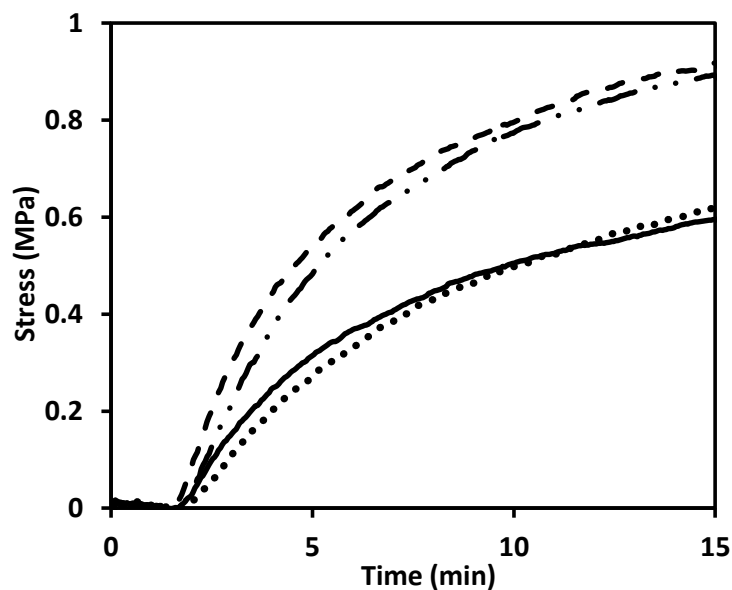


Figure 5.10 Real time shrinkage stress of the resin without filler (-...-), resin with 20 wt% thiol functionalized filler (- - -), hyperbranched oligomer functionalized filler (...) and thiol functionalized filler with additional hyperbranched oligomer (—). The systems were initiated with 1.0 wt% Irgacure 184 and cured by 365nm light at $10\text{mW}/\text{cm}^2$. The curves are the average of triplet replicates.

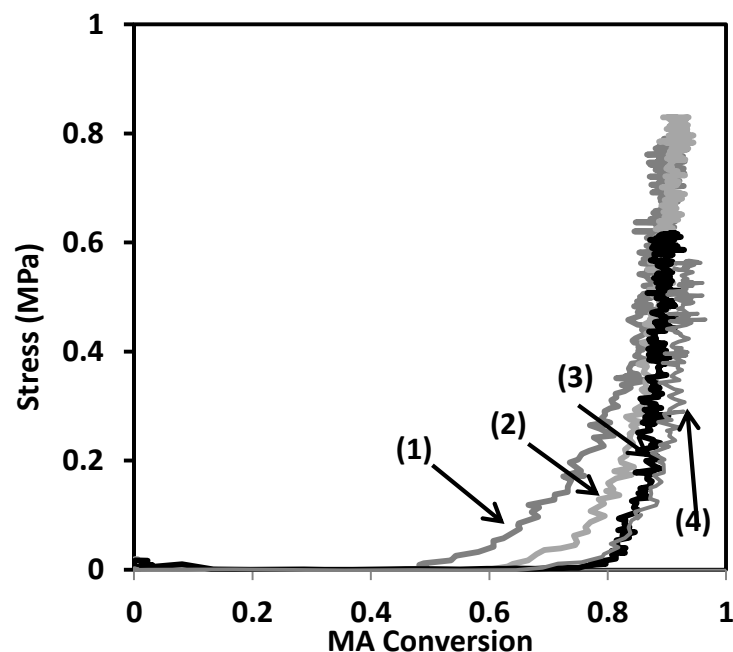


Figure 5.11 Shrinkage stress vs. methacrylate conversion of (1) resin without filler, (2) resin with 20 wt% thiol functionalized filler, (3) hyperbranched oligomer functionalized filler and (4) thiol functionalized filler with additional hyperbranched oligomer. The systems were initiated with 1.0 wt% Irigacure 184 and cured by 365nm light at 10mW/cm².

5.4 Conclusions

OX50 silica nanoparticles were functionalized by a flexible 16 functional alkene-terminated hyperbranched oligomer which was synthesized by various step-wise thiol-ene/yne reactions. 93% of the particle surface is covered by the hyperbranched oligomer and an interfacial layer ranging from 0.8 – 4.5 nm thickness is generated. A composite system with this filler incorporated into a thiol-yne-methacrylate resin was designed and evaluated. Compared with the control systems, this composite system is able to reduce the shrinkage stress by 30% (from 0.9 MPa to 0.6 MPa) without sacrificing modulus and glass transition temperature. Moreover, the shrinkage stress of this composite builds up at much later polymerization stage. These interesting phenomena are observed in both composite systems with (1) immobilized hyperbranched oligomer and (2) in a physical mixture of the oligomer, resin and filler. Since the relative amount of the functional groups on the

filler surface is small compared to those in the bulk resin, the reaction kinetics are not significantly altered.

5.5 Acknowledgements

The authors gratefully acknowledge the National Science Foundation CBET 0626023 and National Institutes of Health NIH/NIDCR Grants DE10959 and DE018233 for funding this work.

5.6 References

1. Fortin, D.; Vargas, M. A., The spectrum of composites: New technologies and materials. *Journal of the American Dental Association* **1999**, *131*, 26S-30S.
2. Cramer, N. B.; Stansbury, J. W.; Bowman, C. N., Recent advances and developments in composite dental restorative materials. *J Dent Res* **2011**, *90* (4), 402-416.
3. Braga, R.; Ballester, R.; Ferracane, J., Factors involved in the development of polymerization shrinkage stress in resin-composites: A systematic review. *Dent Mater* **2005**, *21* (10), 962-970.
4. Davidson, C. L.; Feilzer, A. J., Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. *J Dent* **1997**, *25* (6), 435-440.
5. Ferracane, J., Developing a more complete understanding of stresses produced in dental composites during polymerization. *Dent Mater* **2005**, *21* (1), 36-42.
6. Shah, P. K.; Stansbury, J. W., Polymer-brush modified fillers for dental composites. *Abstracts of Papers Am Chem Soc* **2006**, 231.
7. Shah, P. K.; Stansbury, J. W., Modified filler-matrix interfaces in polymeric composites used as dental restoratives. *Abstracts of Papers Am Chem Soc* **2007**, 233.
8. Mezzenga, R.; Boogh, L.; Manson, J. A. E., A review of dendritic hyperbranched polymer as modifiers in epoxy composites. *Compos Sci Tech* **2001**, *61* (5), 787-795.
9. Wan, Q.; Schrick, S.; Culbertson, B., Methacryloyl derivitized hyperbranched polyester. 2. Photo-polymerization and properties for dental resin systems. *J Macromol Sci, Part A* **2000**, *37* (11), 1317-1331.

10. Hoyle, C. E.; Lowe, A. B.; Bowman, C. N., Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem Soc Rev* **2010**, 39 (4), 1355.
11. Lowe, A. B.; Hoyle, C. E.; Bowman, C. N., Thiol-yne click chemistry: A powerful and versatile methodology for materials synthesis. *J Mater Chem* **2010**, 20 (23), 4745-4750.
12. Franc, G.; Kakkar, A. K., "Click" methodologies: efficient, simple and greener routes to design dendrimers. *Chem Soc Rev* **2010**, 39 (5), 1536.
13. Rissing, C.; Son, D. Y., Application of thiol-ene chemistry to the preparation of carbosilane-thioether dendrimers. *Organometallics* **2009**, 28 (11), 3167-3172.
14. Killops, K. L.; Campos, L. M.; Hawker, C. J., Robust, efficient, and orthogonal synthesis of dendrimers via thiol-ene "Click" chemistry. *J Am Chem Soc* **2008**, 130 (15), 5062-5064.
15. Antoni, P.; Robb, M. J.; Campos, L.; Montanez, M.; Hult, A.; Malmström, E.; Malkoch, M.; Hawker, C. J., Pushing the limits for thiol-ene and CuAAC reactions: Synthesis of a 6th generation dendrimer in a single day. *Macromolecules* **2010**, 43 (16), 6625-6631.
16. Hoogenboom, R., Thiol-yne chemistry: A powerful tool for creating highly functional materials. *Angew Chem Int Edit* **2010**, 49 (20), 3415-3417.
17. Chan, J. W.; Hoyle, C. E.; Lowe, A. B., Sequential phosphine-catalyzed, nucleophilic thiol-ene/radical-mediated thiol-yne reactions and the facile orthogonal synthesis of polyfunctional materials. *J Am Chem Soc* **2009**, 131 (16), 5751-5756.
18. Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N., Thiol-yne photopolymerizations: Novel mechanism, kinetics, and step-growth formation of highly cross-linked networks. *Macromolecules* **2009**, 42 (1), 211-217.
19. Sideridou, I. D.; Karabela, M. M., Effect of the amount of 3-methacyloxypropyltrimethoxysilane coupling agent on physical properties of dental resin nanocomposites. *Dent Mater* **2009**, 25 (11), 1315-1324.

Chapter 6

Induction Curing of Thiol-acrylate and Thiol-ene Composite Systems*

Induction curing is demonstrated as a novel type of *in situ* radiation curing that maintains most of the advantages of photocuring while eliminating the restriction of light accessibility. Induction curing is utilized to polymerize opaque composites comprised of thiol-acrylate and thiol-ene resins, nanoscale magnetic particles, and carbon nanotubes. Nanoscale magnetic particles are dispersed in the resin and upon exposure to the magnetic field, these particles lead to induction heating that rapidly initiates the polymerization. Heat transfer profiles and reaction kinetics of the samples are modeled during the reactions with varying induction heater power, species concentration, species type and sample thickness, and the model is compared with the experimental results. Thiol-ene polymerizations achieved full conversion between 1.5 minutes and 1 hour, depending on the field intensity and the composition, with the maximum reaction temperature decreasing from 146 - 87 °C when the induction heater power was decreased from 8 – 3 kW. The polymerization reactions of the thiol-acrylate system were demonstrated to achieve full conversion between 0.6 and 30 minutes with maximum temperatures from 139 to 86 °C. The experimental behavior was characterized and the temperature profile modeled for the thiol-acrylate composite comprised of sub100nm nickel particles and induction heater power in the range of 32 to 20 kW. A 9°C average deviation was observed between the modeling and experimental results for the maximum temperature rise. The model also was utilized to predict reaction temperatures and kinetics for systems with varying thermal initiator concentration, initiator half-life, monomer molecular weight and temperature gradients in samples with varying thickness, thereby demonstrating that induction curing represents a designable and tunable polymerization method. Finally, induction curing was utilized to cure thiol-acrylate systems

* This chapter is from the publication S. Ye, N.B Cramer, B.E. Stevens, R.L. Sani, C.N. Bowman, *Macromolecules* **2011**,44,4988-4996

containing carbon nanotubes where 1 wt% carbon nanotubes resulted in systems where the storage modulus increased from 17.6 ± 0.2 to 21.6 ± 0.1 MPa and an electrical conductivity that increased from $<10^{-7}$ to 0.33 ± 0.5 S/m.

6.1 Introduction

The vast majority of radical polymerizations are initiated via thermal heating. The heat source is provided externally to the target, which in some cases can result in temperature gradients, reaction rate gradients and non-uniform material properties. Also, traditional heating techniques are limited to applications that do not involve temperature sensitive substrates. Radiation curing is an alternative radical polymerization methodology that represents a highly desirable method for producing crosslinked polymer networks with advantages that include spatiotemporal control of the reaction, solvent-free formulations, ambient curing, and high energy efficiency.^{1,2} X-ray and γ -ray initiation are two forms of radiation curing that have been studied but have only seen limited application because of the hazards associated with these wavelengths to the human body and the subsequent requirements for shielding. Far more commonly, radiation curing utilizes ultraviolet or visible light with widespread applications that include lithography, dental materials, printing inks, and clear coatings to name a few.³ However, in some applications, such as highly filled composite systems, pigmented systems, or systems that are inaccessible to light, photopolymerizations are limited by optical accessibility. In this work we describe a novel radio frequency curing technique, induction curing, that combines aspects of both radiation and thermal curing. Induction curing maintains most of the advantages of photocuring such as rapid, efficient cure with temporal control while being an environmentally friendly technique that cures without the need for solvents. Moreover, induction curing eliminates the restriction of light accessibility that is required in traditional photocuring. Thus, induction curing is demonstrated to be a tunable and promising *in situ* polymerization method.

The mechanism and applications of induction heating have been introduced in Section 1.4 in Chapter 1. Most recently, in polymer area, induction heating has been implemented by embedding ferromagnetic particles in thermoplastic or thermosetting polymer matrices to achieve induction-heating induced melting, welding,⁴ coating,⁵ shape memory actuation,^{6,7} and adhesion^{8,9}. Suwanwatana and co-workers also developed a heat transfer model relating different nickel particle size, loading, magnetic field and frequency to the temperature change in cured polymer substrates.^{10,9} Induction heating has not previously been utilized to induce an *in situ* radical polymerization of thiol-containing monomer formulations and there has not been a model developed for an *in situ* induction polymerization which combines both induction heating process and reaction kinetics. For the induction heating polymerizations described herein, micro ferromagnetic particles are dispersed in a reactive monomer system that also contains thermally sensitive radical initiators. Upon exposure to an alternating magnetic field, the heat generated by the particles heats the system and triggers cleavage of the thermal initiators, initiating the desired radical polymerization. Since the magnetic particles are the only component responding to the magnetic field, the reaction kinetics are not affected by the field itself aside from the temperature increase. By using this method, highly filled composite systems are radiation cured without the limitations of optical accessibility or the hazards associated with X-rays and γ -rays. Also, as compared to external heating techniques (i.e. oven heating), induction heating is much more rapid and efficient and essentially applies targeted heat to the ferromagnetic particles suspended in the resin while leaving any associated substrates only indirectly affected. Thus, induction heating polymerization has the potential for applications in coatings or adhesion to thermally sensitive materials.

In this work, thiol-ene and thiol-acrylate polymerizations have been chosen as model systems. Thiol-ene systems are an emerging area in photopolymerizations as they exhibit several unique, and often advantageous, properties such as delayed gelation, reduced oxygen inhibition, and low shrinkage stress.^{1,11,12,13} These properties are a result of the unique free radical step-growth

reaction mechanism. The step growth mechanism involves a thiyl radical, which adds across an ene functional group to form a carbon-centered radical. The thiyl radical is subsequently regenerated by chain transfer of the carbon-centered radical to another thiol functional group.¹⁴ Thiol-acrylate systems undergo a radical step-growth polymerization between thiols and acrylates and homopolymerization of acrylates, a process which maintain the advantages of thiol-ene systems while providing the ability to achieve higher glass transition temperatures.¹⁴ Nickel and cobalt particles exhibit relatively good stability with thiol-ene and thiol-acrylate systems, are abundant in a variety of sizes and are also inexpensive and are therefore good candidates as model particles for the induction heating process. Carbon nanotubes (CNTs) were chosen as a filler material based on their high aspect ratio, resulting in highly desirable modulus and conductivity properties.¹⁵ Also a heat transfer model of *in situ* induction polymerization was developed and confirmed by experimental data. The model also was utilized to predict reaction temperatures and kinetics for systems with varying thermal initiator concentration, initiator half-life, monomer molecular weight and temperature gradients in samples with varying thickness.

6.2 Experimental

Trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), allyl pentaerythritol (APE) and 2,2'-azobisisobutyronitrile (AIBN) were all purchased from Sigma Aldrich Co. (Milwaukee, WI). Poly(ethylene glycol)200 diacrylate (PEGDA) was purchased from Sartomer Company (Exton, PA). Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Evans Chemetics, Nano scale (<100 nm) and micro scale (3 μ m) nickel particles, and micro scale (2 μ m) cobalt particles were purchased from Sigma Aldrich Co. (Milwaukee, WI). Multiwall hydroxyl functionalized carbon nanotubes (CNT-OH) were purchased from Nanostructured and Amorphous Materials Inc. with a 60-

80 nm diameter range, 10-20 μm length range and 95% purity. Conductive liquid silver paint was purchased from Jed Pella Inc. (Redding, CA). All materials were used without further purification.

Stoichiometric thiol to ene functional group ratios were used in the PETMP-APE resins and 3:7 thiol to acrylate functional group ratios were used in the PETMP-PEGDA resins to minimize the amount of unreacted thiol monomers.¹⁴ TMPTMP, PEGDA, magnetic particles and CNT-OH were mixed for five minutes by an ultrasonic cell crusher (SYJ-650, Sharpertek Corp., Auburn Hills, MI) operating at 24 kHz. AIBN was added to the solution after sonication to prevent polymerization during mixing. The solution was then poured into a 20 x 5 x 0.8 mm cell, which was horizontally inserted into a solenoid coil where a vertical magnetic field was generated by an induction heater (7.5-135, Taylor-Winfield Corp., Brookfield, OH) with variable power settings.

Fourier Transform Infrared (FTIR) spectroscopy (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) was utilized to monitor the functional group conversion. The Near IR light beam was aligned perpendicular to the sample with fiber optic cables enabling real-time kinetic characterization. Conversion was monitored by observing the C=C vibration at 6020 cm^{-1} . An infrared pyrometer (Omega OS550) was arranged vertically to the sample to measure the temperature in real time during polymerization.

Dynamic mechanical analysis (DMA) was performed with a DMA Q800 dynamic mechanical analyzer (TA Instruments). The samples were rectangular films with dimensions of 20 x 5 x 0.8 mm. Multi frequency strain mode was used to measure moduli as a function of temperature by applying a sinusoidal stress of frequency 1 Hz over a temperature range of -40 - 100 $^{\circ}\text{C}$ and a temperature ramping rate of 3 $^{\circ}\text{C}/\text{minute}$.

Electrical conductivity of the composite material was calculated from the reciprocal of the resistivity measured by a Hewlett Packard multi-meter 34401 A (HP, Santa Clara, CA). The samples were coated with conductive silver paint to improve the contact between the probe and the polymer.

Scanning electron microscopy (SEM) (JSM-6480LV) with a low vacuum mode was utilized to observe the microstructure of the composite material by 5 kV. The samples were fractured under nitrogen and sputter coated with gold.

6.3 Results and Discussions

6.3.1 Kinetics of thiol-ene and thiol-acrylate systems cured by induction heating

To demonstrate the feasibility of induction curing of thiol-ene and thiol-acrylate systems, double bond conversion and surface temperature versus time are shown in Figure 6.1 for a PETMP-APE system and in Figure 6.2 for a PETMP-PEGDA system. The reaction kinetics are strongly influenced by both induction heater power and the characteristics of the magnetic particles. In Figure 6.1, the PETMP-APE system achieves a final double bond conversion of 86% in 1.5 minutes at 8 kW, 84% in one hour at 6 kW and only 70% at 3 kW after one hour. Higher induction heater power generates stronger magnetic fields resulting in faster temperature ramping and reaction kinetics. The surface temperature profiles of the systems reacted at 8 kW and 6 kW show a relatively slow temperature increase resultant from induction heating of the nickel particles, followed by a rapid increase in temperature caused by the exothermic nature of the thiol-ene polymerization. The polymerization reaction begins to occur rapidly around 70 °C, which is the temperature where the cleavage rate of AIBN increases dramatically. The system reacted at 8 kW reaches a maximum temperature of 146 °C whereas the system reacted at 6 kW reaches only 87 °C because of the slower reaction. There is no obvious reaction peak in the temperature profile of the system reacted at 3 kW

because the temperature, limited by heat transfer to the environment, reaches only 56 °C which does not result in sufficiently rapid cleavage of AIBN to initiate a viable polymerization. These results demonstrate that the reaction rate and the maximum temperature are controlled by adjusting the induction heater power. Figure 6.2 shows the double bond conversion and surface temperature versus time of the PETMP-PEGDA system polymerized with different particle types and sizes. The system containing cobalt particles heats the most rapidly, achieving complete conversion in 0.6 minutes and also results in the highest maximum reaction temperature of 139 °C and the highest steady state temperature of 76 °C. The Curie temperature of the cobalt particles (1130 °C) is much higher than the nickel particles (358 °C)¹⁶ and therefore heats the resin faster and causes a more rapid reaction, resulting in the achievement of a higher maximum temperature. Nanoscale nickel particles heat the resin faster and reach a higher maximum reaction temperature as compared to micron-scale particles due to the increased susceptibility to the magnetic field. The different heating rates of the particles result in significantly different kinetic and temperature profiles, which demonstrate that induction curing is readily controlled by choosing different magnetic particles.

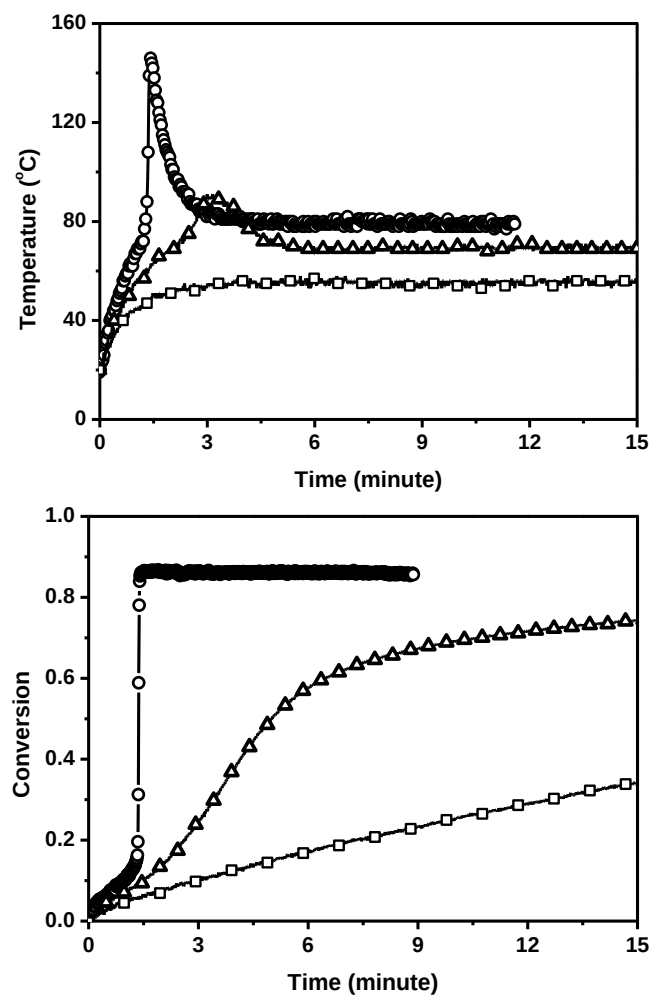


Figure 6.1. (a) Surface temperature versus time and (b) conversion versus time for PETMP-APE initiated by 1 wt% AIBN and 3 wt% Ni particles (3 μ m) cured at induction heater powers of 8 (○), 6 (Δ), and 3 (□) kW.

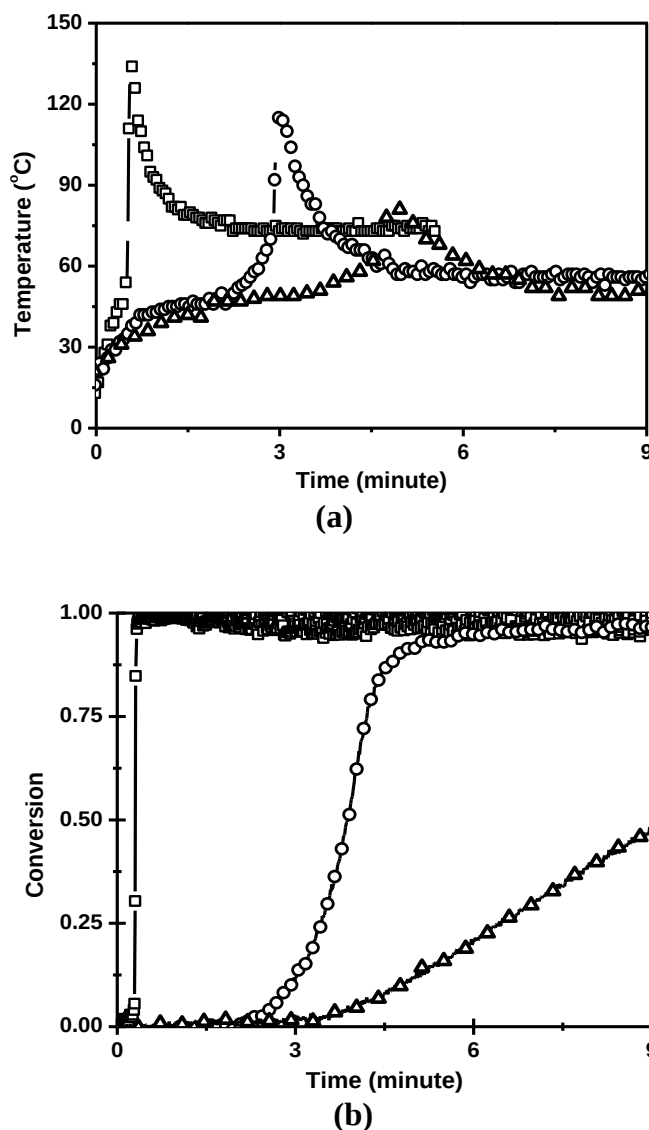


Figure 6.2. (a) Surface temperature versus time and (b) conversion versus time for PETMP-PEGDA initiated by 1 wt% AIBN and 1 wt% particles cured at 20 kW. Samples contain 2 μm cobalt ($\square$), <100 nm nickel ($\circ$), and 3 μm nickel (Δ) particles.

6.3.2 Temperature Profile Modeling

The polymerization reaction rate and final conversion of induction cured systems are strongly affected by temperature which is dictated by both the exothermic heat of reaction and the induction heating. Moreover, temperature gradients that are formed within the sample result in reaction rate

gradients which reciprocally affect the temperature profile in the sample. Modeling of the temperature profile during induction curing helps to understand how factors, such as induction heater power, sample geometry, initiator, or resin formulation, affect the curing; predict the complex curing relationships; and enable better design of the formulations for specific application requirements, for example adhesion to temperature sensitive substrates. Therefore, induction curing broadens the scope of radiation curing capabilities beyond that which is possible by conventional photoinitiated polymerizations.

The thiol-acrylate system is chosen for modeling because it maintains the advantages of thiol-ene systems while achieving higher glass transition temperatures, which facilitates applications in adhesives and coatings. COMSOL program is employed to model the heat transfer and kinetics behavior. TMPTMP-PEGDA with 1.5 wt% Ni (nm) is utilized as a model system with the polymer sandwiched between glass slides. The thickness of the polymer and glass are 0.76 mm and 0.1 mm, respectively; and this direction is defined as the x direction. Based on the radical reaction mechanism, mass balances during curing are described as the consumption of initiator (equation 6.1), inhibitor (equation 6.2), monomer (equation 6.3), and radicals (equation 6.4).¹⁷

$$\frac{d[I]}{dt} = -k_d \cdot [I] \quad (6.1)$$

$$\frac{d[Z]}{dt} = -k_z \cdot [Z] \cdot [P\bullet] \quad (6.2)$$

$$\frac{d[M]}{dt} = -k_p \cdot [M] \cdot [P\bullet] \quad (6.3)$$

$$\frac{d[P\bullet]}{dt} = R_i - 2 \cdot k_t \cdot [P\bullet]^2 - k_z \cdot [Z] \cdot [P\bullet] \quad (6.4)$$

in which $[I]$, $[Z]$, $[M]$ and $[P\bullet]$ are the concentration of initiators, inhibitors, double bonds and radicals, respectively; k_d , k_z , k_p and k_t are the kinetic constants for initiation, inhibition, propagation and termination, respectively. Based on the mixed reaction mechanism of the thiol-acrylate system, the consumption of the double bonds includes both acrylate homopolymerization and chain transfer to thiol. Several of the critical assumptions inherent in these mass balances are that: 1) two primary radicals are generated by the initiation step, 2) chain length does not affect the propagation, termination or inhibition steps, 3) bimolecular termination is the dominant mechanism for termination, and 4) the network is homogeneously formed and there is no significant diffusion that occurs during the reaction.¹⁸

Due to the induction heating process and the exothermic polymerization reaction, the temperature changes substantially during the curing. Each of the kinetic constants is written in an Arrhenius form (equation 6.5)¹⁷

$$k_i = k_{i0} \cdot \exp\left(\frac{-E_{ai}}{R \cdot T}\right) \quad (6.5)$$

where the subscript i refers to the initiation, inhibition, propagation, or termination reaction; k is the kinetic constant, k_0 is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the absolute temperature.

The energy balances are given in equations 6.6 and 6.7. The assumptions inherent to the energy balance are that 1) conduction only occurs in the x direction in the sample, 2) there is no significant convection or radiation, and 3) the decrease in heat generated by the particles with increased sample temperature is small enough that the heat generated by the particles can be considered to be constant throughout the reaction. The transient energy balances on the glass layers and the polymer layer are equations 6.6 and 6.7, respectively.

$$\rho_{glass} \cdot C_{glass} \frac{\partial T}{\partial t} = k_{glass} \frac{\partial^2 T}{\partial x^2} \quad (6.6)$$

$$\rho_{poly/Ni} \cdot C_{poly/Ni} \frac{\partial T}{\partial t} = k_{poly/Ni} \frac{\partial^2 T}{\partial x^2} + Q_{IND} + Q_{REC} \quad (6.7)$$

Here, ρ is the density; C is the heat capacity; k is the heat conductivity; the subscript describes different materials in the modeling; glass is glass surface and poly/Ni is the resin-nickel particle mixture; Q_{IND} and Q_{REC} are the heats generated by inductive heating of the particles and by the exothermic reaction, respectively. The boundary conditions are that the temperature at the glass surfaces contacting the polymer equals the temperature at the polymer surface and that the heat flux at the glass/polymer interface is equal to that at the glass/air interfaces (equation 6.8).

$$k_{glass} \frac{dT}{dx} = h_{air} \cdot (T - T_{air}) \quad (6.8)$$

Here, k_{glass} is the thermal conductivity of glass, h_{air} is the heat transfer coefficient, and T_{air} is the ambient temperature.

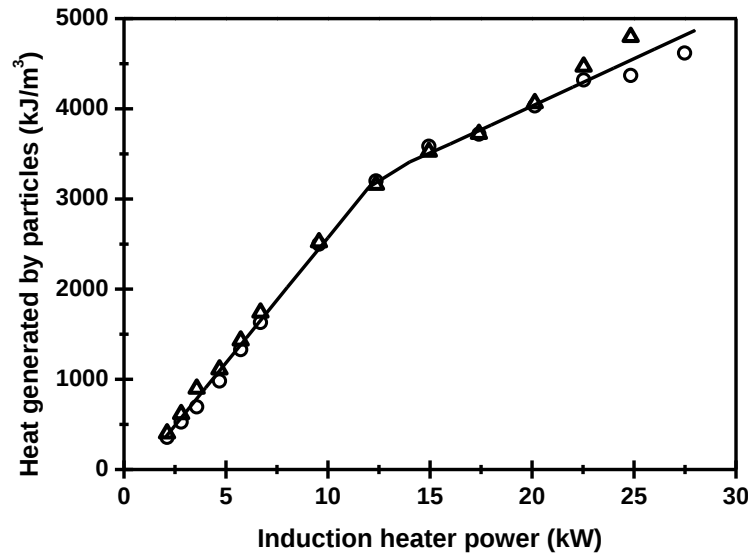
Q_{IND} is a function of the induction heater power, particle loading and particle size and can be determined from the steady state temperature of the cured sample. At steady state, the boundary condition at the glass surface contacting the polymer is that the total heat transfer from the polymer to the glass equals the heat generated by the particles (equation 6.9)

$$k_{glass} \frac{dT}{dx} \cdot A_{glass} = \frac{1}{2} \cdot Q_{IND} \cdot V_{polymer} \quad (6.9)$$

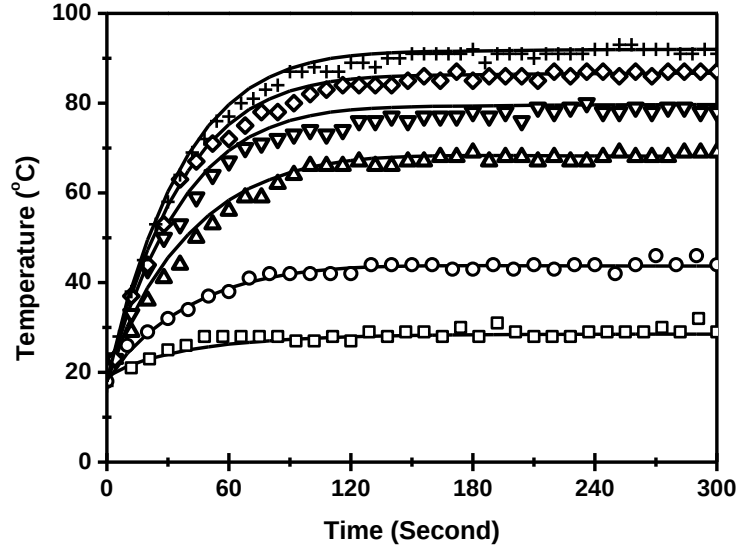
in which, k_{glass} is the thermal conductivity of glass, A_{glass} is the area of the glass, Q_{IND} is the heat generated by induction heating and $V_{polymer}$ is the polymer volume. The value of Q_{IND} is calculated

from equations 6.8 and 6.9, and Q_{IND} as a function of induction heater power is obtained by changing the power.

Figure 6.3a illustrates the heat generated by the particles versus induction heater power for both increasing and decreasing induction curing power. The results indicate that Q_{IND} exhibits a linear relationship between induction heater power at steady state during the processes of increasing and decreasing power. There is no obvious difference between the data obtained from these two processes, which indicates that the thermal history does not have a significant effect on the heat generated by induction heating of the particles. Figure 6.3b shows the surface temperature profile versus time for the experimental and modeling results of the transient, non-reacting system.



(a)



(b)

Figure 6.3 (a) Heat generated by particles in a fully cured polymer sample at different induction power levels during the process of increasing power ($\circ$) and during the process of decreasing power (Δ). The lines represent the data fit. (b) Experimental surface temperature profiles versus time for particles in cured polymer samples heated at (+) 28 kW, ($\diamond$) 23 kW, (∇) 17 kW, (Δ) 12 kW, ($\circ$) 7 kW and ($\square$) 4 kW, along with the lines for the modeling predictions (—). The cured polymers are comprised of TMPTMP-PEGDA with 1.5 wt% Ni (nm) particles.

The heat generated by the exothermic polymerization reaction is the product of the reaction enthalpy and the rate of double bond consumption (equation 6.10)

$$Q_{REC} = \Delta H \cdot \frac{d[M]}{dt} \quad (6.10)$$

in which, ΔH is determined from the experimental results. The heat transfer profile for induction curing is obtained by simultaneously solving equations 6.1 – 6.7 with the given boundary conditions and the parameters in Table 1 with the solution presented in Figure 6.4. The experimental and modeling results at different induction heater powers are extremely consistent with temperature differences of up to only 9 °C, with 7% average variation.

Table 6.1. Physical and kinetic parameters used in heat transfer modeling.

Parameter	Value	Unit	Reference
k_{d0}	2.9×10^{15}	1/s	¹⁹
E_{ad}	130000	J/mol	¹⁹
k_{z0}	5.3×10^7	$m^3/mol/s$	²⁰
E_{az}	18000	J/mol	²⁰
k_{t0}	3.6×10^3	$m^3/mol/s$	²⁰
E_{at}	2900	J/mol	²⁰
k_{p0}	3000	$m^3/mol/s$	experimentally determined*
E_{ap}	8900	J/mol	experimentally determined*
ρ_{glass}	2225	kg/m^3	²¹
C_{glass}	835	J/kg/K	²¹
k_{glass}	1.4	W/m/K	²¹
$\rho_{poly/Ni}$	1230	kg/m^3	Calculated by volumetric ratio
$C_{poly/Ni}$	1541	J/kg/K	Calculated by volumetric ratio
$k_{poly/Ni}$	0.35	W/mK	Calculated by volumetric ratio
h_{air}	25	W/m ² K	Experimental fit
ΔH	36000	W/m ³	Experimental fit

*Determined by photocuring of the same system at room temperature to maintain a constant temperature, since k_{p0} and E_{ap} are not related to the initiation mechanism

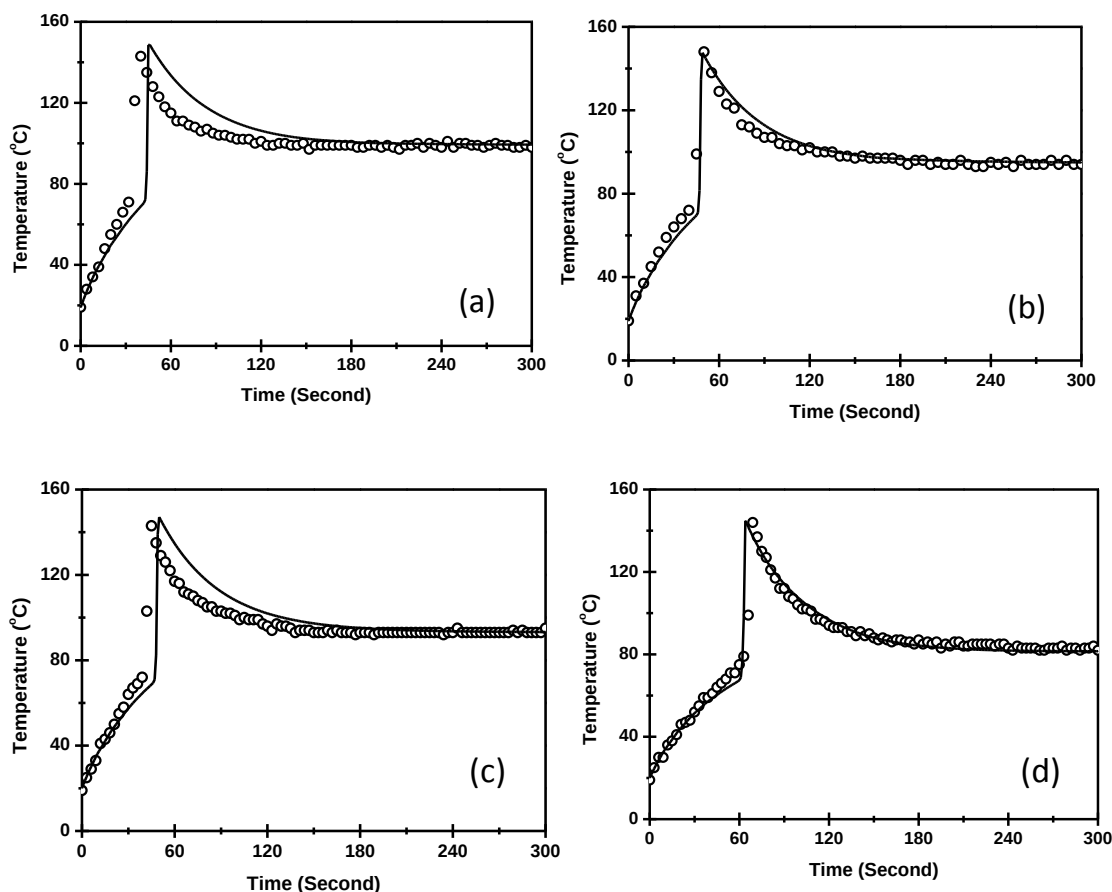


Figure 6.4. Surface temperature profile versus time for (○) experimental data and (—) modeling results of TMPTMP-PEGDA with 1 wt% AIBN and 1.5 wt% Ni (nm) cured with varying induction heater powers: (a) 32 kW, (b) 30 kW, (c) 27 kW and (d) 20 kW.

After verifying the consistency of the modeling and experimental results, the model was utilized to predict reaction temperatures and polymerization kinetics for systems with varying thermal initiator concentration, initiator decay rate, monomer molecular weight and temperature gradients in samples with varying thickness. Figure 6.5 shows the modeling results of surface temperature profile versus time for varying induction power. The data indicates that decreasing the power delays the onset of the polymerization reaction due to the slower rate of AIBN cleavage at lower temperatures. The reaction effectively begins after ~60 seconds when the sample is heated with 20 kW as compared to the reaction initiating at ~270 seconds when the sample is heated with 8

kW. A 20°C difference in the maximum reaction temperatures is observed for polymerizations initiated by 20 kW and 8 kW power.

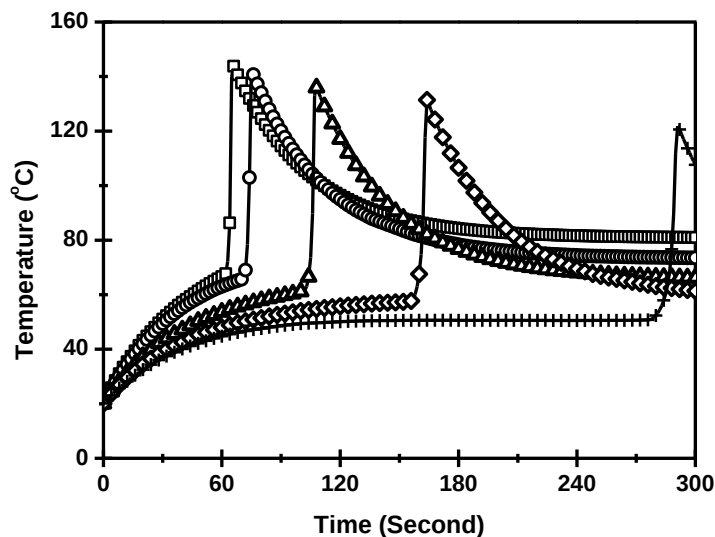


Figure 6.5. Modeling results of surface temperature profile versus time of TMPTMP-PEGDA with 1 wt% AIBN and 1.5 wt% Ni (nm) cured by varying induction power: ($\square$) 20 kW, ($\circ$) 15 kW, (Δ) 12 kW, ($\diamond$) 10 kW and (+) 8 kW.

The initiation step is one of the tunable parameters that control the reaction kinetics and heat profile of induction curing. Here, the model is utilized to predict behavior for different initiator concentrations and initiators with different half-lives. Figure 6.6 shows the modeling results for the surface temperature profile as a function of time when the initiator concentration is varied. Decreasing the AIBN concentration delays the reaction onset because it takes longer to consume the inhibitor given the lower radical generation rate. The maximum reaction temperature is only minimally affected with lower AIBN concentrations leading to higher maximum temperatures due to the increased temperature at which the polymerization reaction escalates. Figure 6.7a shows the modeling results for the surface temperature profile versus time when using different thermal initiators with varying activation energies and decay rates. The half-life and kinetic constants utilized in modeling these initiators are listed in Table 6.2. The onset of the polymerization reaction

is delayed by reducing the initiator decomposition rate. Di(2-ethylhexyl) peroxydicarbonate (DTBP) exhibits the shortest half-life (2 minutes at 90 °C) among these four initiators and as a result initiates the reaction at a lower temperature than all of the other initiators and exhibits a lower maximum temperature resultant from the reaction onset occurring at the lower temperature. The maximum temperatures of polymerizations initiated by AIBN (half-life of 20 minutes at 90 °C) and 1,1'-azodi(hexahydrobenzonitrile) (AHBN) (half-life of 4.8 hours at 90 °C) increase because the polymerization onset is delayed to higher temperatures. Di(tert-butylperoxyisopropyl)benzene (BPIPb) has the longest half-life (10 days at 90 °C) among these four initiators, but exhibits a much lower maximum temperature. This outcome is because the reaction time scale (20 minutes) is very short compared with the 10 day half-life of AHBN at 90 °C. Thus, a steady state temperature from particle heating is reached due to the slow reaction rate. Figure 6.7b illustrates the slow reaction rates of systems initiated by BPIPb. BPIPb systems require 3 minutes to achieve full conversion of double bonds while the other three systems require less than 10 seconds to achieve full conversion once the polymerization reaction is initiated.

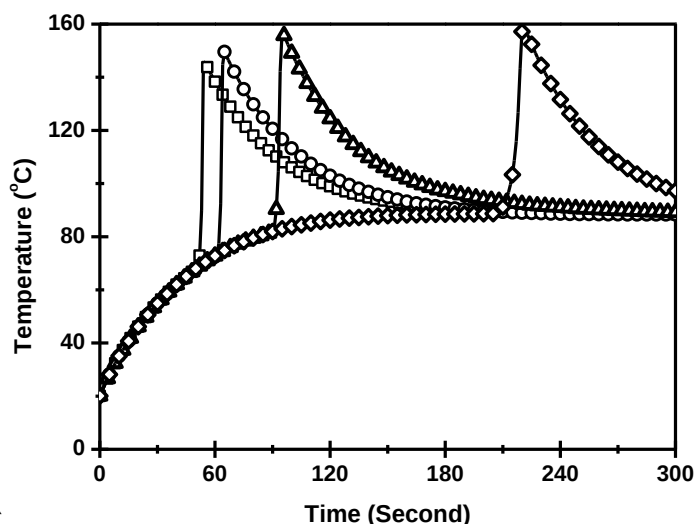


Figure 6.6. Modeling results of surface temperature profile versus time for TMPTMP-PEGDA with 1.5 wt% Ni (nm) initiated by 25 kW and (□) 1, (○) 0.5, (Δ) 0.1, and (◇) 0.01 wt% AIBN.

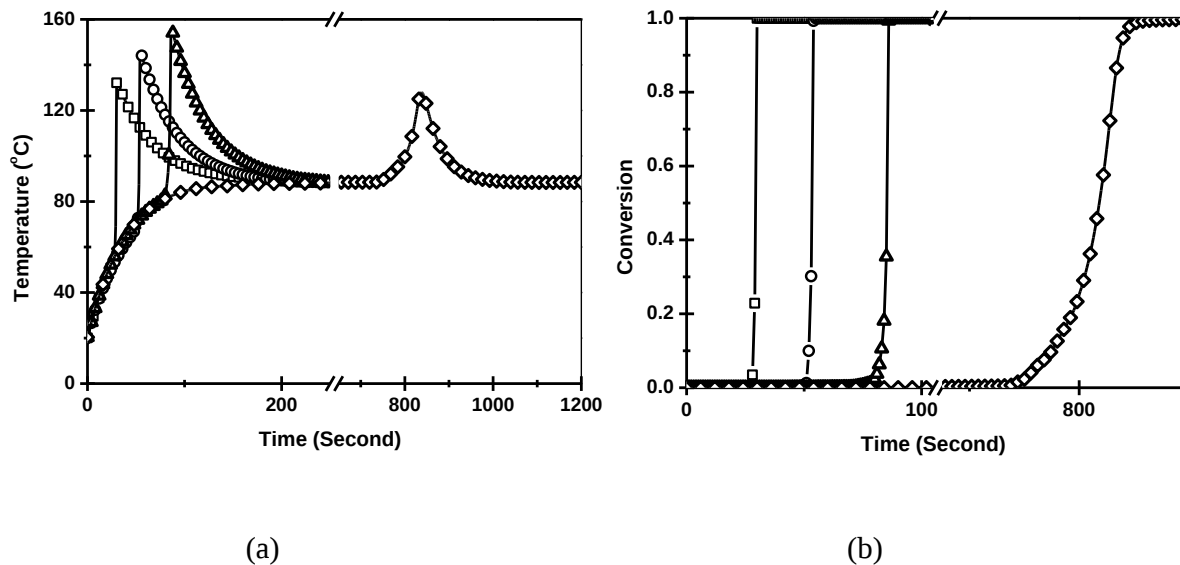


Figure 6.7. Modeling results of (a) surface temperature profile versus time and (b) conversion versus time of TMPTMP-PEGDA with 1 wt% initiator and 1.5 wt% Ni (nm) at 25 kW with (□) DTBP, (○) AIBN, (Δ) AHBN, and (◇) BPIPb.

Table 6.2. Activation energy, pre-factor of kinetic constant and half-life of initiators¹⁹

Initiator	Ea (J/mol)	k _{d0} (1/s)	Half-life at 90 °C
Di(2-ethylhexyl) peroxydicarbonate (DTBP)	126000	7.4×10 ¹⁵	2 min
2-2' azobisisobutyronitrile (AIBN)	130000	2.9×10 ¹⁵	20 min
1,1'-azodi(hexahydrobenzonitrile) (AHBN)	142000	1.1×10 ¹⁶	4.8 hours
Di(tert-butylperoxyisopropyl)benzene (BPIPb)	153000	7.7×10 ¹⁵	10 days

In addition to the initiation step, the monomer formulation also affects the temperature profile and reaction kinetics of induction curing. Figure 6.8 shows the modeling results for the surface temperature profile versus time for samples with different molecular weight PEGDA monomers. The maximum temperature decreases with increasing molecular weight of PEGDA, resulting from the decreased double bond concentration leading to a slower reaction rate and less heat generated by the reaction. Based on these modeling results, the polymerization kinetics and the maximum reaction

temperature are readily controlled by the induction heater power, the thermal decomposition kinetics of the initiator, and the molecular weight and functionality of the monomers.

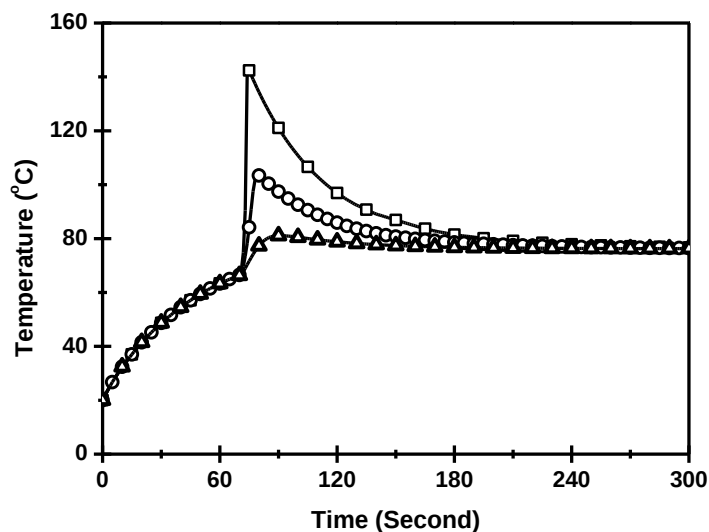
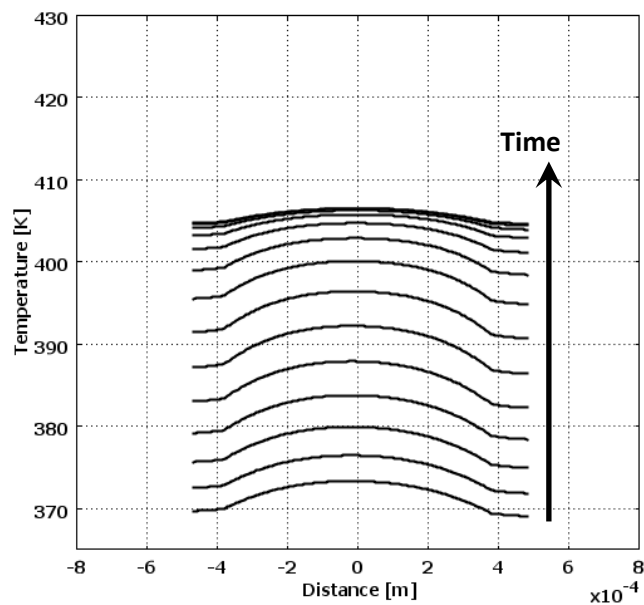
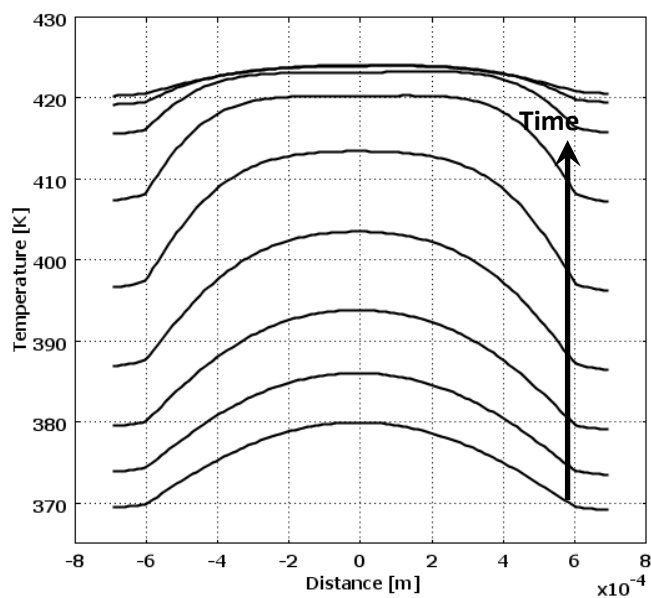


Figure 6.8. Modeling results for the surface temperature profile versus time of TMPTMP-PEGDA with 1 wt% AIBN and 1.5 wt% Ni (nm) cured at 17 kW with PEGDA molecular weights of (□) 302 g/mol, (○) 700 g/mol and (Δ) 2000 g/mol.

Sample thickness is another important factor that affects the temperature and reaction kinetics. When a thick sample is thermally cured, a significant temperature gradient arises in the sample due to heat transfer, which results in a corresponding gradient in the polymerization rate. Since the heat generated by the reaction is proportional to the reaction rate, the reaction rate gradient reciprocally affects the temperature profile in the sample. As temperature and conversion gradients can have a dramatic impact on material properties, it is of interest to study the temperature profiles of thick samples cured by induction heating. Figure 6.9 shows bulk temperature profiles at a cross-section of the samples during curing. Because of the uniform nature of the energy generation associated with the induction curing mechanism, there is only a 4 °C temperature gradient in a 0.76 mm thick sample (Figure 6.9a) at the fastest reaction rate and a 17 °C temperature gradient in an even larger, 1.2 mm thick sample (Figure 6.9b).



a)



(b)

Figure 6.9. Modeling results of bulk temperature profile versus distance at a cross-section of TMPTMP-PEGDA initiated by 1 wt% AIBN and 1.5 wt% Ni (nm) particles at 17 kW with temperature data presented for 0.1 second intervals during the exothermic reaction phase. (a) 0.76 mm thickness sample presented from 162.4 – 163.7 seconds and (b) 1.2 mm thickness sample from 86.5 - 87.3 seconds.

6.3.3 Carbon nanotube composite systems

Induction heating was utilized to cure thiol-acrylate-carbon nanotube composite systems. Composite systems with carbon nanotubes cannot be cured by photopolymerization due to the strong light attenuation associated with light absorption by the carbon nanotubes. To obtain appropriate dispersion, hydroxyl functionalized carbon nanotubes were added to the TMPTMP-PEGDA monomer resin because the hydroxyl group hydrogen bonds with the ether group in PEGDA to promote enhanced dispersion. SEM results of the cured polymer (Figure 6.10) demonstrate dispersion of the carbon nanotubes and the nanoscale nickel particles in the TMPTMP-PEGDA sample. Here, the composite containing 0.1 wt% carbon nanotubes in TMPTMP-PEGDA reaches 92% conversion. When the amount of CNTs is increased to 1 wt%, the sample is totally absorptive and the IR signal cannot penetrate through the sample to determine the conversion. However, the maximum reaction temperature of the sample containing 1 wt% carbon nanotubes TMPTMP-PEGDA is similar to the sample containing 0.1 wt% carbon nanotubes, indicating that a similar conversion was likely achieved. Figure 6.11 shows that the rubbery storage modulus slightly increases to 21.6 ± 0.1 MPa with 1 wt% carbon nanotubes as compared to 17.6 ± 0.2 MPa for the sample without carbon nanotubes. The electrical conductivity increases by at least six orders of magnitude with 1 wt% carbon nanotubes (0.33 ± 0.05 S/m) as compared to $<10^{-7}$ S/m for the pure TMPTMP-PEGDA.

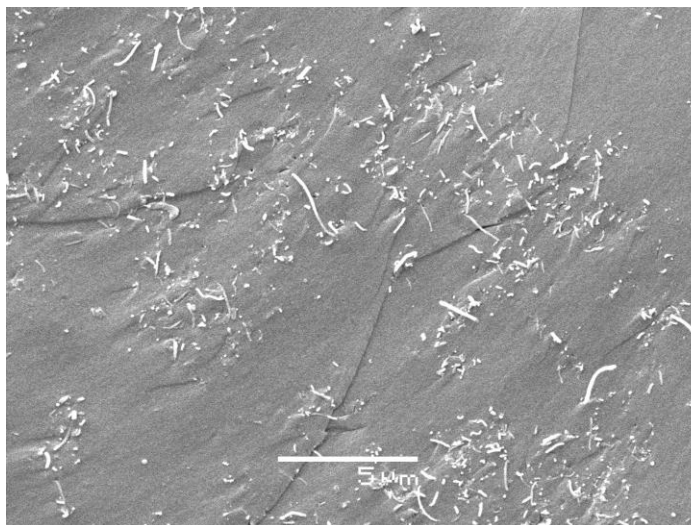


Figure 6.10. SEM image of TMPTMP-PEGDA with 1 wt% AIBN, 1 wt% Ni (nm), and 1 wt% CNT-OH scanned at low vacuum mode 5 kV.

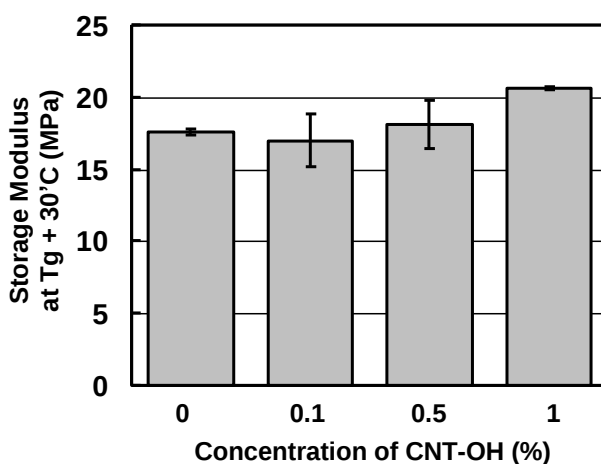


Figure 6.11. Storage modulus at $T_g + 30^\circ\text{C}$ for varying amounts of CNT-OH in TMPTMP-PEGDA with 1 wt% AIBN and 1 wt% Ni (nm). The sample is cured at 22 kW.

6.4 Conclusions

In this work, we have demonstrated a new type of radiation curing based on induction heating of thiol-ene and thiol-acrylate systems with ferromagnetic particles. A model was developed that accurately predicts both temperature profiles and polymerization rates of samples with varying

particle types and sizes, induction heater power, initiator type and concentration, functional group concentration, and sample geometry. Thiol-ene and thiol-acrylate composite systems containing carbon nanotubes, which are completely opaque and uncured by photocuring, were demonstrated to be readily polymerized by induction heating. The addition of only 1 wt% carbon nanotubes increased the storage modulus and resulted in an electrically conductive composite.

6.5 Acknowledgements

The authors gratefully acknowledge the National Science Foundation CBET 0626023, and National Institutes of Health / National Institute of Dental and Craniofacial Research Grant DE10959 for funding this work.

6.6 References

1. Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol-enes: Chemistry of the past with promise for the future. *J Polym Sci Part a-Poly Chem* **2004**, 42 (21), 5301-5338.
2. Kloosterboer, J. G., Network formation by chain crosslinking photopolymerization and its applications in electronics. *Adv Polym Sci* **1988**, 84, 1-61.
3. Fouassier, J.-P.; Rabek, J. F., *Radiation curing in polymer science and technology, volume 1. Fundamentals and methods*. Elsevier Applied Science: London; New York, 1993.
4. Zinn, S.; Semiatin, S. L.; Electric Power Research Institute.; Battelle Memorial Institute. Columbus Laboratories., *Elements of induction heating : design, control, and applications*. ASM International: Metals Park, Ohio, 1988; p xv, 335 p.
5. Martinazzo, F. Induction cured power coatings for temperature sensitive substrates. 2004-983115, 20050123743.

6. Schmidt, A. M. S. A. M., Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles. *Macromol Rapid Comm* **2006**, 27 (14), 1168-1172.
7. Yakacki, C. M.; Satarkar, N. S.; Gall, K.; Likos, R.; Hilt, J. Z., Shape-memory polymer networks with Fe(3)O(4) nanoparticles for remote activation. *J Appl Polym Sci* **2009**, 112 (5), 3166-3176.
8. Tay, T. E.; Fink, B. K.; McKnight, S. H.; Yarlagadda, S.; Gillespie, J. W., Accelerated curing of adhesives in bonded joints by induction heating. *J Compos Mater* **1999**, 33 (17), 1643-1664.
9. Suwanwatana, W.; Yarlagadda, S.; Gillespie, J. W., Hysteresis heating based induction bonding of thermoplastic composites. *Compos Sci Tech* **2006**, 66 (11-12), 1713-1723.
10. Suwanwatana, W.; Yarlagadda, S.; Gillespie, J. W., Influence of particle size on hysteresis heating behavior of nickel particulate polymer films. *Compos Sci Tech* **2006**, 66 (15), 2825-2836.
11. Bowman, C. N.; Kloxin, C. J., Toward an enhanced understanding and implementation of photopolymerization reactions. *AIChE J* **2008**, 54 (11), 2775-2795.
12. Hoyle, C. E.; Bowman, C. N., Thiol-ene click chemistry. *Angew Chem Int Edit* **2010**, 49 (9), 1540-1573.
13. Hoyle, C. E.; Lowe, A. B.; Bowman, C. N., Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem Soc Rev* **2010**, 39 (4), 1355.
14. Cramer, N. B.; Bowman, C. N., Kinetics of thiol-ene and thiol-acrylate photopolymerizations with real-time fourier transform infrared. *J Polym Sci Part a-Poly Chem* **2001**, 39 (19), 3311-3319.
15. Moniruzzaman, M.; Winey, K. I., Polymer nanocomposites containing carbon nanotubes. *Macromolecules* **2006**, 39 (16), 5194-5205.
16. Bozorth, R. M., *Ferromagnetism*. IEEE Press: Piscataway, N.J., 1993; p xvii, 968 p.
17. Odian, G. G., *Principles of polymerization*. 4th ed.; Wiley-Interscience: Hoboken, N.J., 2004; p xxiv, 812 p.
18. Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. N., Mechanism and modeling of a thiol-ene photopolymerization. *Macromolecules* **2003**, 36 (12), 4631-4636.
19. Initiator manuals of Akzo Nobel Corporation.

20. Goodner, M. D.; Bowman, C. N., Development of a comprehensive free radical photopolymerization model incorporating heat and mass transfer effects in thick films. *Chem Eng Sci* **2002**, 57 (5), 887-900.
21. Incropera, F. P., *Introduction to heat transfer*. 5th ed.; Wiley: Hobokenm NJ, 2007; p xxv, 901 p.

Chapter 7

Conclusions

This thesis was focused on understanding and investigating the interrelationships between monomer formulations, curing conditions, and material properties of thiol-ene and thiol-yne photopolymerizations. The goal was to address challenges related to developing photocurable resin and composite systems with high modulus and T_g , as well as low shrinkage stress. Ultimately, we examined the interrelationship of curing mechanism and material properties and based on the enhanced understanding, developed resins and composites as well as curing methodologies that yielded improved material performance.

In Chapter 3, to obtain a better understanding of how the polymer material properties are related to the curing conditions, the final conversions and mechanical properties (T_g and heterogeneity) of various radical photocuring systems including chain-growth (acrylates), step-growth (thiol-ene and thiol-norbornene) and mixed chain-step-growth (thiol-acrylates) systems were evaluated at different curing temperatures. The glass transition temperature (T_g) was quantified as a function of the network mobility which is related to the cure temperature (T_{cure}), the maximum achievable glass transition temperature ($T_{g\text{max}}$), and the network heterogeneity ($T_{g1/2\text{width}}$). For systems cured at temperatures much lower than the maximum glass transition temperature (i.e., where $T_{\text{cure}} < T_{g\text{max}} - T_{g1/2\text{width}}$), diffusion limitations and network heterogeneity dictate the final T_g such that $T_g \approx T_{\text{cure}} + T_{g1/2\text{width}}$. For systems polymerized at temperatures closer to their maximum glass transition temperature (i.e., where $T_{\text{cure}} \geq T_{g\text{max}} - T_{g1/2\text{width}}$), molecular structure becomes the dominant factor and $T_g \approx T_{g\text{max}}$. These relationships were shown to be applicable to resin systems reacted via various curing mechanisms including radical chain growth and step growth reactions as well as condensation reactions. These different mechanisms result in very different network heterogeneity and the different resin systems also exhibited T_g 's ranging from 35 to 205 °C. Despite

this wide range of network heterogeneity and material properties, the data across these systems exhibited only ~10% error between predicted and experimental values.

After evaluating various kinds of radical photopolymerization systems, in Chapter 4 ternary thiol-yne-methacrylate and thiol-yne-acrylate systems were characterized as possible resin systems capable of achieving excellent mechanical properties (i.e., high T_g and modulus) and low shrinkage stress. Formulations with 70 wt% methacrylate were found to increase the T_g from 51 ± 2 to 75 ± 1 °C and the modulus from 1800 ± 100 to 3200 ± 200 MPa over the pure thiol-yne system. Additionally, the shrinkage stress was 1.2 ± 0.2 MPa, which is lower than that of the pure methacrylate, binary thiol-yne and thiol-ene-methacrylate control systems which are all > 2 MPa. A minimum shrinkage stress value (1.0 ± 0.2 MPa) was observed in the 50 wt% methacrylate and 70 wt% acrylate systems. This tunable behavior results from the competitive reaction kinetics and the network evolution resulting from the balance between the methacrylate or acrylate homopolymerization relative to chain transfer to thiol and the accompanying thiol-yne step-growth polymerization. The crosslinking density and the amount of volumetric shrinkage that occurs prior to gelation relative to the total volumetric shrinkage were determined as the two dominant factors that control the final shrinkage stress of the ternary systems.

To increase the modulus further, thiol-yne-methacrylate resin systems incorporating glass fillers were studied in Chapter 5. OX50 silica nanoparticles were functionalized with a flexible 16-functional alkene-terminated hyperbranched oligomer. The 16-functional alkene was synthesized by a multistage reaction scheme employing several thiol-ene/yne reactions. The molecules covered 93% of the particle surface with an interfacial layer ranging from 0.8 – 4.5 nm thick. A thiol-yne-methacrylate composite with these functionalized silica nanoparticles demonstrated a 30% reduction in shrinkage stress (from 0.9 MPa to 0.6 MPa) without sacrificing the modulus (3200 ± 200 MPa) or glass transition temperature (62 ± 3 °C) as compared with the control system. Moreover, the shrinkage stress of the composite builds up at much later stages of the polymerization. We

hypothesize that during polymerization, the chains of the hyperbranched molecule are extended by the resin shrinkage providing more mobility that delays the stress build up.

Chapters 3 – 5 were focused on addressing challenges in the materials area surrounding how to design resin or composite systems with superior mechanical properties and low shrinkage stress. In Chapter 6, an induction polymerization method was developed as an alternative to UV curing to address challenges associated with the restriction of light accessibility in highly filled composite systems. Thiol-acrylate resins with sub100 nm nickel particles were demonstrated to achieve full conversion between 0.6 and 30 minutes with maximum temperatures ranging from 86 to 139 °C by changing the induction heater power and formulation composition. To understand further the induction curing behavior, a model of heat transfer profiles combined with reaction kinetics was developed with varying induction heater power and a 9 °C average deviation was observed between the modeling and experimental results for the maximum temperature rise. The model also was utilized to predict reaction temperatures and kinetics for systems with varying thermal initiator concentration, initiator half-life, monomer molecular weight and temperature gradients in samples with varying thickness; thereby demonstrating that induction curing represents a designable and tunable polymerization method. Moreover, induction curing was utilized to cure thiol-acrylate systems containing 1 wt% carbon nanotubes which increased the storage modulus from 17.6 ± 0.2 to 21.6 ± 0.1 MPa and electrical conductivity from $<10^{-7}$ to 0.33 ± 0.5 S/m.

Recommendations for future work are focused on additional investigation for the ternary resin and the composite system. ISO criteria such as depth of cure, flexural strength and modulus, water sorption and solubility can be tested to further implement the ternary systems as an actual dental composite. Moreover, the concept of utilizing a flexible interfacial layer between the inorganic filler and polymer matrix to reduce shrinkage stress without sacrificing other mechanical properties was demonstrated in this thesis. There are additional studies that can be followed on this

topic to further understand the mechanism resulting in the reduced shrinkage stress and to optimize the composite systems. The thickness of the interfacial layer is tunable by adding another generation of the hyperbranched oligomer during synthesis as an interesting control factor. Another variable is the structure of the hyperbranched oligomer. Compared with tetrahedral shaped molecules synthesized in this thesis, globular molecules are expected to have more facial functional groups as an interfacial layer and might therefore alter the reaction kinetics and the resulting shrinkage stress. Thus, the relationship between the thickness of the interfacial layer and the reaction kinetics and final shrinkage stress could be quantified.

Bibliography

- (1) Anseth, K. S.; Bowman, C. N., Reaction Diffusion Enhanced Termination in Polymerizations of Multifunctional Monomers. *Polym. React. Eng.* **1993**, 1 (4), 499-520.
- (2) Anseth, K. S.; Newman, S. M.; Bowman, C. N., Polymeric Dental Composites: Properties and Reaction Behavior of Multimethacrylate Dental Restorations. *Adv Polym Sci* **1995**, 122, 177-217.
- (3) Anseth, K. S.; Wang, C. M.; Bowman, C. N., Kinetics Evidence of Reaction-Diffusion during the Polymerization of Multi(meth)acrylate Monomers. *Macromolecules* **1994**, 27 (3), 650-655.
- (4) Anseth, K. S.; Wang, C. M.; Bowman, C. N., Reaction Behavior and Kinetics Constants for Photopolymerizations of Multi(meth)acrylate Monomers. *Polymer* **1994**, 35 (15), 3243-3250.
- (5) Antoni, P.; Robb, M. J.; Campos, L.; Montanez, M.; Hult, A.; Malmström, E.; Malkoch, M.; Hawker, C. J., Pushing the Limits for Thiol-Ene and CuAAC Reactions: Synthesis of a 6th Generation Dendrimer in a Single Day. *Macromolecules* **2010**, 43 (16), 6625-6631.
- (6) Aronhime, M. T.; Gillham, J. K., Time Temperature Transformation (TTT) Cure Diagram of Thermosetting Polymeric systems. *Adv. Polym. Sci.* **1986**, 78, 83-113.
- (7) Bowman, C. N.; Kloxin, C. J., Toward an Enhanced Understanding and Implementation of Photopolymerization Reactions. *AIChE J.* **2008**, 54 (11), 2775-2795.
- (8) Bozorth, R. M., Ferromagnetism. IEEE Press: Piscataway, N.J., 1993; p xvii, 968 p.
- (9) Braga, R.; Ballester, R.; Ferracane, J., Factors Involved in the Development of Polymerization Shrinkage Stress in Resin-Composites: A Systematic Review. *Dent Mater* **2005**, 21 (10), 962-970.
- (10) Bretscher, K. R.; Rusin, R. P.; Craig, B. D.; Mitra, S. B.; Oxman, J. D.; Gust, J. R.; Hayne, C. A.; Westberg, J. W.; Trom, M. C.; Kolb, B. U.; Jacobs, D. W.; Kaisaki, D. A.; Baker, J. A. Radiopaque Cationically Polymerizable Compositions Comprising a Radiopacifying Filler. **1999-US5717**
- (11) Bueche, F., Physical properties of polymers. Interscience Publishers: New York, 1962.
- (12) Cao, X.; Lee, L. J., Control of Shrinkage and Final Conversion of Vinyl Ester Resins Cured in Low-Temperature Molding Processes. *J Appl Polym Sci* **2003**, 90 (6), 1486-1496.

- (13) Carioscia, J. A.; Schneidewind, L.; O'Brien, C.; Ely, R.; Feeser, C.; Cramer, N.; Bowman, C. N., Thiol–Norbornene Materials: Approaches to Develop High Tg Thiol–Ene Polymers. *J. Polym. Sci. Part A: Poly. Chem.* **2007**, 45 (23), 5686-5696.
- (14) Chan, J. W.; Hoyle, C. E.; Lowe, A. B., Sequential Phosphine-Catalyzed, Nucleophilic Thiol-Ene/Radical-Mediated Thiol-Yne Reactions and the Facile Orthogonal Synthesis of Polyfunctional Materials. *J. Am. Chem. Soc.* **2009**, 131 (16), 5751-5754
- (15) Chen, X. X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H. B.; Nutt, S. R.; Sheran, K.; Wudl, F., A Thermally Remendable Cross-Linked Polymeric Material. *Science* **2002**, 295 (5560), 1698-1702.
- (16) Chiu, Y. Y.; Lee, L. J., Microgel Formation in the Free-Radical Cross-Linking Polymerization of Ethylene-Glycol Dimethacrylate (EGDMA) .1. Experimental. *J. Polym. Sci. Part A:Poly. Chem.* **1995**, 33 (2), 257-267.
- (17) Cook, W. D.; Forsythe, J. S.; Irawati, N.; Scott, T. F.; Xia, W. Z., Cure kinetics and Thermomechanical Properties of Thermally Stable Photopolymerized Dimethacrylates. *J Appl Polym Sci* **2003**, 90 (14), 3753-3766.
- (18) Cook, W. D.; Scott, T. F.; Quay-Thevenon, S.; Forsythe, J. S., Dynamic Mechanical Thermal Analysis of Thermally Stable and Thermally Reactive Network Polymers. *J Appl Polym Sci.* **2004**, 93 (3), 1348-1359.
- (19) Cook, W. D.; Simon, G. P.; Burchill, P. J.; Lau, M.; Fitch, T. J., Curing Kinetics and Thermal Properties of Vinyl Ester Resins. *J Appl Polym Sci* **1997**, 64 (4), 769-781.
- (20) Cramer, N. B.; Bowman, C. N., Kinetics of Thiol-Ene and Thiol-Acrylate Photopolymerizations with Real-Time Fourier Transform Infrared. *J.Polym. Sci. Part A: Poly. Chem.* **2001**, 39 (19), 3311-3319.
- (21) Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Boulden, J. E.; Wydra, R.; Stansbury, J. W.; Bowman, C. N., Properties of Methacrylate–Thiol–Ene Formulations as Dental Restorative Materials. *Dent Mater* **2010**, 26 (8), 799-806.
- (22) Cramer, N. B.; Couch, C. L.; Schreck, K. M.; Carioscia, J. A.; Boulden, J. E.; Stansbury, J. W.; Bowman, C. N., Investigation of Thiol-Ene and thiol-Ene–Methacrylate based Resins as Dental Restorative Materials. *Dent Mater* **2010**, 26 (1), 21-28.
- (23) Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. N., Mechanism and Modeling of a Thiol-Ene Photopolymerization. *Macromolecules* **2003**, 36 (12), 4631-4636.

- (24) Cramer, N. B.; Reddy, S. K.; O'Brien, A. K.; Bowman, C. N., Thiol-Ene Photopolymerization Mechanism and Rate Limiting Step Changes for Various Vinyl Functional Group Chemistries. *Macromolecules* **2003**, 36 (21), 7964-7969.
- (25) Cramer, N. B.; Stansbury, J. W.; Bowman, C. N., Recent Advances and Developments in Composite Dental Restorative Materials. *J Dent Res* **2011**, 90 (4), 402-416.
- (26) Davidson, C. L.; Feilzer, A. J., Polymerization Shrinkage and Polymerization Shrinkage Stress in Polymer-based Restoratives. *J Dent* **1997**, 25 (6), 435-440.
- (27) Dodiuk-Kenig, H.; Lizenboim, K.; Eppelbaum, I.; Zalsman, B.; Kenig, S., The Effect of Hyper-branched Polymers on the Properties of Dental Composites and Adhesives. *J Adh Sci Tech* **2004**, 18 (15-16), 1723-1737.
- (28) Eick, J. D.; Kostoryz, E. L.; Rozzi, S. M.; Jacobs, D. W.; Oxman, J. D.; Chappelow, C. C.; Glaros, A. G.; Yourtee, D. M., In vitro Biocompatibility of Oxirane/Polyol Dental Domposites with Promising Physical Properties. *Dent Mater* **2002**, 18 (5), 413-421.
- (29) Enns, J. B.; Gillham, J. K., Time Temperature Transformation (TTT) Cure Diagram – Modeling the Cure Behavior of Thermosets. *J Appl Polym Sci* **1983**, 28 (8), 2567-2591.
- (30) Fairbanks, B. D.; Scott, T. F.; Kloxin, C. J.; Anseth, K. S.; Bowman, C. N., Thiol-Yne Photopolymerizations: Novel Mechanism, Kinetics, and Step-Growth Formation of Highly Cross-Linked Networks. *Macromolecules* **2009**, 42 (1), 211-217.
- (31) Fairbanks, B. D.; Sims, E. A.; Anseth, K. S.; Bowman, C. N., Reaction Rates and Mechanisms for Radical, Photoinitiated Addition of Thiols to Alkynes, and Implications for Thiol-Yne Photopolymerizations and Click Reactions. *Macromolecules* **2010**, 43 (9), 4113-4119.
- (32) Feng, L.; Suh, B. I.; Shortall, A. C., Formation of Gaps at the Filler-Resin Interface Induced by Polymerization Contraction Stress Gaps at the Interface. *Dent Mater* **2010**, 26 (8), 719-729.
- (33) Ferracane, J., Developing a more Complete Understanding of Stresses Produced in Dental Composites During Polymerization. *Dent Mater* **2005**, 21 (1), 36-42.
- (34) Fortin, D.; Vargas, M. A., The Spectrum of Composites: New Technologies and Materials. *J Am Dent Assoc* **1999**, 131, 26S-30S.
- (35) Fouassier, J.-P.; Rabek, J. F., Radiation Curing in Polymer Science and Technology, volume 1. Fundamentals and Methods. Elsevier Applied Science: London; New York, 1993.

- (36) Franc, G.; Kakkar, A. K., Click Methodologies: Efficient, Simple and Greener Routes to Design Dendrimers. *Chem Soc Rev* **2010**, 39 (5), 1536.
- (37) Funke, W.; Okay, O.; Joos-Muller, B., Microgels Intramolecularly Crosslinked Macromolecules with a Globular Structure. *Microencapsulation - Microgels - Iniferters* **1998**, 136, 139-234.
- (38) Goodner, M. D.; Bowman, C. N., Development of a Comprehensive Free Radical Photopolymerization Model Incorporating Heat and Mass Transfer Effects in Thick Films. *Chem. Eng Sci* **2002**, 57 (5), 887-900.
- (39) Hoogenboom, R., Thiol-Yne Chemistry: A Powerful Tool for Creating Highly Functional Materials. *Angew Chem Int Edit* **2010**, 49 (20), 3415-3417.
- (40) Hoyle, C. E.; Bowman, C. N., Thiol-Ene Click Chemistry. *Angew Chem Int Edit* **2010**, 49 (9), 1540-1573.
- (41) Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol-enes: Chemistry of the past with promise for the future. *J Polym Sci Part A: Poly Chem* **2004**, 42 (21), 5301-5338.
- (42) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N., Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis. *Chem Soc Rev* **2010**, 39 (4), 1355.
- (43) Incropera, F. P., Introduction to Heat Transfer. 5th ed.; Wiley: Hobokenm NJ, 2007; p xxv, 901 p.
- (44) Initiator Manuals of Akzo Nobel Corproation.
- (45) Inoue, K., Functional Dendrimers, Hyperbranched and Star Polymers. *Prog Polym Sci* **2000**, 25 (4), 453-571.
- (46) Kannurpatti, A. R.; Anderson, K. J.; Anseth, J. W.; Bowman, C. N., Use of "Living" Radical Polymerizations to Study the Structural Evolution and Properties of Highly Crosslinked Polymer Networks. *J Polym Sci Part B: Poly Phys* **1997**, 35 (14), 2297-2307.
- (47) Kannurpatti, A. R.; Lu, S.; Bunker, G. M.; Bowman, C. N., Kinetic and Mechanistic Studies of Iniferter Photopolymerizations. *Macromolecules* **1996**, 29 (23), 7310-7315.
- (48) Killops, K. L.; Campos, L. M.; Hawker, C. J., Robust, Efficient, and Orthogonal Synthesis of Dendrimers via Thiol-Ene Click Chemistry. *J Am Chem Soc* **2008**, 130 (15), 5062-5067.

- (49) Kloosterboer, J. G., Network Formation by Chain Crosslinking Photopolymerization and its Applications in Electronics. *Adv Polym Sci* **1988**, 84, 1-61.
- (50) Kloosterboer, J. G.; Lijten, G., Photopolymers Exhibiting a Large Difference between Glass-Transition and Curing Temperature. *Polymer* **1990**, 31 (1), 95-101.
- (51) Lee, T. Y.; Carioscia, J.; Smith, Z.; Bowman, C. N., Thiol-Allyl Ether-Methacrylate Ternary Systems. Evolution Mechanism of Polymerization-Induced Shrinkage Stress and Mechanical Properties. *Macromolecules* **2007**, 40 (5), 1473-1479.
- (52) Lee, T. Y.; Smith, Z.; Reddy, S. K.; Cramer, N. B.; Bowman, C. N., Thiol-Allyl Ether-Methacrylate Ternary Systems. Polymerization Mechanism. *Macromolecules* **2007**, 40 (5), 1466-1472.
- (53) Lovell, L. G.; Berchtold, K. A.; Elliott, J. E.; Lu, H.; Bowman, C. N., Understanding the Kinetics and Network Formation of Dimethacrylate Dental Resins. *Polym Adv Tech* **2001**, 12 (6), 335-345.
- (54) Lovell, L. G.; Lu, H.; Elliott, J. E.; Stansbury, J. W.; Bowman, C. N., The Effect of Cure Rate on the Mechanical Properties of Dental Resins. *Dent Mater* **2001**, 17 (6), 504-511.
- (55) Lozinski, M. G., Industrial Applications of Induction Heating. [1st English ed.; Pergamon Press: Oxford, New York,, 1969; p xviii, 672 p.
- (56) Lu, H.; Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N., Investigations of Step-Growth Thiol-Ene Polymerizations for Novel Dental Restoratives. *Dent Mater* **2005**, 21 (12), 1129-1136.
- (57) Lu, H.; Lovell, L. G.; Bowman, C. N., Exploiting the Heterogeneity of Cross-Linked Photopolymers to Create High-T(g) Polymers from Polymerizations Performed at Ambient Conditions. *Macromolecules* **2001**, 34 (23), 8021-8025.
- (58) Lu, H.; Stansbury, J. W.; Dickens, S. H.; Eichmiller, F. C.; Bowman, C. N., Probing the Origins and Control of Shrinkage Stress in Dental Resin-Composites: I. Shrinkage Stress Characterization Technique. *J Mater Sci: Mater Med* **2004**, 15 (10), 1097-1103.
- (59) Martinazzo, F. Induction Cured Power Coatings for Temperature Sensitive Substrates. 2004-983115
- (60) Mezzenga, R.; Boogh, L.; Manson, J. A. E., A Review of Dendritic Hyperbranched Polymer as Modifiers in Epoxy Composites. *Comp Sci Tech* **2001**, 61 (5), 787-795.

- (61) Mishra, M. K.; Kobayashi, S., Star and Hyperbranched Polymers. Marcel Dekker: New York, 1999; p ix, 350 p.
- (62) Moniruzzaman, M.; Winey, K. I., Polymer Nanocomposites Containing Carbon Nanotubes. *Macromolecules* **2006**, 39 (16), 5194-5205.
- (63) Moraes, R. R.; Garcia, J. W.; Barros, M. D.; Lewis, S. H.; Pfeifer, C. S.; Liu, J.; Stansbury, J. W., Control of Polymerization Shrinkage and Stress in Nanogel-Modified Monomer and Composite Materials. *Dent Mater* **2011**, 27 (6), 509-519.
- (64) Morgenroth, F.; Mullen, K., Dendritic and Hyperbranched Polyphenylenes via a Simple Diels-Alder Route. *Tetrahedron* **1997**, 53 (45), 15349-15366.
- (65) Newkome, G. R.; Moorefield, C. N.; Vögtle, F., Dendrimers and Dendrons : Concepts, Syntheses, Applications. Wiley-VCH: Weinheim ; New York, 2001; p xii, 623 p.
- (66) Nilsson, C.; Simpson, N.; Malkoch, M.; Johansson, M.; Malmstrom, E., Synthesis and Thiol-Ene Photopolymerization of Allyl-Ether Functionalized Dendrimers. *J Polym Sci Part A: Poly Chem* **2008**, 46 (4), 1339-1348.
- (67) O'Brien, A. K.; Bowman, C. N., Impact of Oxygen on Photopolymerization Kinetics and Polymer Structure. *Macromolecules* **2006**, 39 (7), 2501-2506.
- (68) O'Brien, A. K.; Bowman, C. N., Modeling Thermal and Optical Effects on Photopolymerization Systems. *Macromolecules* **2003**, 36 (20), 7777-7782.
- (69) Odian, G. G., Principles of Polymerization. 4th ed.; Wiley-Interscience: Hoboken, N.J., 2004; p xxiv, 812 p.
- (70) Oleinik, E. F., Epoxy-Aromatic Amine Networks in the Glassy State Structure and Properties. *Advances in Polymer Science* **1986**, 80, 49-99.
- (71) Otsu, T.; Yoshida, M.; Tazaki, T., A Model for Living Radical Polymerization. *Makromolekulare Chemie-Rapid Communications* **1982**, 3 (2), 133-140.
- (72) Oxman, J. D.; Jacobs, D. W. Ternary Photoinitiator System for Curing of Epoxy Resins. 1998-US4029
- (73) Park, H. Y.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N., Covalent Adaptable Networks as Dental Restorative Resins: Stress Relaxation by Addition–Fragmentation Chain Transfer in Allyl Sulfide-Containing Resins. *Dent Mater* **2010**, 26 (10), 1010-1016.

- (74) Pfeifer, C. S.; Wilson, N. D.; Shelton, Z. R.; Stansbury, J. W., Delayed Gelation through Chain-Transfer Reactions: Mechanism for Stress Reduction in Methacrylate Networks. *Polymer* **2011**, 52 (15), 3295-3303.
- (75) Rapoport, E.; Pleshivtseva, Y., Optimal Control of Induction Heating Processes. CRC/Taylor & Francis: Boca Raton, FL, 2007.
- (76) Reddy, S. K.; Cramer, N. B.; Bowman, C. N., Thiol-Vinyl Mechanisms. 2. Kinetic Modeling of Ternary Thiol-Vinyl Photopolymerizations. *Macromolecules* **2006**, 39 (10), 3681-3687.
- (77) Reddy, S. K.; Cramer, N. B.; Kalvaitas, M.; Lee, T. Y.; Bowman, C. N., Mechanistic Modelling and Network Properties of Ternary Thiol-Vinyl Photopolymerizations. *Aust J Chem* **2006**, 59 (8), 586-593.
- (78) Rissing, C.; Son, D. Y., Application of Thiol-Ene Chemistry to the Preparation of Carbosilane-Thioether Dendrimers. *Organometallics* **2009**, 28 (11), 3167-3172.
- (79) Rozenberg, B. A., Thermodynamics and Mechanism of Reactions of Epoxy Oligomers with Amines. *Adv Polym Sci* **1986**, 75, 113-165.
- (80) Sandler, S. R., Polymer Synthesis and Characterization : a Laboratory Manual. Academic Press: San Diego, 1998.
- (81) Scheirs, J.; Priddy, D. Modern Styrenic Polymers Polystyrenes and Styrenic Copolymers. John Wiley & Sons, Inc.: West Sussex, U.K., 2003.
- (82) Schmidt, A. M. S. A. M., Electromagnetic Activation of Shape Memory Polymer Networks Containing Magnetic Nanoparticles. *Macromol Rapid Comm* **2006**, 27 (14), 1168-1172.
- (83) Scott, T. F.; Draughon, R. B.; Bowman, C. N., Actuation in Crosslinked Polymers via Photoinduced Stress Relaxation. *Adv Mater* **2006**, 18 (16), 2128-2132.
- (84) Senyurt, A. F.; Wei, H. Y.; Hoyle, C. E.; Piland, S. G.; Gould, T. E., Ternary Thiol-Ene/Acrylate Photopolymers: Effect of Acrylate Structure on Mechanical Properties. *Macromolecules* **2007**, 40 (14), 4901-4909.
- (85) Shah, P. K.; Stansbury, J. W., Modified Filler-Matrix Interfaces in Polymeric Composites Used as Dental Restoratives. *Abstracts of Papers of the Am. Chem. Soc.* **2007**, 233.
- (86) Shah, P. K.; Stansbury, J. W., Polymer-Brush Modified Fillers for Dental Composites. . *Abstracts of Papers of the Am. Chem. Soc* **2006**, 231.

- (87) Sideridou, I. D.; Karabela, M. M., Effect of the Amount of 3-Methacyloxypropyltrimethoxysilane Coupling Agent on Physical Properties of Dental Resin Nanocomposites. *Dent Mater* **2009**, 25 (11), 1315-1324.
- (88) Suwanwatana, W.; Yarlagadda, S.; Gillespie, J. W., Hysteresis Heating Based Induction Bonding of Thermoplastic Composites. *Compos Sci Tech* **2006**, 66 (11-12), 1713-1723.
- (89) Suwanwatana, W.; Yarlagadda, S.; Gillespie, J. W., Influence of Particle Size on Hysteresis Heating Behavior of Nickel Particulate Polymer Films. *Compos Sci Tech* **2006**, 66 (15), 2825-2836.
- (90) Tay, T. E.; Fink, B. K.; McKnight, S. H.; Yarlagadda, S.; Gillespie, J. W., Accelerated Curing of Adhesives in Bonded Joints by Induction Heating. *J Compos Mater* **1999**, 33 (17), 1643-1664.
- (91) Van Ende, A.; De Munck, J.; Mine, A.; Lambrechts, P.; Van Meerbeek, B., Does a Low-Shrinking Composite Induce Less Stress at the Adhesive Interface? *Dent Mater* **2010**, 26 (3), 215-222.
- (92) Venditti, R. A.; Gillham, J. K., Relationship between the Glass Transition Temperature (T_g) and Fractional Conversion for Thermosetting Systems. *J Appl Polym Sci* **1997**, 64 (1), 3-14.
- (93) Wan, Q.; Schricker, S.; Culbertson, B., Methacryloyl Derivatized Hyperbranched Polyester. 2. Photo-Polymerization and Properties for Dental Resin Systems. *J Macromol Sci Part A* **2000**, 37 (11), 1317-1331.
- (94) Wang, X. R.; Gillham, J. K., Analysis of Cross-Linking in Amine-cured Epoxy Systems – the One-to-One relationship between T_g and Conversion. *J Appl Polym Sci* **1992**, 45 (12), 2127-2143.
- (95) Wang, X. R.; Gillham, J. K., TG-Temperature Property (TGTP) Diagram for Thermosetting Systems – Anomalous Behavior of Physical Properties vs Extent of Cure. *J Appl Polym Sci* **1993**, 47 (3), 425-446.
- (96) Wei, H. Y.; Senyurt, A. F.; Jonsson, S.; Hoyle, C. E., Photopolymerization of Ternary Thiol-Ene/Acrylate Systems: Film and Network Properties. *J Polym Sci Part A: Poly Chem* **2007**, 45 (5), 822-829.
- (97) Willard, M. A.; Francavilla, T.; Harris, V. G., Core-Loss Analysis of an (Fe, Co, Ni)-Based Nanocrystalline Soft Magnetic Alloy. *J Appl Phys* **2005**, 97 (10).

- (98) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless, K. B.; Fokin, V. V., Efficiency and Fidelity in a Click-Chemistry Route to Triazole Dendrimers by the Copper(I)-Catalyzed Ligation of Azides and Alkynes. *Angew Chem Int Edit* **2004**, 43 (30), 3928-3932.
- (99) Yakacki, C. M.; Satarkar, N. S.; Gall, K.; Likos, R.; Hilt, J. Z., Shape-Memory Polymer Networks with Fe(3)O(4) Nanoparticles for Remote Activation. *J Appl Polym Sci* **2009**, 112 (5), 3166-3176.
- (100) Zinn, S.; Semiatin, S. L.; Electric Power Research Institute.; Battelle Memorial Institute. Columbus Laboratories., Elements of induction heating : Design, Control, and Applications. ASM International: Metals Park, Ohio, 1988; p xv, 335 p.