DESIGN OF HETEROGENEOUS NETWORK STRUCTURES THROUGH POLYMERIZATION INDUCED PHASE SEPARATION

by

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The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline.

ABSTRACT

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Design of Heterogeneous Network Structures Through Polymerization-Induced Phase Separation

Thesis directed by Professor Jeffrey W. Stansbury

The design of heterogeneous polymer networks has been used to combine the properties of different constituents in a single material. Heterogeneous networks with enhanced mechanical integrity, processing, and defined covalent interactions have been developed utilizing methods such as blending, block copolymer synthesis, and phase separation. However, these approaches have not yet been exploited to tailor heterogeneity in densely cross-linked networks formed under ambient photopolymerization conditions. This limits the utility of heterogeneous networks in many biomaterials, coatings, adhesive, and lithographic applications, as they often require *in situ*, ambient processing. To successfully engineer these materials, this thesis studies polymerization-induced phase separation (PIPS) as an approach to design network heterogeneity. Furthermore, this work identifies control parameters that can be utilized to tailor the development of phase morphology during polymerization.

A model system composed of a dimethacrylate homopolymer modified with thermoplastic, linear prepolymers was studied. Phase separation was detected at very early stages of polymerization, resulting in the formation of two phases, one enriched in homopolymer, and another composed of both homopolymer and prepolymer. The efficacy of this model system at reducing polymerization stress was probed. Significant stress reduction was observed when PIPS delayed the onset of macrogelation. The delay in macrogelation permits the formation of cocontinuous network structure, providing maximum interfacial area for internal rearrangement that compensates for volumetric shrinkage.

The influence of thermoplastic prepolymer properties on PIPS were studied, specifically chain-length and glass transition temperature (T_g). With decreasing chain-length, the system free energy decreases due to entropic changes, thus decreasing the thermodynamic driving force for

PIPS. However, with increasing chain-length physical limitations become more significant, and PIPS can be suppressed under rapid polymerization conditions. The prepolymer T_g was found to influence stress and modulus development. When the prepolymer T_g was significantly lower than that of the bulk matrix, the development of stress was delayed during polymerization as the lower T_g domains can flow readily to compensate for volume changes. The difference in relative reaction rate between phases formed was probed through analysis of T_g during cure. In the model system studied here, polymerization is preferred and accelerated in the homopolymer-enriched domains at the start of polymerization.

Finally, the influence of bulk matrix structure on phase separation was evaluated. Introducing structurally similar mono-vinyl monomers was found to enhance the period for phase separation via diffusion. This extended period permitted the use of incident UV-irradiation to tune the resulting size and morphology of heterogeneous domains formed. Inert particulate filler was introduced into the bulk matrix to probe the efficacy of PIPS in spatially constricted domains. Physical suppression of PIPS, due to decreased interparticle spacing and increased solution viscosity, was observed at a sufficiently high loading of filler into the matrix.

DEDICATION

To my mother, Lois.

Thank you for the countless lessons in life, humor, and chemistry.

"All that I am or ever hope to be, I owe to my angel mother." – Abraham Lincoln

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CHAPTER 1

INTRODUCTION

1.1 Purpose of Work

The work presented here will explore the advantages and control parameters associated with polymer networks that undergo phase separation during ambient photopolymerizations. While phase-separating polymerizations have been explored as an approach to design heterogeneous polymeric materials, little work has been done to expand this method into densely cross-linked network structures. There are even fewer examples of utilizing phase separation in combination with the additional spatial and temporal control afforded when using photoirradiation as the initiating mechanism for the polymerization. Here, we highlight material systems and characterization techniques that are appropriate for studying heterogeneous network formation under these conditions. Additionally, this thesis identifies approaches based in formulation chemistry as well as the processing parameters that can be utilized to tune the phase separation and resulting heterogeneous network structure.

1.2 Cross-linking Photopolymerization Overview

The cross-linking reaction of multi-functional vinyl monomers by free-radical polymerization has shown great promise in the development of polymer-based materials as these networks offer significant advantages when compared to their linear counterparts. Some of these benefits include: high strength, good thermal and mechanical stability, and excellent moisture resistance. These properties, amongst many others, have made cross-linked polymer networks attractive for a number of applications such as coatings, adhesives, printing, and biomaterials. A variety of multi-functional monomers have been explored for the application of cross-linked networks, and some primary examples include: methacrylate, acrylate, epoxy, vinyl chloride,

urethane, ethylene, alkyne, thiol, amine, siloxane and styrene based.¹⁻⁵ The work presented in this thesis will focus mainly on the use of the methacrylate functionality, which has been applied widely in different biomedical applications. For example, tissue engineering utilizes low modulus, hydrophilic poly(ethylene glycol)-based methacrylate monomers and dental restorative materials have been developed with more rigid, relatively hydrophobic methacrylate monomers to form networks with high cross-link density and strength.

The use of photoactivation as a means to produce radicals that will initiate cross-linking polymerizations enhances these reactions by adding spatial and temporal control, making it very easy for these materials to be formed *in situ*.⁶ Besides the control in space and time offered by utilizing light to initiate the polymerization, photoactivation has many additional advantages compared to other methods, namely thermal or redox initiations that are used in a variety of industrial applications. The first advantage is that photoinitiation can be incredibly energy efficient, especially when compared to thermal activation. For example, the absorption of one photon can initiate the growth of a polymer composed of 10⁵ monomer units.⁷ Photoactivation also allows the polymerization to be conducted under ambient conditions compared to thermallyinitiated systems. While this is also possible in redox-initiated polymerizations, these systems require pre-mixing immediately before use and do not have the spatial control available with photoinitiation. Additionally, photopolymerizations can be conducted in a bulk resin system, without the aid of solvent. These benefits make the application and implementation of photopolymers very attractive for a variety of fields where well-controlled ambient conditions are essential. Major examples of this are dental restorative and composite-based materials, where in situ formation at nearly ambient conditions is necessary while the final restorative material

needs to have strength close to that of the native tooth, known to be the hardest tissue in the body.⁴

A wide variety of photoactive molecules have been studied in detail for their use in initiating reactions through the formation of primary radicals upon excitation by light. Most relevant photoinitiators are responsive to light that falls in either the ultraviolet (UV, $\lambda \sim 200$ -400nm) or the visible region ($\lambda \sim 400$ -700nm) of the electromagnetic spectrum. Typically, visible light initiation is utilized in biological applications to avoid potential biological damage from UV exposure and to provide better depth of cure in thick samples; the longer wavelength of light will have greater penetration into the sample. However, UV irradiation does provide a higher amount of energy per photon, and is often more efficient at direct decomposition of photoinitiator molecules.⁵

The formation of radicals upon exposure to either UV or visible irradiation occurs primarily through one of two different mechanisms. The first, referred to as Norrish Type I, occurs by direct cleavage of a chemical bond, resulting in two radicals. The second mechanism, Norrish Type II, involves electron transfer and hydrogen abstraction, and is often referred to as sensitization.^{2, 6} With Norrish Type II photoinitiation, once the initiator molecule enters an excited state, a labile hydrogen molecule is abstracted from a donor compound (commonly referred to as a co-initiator and is often an amine, ether, or thiol). This mechanism results in the formation of one initiating radical (typically from the donor compound),⁸ while the second radical formed from the photoinitiator molecule is relatively inefficient towards the initiation process.

An example of a photoinitiator that undergoes Norrish Type I cleavage is displayed in Figure 1.1 below. The photoinitiator highlighted here is 2,2-dimethoxyphenyl acetophenone (DMPA, Irgacure 651), a benzilketal, which will be utilized for all photoinitiated polymerizations discussed in this thesis. Upon exposure to irradiation, a carbon-carbon single bond cleaves (Norrish Type I), resulting in two benzyl radicals. A unique aspect of this photoinitiator is that a secondary rearrangement of one of the primary radicals occurs, releasing a methyl radical. This methyl radical, being much smaller than the benzyl radical formed, is a main advantage of using DMPA in photopolymerizations. Being so small in size, it is very diffusive and efficient at propagating radicals, and thus promoting the polymerization process.⁷ The application of DMPA as a UV photoinitiator has been widespread and well studied.



Figure 1.1 – Cleavage mechanism of 2,2-dimethoxy phenyl acetophenone (DMPA, Irgacure 651) upon exposure to ultraviolet irradiation.

Beyond DMPA, a large number of photoinitiators have been developed and characterized.⁹ In addition to the type of photoinitiators, photoinitiation has been studied rigorously to understand the effects of irradiation intensity, wavelength, initiator efficiency, and molar absorptivity on the resulting polymerization kinetics.¹⁰

While the use of multi-functional monomers in the presence of photoinitiators to form cross-linked networks by free-radical polymerizations provides many advantages of the resulting materials, there are numerous difficulties in understanding and analyzing cross-linking polymerizations. The presence of more than one reactive group per monomer unit leads to some interesting physical, kinetic and mechanical behaviors during polymerization that have been studied extensively. A short summary of some critical aspects of these polymerizations follows.

During cross-linking polymerizations, there is a dramatic increase in the viscosity of the material as it transitions from a liquid monomer to a gel. Often during these polymerizations, the material viscosity will also increase significantly beyond gelation as it vitrifies and transitions from a gel to a rubbery and then a glassy material. It is quite common that during the polymerization of multi-functional methacrylate-based monomers, the resulting material is a glass with an ultimate glass transition temperature (T_g) greater than 100 or 150°C. The resulting T_g is dependent on the temperature at which the reaction is conducted. Typically, ambient photocuring leads to a T_g that ranges from 20-40°C above the cure temperature, but has been shown to be as great as 100°C above cure temperature in the ambient polymerization of dimethacrylate monomers.¹¹ The increase in viscosity as well as the formation of cross-links leading to a glassy material imposes certain diffusion limitations to the kinetic development of the network.

A variety of studies have focused on this anomalous kinetic behavior as a result of changes in diffusivity during polymerization in the reaction of multi-functional monomers, specifically those where the functional group is acrylate or methacrylate based in free-radical polymerizations.^{7, 12-17} Typically, the effect of the increase in viscosity results in an autoacceleration period, in which the overall polymerization rate increases rapidly. This is

followed by an autodeceleration period, in which the rate decreases severely until the polymerization effectively ceases, and no further conversion of functional groups is observed. These two periods of autoacceleration and autodeceleration have been explained well in the context of kinetic rate constants and diffusion constraints that change during a free-radical cross-linking polymerization.¹²⁻¹⁴

At the early stages of the polymerization of multi-functional monomers, the reaction is constrained by physical diffusion. This means that the polymerization rate is limited by the rate at which small initiating radicals, monomer molecules and macro-radical chains, can diffuse to reactive functionalities to initiate and/or propagate the polymerization process.^{7, 12-14} During this period, the viscosity of the solution rises gradually with the increased formation of polymer chains. These chains will vary in length based on whether the reaction follows a chain growth mechanism, forming high molecular weight chains from the beginning of the reaction, or if it proceeds via the step-growth mechanism where high molecular weight chains are not obtained until late in the reaction. Independent of the reaction mechanism, the absolute viscosity during the pre-gel stage of the reaction remains relatively low, especially when compared to the viscosity of the final network. During this period in a chain-growth process, local heterogeneities typical in cross-linking polymerizations such as microgels begin to form.^{15, 16} The kinetic constant associated with propagation of polymer chains (k_p) will decrease modestly, as the viscosity does not yet significantly limit the diffusion of monomer molecules. However, the kinetic constant associated with termination (k_t) decreases by a significantly larger fraction as the physical diffusion of large macro-radicals becomes limited with small increases in solution viscosity.^{12, 13} This leads into the observed increase in overall polymerization rate characterized by autoacceleration, often referred to as the Trommsdorff-Norrish effect.⁷ During this period, the

concentration of radicals may be increasing from initiation events, depending on the relative concentration and type of photoinitiator as well as the irradiation source, which continues to promote the conversion of monomer.

During early stages of the polymerization, the rate of network formation is also influenced by the onset of network macrogelation, where the storage (elastic) modulus overcomes that of the rubbery (viscous) modulus, thus the network spans the entire reaction vessel and has an infinite molecular weight.¹⁸ At this point, while network chains may still be elastic, significant diffusion of macro-radical chains is limited. In a cross-linking polymerization, gelation can occur very early in the reaction, at or below 5% conversion of functionalities.¹⁴ Accompanying this increase in viscosity is an increase in the network's T_g. As stated, depending on the nature of the monomers or comonomers in use as well as the temperature at which the polymerization is conducted, the network may also vitrify and transition from a gel to a glass as the polymerization proceeds further.

Once vitrification occurs, there is little to no mobility or elasticity of segmental chains available, and diffusion of macro-radicals is completely restricted.^{7, 12-14, 17} Additionally, if primary or initiating radicals still exist and have not yet been consumed at this point in the reaction, the radicals may also become trapped within the cross-linked network.⁷ Here, the existence of radicals mid-reaction is expected because free-radical cross-linking polymerizations are often engineered so that there is no risk of limiting the ultimate conversion due to a lack of initiation events. While the ultimate T_g in networks that undergo vitrification during polymerization can be higher than the temperature at which the cure is conducted, it is well below the T_g of a fully cured network. This phenomenon is due to the transition to a glassy state,

which results in the trapping of many un-reacted monomers as well as pendant double bonds attached to the bulk network.

The onset of vitrification usually coincides with the onset of autodeceleration, or a decrease, occurring more rapidly than expected based on the change in reactive group concentration, in the bulk polymerization rate throughout the remainder of the polymerization. This behavior occurs as the polymerization transitions to being limited by reaction diffusion, as opposed to the physical diffusion described previously. When the polymerization is limited by reaction diffusion, the viscosity of the material is so high that physical diffusion of all species (large macro-radicals, initiating radicals, and monomer molecules) is limited. This results in a decrease in both the propagation and termination rate constants (k_p and k_t, respectively).¹² However, the reaction still proceeds even though it is in a vitrified state, as some residual monomer will diffuse through unreacted functional groups until encountering a second radical with which to terminate.¹⁷ The structural heterogeneity associated with cross-linked networks also contributes to conversion in the vitrified state, as mobility in some regions will be less limited than in others, thereby permitting more diffusion. Eventually the reaction comes to completion and the observed rate reaches zero; however, the reaction typically occurs without complete conversion of all functionalities.⁷

While the general autoacceleration and autodeceleration behaviors are exhibited in various monomer systems, the onset of gelation, vitrification, autodeceleration, and relative magnitude of the increase in bulk polymerization rate can vary significantly based on the monomer structure. For instance, when utilizing bisphenol A glycerolate dimethacrylate (BisGMA) as the bulk resin, which has a high initial monomer viscosity and is used extensively in dental material applications, vitrification occurs relatively early in the polymerization and the

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final conversion of the resin may only reach $\sim 35\%$.¹⁹ However, when using a slightly different dimethacrylate monomer, tri-ethylene glycol dimethacrylate (TEGDMA), with a lower viscosity, vitrification is delayed and the limiting conversion can be as great as 75%.⁵

1.3 Polymerization Shrinkage and Stress

Despite the advantages offered by photoinitiated, cross-linking polymerizations, the main drawback to this class of reactions is the development of polymerization shrinkage and stress. As monomer molecules convert to polymer, either cross-linked or linear in nature, there is an associated loss in free volume that leads to volumetric shrinkage of the polymerizing resin. If the resin is not bonded to any surface or interface, this change of volume will happen freely in all dimensions. However, in applications where a bonded interface is necessary (i.e., coatings, dental restoratives), the now-constrained, volumetric shrinkage leads to a complex build-up of stress in both the reacting polymer and potentially in the substrate as well. This depends on the relative modulus of the formed material. The stress is a result of the competition between the shrinkage occurring within the resin and the adhesive force acting between the resin and the bonded interface. This behavior is illustrated below in Figure 1.2.

For a methacrylate-based reaction, the extent of volumetric shrinkage during polymerization can be predicted with reasonably good accuracy since molar change in volume from the reaction of either a methacrylate or acrylate moiety has been determined experimentally to be approximately 22 cm³/mol (independent of the monomer structure).²⁰ The level of polymerization stress experienced by a network is much harder to predict when based solely on the reactive functionality. The magnitude of polymerization stress is complex and dynamic and evolves during a reaction. Factors such as: the extent of conversion, elastic modulus, viscosity, extent of volumetric shrinkage and polymerization rate contribute to the relative magnitude of

stress during a polymerization.²¹⁻²⁶ Since it is not a fundamental property of materials, the magnitude of stress also depends directly on the sample geometry and the compliance of the bonded substrates.²⁷ Additionally, many studies have shown that when photoirradiation is employed as the mechanism of initiation, the irradiation intensity also contributes to the magnitude of polymerization stress.²⁸



Figure 1.2 – Volumetric shrinkage and interfacial stress development during polymerization, and the influence of bonded interfaces as compared to free shrinkage. (Red arrows indicate direction in which stress combats adhesive bonding between polymer resin and interface.)

Prior to network gelation, the volumetric shrinkage as a result of functional group conversion is compensated for by viscous flow of the polymerizing resin. However, once gelation is encountered, bulk shrinkage continues and stress development is observed, with the polymerization stress increasing most dramatically along with the onset of vitrification.²⁴ The level of stress scales with the final modulus of the material, meaning a system that has a lower

modulus will typically display a lower level of polymerization stress than materials that have higher resulting modulus, given the same sample geometry and constraining substrates. Depending on the relative magnitude of the different forces, the build-up of polymerization stress can lead to de-lamination of the material from the substrate to which it is applied, as well as internal defects such as cracking within the bulk material. Both the internal and interfacial defects will compromise material performance in a variety of applications and often results in the need for replacement materials.

Many different approaches to combatting and alleviating the effect of polymerization shrinkage and stress have been proposed and studied. One such example is the use of inorganic fillers, which have shown promise in the reduction of polymerization shrinkage in composite-based systems.²⁹⁻³¹ In studies utilizing inert barium aluminosilicate glass filler, the reduction in shrinkage strain was found to scale proportionally with the volume fraction of filler loaded into the system. The presence of the filler reduces the overall concentration of reactive functional groups that directly contribute to the reaction-induced polymerization shrinkage.³² The most extensively explored glass-based fillers, such as the barium aluminosilicate, typically have a modulus much higher than that of the final polymer. This difference in modulus means the particulate introduced into the system will not change dimension in response to the shrinkage occurring within the matrix during polymerization.

Many other effects beyond shrinkage reduction are exploited by utilizing inorganic filler within a polymer matrix. One important effect is an associated increase in modulus and toughness based directly on the type of filler and resin in use.³³ This increase in modulus scales with the volume fraction of filler in the composite, similarly to that mentioned above. Since polymerization shrinkage stress is a function of both shrinkage strain and modulus, highly filled

resins with a large final modulus can actually experience little to no stress reduction despite a substantial reduction in shrinkage. Another effect of introducing inorganic filler is a change in transparency and color of the polymer formed compared to the unfilled material. Depending on the intended application, these changes in optical properties can be beneficial or detrimental to the material. The optical changes typically vary with both the extent of conversion as well as the loading level of filler in the resin.³⁴ To develop filled systems that combine both increased modulus and stress reduction, inorganic fillers with functionalized surfaces have been developed.^{31, 35-38} These coupling agents allow for covalent attachment between the filler and the resin matrix. It has been shown that the functionalization of fillers with polymer brushes or hyper-branched moieties have been effective at stress reduction by providing compliant interfaces, which compensate for volume changes during polymerization.³¹

The thiol-ene click reaction has been investigated recently as an approach towards developing cross-linked photopolymers with reduced polymerization shrinkage and stress.^{1, 3} In this reaction mechanism, the polymerization proceeds through alternating propagation and chain transfer events. The propagation step occurs across the ene-group, where the resulting carbon-centered radical undergoes chain transfer by abstraction of a hydrogen radical from the thiol. This mechanism results in the step-wise growth of molecular weight and network structure, meaning the molecular weight does not increase significantly until late stages of the reaction. This is opposed to chain-growth polymerizations where high molecular weight polymer is generated almost immediately at the onset of the polymerization. The step-growth nature of a thiol-ene reaction leads to delayed gelation, in turn reducing the magnitude of the polymerization stress. Since each -ene double bond reacts with only one thiol monomer, instead of two monomers as in the chain growth mechanism, there is a less significant decrease in the free

volume as a function of double bond conversion. This has been characterized as ~12-15 cm³/mol, which is close to half the value estimated in (meth)acrylate chain-growth polymerizations.³⁹ Beyond the reduction in polymerization shrinkage and stress, thiol-ene polymerizations can be formed very rapidly, resulting in the formation of a very homogeneous, nearly ideal uniform polymer network while overcoming issues with oxygen inhibition. Typically, thiol-ene networks have a lower T_g and modulus than methacrylate-based cross-linked systems, which can be a limitation depending on the material's intended use. Additionally, issues with distinct odors, higher toxicity and limited shelf-life have been noted as concerns with the use of thiol-ene chemistry for certain applications.³

Another mechanism proposed for stress relaxation in cross-linked polymer networks is through stimuli-responsive covalent adaptable networks (CANs) that undergo bond rearrangement.⁴⁰⁻⁴³ Exchangeable chemical bonds in these networks are incorporated into the elastic chains. Depending on the rate of bond exchange and corresponding duration of an applied stress, this rearrangement will lead to stress relaxation while active radical species are present. While the exchangeable bonds undergo both cleavage and reformation, mechanical properties such as modulus and T_g are conserved during the rearrangement since the total number of bonds formed remains equivalent.^{6, 40} Some of the most common moieties explored to incorporate the exchangeable bond are allyl sulfides and trithiocarbonates, both of which can undergo additionfragmentation chain transfer in the presence of radicals. If a photoinitiator is incorporated in the network formation process, the relaxation and bond rearrangement can be controlled both spatially and temporally. Like the thiol-ene systems, many CAN-based networks have sufficiently lower T_gs and modulus than (meth)acrylate based cross-linked resins. For this reason, much work has been done to optimize these material properties in systems that combine the aspects of methacrylate, allysulfide, and thiol-ene polymerizations.^{43, 44}

A different approach towards polymerization stress reduction is the development of heterogeneous networks with domains of differing physical properties. This relies on developing interfaces that can compensate for volumetric changes during polymerization. One method towards this is polymerization-induced phase separation, induced by the addition of organic lowprofile additives (LPAs) to a bulk monomer or comonomer resin.⁴⁵⁻⁴⁸ Commonly, the observed reduction in shrinkage and stress in these systems is attributed to cavitation or microvoid formation along interfaces of chemically different domains.⁴⁵⁻⁵¹ This microvoid formation occurs as phases with differing thermal expansion coefficients are brought from an elevated processing temperature to ambient conditions.⁴⁵ Here, the heating and cooling process contributes not only to the shrinkage reduction, but also promotes the phase separation process. This approach has been proven effective for shrinkage reduction through phase separation in thermal polymerization applications, e.g., the development of molded thermosets.⁴⁹⁻⁵¹ However, limited work has been done to explore methods that could extend this approach to applications where ambient polymerization conditions are necessary. This thesis will focus on identifying and characterizing similar approaches towards heterogeneous network development that could have the added benefit of shrinkage and stress reduction in ambient photopolymerizations.

1.4 Heterogeneous Network Development

Heterogeneous polymeric materials offer many advantages compared to their single phase counterparts since the combined properties of different components can contribute synergistically to the performance and utility of a single material.⁵² This was the desire and driving force behind the research and development of one of the first classes of heterogeneous

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polymer systems: polymer blends. In these systems, two components already in the polymeric state are mixed or *blended* together to form a heterogeneous material. Typically, the two components are linear pre-formed polymers. To effectively combine both polymers' characteristics, it is often necessary to have co-continuous morphology in the resulting blend. Whether the morphology is co-continuous or dispersed relies heavily on the viscosity, volume fraction and resulting interfacial tension of the components.^{53, 54} For example, it has been demonstrated in the blend of two widely-used commercial plastics, polystyrene and polyethylene, that a higher interfacial tension minimizes the compositional range where the resulting morphology is co-continuous.⁵³

Also contributing to the resulting morphology in blended polymers is the processing approach and its associated parameters. Processes that have been described to achieve this aim include a blend of extrusion and mixing as well as annealing.⁵³⁻⁵⁶ Willemse et al. have proposed simultaneous blending and melting as an effective approach to dispersion in commercially relevant blends, such as polystyrene/polyethylene. The dispersion proceeds through a 'sheeting' mechanism, where layers of different polymer components break-up during shear flow.⁵⁶ Work has also been done to elucidate the stability of blends with varying morphologies when annealed after blending. Annealing has been shown to lead to an increase in phase sizes through coalescence, and even leads to the development of dispersed morphology in blends with initially co-continuous structure.^{54, 56} Again, the extent of coalescence upon annealing depends on the relative viscosity and interfacial tension in the blend. If there is some degree of cross-linking in the blend, no significant change in phase morphology is observed upon annealing.⁵⁴

While blending as an approach towards heterogeneous polymer networks has been well characterized, the energetic needs for processing – whether mechanical, thermal or a

combination of both – are large, which limits the applications of these materials. Specifically, the studies outlined here all require processing temperatures of at least 200°C. This thermal input, as well as the mechanical energy required from the use of an extruder and/or mixer, makes these materials ill suited for applications that require *in situ* formation.

Another approach to develop heterogeneous polymer materials has been through the formation of block copolymers.^{57, 58} Here, morphology and volume fraction of the resulting heterogeneous structure are controlled through precise design and synthesis of monomers as well as the relative concentration of the different components. In several of these studies, miscibility of the copolymers is controlled through hydrogen bonding strength.^{57, 58} To achieve these differing morphologies, the block copolymers are formed in the presence of solvent that is removed during processing; the resulting phase morphologies are greatly varied from cylindrical, spherical and lamellar shapes. Again, similarly to blended systems, this approach typically utilizes linear, pre-formed polymers as the main components of the material formulation.

Variation in miscibility and the potential for phase separation of polymeric components have been exploited towards the development of heterogeneous networks. One such example is the development of networks through thermally-induced phase separation.⁵⁹⁻⁶¹ This can be accomplished by taking a solution of multiple polymer components at an elevated temperature and inducing phase separation by cooling or quenching the solution. This approach is appropriate when the multi-component system displays upper critical solution temperature (UCST) behavior, i.e., above a certain temperature threshold the mixture will be homogeneous.^{60, 61} Thermally-induced phase separation is actually more commonly utilized in lower critical solution temperatures and thus, phase separation is promoted by increasing the overall temperature of the solution.^{59, 61}

This approach is used often in the development of membranes, where pore size and shape can be controlled through the rate and temperature at which the system is quenched.⁶⁰

1.4.1 Polymerization Induced Phase Separation

An attractive approach towards ambient heterogeneous network formation, which will be the focus of this thesis, is to develop heterogeneous networks *in situ* through polymerizationinduced phase separation (PIPS). This method takes advantage of thermodynamic instability introduced by the polymerization process. The instability leads to phase separation, promoting the formation and evolution of multi-phase structure in a polymeric material. This eliminates the need for external apparatuses such as mixers and extruders to form the compositionally heterogeneous domains. Thus, PIPS is a very attractive approach to develop heterogeneous materials for *in situ* applications. Typically, formation of heterogeneous materials via PIPS starts with a homogeneous formulation. Increases in the overall free energy of the formulation, either from entropic or enthalpic changes once the polymerization reaction initiates, promote phase separation of components that are either completely or partially immiscible. The extent to which different components will phase separate depends on several factors such as, but not limited to, the kinetics of the reaction, relative miscibility, viscosity of the solution, and formation of crosslinks. These factors that can either hinder or promote phase separation during polymerization are generally categorized as related to the thermodynamics or kinetics of the reaction. Heterogeneous network formation through PIPS relies heavily on the dynamic interplay, and in some ways competition, between the thermodynamic and kinetic constraints.

Thermodynamic factors that can either promote or suppress PIPS are best understood in the context of the overall free energy of the polymerizing system. This has been described theoretically for heterogeneous polymer solutions with the Flory-Huggins lattice model.⁶²⁻⁶⁶ The

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core of this model is the calculation of the overall Gibb's free energy of mixing (ΔG). Equation 1 shows the Gibbs calculation for a multi-component mixture:

$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix} \tag{1}$$

Where:

 ΔH = Enthalpy, ΔS = Entropy, and T = Temperature (K)

If the value of the free energy is negative, $\Delta G^{mix} < 0$, then the multi-component system is in a stable energy state and will remain in a single phase. However, if the free energy of mixing is sufficiently high, $\Delta G^{mix} > 0$, then phase separation is preferred to reduce the overall free energy of the system.

Both the overall enthalpy (ΔH^{mix}) and entropy (ΔS^{mix}) contribute to the free energy of a mixture. The enthalpy of mixing relates to the heat absorbed or released by mixing the different components present in the system. For instance, if two components that are chemically dissimilar and immiscible are mixed in equal volumes, the ΔH value is likely to be positive since the mixing will be an endothermic process. In general, the property of enthalpy relates to the relative miscibility of all the components included in a mixture. The entropy of mixing (ΔS^{mix}) describes the degree of randomness or disorder in the system. ΔS is often explained as the number of ways in which different components can be arranged in a system assuming a given model (e.g., a lattice).⁶³ For example, a cross-linked network will likely have a lower ΔS than a system based in linear polymers, as the cross-links restrict the possible arrangements available for the network.

As the reaction progresses, the overall ΔG^{mix} will change as a result of variations in one or both of the enthalpy and entropy of mixing (see Equation 1). This is why an initially stable and homogeneous multi-component monomer formulation, with $\Delta G^{mix} < 0$, can undergo phase separation during polymerization. The absolute value of these enthalpic and entropic changes is difficult to predict due to their complexity, especially in a cross-linking polymerization, which inherently forms a network with a degree of heterogeneity to it. For instance, at the early stages of the reaction, initiation, propagation and termination events may all be occurring simultaneously in different locations of the forming network. However, some general trends that contribute to changes in overall free energy can be reasonably assumed and will be discussed.

The change in entropy of mixing is fairly easy to predict given a polymerization. As conversion increases, the number of individual components within the system will decrease as monomer molecules combine to form polymer chains. If there are multi-functional monomers then formation of cross-links will further reduce the number of components within the system. Further, this correlates with a decrease in the number of conformations the system can undergo, which results in a decrease in the overall entropy.⁶² Since entropy will continue to decrease throughout the reaction, increases in conversion will promote increases in the overall free energy, thus making phase separation more favorable or likely during the reaction.

The enthalpy of mixing is much more difficult to quantify during the reaction; there is no clear indication of whether ΔH^{mix} will increase or decrease with conversion. Again, this relates to the relative miscibility of the different components and the attractive or repulsive interactions between them. During a polymerization, the relative miscibility will not change dramatically given the repeat unit, either in the monomer or polymer form, remains the same. However, the density of chain ends will change with conversion and could impact miscibility.

While phase separation is favored when $\Delta G^{mix} > 0$, there are two possible mechanisms that can occur once entering a high free energy state. The mechanism through which phase separation proceeds depends on whether the free energy state is either metastable or highly unstable. The barriers between the metastable and highly unstable regions are typically illustrated through a phase diagram, such as Figure 1.3. This phase diagram shows typical phase behavior for a multi-component mixture with upper critical solution temperature (UCST) behavior, i.e. at a sufficiently high temperature, only one phase is observed. In this diagram, the natural variable that alters the free energy of the mixture is temperature. Figure 1.3 displays the binodal and spinodal curves in red and blue, respectively. The binodal curve represents the boundary between stability and metastability, while the spinodal curve represents the boundary between metastability and complete instability. Phase diagrams like this can also be plotted as a function of pressure, or in the case of PIPS, the y-axis can be the extent of reaction.



Composition

Figure 1.3 – Example phase diagram showing metastable and unstable regions in a multicomponent solution.

When a multi-component mixture becomes metastable, which is depicted as the regions between the red and blue phase curves in Figure 1.3, phase separation will proceed through the Nucleation and Growth (N&G) mechanism. The metastable domain is described mathematically as regions of local minima in the overall free energy. In N&G, small spherical domains of the phase with a lower volume fraction, otherwise referred to as the minor phase, will form. As time progresses, and assuming no additional constraints limiting phase separation develop, these dispersed domains will grow in size and eventually coalesce.^{46, 59, 67, 68} The resulting size and fraction of dispersed domains is dependent on the initial concentration of the different components.

The second mechanism of phase separation, Spinodal Decomposition (SD), occurs when a system enters a highly unstable free energy state, or in other words crosses the spinodal curve in the multi-phase region. This state is also characterized by the following: $\frac{\partial^2 \Delta G^{mix}}{\partial x_1^2} = 0$, where x_1 is a compositional variable. In SD, co-continuous phase structure forms immediately upon entering the highly unstable free energy state.^{46, 59, 68} If this mechanism can proceed without any physical constraints, the co-continuous domains will eventually coalesce to form dispersed domains which are similar to those observed in systems that underwent N&G.⁶⁹ However, if the phase separation is halted prior to coalescence, phase structure that is co-continuous will remain. Many theoretical studies have investigated phase separation and the evolution of the free energy in polymer solutions^{63, 65, 70} as well as during polymerizations.^{67, 71} This thesis will focus on wellcontrolled experimental methodology with support taken from these theories.

Thus far, this discussion has only considered the thermodynamic contributions to phase separation, but as mentioned, the process of PIPS involves the dynamic interplay between both the thermodynamic changes in free energy as well as the kinetic and physical limitations imposed during polymerization. The limitations on diffusion mainly result when viscosity increases during polymerization. This can dramatically suppress the phase separation process. As described previously, the viscosity of a polymerizing formulation will increase dramatically as polymeric material transitions from a liquid to a gel to a glass. These viscous effects prohibit diffusion, especially of large molecules within the polymer solution or network. For example, if multi-functional monomers are utilized and form a cross-linked network, phase separation will

likely be suppressed after the onset of macrogelation. The extent to which phase separation is suppressed will depend on the elasticity of the network chains as well as the relative size and diffusivity of the other components within the system. If and when vitrification occurs (which will depend on the monomers utilized, as well as the temperature at which the polymerization is conducted), diffusion will be severely limited and thus, phase separation via diffusion can be restricted significantly.

The imposition of kinetic limitations on phase separation during polymerization has been studied specifically in the context of the Trommsdorrff-Norrish effect.⁷²⁻⁷⁵ In general, the onset of autodeceleration in linear polymers corresponds to the arrest of phase separation through diffusion. Therefore, gelation and vitrification impose kinetic constraints on the phase separation process during polymerization, which can dramatically alter the extent to which phase separation via diffusion can occur during the reaction. For example, consider a system that only enters an unstable free energy state at late stages of conversion. While phase separation may be energetically favorable, if the reaction proceeds beyond gelation or vitrification of the polymer network, phase separation may be physically limited and will not occur even though, thermodynamically speaking, separation should proceed readily. This behavior is illustrated schematically in Figure 1.4 below. The effects of both gelation and vitrification during a polymerization have been cited as imposing significant barriers to phase separation during polymerization in numerous studies.^{45-47, 52, 69, 72, 73, 76-88}



Figure 1.4 – Schematic illustration of physical limitations to phase separation during polymerization, specifically the onset of network macrogelation.

1.4.2 Previous Approaches to Heterogeneous Polymer Networks via PIPS

A number of different approaches have been characterized towards heterogeneous polymer formation via PIPS, taking into account both the thermodynamic and kinetic limitations to this process. A solvent is often used to drive thermodynamic immiscibility during polymerization. In some cases, the resulting phase separation has been an unexpected or undesired response, such as in the study of dental adhesive formulations.⁸⁹⁻⁹¹ Here, during the copolymerization of BisGMA and hydroxyl-ethyl methacrylate (HEMA), the aqueous nature of the enamel or dentine surface leads to phase separation into hydrophobic (BisGMA-rich) and hydrophilic (HEMA-rich) domains. This copolymerization process ultimately leads to lower

conversion in both phases due to interactions of the initiator with water in the HEMA-rich regions and early vitrification in the BisGMA-rich domains, both of which compromise the adhesive strength of the material. This is not to be confused with the controlled phase separation observed in the copolymerization of dimer acid-derived dimethacrylates with traditional dimethacrylate monomers (TEGDMA, BisGMA) that has also been explored for dental applications. In this copolymerization, the phase separation occurs in the bulk material and is not a result of solvent interactions from the environment in which the material is formed; this results in higher conversion, reduced shrinkage and reduced stress of the network.⁹²

In contrast, there have been studies where the desired outcome is phase separation induced by a polymer/solvent mixture.^{93, 94} For instance, the thermal phase separation of acrylamide-based polymers have been explored for drug delivery applications.⁹³ These polymers transition from coil-like structures to globules after passing through their lower critical solution temperature. Another example is the phase separation between acrylate-based polymers and water, which is exploited to create hydrogels.⁹⁴ In some approaches, the activity and relative miscibility between solvent and polymer are altered during processing by inducing solvent evaporation.^{95, 96} Here, simultaneous polymerization and solvent evaporation are utilized to influence the formation of microstructures in the polymer network. The rates of solvent evaporation and network formation influence the phase structure; in one study, these were controlled utilizing photoirradiation.⁹⁶ This approach has been successful for creating skin layers with phase-separated morphology on the surface of a material while at the same time maintaining a more densely cross-linked bulk that does not undergo distinct phase separation.⁹⁶

Significant work has been done toward developing networks utilizing phase separation in semi- and interpenetrating polymer networks (semi-IPNs, IPNs).^{69, 77-81} Dean and Cook have

done the majority of this work utilizing dual-cure networks to selectively control the order of phase formation. To achieve control, two different monomer components are used, one based in epoxy functionality and the other in methacrylate. While both can polymerize through a freeradical polymerization, two separate initiators with varying miscibility in one of the monomers were used. Differing initiator schemes have been employed to control the cure order. In one approach, the entire matrix was cured thermally, but initiators were chosen for their varying decomposition rates at the processing temperatures to selectively control development in the different phases.^{78, 80} In another approach, different curing mechanisms were utilized; the epoxy component was mixed with a thermal initiator and the methacrylate with a photoinitiator.⁷⁷ As described, the polymerization could be initiated in the individual phases by the introduction of either thermal or photonic energy. It was found that varying morphologies could be achieved by simply varying the order of polymerization or by altering the ratio of the two different components in the bulk resin.^{79, 81} In one study, a less heterogeneous network was formed when the more rigid epoxy component was allowed to polymerize first. However, if the cure order was reversed, and the more flexible methacrylate component was cured first by photoinitiation, a much more heterogeneous network formed, as indicated by broad peaks observed in the tan delta profile.⁷⁷ While this approach provides direct control over the order of phase formation, the first phase formed, regardless of the order, puts significant limitations on the rate and extent of cure of the latter forming domains.

Other approaches have focused on developing different phase morphologies by varying the extent of phase separation that can occur during PIPS. One approach towards this aim that also utilizes free-radical polymerizations has been the polymerization of copolymers with varying reactivity ratios.^{46-48, 52, 97, 98} Here, larger differences in reactivity ratios result in an

earlier onset of phase separation as well as a significant difference in composition throughout regions of the copolymer. A common approach to varying morphology is by adjusting the amount of time between phase separation and network gelation during polymerization or eliminating limitations to diffusion. This is often accomplished by increasing the processing temperature, so diffusion limitations decrease and further phase development can occur.^{45, 88} Another approach to extend the time for diffusion during phase separation is by utilizing epoxybased resins, which polymerize very slowly. As a result, the physical time prior to gelation is quite long when compared to an acrylic-based polymerization.^{76, 82, 99} The use of a slow reacting epoxy system not only maximizes the time for phase separation during polymerization, but also makes dynamic characterization of the evolving phase structure more accessible. In these studies, strong correlations between the phase morphology (co-continuous versus dispersed) and resulting stress reduction have been found. It is worth noting that networks resulting in co-continuous morphology have a larger degree of stress reduction.⁴⁷

Systems that undergo PIPS and take advantage of the additional control offered by photoinitiation have been explored recently.^{71-75, 83-88, 96, 100-102} The majority of these studies have focused on the development of materials for polymer-dispersed liquid crystals (PDLCs).^{71, 84-87, 100, 102} In these applications, the majority of the bulk material is liquid crystal (usually at a mass fraction of 50% or higher), and the polymer component is often linear in nature. These do not form chemical cross-links, so the impact of a viscosity increase or dense cross-linking is minimized. An additional control that has been demonstrated in linear-PDLC examples is the LC morphology prior to photopolymerization. This is accomplished by varying the temperature at which the material is photocured; the liquid crystal fraction can be in either a nematic or isotropic phase.¹⁰² Using these combined controls, a variety of phase domains including

dispersed,^{84, 86, 100} co-continuous,⁸⁶ and fibrous¹⁰² have been demonstrated. In these systems, relatively low irradiation intensities are utilized (less than 1mW/cm²) so as not to completely suppress the phase separation process.^{85, 86, 100} Additionally, the impact of the dispersion type on material properties has been explored, e.g. transmittance, driving voltage, and contrast ratio.^{87, 100}

Photo-induced PIPS in a network with chemical cross-links has been explored in PDLC applications.^{71, 84-86} The impact of the kinetics of polymerization on the resulting morphology and physical properties has been well characterized. While this system utilizes a cross-linked polymer resin, the liquid crystal fraction is again significant (ranging from 50-70 wt%) and cited to act like a solvent.^{71, 85, 86} The resulting cross-linked network has a greater degree of elasticity and lower overall viscosity. For this reason, some studies have observed phase separation postnetwork gelation proceeding via liquid-gel de-mixing, which becomes permissible when these systems form very elastic cross-links during the reaction.^{71, 85, 86, 100} The elasticity allows for phase separation to occur during a much larger portion of the reaction and access to a variety of domain morphologies. However, if the cross-link fraction were increased, diffusion would be restricted and post-network gelation would likely not occur.

Photo-induced PIPS has been studied in totally polymeric systems where, despite the initial monomer formulation being a liquid, the resulting material is a solid. There is no significant liquid component as was the case in the PDLC or solvent-based approaches. This phenomenon has been explored most commonly in linear polymeric resins.^{72-75, 88, 101} These studies have shown very good control over phase structure and domain size as a function of both visible and UV irradiation intensity.^{73-75, 101} Typically, with increasing irradiation intensity, there is an associated decrease in domain size. This effect has only been explored in ambient

polymerizations with UV intensities less than $1 \text{mW/cm}^{2 \ 72, \ 73}$ and visible intensities less than $2.5 \text{mW/cm}^{2. \ 74, \ 75}$

1.5 Scope of Work

In this thesis, the material system we highlight takes advantage of photo-induced PIPS in cross-linking resin systems. By modifying a dimethacrylate resin with thermoplastic prepolymers, high T_g, densely cross-linked, phase-separated polymeric networks with promising potential for ambient photopolymerization applications were developed. The influence of PIPS on interfacial polymerization stress development was studied, and a mechanism is presented for the reduction of polymerization stress during phase separating polymerizations. The influences of thermoplastic prepolymer chain length and thermal stability (specifically Tg) were studied in the context of phase separation, specifically for changes in thermodynamic parameters and local diffusion behavior. Structurally similar monomethacrylate moieties were introduced as comonomers into the dimethacrylate matrix to probe how bulk matrix properties influence the extent of phase separation during a polymerization. Similarly, inert particulate filler was introduced into the bulk matrix to probe the efficacy of PIPS in systems where the continuous network formation is spatially constricted. Finally, a range of photoirradiation intensities spanning 300μ W/cm²-100mW/cm² were employed to initiate the polymerization reaction in all studies. The influence of this tunable parameter on the extent of phase separation and resulting phase morphology was characterized.

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CHAPTER 2

OBJECTIVES

The development of cross-linked polymer networks through chain-growth polymerizations has been studied for a variety of applications, as these reactions occur rapidly and the resulting materials have many desirable properties: including thermal stability, moisture resistance, and high strength. With the use of photonic energy to initiate the polymerization, there is the additional advantage of spatial and temporal control over the reaction, as well as the ability to form these networks under ambient conditions. Despite these advantages, the formation of cross-linked networks through chain-growth polymerizations still have the consequence of polymerization shrinkage and the associated development of polymerization stress during polymerization. One approach to combat polymerization shrinkage and stress is to develop heterogeneous polymer networks, where the interfaces between compositionally different domains can provide an avenue for internal stress reduction during polymerization.

Furthermore, beyond the ability to reduce polymerization shrinkage and stress, heterogeneous networks are often employed to engineer materials that have bulk properties that are not easily accessible from a single precursor or a unified processing step. An elegant approach to develop heterogeneous networks is through polymerization-induced phase separation (PIPS), in which a stable and homogeneous monomer formulation will undergo phase separation during a polymerization due to increases in the overall free energy of the material system. Unfortunately, the use of PIPS has yet to be exploited to tailor heterogeneity in densely cross-linked networks formed under ambient photopolymerization conditions. This limitation restricts the use of PIPS in many materials applications: such as dental composites, coatings, and adhesives where ambient photocuring is preferred, if not required.

The objective of this thesis is to demonstrate the efficacy of PIPS in cross-linking reactions, and to study the relationship between phase separation and the resulting network properties in ambient photopolymerizations. The following specific aims serve as the main objectives of this study, and are designed to expand our understanding of this interesting approach towards heterogeneous network formation. Additionally, we aim to understand how materials and processing factors can be used to tune the phase separation process, so the resulting network structure can be precisely engineered with this approach.

Specific Aim 1: Identify and characterize model photopolymeric systems that undergo polymerization-induced phase separation and are appropriate for ambient cure, freeradical, bulk polymerizations.

Since limited work has been done previously towards developing cross-linked, phaseseparated networks in ambient photopolymerizations, a model material system was developed and characterized in depth. A bulk, dimethacrylate homopolymer matrix of triethylene glycol dimethacrylate (TEGDMA) was modified with three different, non-reactive, linear thermoplastic prepolymers (poly-methyl, ethyl and butyl methacrylate) to induce phase separation during polymerization. The thermal stability of all TEGDMA/prepolymer monomer formulations was probed through the upper critical solution temperature, to ensure homogeneity at ambient conditions prior to polymerization. The polymerization kinetics were monitored at varying loadings of prepolymer, and it was found that the loading level has a significant impact on the autoacceleration behavior, maximum rate of polymerization and limiting conversion compared to a TEGDMA homopolymerization. The magnitude of the changes in the polymerization rate depended on the individual prepolymer and its impact on solution viscosity. The onset of phase separation and the onset of network gelation were probed utilizing optical density and photo-rheometric measurements, respectively. The optical density measurements were also used to monitor dynamic changes in refractive index difference between compositionally different phases during polymerization. An attractive aspect of the prepolymerbased approach employed here is that near-optically transparent, phase-separated photopolymers were typically achieved. Analysis of the thermal properties of the networks, specifically glass transition temperature (T_g), post-ambient polymerization, was used to detect multi-phase structure. The composition of resulting phases formed was estimated through the observed shift in glass transition temperature. Regardless of modifying prepolymer, PIPS in the bulk dimethacrylate resin resulted in the formation of two phases: one enriched in TEGDMA-homopolymer, and a second composed of a mixture TEGDMA and prepolymer.

Specific Aim 2: Demonstrate that PIPS can lead to materials with reduced volumetric shrinkage and polymerization stress in ambient photopolymerizations. Seek to understand the physical mechanism of how and why stress reduction may occur in these materials.

Previous work has indicated that co-continuous phase structure is most efficient at compensating for polymerization shrinkage in a phase-separated matrix. With this knowledge, the aim of this study was to identify the optimal material formulations that permit the formation of co-continuous phase structure during polymerization to provide the most significant compensation of polymerization shrinkage and interfacial stress. The model TEGDMA/prepolymer polymerization was monitored in terms of polymerization interfacial stress. Additionally, the resulting phase morphology was probed post-polymerization.

When the TEGDMA-resin was modified with a significant loading of prepolymer (10-20 wt%) the onset of gelation was significantly delayed, providing more time for structural

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evolution by diffusion of immiscible components prior to network macrogelation. A fluorescently tagged prepolymer was introduced into the matrix to probe the phase structure post-ambient photopolymerization. As prepolymer loading level increases the phase structure evolves from a prepolymer dispersion to a co-continuous, regular phase structure. The material formulations with extended periods prior to network macrogelation displayed co-continuous network structure post-polymerization. This corresponded to an enhanced reduction, beyond that of the volume fraction of prepolymer, in both polymerization stress and shrinkage. This work provides an avenue to develop high T_g, densely cross-linked polymeric materials with significantly reduced stress, without relying on thermal processing parameters to aid the stress reduction.

Specific Aim 3: Understand how the physical properties of a modifying material (used to induce phase separation) can alter the phase separation process. Specifically look at the impact of molecular weight and glass transition temperature (T_g).

The studies included in this aim intend to understand and demonstrate how the modifying prepolymer can alter the interplay between the competing kinetic and thermodynamic constraints during a phase-separating polymerization. Additionally, with this understanding, these studies also demonstrate the ability to use prepolymer modification to tune the resulting bulk network properties and adjust processing constraints.

To isolate the impact of prepolymer chain length, three poly(methyl methacrylate) prepolymers, varying by an order of magnitude in molecular weight, were synthesized and introduced into a TEGDMA-resin. The overall free energy of the polymerizing system increases with prepolymer molecular weight as it decreases the system entropy, meaning that when the prepolymer chain length becomes sufficiently small, even though potential diffusion rates are

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enhanced, phase separation does not proceed during polymerization and the prepolymer acts essentially as an inert filler in the matrix. However, when the prepolymer molecular weight is significantly higher, kinetic limitations become significant and phase separation can be suppressed at high rates of network formation. Therefore, staged curing approaches, implemented by adjusting the incident irradiation intensity were utilized. In this method, an initial low-intensity cure is employed at the beginning of the reaction to permit phase separation via diffusion followed by a high-intensity cure to ensure a high degree of conversion. With this approach, phase-separated morphology that compensates for polymerization stress forms, while maintaining a high modulus and limiting conversion of the resulting network.

To investigate the impact of prepolymer thermal properties on phase separation during polymerization, the T_g development was monitored as a function of conversion. To probe this, a photo-iniferter was introduced into the polymerizing resin. With a photo-iniferter, partially cured networks that have not reached the full extent of conversion can be analyzed at above ambient temperatures without the risk of additional conversion, since the iniferter will cap active radicals that could provide avenues for re-initiation at higher temperatures. It was found that despite obtaining equivalent phase compositions at the end of polymerization, the rate at which individual phases developed varied based on the T_g of the modifying prepolymer. The differential between the prepolymer and homopolymer matrix T_g was found to have a significant impact on the modulus development and internal stress reduction during polymerization.

Specific Aim 4: Understand how structural limitations of the bulk homopolymer matrix influences phase separation, and how the control offered by photoinitiation can allow for more distinct control over resulting phase structure

This study aims to identify how the bulk matrix can be adjusted to expand the resulting phase morphologies that have been observed from ambient, phase-separating polymerizations. The work detailed up to this point has utilized a dimethacrylate-based resin, which while effective, does not offer significantly varied phase structure based on the irradiation intensity employed. Additionally, the phase separation process is suppressed at higher irradiation intensities.

In the first study presented under this aim, a structurally similar monomethacrylate was introduced into the bulk dimethacrylate matrix. The comonomer matrix was still modified with non-reactive prepolymer to induce phase separation, however the decrease in cross-link density and solution viscosity delays the onset of network gelation more significantly than in the purely dimethacrylate based resins. This delay in gelation extends the period for phase separation significantly when compared to purely dimethacrylate-based polymerizations, allowing for a phase that is richer in prepolymer to form as limitations to diffusion are minimized. Additionally, the extended period for phase separation allows distinct phase morphology to form under a much broader range of irradiation intensities than those employed in previous studies. With this material system, adjustments to the irradiation intensity can be used to alter the resulting phase morphology.

A short study into the impact on phase separation upon introducing reinforcing inorganic filler into the resin is also presented in this section. The introduction of filler spatially constricts the domains in which a continuous network can form. With increasing filler content, the

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interparticle spacing between filler particles decreases exponentially. This leads to an associated exponential increase in solution viscosity prior to polymerization. It was found that phase separation can persist in TEGDMA/prepolymer-filled resins. However, there does exist a threshold in the filler content above which phase separation is suppressed. This threshold varies based on prepolymer, and its impact on solution viscosity. This study addresses the ability to form phase-separated domains in composite-based materials, which is a topic that has yet to be explored in ambient photopolymerizations.

CHAPTER 3

A NEW APPROACH TO NETWORK HETEROGENEITY: POLYMERIZATION INDUCED PHASE SEPARATION IN PHOTO-INITIATED, FREE-RADICAL METHACRYLIC SYSTEMS^{*}

Non-reactive, thermoplastic prepolymers (poly- methyl, ethyl and butyl methacrylate) were added to a model homopolymer matrix composed of triethylene glycol dimethacrylate (TEGDMA) to form heterogeneous networks via polymerization induced phase separation (PIPS). PIPS creates networks with distinct phase structure that can partially compensate for volumetric shrinkage during polymerization through localized internal volume expansion. This investigation utilizes purely photoinitiated, free-radical systems, broadening the scope of applications for PIPS since these processing conditions have not been studied previously.

The introduction of prepolymer into TEGDMA monomer resulted in stable, homogeneous monomer formulations, most of which underwent PIPS upon photoirradiation, creating heterogeneous networks. During polymerization the presence of prepolymer enhanced autoacceleration, allowing for a more extensive ambient cure of the material. Phase separation, as characterized by dynamic changes in sample turbidity, was monitored simultaneously with monomer conversion and either preceded or was coincident with network gelation. Dynamic mechanical analysis shows a broadening of the tan delta peak and secondary peak formation, characteristic of phase-separated materials, indicating one phase rich in prepolymer and another depleted form upon phase separation. In certain cases, PIPS leads to an enhanced physical reduction of volumetric shrinkage, which is attractive for many applications including dental composite materials.

^{*} Manuscript was adapted from *Polymer*, 2012, 53, 4694-4701.

3.1 Introduction

Photopolymerized materials have been researched extensively because of the advantages they offer during cure, mainly spatial and temporal control along with rapid, on demand curing. This enhanced control is advantageous for applications in the stereo-lithography, coatings, and biomedical fields. Another advantage of photoinitiation is the ability to cure at ambient conditions, which is especially important when studying photopolymerizable dimethacrylate resins utilized as dental materials. These resins are chosen since they can form glassy, densely cross-linked networks upon polymerization and the majority have good biocompatibility and can withstand the challenging oral environment.¹⁻⁴ Dimethacrylate photopolymerizations, however, do not avoid the inherent shrinkage and associated stress upon cure that is typical of polymerizations.¹⁻⁹ This shrinkage is caused by a reduction in associated free volume as monomer is converted to polymer, and in methacrylic systems leads to a volume reduction ~23 cm³ per mol of converted reactive group.³⁻⁵

When dimethacrylates are utilized in dental composites the associated stress can lead to internal defects as well as separation of the interface from the substrate to which it is bonded.² These failures may lead to staining and secondary caries formation. To avoid this, studies have explored methods to compensate for, and potentially eliminate polymerization shrinkage and the associated stress in methacrylic systems, including heterogeneous network formation.^{1, 3-10}

The Gibbs Free Energy of Mixing thermodynamically dictates phase separation in a multi-component mixture:

$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix} \tag{1}$$

A value of $\Delta G^{mix} > 0$ indicates thermodynamic instability, and if diffusion is allowed, will induce phase separation.¹⁰⁻¹² During a polymerization the entropic contribution (ΔS^{mix}) is

constantly negative as monomer converts to polymer and the number of molecules in the system decreases; favoring phase separation.^{10, 13} The enthalpic contribution (ΔH^{mix}) is more difficult to generalize; the conversion of π -bonds in monomers to σ -bonds in polymers is an exothermic ($\Delta H^{mix} < 0$) process.¹⁴ However the energetic interactions between neighboring molecules also contribute to ΔH^{mix} , so it can be negative or positive depending on the system.¹⁵

There are two mechanisms of phase separation: Nucleation and Growth (N&G) and Spinodal Decomposition (SD).^{6, 16} N&G is initiated by a system that is in a meta-stable state and has phase structure characterized by small, dispersed droplets in a continuous matrix. Assuming diffusion is possible, the dispersed phase increases in size through coalescence while maintaining the same overall shape.^{6, 16} In SD, phase separation is initiated by a system in a highly unstable state, characterized by a spinodal, where the following holds true:^{6, 16, 17}

$$\frac{\partial^2 \Delta G^{mix}}{\partial x_1^2} = 0 \tag{2}$$

This mechanism yields a co-continuous phase structure that is inter-connected.^{6, 16-18} If phase separation persists long enough, coalescence will occur and the phase structure will approach that achieved with N&G. Prior work has cited SD as a more appropriate mechanism for overall shrinkage control.⁶

Equally as important as thermodynamics to the phase separation process are the kinetics of network development.^{10, 11, 18} One critical aspect is the gel point, which is defined as either the first time during the polymerization where one macromolecule spans the entire vessel of reaction, or when the material develops a significant loss of fluidity.¹⁴ It is related directly to the kinetics of the reaction, so the point in conversion at which gelation occurs can shift if there is change in the rate of reaction. Since there is a large reduction in fluidity of the material past the gel point, if its occurs early in conversion, which is known to be the case in dimethacrylate polymerizations,

diffusion of incompatible phases may be prohibited thus preventing phase separation despite any thermodynamic instability.^{12, 19, 20}

Previous work with polymerization-induced phase separation has typically looked at approaches that are inappropriate for the application of dental and other biomaterials. For instance, thermally initiated polymerization-induced phase separation has been shown to yield phase structure typical of N&G as well as SD mechanisms.¹⁶ There has also been significant interest in orthogonal dual-cure systems that result in interpenetrating polymer networks; one example is the combination of methacrylate and epoxy components that are cured by photo or thermal initiation, respectively.^{10, 11, 18} Changing the order of cure, as well as the ratio of methacrylate to epoxy components can alter the phase structure in these materials. Allowing the epoxy component, which in this case had the higher modulus, to cure first leads to less heterogeneous materials due to a lack of mobility in the system. However if the cure order is reversed, a more heterogeneous material (indicated by a broader peak in the tan delta profile) is formed resulting in residual unreacted epoxy components residing in the pre-formed methacrylate phase.^{10, 11, 18} Unfortunately, this approach is inappropriate for in-situ formed biomaterials since it requires thermal initiation and much longer polymerization times associated with cure of the epoxy components. Additionally, whether applied to IPN systems or single mechanism curing processes, the use of thermal initiation potentially creates greater internal stresses due to post-polymerization thermal contraction effects that can lead to poorly controlled micro/macro void formation in phase-separated polymers.

In this work we modify a bulk homopolymer matrix with non-reactive prepolymer to investigate polymerization-induced phase separation (PIPS) in a purely photoinitiated system. Both the chemical structures of the prepolymers, as well as the amounts added to the bulk

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homopolymer are varied to explore the impact on the phase-separation process and the final phase composition. The physical mechanism of shrinkage control in materials undergoing PIPS has been explored and discussed to a limited extent; therefore it is our aim to use a relatively simple model system where changes in the material during polymerization are related directly to a single reactive component.

3.2 Experimental

Materials - Triethylene glycol dimethacrylate (TEGDMA, Esstech) was utilized in all studies as the bulk homopolymer matrix, which was modified by the addition of commercially obtained (Aldrich): poly(methyl methacrylate), poly(ethyl methacrylate), and poly(butyl methacrylate) (PMMA, PBMA, and PMMA, respectively). The three prepolymers have different molecular weights and glass transition temperatures (measured using a dynamic mechanical analyzer equipped with powder pockets), as indicated in Table 3.1, where:

 M_w = weight average molecular weight T_g = glass transition temperature n_D^x = refractive index measured at temperature x (°C)

The photoinitiator in all samples was 2,2-dimethoxy-2-phenylacetophenone (DMPA). It is soluble in TEGDMA, and absorbs in the UV region. All experiments utilized 365 (\pm 10) nm light unless otherwise noted.

Table 3.1 – Prepolymer Properties		
Poly(butyl methacrylate)	Poly(ethyl methacrylate)	Poly(methyl methacrylate)
(PBMA)	(PEMA)	(PMMA)
M _W ~337,000 Da	M _W ~515,000 Da	M _W ~120,000 Da
T _g ~22.4(±2.5) °C	$T_{g} \sim 72.5(\pm 1.1)^{\circ}C$	T _g ~117(±6.0) °C
ρ=1.07 g/mL	ρ=1.11 g/mL	ρ=1.19 g/mL
$n_D^{25}=1.4804 \ (\pm 6E-4)$	n_D^{25} =1.4904 (±4E-4)	n_D^{25} =1.4906 (±1E-3)

Sample Preparation - For samples with low prepolymer content (up to 10 wt%), the appropriate mass of initiator and volume of TEGDMA were placed in a sample vial and allowed to stir for approximately 10 min until all of the initiator was incorporated. The appropriate mass of prepolymer was then added to the vial and allowed to stir vigorously overnight. For samples with higher prepolymer contents (greater than 10 wt%) the same procedure was followed as above, except that the monomer was diluted with an equal volume of acetone. Once the prepolymer was completely incorporated into the TEGDMA/DMPA/acetone solution, the solvent was removed under reduced pressure with complete removal verified gravimetrically.

Cloud Point Determination - A polarizing light microscope (Leica DMRXP) equipped with a thermal stage (Linkam LTS 350) and temperature controller (Linkam CI 94) was used to determine the de-mixing temperature in monomer/prepolymer samples. A disc-shaped sample (240 µm thick x 10 mm diameter) sandwiched between a glass slide and a microscope coverslip was placed on the thermal stage. The temperature of the stage was brought to 25 °C and allowed to equilibrate for 1 min. The stage was then cooled to -75 °C at 3 °C/min. Low intensity polarized light was transmitted through the sample throughout the entire temperature profile and the intensity of transmitted light was measured in real time. The de-mixing (cloud point) temperature was determined as the temperature at which a dramatic reduction in the light transmitted through the monomer/prepolymer sample was observed during the cooling cycle.^{17, 21, 22} The analogous heating cycle was also observed to validate the cloud point temperature measured.

Viscosity - A parallel-plate rheometer (TA Ares) was employed to measure the initial viscosities of TEGDMA/prepolymer syrups. To accomplish this constant strain (100 s⁻¹) runs of approximately 1.5 min in duration were analyzed for each sample.

Photo-Rheometry - The rheometer was also equipped with a UV light source (λ =365±10 nm) that was coupled to an in-house designed optical attachment that provides measurement of the gel point (assigned as the G'/G'' crossover point) and methacrylate conversion simultaneously. The methacrylate conversion was monitored using a Fourier transform infrared spectrometer (Thermo Scientific, Nicolet 6700) equipped with near-IR fiber optic cables. The optical attachment, constructed specifically for this set-up facilitated both the uniform irradiance of the UV curing light and the near-infrared source to be directed through the sample, which was sandwiched between two quartz plates (22 mm diameter). Sample thickness was maintained at 300 µm in all experiments. The change in the methacrylate (=CH₂) peak area (first overtone at 6165 cm⁻¹) was used to calculate conversion in real time. A chamber was constructed to allow for nitrogen purging of all samples. Each sample underwent one hour of N₂ purge before analysis, with the plates separated to approximately 1.5 mm to remove dissolved oxygen and avoid oxygen-inhibited edge effects that otherwise confound the rheologic data. Incident UV light irradiance (I₀) was 300 µW/cm² in all experiments.

Optical Density during Polymerization - To measure optical properties during polymerization a UV/vis portable spectrometer (Ocean Optics, USB2000) was used. A disc-shaped sample (thickness=240 µm, diameter=10 mm) was secured so that a near-IR source, visible light source, and UV curing light source could transmit simultaneously through the material. The near-IR source was employed to monitor conversion under the same conditions as described above. To follow the changes in optical clarity of the polymerizing sample, the UV/vis spectrometer was employed. A visible light source that emits 400-800 nm wavelength light as a photo probe independent of the photoinitiator was used to transmit visible light through the sample. The intensity of the 600 nm light transmitted was monitored in real time.
Dynamic Mechanical Analysis - A dynamic mechanical analyzer (DMA, Perkin Elmer 8000) configured with thin aluminum pockets, each containing 10 mg of bulk polymer, was used to determine the T_g of the different prepolymers. A single cantilever cyclic displacement of 50 μ m at 1 Hz in air was applied as the specimens (n=3) were heated to 180 °C with tan δ data collected as the sample was cooled to 25 °C at 2 °C/min. A separate DMA (TA Q800) was used to characterize polymer structure post-cure. Samples had approximate dimensions of 9.0 x 3.6 x 1.0 mm (*length x width x thickness*) and were analyzed using a temperature sweep under 0.01 % strain. After allowing the sample to equilibrate for 5 min at -50 °C, samples were brought to a temperature of 200 °C at a rate of 3 °C/min, and then cooled to -50 °C at the same rate. All results reported are from the initial scan (ramp up in temperature), and were compared with the secondary scan to ensure no additional thermal cure during analysis. All samples were photopolymerized and then thermally post-cured to ensure conversion greater than 90 % before thermal analysis.

Volumetric Shrinkage - TEGDMA/prepolymer samples were measured before and after polymerization using a helium-purged gas pycnometer (Micrometrics AccuPyc II 1340, Serial No. 841). Polymer densities were measured after TEGDMA/prepolymer samples were exposed to 10 min of UV irradiation ($I_0=5 \text{ mW/cm}^2$). The cell used in all tests was cylindrical and had a total volume of 1 cm³. The experimental volumetric shrinkage was calculated using measured monomer and polymer densities as shown in Equation 3:

$$\% VS_{\text{exp}} = \frac{\rho_{poly} - \rho_{mono}}{\rho_{poly}} x100$$
(3)

3.3 Results and Discussion

Monomer/Prepolymer Formulations Viscosity The viscosity of all monomer/prepolymer syrups increases exponentially with increasing prepolymer content (Figure 3.1). This is attributed to an increase in entanglements between prepolymer and monomer chains. The difference in viscosities between the various prepolymers is primarily due to differences in molecular weight (Table 3.1). PEMA, with the highest molecular weight, also has the highest viscosity. However, following this logic, PBMA should have the intermediate viscosity, and PMMA the lowest. For this latter pair, the opposite is observed. Since PBMA has the longest side chain group on the repeat unit, it allows for more chain mobility and space between chains, which reduces the entanglement interactions, producing a lower solution viscosity. Sample viscosity imposes a practical limit on prepolymer content when considering an ambient temperature photocurable material. The large increase in viscosity made application as well as analysis of certain samples impractical (TEGDMA/30 wt% PEMA, TEGDMA/30 wt% PMMA).



Figure 3.1 – Viscosity of TEGDMA/Prepolymer Syrups (n=3). Materials were analyzed under constant strain (100 s⁻¹) for 1.5 min.

Monomer/Prepolymer Formulation De-mixing Temperature - Thermal de-mixing (or cloud point) temperatures as a function of prepolymer content are shown in Figure 3.2. All samples displayed upper critical solution temperature (UCST) behavior, although over the range covered here, the phase boundary for TEGDMA/PMMA was essentially flat. For all samples the UCST was below 0 °C. This indicates that all samples are stable homogeneous mixtures under ambient conditions. This is advantageous for the system at hand, since the desire is to induce phase separation during polymerization, not prior to initiation. Two samples, 1 wt% PBMA and 1 wt% PMMA displayed no cloud point behavior within limitations of the test. It should be noted, TEGDMA transitions from a liquid to an amorphous glass at -81 °C (monomeric T_g) and no cloud point below this temperature would be expected.²³



Figure 3.2 – Cloud Point Temperatures (TEGDMA/Prepolymer, n=3). Taken as the onset of turbidity when materials were cooled from 25 °C to -75 °C at a rate of 3 °C/min.

Polymerization Kinetics - To begin analyzing the PIPS process, the effect of prepolymer on polymerization kinetics was investigated. A representative plot of the normalized (by initial monomer concentration) rate of polymerization, as a function of conversion for different PEMA contents is displayed in Figure 3.3 (averaged kinetic data with associated error is reported in Tables 3.2-3.4). Since the amount of prepolymer loading directly impacts the monomer concentration (and thus, the polymerization rate), all calculations were normalized by the initial monomer concentration to account for behavior due to reduced double bond concentration.



Figure 3.3 – Kinetic Impact of Prepolymer in TEGDMA/PEMA materials. $R_p = -\frac{d[M]}{dt}$ (mol*ml⁻¹*min⁻¹). Real-time monomer concentration calculated by monitoring methacrylate (=CH₂) peak area (first overtone at 6165 cm⁻¹). I_o=5 mW/cm² λ_{cure} =365 nm.

As can be seen, the prepolymer-modified syrup with 1 wt% PEMA has a dramatically enhanced reactivity compared to pure TEGDMA. This is attributed to the increased viscosity that favors early autoacceleration with the high reaction rate leading to a delay in the polymerization rate maximum to approximately 50 % conversion. At this loading, the increase in viscosity selectively restricts diffusion of long chain radical species in the material and, presumably to a lesser extent, diffusion of the inert prepolymers as well. This leads to higher overall conversion in 1 wt% PEMA samples (80 ± 1 %) compared to pure TEGDMA (76 ± 3 %). PEMA also has a T_g lower than that of ambient cured TEGDMA, therefore higher conversion is expected, but the reaction kinetics also affect the ultimate conversion. It should be noted that this increase in initial viscosity does not limit diffusion of prepolymer in the low conversion, pre-gel regime as will be discussed shortly.

There exists a threshold where continued increase in prepolymer loading and initial viscosity actually inhibits the polymerization rate (indicated by the 20 wt% PEMA trend in Figure 3.3) compared to the control. Depending on the prepolymer additive, this threshold occurs at different loading levels. Beyond the threshold, the viscosity increase is so high that diffusion of all species is restricted and the polymerization rate is decreased. To further show this trend, Tables 3.2-3.4 displays the maximum rate of polymerization (R_p^{max}), as well as the conversion at which it is observed for all modified materials. In all cases n=3, I_o=5 mW/cm².

Table 3.2 – TEGDMA/PMMA Kinetics				
Prepolymer Content (wt %)	R _p ^{max} (mol/L/min)	Conversion @ R _p max	Final Conversion	
0	13.1 (±1.2)	0.30 (±0.04)	0.76 (±0.03)	
1	23.3 (±2.8)	0.41 (±0.03)	0.78 (±0.03)	
5	15.4 (±0.7)	0.39 (±0.01)	0.81 (±0.02)	
10	13.9 (±0.6)	0.35 (±0.01)	0.80 (±0.03)	
15	14.3 (±1.2)	0.37 (±0.03)	0.80 (±0.01)	
20	4.41 (±0.5)	0.14 (±0.03)	0.81 (±0.01)	

is observed for an modified materials. In an cases in $3, 1_0, 5$ m/v/

Table 3.3 – TEGDMA/PEMA Kinetics				
Prepolymer Content (wt %)	R _p ^{max} (mol/L/min)	Conversion @ R _p max	Final Conversion	
0	13.1 (±1.2)	0.30 (±0.04)	0.76 (±0.03)	
1	21.4 (±0.5)	0.39 (±0.01)	0.80 (±0.01)	
5	19.1 (±2.7)	0.36 (±0.02)	0.80 (±0.01)	
10	11.6 (±0.9)	0.32 (±0.02)	0.85 (±0.01)	
15	11.0 (±0.4)	0.35 (±0.01)	0.80 (±0.01)	
20	11.8 (±0.3)	0.37 (±0.02)	0.84 (±0.01)	

Table 3.4 - TEGDMA/PBMA Kinetics				
Prepolymer Content (wt %)	R ^{max} (mol/L/min)	Conversion @ R _p max	Final Conversion	
0	13.1 (±1.2)	0.30 (±0.04)	0.76 (±0.03)	
1	18.7 (±1.4)	0.38 (±0.02)	0.81 (±0.01)	
5	31.0 (±2.6)	0.47 (±0.04)	0.90 (±0.04)	
10	12.8 (±2.6)	0.31 (±0.05)	0.85 (±0.02)	
15	5.25 (±0.3)	0.18 (±0.03)	0.82 (±0.01)	
20	7.74 (±1.2)	0.22 (±0.05)	0.83 (±0.01)	
30	5.20 (±0.7)	0.19 (±0.03)	0.83 (±0.01)	

Phase Separation Characterization - To better understand the potential polymerizationinduced phase separation process in these materials, both the gel point and the onset of phase separation were determined as a function of conversion. The gel point was assigned as the G'/G'' crossover from the photo-rheological analyses. The onset of phase separation was characterized as the point at which a reduction in intensity of 600 nm light transmitted through the polymerizing sample was observed (i.e. onset of turbidity). This point may actually be an overestimation of the start of phase separation, because the detection is limited to length scales on the order of the wavelength of light in use. Using this method, phase separation was detected in all formulations except for TEGDMA/1 wt% PMMA and TEGDMA/1 wt% PBMA.

The gel point and onset of phase separation are plotted together in Figure 3.4 for TEGDMA/PEMA samples. Phase separation either effectively coincides with or precedes gelation, which is true for all the prepolymer compositions tested, which indicates there is a period of time where diffusion of incompatible phases occurs more readily than post-gelation where diffusivity decreases dramatically. In the 1 and 5 wt% PEMA formulations, the gel point occurs earlier in the reaction when compared to the control (0.065 conversion). This is a result of the enhanced autoacceleration occurring in low prepolymer content samples as suppressed termination means longer chains, and this correlates with earlier gelation. Delayed gelation is observed in samples containing greater than 10 wt% PEMA. In these cases, polymerization in the dispersed phase or one of the co-continuous phases is faster and occurs before the overall matrix or secondary co-continuous phase gels.



Figure 3.4 – TEGDMA/PEMA Gelation and Phase Separation onsets during polymerization (n=3), as measured by G'/G'' crossover point and onset of turbidity respectively, $I_0=300 \ \mu W/cm^2$, $\lambda=365 \ nm$.

Not only is the onset of phase separation important, but also the characterization and comparison of the phase separation process within the different materials. As previously stated, the onset of phase separation is indicated by a reduction in visible light transmission, or in other words, an increase in turbidity of the material.²⁴ The increase in turbidity indicates a difference in refractive indices between the two incompatible phases, one prepolymer-rich (see Table 3.1) and one depleted $(n_D^{25}_{TEGDMA}=1.4598)$, which can be assumed to undergo polymerization at different rates. There exists a point where the turbidity is at a maximum, which is followed by a recovery period where light transmission increases. While potentially related to decreasing numbers or dimensions of light scattering centers, this decrease in optical density is most likely associated with the secondary phase (or more slowly polymerizing phase) 'catching up' or polymerizing to a point that the difference in refractive indices between phases is decreasing. The beginning of this recovery phase appears to coincide with the onset of deceleration in low prepolymer content (up to 15 wt%) materials. This indicates that the observed deceleration period is not just an artifact of viscous development within the material, but suggests that limiting conversion is approached in the one phase while a slower network progression continues in the secondary phase. This behavior is not observed in higher prepolymer content materials, mostly because the kinetics in both phases is hindered significantly because of high material viscosity, that the R_p development due to enhanced autoacceleration is not observed.

To characterize this process, the change in intensity for the different materials was plotted as a function of conversion. In Figure 3.5 the process is compared for the three prepolymers at the same loading (20 wt%). There is a distinct difference between the intensity profiles for PBMA when compared to PMMA or PEMA. PBMA induces a much more dramatic intensity reduction while the PMMA and PEMA modified materials experience relatively small intensity reductions. This appears to be an artifact of the difference in viscosities of the samples. Since PBMA has a comparatively much lower initial viscosity, phase separation may proceed more readily with the development of phases that are more divergent in refractive indices, both because of initial compositional drift between phases as well as differences in local reaction rate between phases (this is supported by phase compositions calculated using DMA, discussed later). In the samples containing PMMA and PEMA, viscosity is so high that diffusion of incompatible phases is more restricted. Therefore the phase separation process does not exhibit such dramatic differences in refractive indices and local reaction rate, even though the refractive indices of PEMA and PMMA are marginally more different from TEGDMA (Table 3.1).



Degree of Conversion

Figure 3.5 – Light Transmission during Polymerization for Different Prepolymers (20 wt% PMMA/PEMA/PBMA), $I_0=300 \ \mu\text{W/cm}^2$, $\lambda_{cure}=365 \text{ nm}$, $\lambda_{visible}=600 \text{ nm}$.

The phase separation process was also compared for each material at different prepolymer loadings. The comparison for PBMA is displayed in Figure 3.6. Without any

prepolymer, there is little relative change in intensity throughout the entire polymerization. Once prepolymer is added, and phase separation is observed, there is a dip in light transmission intensity. The minimum intensity with respect to conversion depends on the amount of PBMA in the sample. At lower loadings, where autoacceleration is enhanced, the minimum intensity occurs at a later conversion.



Figure 3.6 – Light Transmission during Polymerization at Different Prepolymer Loadings (TEGDMA/PBMA), I_o=300 μW/cm², λ_{cure}=365 nm, λ_{visible}=600 nm.

The relative value of the minimum intensity is not dependent on kinetics and is the same for 5 wt% or 20 wt% PBMA. This indicates that the compositions of the phases formed in each sample are similar because they produce the same difference in refractive index. The same behavior was observed for PMMA. Samples containing PEMA, however, showed a difference in the value of minimum intensity – indicating that different phases are formed at 5 wt% versus 20 wt% loading (Figure 3.7). This is validated by DMA data (discussed below). PEMA has the highest molecular weight of all prepolymers tested (Table 3.1). This may limit its diffusional mobility during early-stage polymer matrix formation, which likely results in different phase compositions based on prepolymer loading.



Figure 3.7 – Light Transmission during Polymerization at Different Prepolymer Loadings (TEGDMA/PEMA), I_o=300μW/cm², λ_{cure}=365 nm, λ_{visible}=600 nm.

Dynamic Mechanical Analysis - Dynamic mechanical analysis was used to detect single versus multi-phase structure. It was also utilized to estimate the compositions of different phases in the fully polymerized materials. All samples were post-cured thermally after photoirradiation to ensure that final conversion was greater than 95% before analysis. This post-cure processing is not expected to alter the phase structure set in place during the initial, ambient photopolymerization, which forms a dense network structure with high TEGDMA conversion (>75 %).

Multi-phase structure was verified in samples that exhibited multiple glass transition temperatures (T_g's) or maximums in tan delta behavior as a function of temperature. For pure

TEGDMA homopolymer, one broad, asymmetric tan delta curve is observed (T_g of 161 ± 4 °C), which is characteristic of the significant variation in crosslink density associated with structurally heterogeneous dimethacrylate networks. As shown in Figure 3.8, with increasing prepolymer content a secondary phase, rich in prepolymer develops. The same behavior is observed in PEMA and PMMA modified materials.



Figure 3.8 – Tan Delta Behavior Post-polymerization (TEGDMA/PBMA), Temperature Ramp: 3 °C /min.

All prepolymers used in this study are non-reactive, and therefore other than any chain transfer to polymer, which does not readily occur in methacrylic systems until very high conversions, they do not change chemical character or T_g during the TEGDMA polymerization. All prepolymers have a T_g that is distinctly different and separate from that of pure fully cured TEGDMA homopolymer (161 °C) by a difference of at least 44 °C (Table 3.1). Because of this, the shift in T_g 's observed in phase-separated samples can be used to calculate composition of the

phases in the final material, based on the Fox equation which has been utilized for both sequential and simultaneous IPNs.²⁵ Our system most closely resembles a sequential IPN with the selective formation of the linear polymer in a first step, followed by TEGDMA homopolymerization. The relationship used to calculate the composition of TEGDMA in each phase based on the Fox equation:²⁶

$$\% TEGDMA = \left(1 - \frac{(T_g^{TEGDMA} - T_g^{NewPhase})}{(T_g^{TEGDMA} - T_g^{Prepolymer})}\right) * 100 \tag{4}$$

The homopolymer T_g of TEGDMA ambiently cured by photopolymerization (with no post-cure processing) is ~ 80 °C.²⁷ Therefore in TEGDMA/PBMA materials, the local T_g is reduced by PBMA in prepolymer-rich regions (Table 3.1). However in TEGDMA/PMMA materials the local T_g of prepolymer-rich regions is actually raised and in TEGDMA/PEMA samples it remains similar to that of the photocured matrix. These differences could impact how the different prepolymers interact with the homopolymer matrix during phase polymerization.

The TEGDMA compositions in both the phases formed for TEGDMA/PBMA and TEGDMA/PEMA samples are shown in Figures 3.9-3.10. In PMMA and PBMA containing materials, a relatively pure TEGDMA phase exists whether the sample is single or multi-phase. The prepolymer-rich phase has a TEGDMA composition of ~40-50 % for PMMA and PBMA. This TEGDMA composition is consistent at all prepolymer loadings where PIPS is observed, indicating that once a thermodynamic instability is encountered similar incompatible phase compositions are formed in varying volume fractions related to the initial prepolymer content. At 1 wt% PBMA no optical evidence of PIPS was observed and this coincides with no secondary phase structure apparent in the DMA tan delta plot.



Figure 3.9 – Post-polymerization Phase Compositions (TEGDMA/PBMA, n=3), measured by shift in T_g.

As indicated by Figure 3.10, TEGDMA/PEMA samples do not display the same stability in phase composition. In particular, samples containing 5 and 20 wt% PEMA have much different phase compositions than 1, 10 and 15 wt% PEMA materials. In the phase separation characterization, it was noted that the minimum relative intensity achieved during polymerization (corresponding to a maximum difference in refractive indices of polymerizing phases) varied depending on the amount of PEMA introduced into the monomer matrix. Since the difference in refractive index of polymerizing phases varies with PEMA content it is expected that the final phase compositions would vary as well.



Figure 3.10 – Post-polymerization Phase Compositions (TEGDMA/PEMA, n=3), measured by shift in T_g.

Volumetric Shrinkage - Equation 3 is used to calculate the ambient cure volumetric shrinkage in all materials. However, this measurement alone does not provide sufficient information as to whether there is an actual reduction in volumetric shrinkage due to the phase separation process. For that reason, a theoretical volumetric shrinkage was calculated using Equation 5:

$$\% VS_{theo} = [C = C] * \chi * \Delta VS_{C=C}$$
(5)

Where χ = experimentally observed final conversion [C=C] = initial methacrylate concentration (mol/ml) $\Delta VS_{C=C}$ = molar coefficient of shrinkage for methacrylate group (22.5 cm³/mol)^{3, 4}

This equation accounts for decreases in shrinkage due to changes in the initial methacrylate concentration, which is a significant factor in high prepolymer content samples.

Since phase separation impacts the overall conversion in these materials (Tables 3.3-3.5), both the experimental and theoretical shrinkage were normalized by conversion.

The normalized experimental and theoretical volumetric shrinkage for TEGDMA/Prepolymer samples are displayed in Figures 3.11-3.12. Here, the results are presented as a function of volume fraction (as opposed to mass). In previous results, mass fraction was used for simplicity; however, when measuring volumetric shrinkage the volume fraction of prepolymer added to the bulk matrix is more critical than the mass added.

It is noted that the control, pure TEGDMA, has an experimental shrinkage that falls within error to the theoretical calculation. However, in some cases the experimental shrinkage falls significantly below the theoretically predicted value based on initial reactive group concentration and the degree of conversion achieved. This demonstrates an additional physical bulk volume recovery effect associated with the internal heterogeneous structure.



Figure 3.11 – Volumetric Polymerization Shrinkage (TEGDMA/PMMA, n=3), calculated by change in density post-polymerization.

In both TEGDMA/PMMA and TEGDMA/PEMA samples there is an enhanced reduction in volumetric shrinkage that occurs at 5 wt% prepolymer loading level. The maximum reduction is observed at 10 wt% prepolymer in both cases. However for the TEGDMA/PBMA samples (Figure 3.12), considering the experimental error of the density-based measurements, there is essentially no significant shrinkage reduction regardless of the prepolymer loading level. A more detailed study that employs techniques with significantly lower statistical error is presented in the next chapter of this thesis to probe both the development of polymerization shrinkage and stress during phase-separating polymerizations.



Figure 3.12 – Polymerization Volumetric Shrinkage (TEGDMA/PBMA, n=3), calculated by change in density post-polymerization.

As indicated in Table 3.1, the three prepolymers have T_g 's at 117(±6.0), 72.5(±1.1), and 22.4(±2.5) °C for PMMA, PEMA, and PBMA, respectively. PBMA is the only prepolymer in use that has a T_g below room temperature. Therefore TEGDMA/PBMA samples were the only materials in which the additive was in the rubbery state throughout the polymerization, this may

have a significant impact on the evolution of polymerization shrinkage and stress. PMMA and PEMA contribute T_g 's that are significantly or modestly higher than that of the ambient-photocured TEGDMA matrix that evolves during photopolymerization.²⁸

The shrinkage control mechanism proposed for thermoplastic modifiers, which are also known as low profile additives, relies on chemical or physical connectivity between two phases that develop at different rates. The later development of the secondary phase can lead to nano/micro-scale cavitation at the interface or within the primary phase. This can compensate for some of the initial volumetric shrinkage occurring in the primary phase, resulting in an overall shrinkage reduction due to phase separation.^{1, 7, 9} In the TEGDMA/prepolymer model studied here, the linkage between the primary and secondary phases is due to the presence of TEGDMA in both phases as well as physical entanglements involving the prepolymer chains integrated into the bulk homopolymer matrix. Since PBMA has a rubbery character throughout the polymerization (and consequently, a lower modulus), it may have lower efficacy at distorting the adjacent phase structure. The influence of prepolymer T_g on phase separation and mechanical properties will be studied in more detail in a following chapter.

3.4 Conclusions

Here, we have presented a simplified approach to achieve and study polymerizationinduced phase separation. Pre-gel phase separation was demonstrated with these initial experiments indicating that under certain conditions, PIPS leads to a significant physical reduction in volumetric shrinkage compared to that expected based on solely chemical considerations of double bond concentration and final conversion. These PIPS-based reductions in polymerization shrinkage are also expected to convey a practically important internal stress relaxation mechanism in photopolymers as well.

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CHAPTER 4

STRESS REDUCTION IN PHASE-SEPARATED, CROSS-LINKED NETWORKS: INFLUENCES OF PHASE STRUCTURE AND KINETICS OF REACTION^{*}

A mechanism for polymerization shrinkage and stress reduction was developed for heterogeneous networks formed via ambient, photoinitiated polymerization-induced phase separation (PIPS). The material system used consists of a bulk homopolymer matrix of triethylene glycol dimethacrylate (TEGDMA) modified with one of three non-reactive, linear prepolymers (poly-methyl, ethyl and butyl methacrylate). At higher prepolymer loading levels (10-20 wt%) an enhanced reduction in both shrinkage and polymerization stress is observed. The onset of gelation in these materials is delayed to a higher degree of methacrylate conversion (~15-25%), providing more time for phase structure evolution by thermodynamically driven monomer diffusion between immiscible phases prior to network macrogelation. The resulting phase structure was probed by introducing a fluorescently tagged prepolymer into the matrix. The phase structure evolves from a dispersion of prepolymer at low loading levels to a fully cocontinuous heterogeneous network at higher loadings. The bulk modulus in phase separated networks is equivalent or greater than that of poly(TEGDMA), despite a reduced polymerization rate and cross-link density in the prepolymer-rich domains.

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4.1 Introduction

Currently, a main issue in the implementation of polymeric materials is the volumetric shrinkage that occurs during cure. This shrinkage, caused by a reduction in free volume as monomer converts to polymer, leads to a build-up of polymerization stress both internally and at the interface of the substrate to which the material is applied, causing defects such as cracks within the material and delamination of a bonded surface. It is well known that volumetric shrinkage and stress development within a polymer network is a complex and dynamic process that evolves with the modulus and shrinkage strain during the polymerization. The relative magnitude is dependent on a variety of factors that are based in either the formulation chemistry or the processing conditions. Formulation factors determine the polymerization mechanism based on the monomer selection that sets the initial reactive group concentration and to some extent, the limiting overall conversion. The initiator selection and concentration, as well as any filler or additives in the matrix can also be considered formulation factors. Processing conditions that impact the development of polymerization stress include the rate of polymerization, which in a photoinitiated system is related to the irradiation intensity in combination with the initiator used, and other factors such as the cure temperature, pressure and oxygen exposure.¹ In methacrylic based materials, the average volume reduction is approximately 23 cm³ per mole of converted reactive group.² To address this issue, research has focused on the development of methods that employ both formulation and processing factors to create materials that have low volumetric shrinkage during cure, but also can maintain critical performance properties such as strength, appearance and thermal stability necessary for a specific application.^{1, 3-8}

One such approach directed toward shrinkage control has been to develop heterogeneous networks via polymerization-induced phase separation (PIPS). With this method, a

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heterogeneous network is formed from an initially homogeneous multi-component monomer formulation. The reaction of monomer into polymer leads to limited miscibility of the components in the formulation. This thermodynamic instability promotes phase separation during the reaction to obtain an overall lower free energy. If diffusion is possible at the onset of phase separation, partially or fully immiscible phases will form based on monomer diffusion processes. When applied to cross-linking polymerizations, the extent of phase separation is dependent on order of gelation and phase separation, and the time allowed for morphologic evolution between these two reaction benchmarks.⁹ For instance, if gelation precedes the onset of phase separation, diffusion may be so hindered that heterogeneous network development via phase separation is limited or even precluded despite any thermodynamic instability. This incomplete phase separation results in a network that may have a degree of heterogeneity to it, but no distinct phase structure. However if the reverse occurs and phase separation precedes gelation, a more complete diffusion of immiscible phases can occur. The longer the interval between phase separation and gelation, more phase structure evolution can occur before being locked into place by the network formation.¹⁰ Heterogeneous network formation via PIPS has many advantages, one of which being that the final network structure and material properties can be tuned based on a balance between the kinetics and thermodynamics of the polymerization reaction.11-13

As previously stated, the development of volumetric shrinkage and stress during a polymerization has been studied extensively in the context of curing method, polymerization rate, degree of conversion and the relative modulus of the polymer formed.^{1, 3-7} Materials developed via PIPS potentially display a reduction in volumetric polymerization shrinkage.^{10, 14-17} However, current research is limited to this observation with an incomplete understanding of how and why

this physical reduction occurs. One study into PIPS in an acrylic-based copolymer system hypothesizes that the largest degree of shrinkage reduction occurs with a maximum interfacial volume between the incompatible phases.¹⁸ While another study into an epoxy-based system suggests that a continuous phase rich in a thermoplastic material is necessary for effective shrinkage control.¹¹ Another study attributes stress reduction to micro-void formation along interfaces between continuous phases, which can be controlled through the temperature at which the polymerization is conducted.¹⁴ Unfortunately, these specific approaches and studies are not well suited for many *in-situ* or biomedical applications based on the curing mechanisms and conditions, monomer formulations, and curing time. Additionally, these studies rely heavily on the effect of thermal contraction working on phases fully cured at elevated temperatures. Limited work has been done to elucidate the physical process that leads to enhanced shrinkage and stress reduction, especially under ambient photopolymerization conditions,^{19, 20} which constitutes a growth segment across a wide variety of polymer applications.

Previously, we reported a method to develop heterogeneous networks via PIPS in a photoinitiated, ambient, free-radical dimethacrylate polymerizations.²¹ This method has many advantages including: spatial and temporal control of the photocuring process, high strength and cross-link density of the final material and fast reaction times, making it suitable for many *in-situ* applications. In this system, a bulk homopolymer matrix of triethylene glycol dimethacrylate (TEGDMA) was modified by the addition of three non-reactive, linear prepolymers (poly-methyl, ethyl and butyl methacrylate). In our studies, we were able to measure both the onset of gelation and phase separation as a function of conversion, and found that phase separation either coincides with, or precedes gelation, allowing some time for diffusion of incompatible phases, resulting in networks with two phases: one rich in poly(TEGDMA) and the other rich in a

mixture of poly(TEGDMA)/prepolymer. At specific loadings of prepolymer an enhanced reduction in volumetric shrinkage was observed. Here, we continue our study of this system and focus on better understanding the physical mechanism of shrinkage reduction in a network formed via PIPS in an ambient photopolymerization. Additionally, we explore this mechanism in the context of polymerization stress development, which has only been studied in all-monomeric (no prepolymer present in the matrix) PIPS-based networks,²² but is at least equally important as volumetric shrinkage when applying materials to an application where one, or multiple bonded interfaces are necessary.

4.2 Experimental

Materials - Triethylene glycol dimethacrylate (TEGDMA, Esstech) was utilized for the bulk homopolymerizations in these studies. The matrix was modified by the addition of three commercially obtained (Aldrich) prepolymers: poly-methyl, -ethyl, and -butyl methacrylate (PMMA, PEMA, and PBMA). The weight-average molecular weights, glass transition temperatures (T_g) and densities of each are presented in Table 4.1. The photoinitiator in all studies was 2,2-dimethoxy-2-phenylacetophenone (DMPA), which absorbs in the UV-region. In all studies, a loading of 0.5 wt% (relative to monomer/prepolymer mass) DMPA was used, and 365 (±10) nm UV light was the irradiation source. The preparation of TEGDMA/prepolymer formulations was described in our previous work.²¹

Table 4.1 – Prepolymer Properties					
Poly (methyl methacrylate) (PMMA)	Poly (ethyl methacrylate) (PEMA)	Poly (butyl methacrylate) (PBMA)			
M _W ~120,000 Da	M _W ~515,000 Da	M _W ~337,000 Da			
Tg~117(±6.0) °C	Tg~72.5(±1.1) °C	$T_{g} \sim 22.4 (\pm 2.5) \ ^{\circ}C$			
$\rho = 1.19 \text{ g mL}^{-1}$	$\rho = 1.11 \text{ g mL}^{-1}$	$\rho = 1.07 \text{ g mL}^{-1}$			

Poly-Fluor-PMMA Synthesis - To evaluate the network structure of phase-separated materials, a fluorescently tagged prepolymer was developed. This pink-colored prepolymer was synthesized by introduction of a methacrylate-substituted fluorescent group (methacryloxyethyl thiocarbamoyl rhodamine B, Poly Fluor 570, Polysciences) into a bulk thermal polymerization of methyl methacrylate. The fluorescent group was introduced at a level of 0.02 wt% relative to methyl methacrylate. Conversion was monitored through the change in methacrylate peak area (1635 cm⁻¹) in the mid-IR with the carbonyl absorption (1720 cm⁻¹) used as an internal reference. Molecular weight was measured by gel permeation chromatography (M_w~52,000, PDI~1.67). The polymer structure was verified by NMR spectroscopy. The fluorescent group on this prepolymer (referred to as PF-PMMA) has an excitation maximum at 548 nm and an emission maximum at 570 nm.

Three point bending - Bar-shaped samples (~20 mm x 2 mm x 2 mm, $l \ge w \ge t$) were fabricated via ambient photopolymerization (I_o =5mW/cm²). The samples were tested in a universal testing machine (Mini Bionix 858, MTS, Eden Prairie, MN, USA) equipped with a 10 N load cell for flexural strength and elastic modulus (n=3). All analyses were performed with a crosshead speed of 1mm/min and a 15 mm span between supporting rollers. The flexural modulus was calculated by extracting data from the initial linear portion of the load vs. displacement curve, and applying the formula:

$$\mathbf{E} = \frac{\mathbf{C}\mathbf{L}^3}{4\mathbf{b}\mathbf{h}^3\mathbf{d}}\mathbf{x}\mathbf{10}^{-3}$$

Where: C=load at fracture (N) d=displacement (mm) L= distance between the supports (mm) b= width of specimen (mm) h= height of specimen (mm). **Tensometer** - Real-time polymerization stress was monitored under ambient conditions using a cantilever beam-based tensometer (Paffenberger Research Center, American Dental Association Health Foundation, Gaithersburg, MD) combined with a UV light source to facilitate cure of the material (λ =365±10nm). The setup allowed simultaneous monitoring of material conversion with a Fourier transform infrared spectrometer (FTIR) equipped with near-IR fiber optic cables (Thermo Scientific, Nicolet 6700). The degree of conversion (DC) of each sample was calculated by monitoring the dynamic change in peak area of the methacrylate (=CH₂, first overtone at 6165 cm⁻¹). All samples (n=3) were disc-shaped, with 6mm diameter and 1mm thickness. The details of this instrument and its operation are described more fully in other publications.^{23, 24}

Confocal Microscopy - A microscope (Nikon A1R) was used to image phase structure of polymerized materials. In all experiments, a 20x (Numerical aperture ~ 0.75) objective was used in the confocal imaging mode. The 4CH+DIC (four channel detector + differential interference contrast) setting was used to selectively excite at 561 nm and collect fluorescence from a 525/±25 bandpass filter (based on the fluorescent probe present in polymeric materials). All images were collected in the 'Galvano' mode, with a laser power of 5 % and a gain of 90. Thin-film samples for confocal analysis were prepared by photocuring monomer formulations between a glass slide and coverslip. In all experiments the irradiation intensity was measured from the top surface of the coverslip. Sample thickness was maintained between 70-100 μ m. To ensure no difference in phase structure as a function of the z-dimension, z-stack images were collected. Since the domain size (discussed below) was the same order as the thickness of the samples, no variations in phase structure were observed in the z-direction. Therefore, all images presented here are 2-dimensional. **Photo-Rheometry** - A parallel-plate rheometer (TA Ares) was equipped with a UV light source (λ =365±10 nm) that was coupled to an in-house designed optical attachment²⁵ that provides measurement of the gel point (assigned as the G'/G'' crossover point²⁶) and methacrylate conversion simultaneously. The methacrylate conversion was monitored, as described previously using an FTIR spectrometer (Thermo Scientific, Nicolet 6700) equipped with near-IR fiber optic cables. The optical attachment, constructed specifically for this set-up facilitated both the uniform irradiance of the UV curing light and the near-infrared source to be directed through the sample, which was sandwiched between two quartz plates (22 mm diameter). Sample thickness was maintained at 300 µm in all experiments. A chamber was constructed to allow for nitrogen purging. Each sample underwent 1 h of nitrogen purge before analysis, with the plates separated to approximately 1.5 mm to remove dissolved oxygen and avoid oxygen-inhibited edge effects that otherwise confound the rheologic data. Incident UV light irradiance (I_o) was 300 µW/cm² in all experiments (n=3).

Volumetric Shrinkage - Volumetric shrinkage was measured with a linometer (ACTA, The Netherlands). A drop of monomer was sandwiched between a glass slide and an aluminum disc that was placed on top of a non-contact probe. A light guide was positioned so that the monomer was irradiated from above the glass slide, and the irradiation intensity was measured from the top surface of the glass slide. As the material polymerized and contracted, the aluminum disc was lifted and the differences in potential sensed by the probe was recorded by the instrument software. The dynamic linear shrinkage results (n=3) were converted into volumetric shrinkage data as previously described.²⁷ Methacrylate conversion was monitored simultaneously utilizing FTIR equipped with near-IR fiber optic cables.⁷

Optical Density during Polymerization - To measure optical properties during polymerization a UV/Vis portable spectrometer (Ocean Optics, USB2000) was used. A disc-shaped sample (thickness = 240 μ m, diameter =10 mm) was secured so that a near-IR source, visible light source, and UV curing light source could transmit simultaneously through the material. The near-IR source was employed to monitor conversion under the same conditions as described above. To follow the changes in optical density of the polymerizing sample, the UV/Vis spectrometer was employed. A visible light source that emits broadband 400-800 nm wavelength light as a photo probe independent of the photoinitiator was used with the intensity of the 600 nm wavelength transmitted through the sample monitored in real time. The photoinitiator in this study (DMPA) does not absorb above 380nm,²⁸ so the visible light source did not alter the photopolymerization kinetics.

4.3 Results and Discussion

Volumetric Shrinkage - Figure 4.1 displays volumetric shrinkage as a function of conversion for three different material formulations: poly(TEGDMA), TEGDMA/10 wt% PEMA, and TEGDMA/20 wt% PEMA. Shrinkage measurements were conducted in triplicate, however in Figure 4.1, each curve denotes a single representative experiment. The two resins modified with PEMA have been shown to undergo PIPS.²¹ When prepolymer is introduced into the matrix, there is a decrease in the overall volumetric shrinkage experienced by the network. One would expect this result to a certain degree, as introducing the prepolymer into the monomer formulation decreases the overall double-bond concentration, which directly contributes to polymerization shrinkage.



Figure 4.1 - Real-time volumetric shrinkage of TEGDMA/PEMA materials at varying prepolymer loading levels; I_o=5mW/cm².

The extent of shrinkage reduction can be predicted in these materials, based on the double bond concentration, the final degree of conversion, and the molar volume change associated with methacrylate conversion² through the relationship in Equation 1.

$$%VS_{theo} = [C = C] * \chi * \Delta VS_{C=C}$$
(1)

Where χ = degree of conversion

[C=C] = initial methacrylate concentration (mol ml⁻¹)

 $\Delta VS_{C=C}$ = molar coefficient of shrinkage for methacrylate group (22.5 cm³ mol⁻¹)

With this relationship, the expected volumetric shrinkage for the poly(TEGDMA) control is $\sim 12.4 \%$ (±0.03). The observed poly(TEGDMA) shrinkage was 13.0 % (±1.20), validating that Equation 1 is an accurate and appropriate relationship. The expected final volumetric shrinkage of the PEMA-modified materials in Figure 4.1 based on this equation are 10.7 and 9.5 % for the 10 wt% PEMA and 20 wt% PEMA, respectively. In the network modified with 10 wt% PEMA,

this expected value is in good agreement with the observed value (10.5 %), and in the 20 wt% modification the volumetric shrinkage observed is significantly lower (7.3 %) than expected, indicating that phase separation does result in a physically enhanced shrinkage reduction amounting to more than 20 % beyond that expected from monomer displacement by the prepolymer.

Polymerization Stress - Volumetric shrinkage often has been the property of primary interest when characterizing the benefits of phase-separated networks.^{14, 15, 29} However, also of significance is the related build-up of polymerization stress, especially when utilizing polymer networks in applications where one or multiple bonded interfaces are necessary. To understand the impact of PIPS on this property, the real-time development of polymerization stress during ambient photopolymerization was measured *in situ* using a cantilever beam tensometer. Methacrylate conversion was measured simultaneously utilizing an FTIR spectrometer equipped with near-IR fiber optic cables thereby permitting stress development to be monitored as a function of conversion.

Figures 4.2-4.4 display the stress development with respect to conversion for each modifying prepolymer (PMMA, PEMA, PBMA) at loading levels of 0, 1, 10 and 20 wt%. As with the volumetric shrinkage study, each material was tested in triplicate with a single, representative profile presented. The loading levels were chosen since they promote differences in reaction kinetics and gelation behavior.²¹ Here, the incident light intensity is $I_0=5 \text{ mW/cm}^2$. In all cases, the addition of prepolymer to the TEGDMA matrix reduces the overall polymerization stress. As with volumetric shrinkage, one would expect a reduction in stress relative to the loading level of prepolymer, since the introduction of prepolymer to the matrix reduces the overall polymerization stress the overall polymer, since the introduction of prepolymer to the matrix reduces the matrix reduces the overall polymerization the loading level of prepolymer, since the introduction of prepolymer to the matrix reduces the matrix reduces the overall polymerization to the matrix reduces the matrix reduces the matrix reduces the loading level of prepolymer, since the introduction of prepolymer to the matrix reduces the polymer to high concentration of reactive methacrylate groups. In all the materials with moderate to high

prepolymer loading levels, with the exception of TEGDMA/10 wt% PMMA, the reduction in polymerization stress is greater than the prepolymer volume fraction, indicating that in these cases PIPS may further alleviate the effect of polymerization stress. In some material formulations, specifically, TEGDMA/20 wt% PBMA, there is a reduction in stress as great as 40 %.



Figure 4.2 - Real-time polymerization stress of TEGDMA/PMMA materials at varying prepolymer loading levels; I₀=5 mW/cm².



Figure 4.3 - Real-time polymerization stress of TEGDMA/PEMA materials at varying prepolymer loading levels; I₀=5 mW/cm².

At higher prepolymer loading levels of PMMA (20 wt%) and PBMA (10 and 20 wt%), the reduction in overall stress is accompanied by a delay (i.e. higher degree of conversion) in the onset of stress development. These materials also obtain an equivalent, or in some cases higher, degree of final conversion than the poly(TEGDMA) control, which is desirable for any type of *in-situ* application where diffusion of unreacted monomer out of the polymer network over time is unfavorable. These effects can be attributed to an enhanced autoacceleration effect caused by low concentrations (1-5 wt%) prepolymer in the poly(TEGDMA)-rich domains during polymerization,²¹ resulting in an overall higher degree of conversion. Although they also experience a reduction in overall polymerization stress (Figure 4.3), materials modified by PEMA experience no delay in the onset of stress development nor do they have a higher degree of final conversion. Formulations modified by PEMA, due to its relatively high molecular weight

(Table 4.1) have a higher viscosity than the PMMA or PBMA modified counterparts at any given loading level. This increase in viscosity reduces the overall rate of polymerization significantly (compared to a poly(TEGDMA) polymerization) at loading levels as low as 5 wt%, such that a lower overall conversion is achieved.



Degree of Conversion

Figure 4.4 - Real-time polymerization stress of TEGDMA/PBMA materials at varying prepolymer loading levels; I_o=5 mW/cm².

The observed reduction in polymerization stress could also occur if modification of the bulk matrix with prepolymer reduces the modulus of the network formed upon polymerization. If this is true, then it is very difficult to make a connection between stress reduction and PIPS. To probe this, the elastic modulus was measured via three-point bending. The samples utilized for three-point bending were prepared under identical ambient conditions and irradiation intensity as used in real-time stress measurements. Figures 4.5-4.7 display the bulk elastic modulus of
poly(TEGDMA) compared to the networks formed when the starting matrix is modified by prepolymer at 1, 10 or 20 wt% loading.





All prepolymer modified networks display a slight increase in modulus with initial additions (1 wt%) of prepolymer. This increase, however is not significant at the 95 % confidence interval, as a paired t-test between the poly(TEGMA) and the networks modified by 1 wt% PMMA, PEMA or PBMA all resulted in a p-value > 0.5. At this low loading level, we suspect that the prepolymer is acting as filler, and the modulus of the prepolymer adds to the modulus of the bulk matrix causing a slight, yet insignificant increase.

At moderate to high loading levels (10 and 20 wt%), the reduction in polymerization stress is accompanied by an equivalent, or in some cases increased bulk modulus compared to the poly(TEGDMA) control. When TEGDMA is modified by PEMA or PBMA the modulus of final network is significantly higher (as determined by a paired t-test with a 95% confidence interval) with 10 wt% prepolymer loading. When the loading level is increased to 20 wt% PEMA or PBMA the bulk modulus returns to a value statistically similar to that of poly(TEGDMA). In

these materials, the limiting final conversion decreases at 20 wt% prepolymer loadings, thus decreasing the network modulus. PMMA-modified resins only have a statistically higher bulk modulus at the 20 wt% loading level.



Figure 4.6 - Elastic Modulus, post-cure, of TEGDMA/PEMA materials (n=3)



Figure 4.7 - Elastic Modulus, post-cure, of TEGDMA/PBMA materials (n=3)

These results indicate that the bulk modulus does not significantly decrease upon multiphase, heterogeneous network formation through PIPS, and that the observed stress reduction is due to the PIPS process, and is not a result of compromised bulk network formation. In the materials tested here, PIPS results in networks with two phases: one rich in poly(TEGDMA) and the other rich in poly(TEGDMA)/prepolymer. With these differences in phase composition, we anticipate that there is local variation in modulus arising from the differences in overall cross-link density and prepolymer T_g . The phase rich in poly(TEGDMA)/prepolymer will have a reduced overall cross-link density, which could lead to a relative decrease in modulus in these regions. However, the presence of the entangled prepolymer in these more loosely cross-linked regions actually reinforces and strengthens the local network, since the bulk modulus does not decrease at higher prepolymer loadings, where the poly(TEGDMA)/prepolymer rich phase may be co-continuous with the poly(TEGDMA) phase. The absolute value of the local modulus likely varies with the T_g and molecular weight of prepolymer in use.

With these findings, there are two effects to investigate. The first being, how does phase structure evolve with increasing prepolymer loading, leading to more effective stress reduction? Secondly, what property differences amongst the three different prepolymers leads to differences in phase behavior and stress reduction efficiency? This second thrust will be explored in more detail in future chapters, and here we will focus on elucidating the stress reduction mechanism as a function of prepolymer loading level. To investigate the impact of prepolymer loading, the overall phase structure and domain size of phase-separated networks was analyzed with confocal microscopy imaging, as discussed below.

Phase Structure Imaging via Confocal Microscopy - There exist two modes of phase separation, Spinodal Decomposition (SD) and Nucleation and Growth (N&G). The difference

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between the two is that SD is initiated when a multi-component system is in a highly unstable state while N&G occurs when a system is in a metastable state.¹⁰ The highly unstable state characteristic of SD is defined as where the following holds true:

$$\frac{\partial^2 \Delta G^{mix}}{\partial x_1^2} = 0$$

Where: $\Delta G^{mix} = Gibbs$ Free energy of mixing x = any natural variable (i.e. temperature, volume, etc.)

Typically, materials that undergo N&G mechanism initially have a dispersed phase structure and those undergoing SD have a co-continuous phase structure. However, if the SD mechanism persists for long enough periods of time, coalescence will occur and the phase structure will approach dispersed morphology as a means to reduce the interfacial surface area. Co-continuous phase structure formed under SD has been cited as a more appropriate and effective means of shrinkage control in polymeric systems.¹⁰

To determine what type of phase structure results from PIPS in prepolymer-modified TEGDMA materials, confocal microscopy was utilized. A prepolymer with a fluorescent probe covalently attached to the backbone was synthesized (details in the Experimental section) and blended with the conventional PMMA used here to modify the TEGDMA matrix. The fluorescently tagged material (PF-PMMA) was developed so that when substituted in small quantities to a TEGDMA/PMMA formulation, the phase separation process would proceed in the same manner as when the unmodified PMMA was present in the TEGDMA matrix. Formulations used for confocal studies varied in ratio of PMMA to PF-PMMA depending on the prepolymer loading in the monomer matrix (to maximize image resolution and to avoid saturation in images due to an overabundance of the fluorescent probe). The two numbers following the label 'PF-PMMA' refer to the ratio (wt%) of PMMA to fluorescent PMMA (i.e.

PF-PMMA 3:1 is composed 75 wt% PMMA and 25 wt% fluorescent PMMA). To validate that PF-PMMA did not behave differently than PMMA during the TEGDMA polymerization, the kinetic profiles of TEGDMA modified materials (at the same loading level) were compared, and found to be identical (Figure 4.8).



Figure 4.8 - Kinetic Profile of TEGDMA polymerizations modified by 5 wt% PMMA (red) or a 3:1 (mass ratio) of PMMA: PF-PMMA; I_o=5 mW/cm².

A second measure to ensure that the fluorescent prepolymer did not alter the phase separation process was to evaluate the tan delta profiles post-cure. Although slight shifts were observed (Figure 4.9), each peak was de-convoluted into Gaussian peaks with very similar centers. For the PMMA sample, they occur at 133 and 167 °C. The 167 °C peak corresponds to a poly(TEGDMA) rich phase, and the 133 °C peak corresponds to a phase that composed of both poly(TEGDMA) and PMMA. For the fluorescent sample the peak centers occur at 127 and 167°C, indicating that after phase separation, even when using the fluorescent prepolymer,

similar phases are formed. It should be noted, that when the modifying prepolymer is PBMA or PEMA an identical peak at ~167 °C is observed, corresponding to the poly(TEGDMA)-rich phase. However, the poly(TEGDMA)/prepolymer-rich phase shifts to ~85 or ~110 °C, respectively, based on the pure prepolymer T_g (Table 4.1). As previously stated, there is no observed effect of prepolymer T_g on bulk properties such as modulus (Figures 4.5-4.7). However, there is an expected effect of prepolymer T_g on local property differentials, and this will be explored more thoroughly in a future chapter.



Figure 4.9 - Tan Delta Profile of TEGDMA polymers modified by 5 wt% commercial PMMA (red) or a 3:1 (mass ratio) of commercial PMMA: PF-PMMA; I_o=5 mW/cm².

Using this fluorescent material, we aimed to determine the final overall phase structure (post-ambient cure) as a function of prepolymer loading. For this series of experiments, thin films were prepared by curing \sim 1 ml of monomer formulations sandwiched between an untreated glass slide and glass coverslip at I_o=5 mW/cm². The final degree of conversion (DC) of the thin film samples varied from 75-85 % depending on the loading level of prepolymer. Figure 4.10

shows the changes in phase structure as a function of prepolymer loading, from 0 - 20 wt% PF-PMMA.



Figure 4.10 - Confocal microscopy images of materials, post-cure, having undergone PIPS; scale bar represents 50 μm. A) TEGDMA, DC=77 %, B) TEGDMA/1 wt% PMMA (3:1), DC=82 %, C) TEGDMA/3 wt% PMMA (3:1), DC=93 %, D) TEGDMA/5 wt% PMMA (3:1), DC=85 %, E) TEGDMA/10 wt% PMMA (3:1), DC=75 %, F) TEGDMA/20 wt% PMMA (19:1), DC=70 %.

At very low prepolymer loadings (1 wt% PF-PMMA), a dispersed prepolymer-rich phase structure is observed. The dispersed phase is roughly spherical in shape, and scales anywhere from 5-25 μ m in diameter. At 3 wt% PF-PMMA, the phase structure begins to transition from a dispersed to co-continuous phase structure, as there is both a mixture of spherical phase domains (~10-20 μ m diameter) as well as extended phase domains on the order of 100's of microns. At loading levels of 5, 10 and 20 wt% prepolymer, a co-continuous phase structure is observed, indicative of the SD mechanism. Here, as the loading level of prepolymer increases, the

TEGDMA-rich or 'dark' phase decreases in volume and size. Only at 20 wt% loading does the co-continuous structure appear uniform in both size and shape in either phase.

Histogram analyses of the distribution of red versus black pixels in each image were performed using ImageJ, and the results are shown in Figure 4.11. For the image of poly(TEGDMA), a very narrow distribution close to the value of 0 (pure black) is observed. As prepolymer is introduced, a shoulder appears on the right-hand side of the distribution, attributed to the small domains of prepolymer-rich phase present. This shoulder increases in size at 5 wt% loading, and at 10 wt% loading, a shoulder no longer exists in the distribution, but it has broadened. This implies closer to equivalent volume fraction of the TEGDMA-rich and prepolymer-rich phases. At loading levels of 20 wt%, the prepolymer-rich phase dominates the histogram distribution, and the contribution from the darker, TEGDMA-rich regions is apparent in a shoulder, now on the left side.



Figure 4.11 - Histogram analysis of red versus black pixel distribution (from images presented in Figure 4.10): A) TEGDMA, DC=77 %, B) TEGDMA/1 wt% PMMA (3:1), DC=82 %, C) TEGDMA/3 wt% PMMA (3:1), DC=93 %, D) TEGDMA/5 wt% PMMA (3:1), DC=85 %, E) TEGDMA/10 wt% PMMA (3:1), DC=75 %, F) TEGDMA/20 wt% PMMA (19:1), DC=70 %.

These results can be de-convoluted and quantified to estimate the volume fraction of each phase (Figure 4.12). From these results, it is easy to see that the prepolymer-rich phase volume fraction increases, as expected, with increasing prepolymer loading. Once continuity of the prepolymer-rich phase is established, the volume fraction of this phase increases in a linear manner with additional prepolymer. At these loading levels the prepolymer-rich volume fraction is greater than expected, which corresponds to observed decreases in volumetric shrinkage in these materials.



Figure 4.12 - Estimated volume fractions of poly-TEGDMA-rich phase and PMMA-rich phase based on red versus black pixel distribution: A) TEGDMA, DC=77 %, B) TEGDMA/1 wt% PMMA (3:1), DC=82 %, C) TEGDMA/3 wt% PMMA (3:1), DC=93 %, D) TEGDMA/5 wt% PMMA (3:1), DC=85 %, E) TEGDMA/10 wt% PMMA (3:1), DC=75 %, F) TEGDMA/20 wt% PMMA (19:1), DC=70 %.

Previously, we presented and described two techniques that can be used to measure the conversion at the onset of gelation via photo-rheometry, and the conversion at the onset of phase separation via optical clarity measurements during polymerization.²¹ The onset of phase separation consistently coincided with or preceded the onset of gelation in all TEGDMA

polymerizations modified by PMMA, PEMA, or PBMA. Depending on the modifying prepolymer, as well as the loading level, a significant degree of conversion may or may not occur between these two benchmarks. For instance, at 10 wt% loadings of PEMA or PBMA, gelation is delayed extensively with 7 (\pm 1.0) or 13 (\pm 2.6) % conversion of methacrylate groups respectively, that occurs between the onset of phase separation and gelation. This behavior is displayed in Figure 4.13 for PBMA-modified networks.



Figure 4.13 - TEGDMA/PBMA gelation and phase separation onsets during polymerization (n=3), as measured by G'/G'' crossover point and onset of turbidity respectively; $I_0=300 \ \mu\text{W/cm}^2$, $\lambda=365 \ \text{nm}$.

However, at the same loading (10 wt%) of PMMA into a TEGDMA matrix (Figure 4.14), there is little delay between phase separation and gelation ($3.3 \pm 3.4\%$), indicating that the amount of time for diffusion of incompatible phases is much less. When the loading level of PMMA is increased to 20 wt%, gelation is delayed such that $26 \pm 6.1\%$ conversion methacrylate groups is observed. This delay in the onset of network gelation increases the time between phase separation and gelation from ~12 seconds in the network modified by 10 wt% PMMA to 44 seconds at the 20 wt% PMMA loading under the low irradiance conditions used in the theometric study. This significant delay in gelation as loading is increased from 10 to 20 wt% PMMA is due to the changes in the overall reaction rate. The reaction rate maximum for the TEGDMA/10 wt% PMMA matrix is equivalent to that of the poly(TEGDMA) control (13.9 ± 0.6 versus 13.1 ± 1.2 L mol⁻¹ min⁻¹), but once the loading is increased to 20 wt% the reaction rate becomes significantly slower (4.4 ± 0.5).²¹ The slower reaction rate provides sufficient time for a completely co-continuous phase structure to form via diffusion of incompatible phases (Figure 4.10). This phase structure delays the onset of gelation, as polymerization proceeds in the two phases formed, but at non-equivalent rates. Macrogelation is not observed until one of these co-continuous domains gels. Thus, an observed gel point conversion at 20% combines methacrylate conversion occurring in both phases formed, and the co-continuous phase that has gelled may actually have a lower local methacrylate conversion. A similar decrease in reaction rate begins at a 10 wt% loading level of PEMA and PBMA, thus accounting for the differences in stress reduction behavior as a function of loading level between these prepolymers.



Figure 4.14 - TEGDMA/PMMA gelation and phase separation onsets during polymerization (n=3), as measured by G'/G'' crossover point and onset of turbidity respectively; $I_0=300 \ \mu\text{W/cm}^2$, $\lambda=365 \ \text{nm}$.

With these observations and the images in Figure 4.10, we can conclude that a delay in gelation, resulting in significant network development post-phase separation and pre-gelation allows for regular, co-continuous network formation with maximum interfacial area. Additionally, the polymerizations that have an observed delay in gelation also experience a delay in the onset of stress development. The co-continuous network structure formed in these cases allows for network rearrangement throughout a greater portion of the polymerization, delaying the stress development and decreasing the overall polymerization stress (i.e. TEGDMA/20 wt% PBMA). The loading level where this co-continuous structure is first observed depends on the specific modifying prepolymer, and its impact on gelation.

Combining the studies detailed here, the following stress reduction mechanism is proposed for the TEGDMA/ prepolymer system. Upon photoirradiation, phase separation is initiated via thermodynamic instability between the prepolymer additive and the initially formed TEGDMA homopolymer that is accompanied by a change in opacity of the polymerizing material, as the two phases formed have differing refractive indices. With moderate loading levels, due to the amount of prepolymer present and the time available for diffusion of incompatible phases, a continuous phase rich in prepolymer will form. Polymerization will proceed more rapidly in the TEGDMA-rich phase as it has a higher concentration of double bonds and lower local viscosity. The composition of the poly(TEGDMA)/prepolymer-rich phase is approximately 40-50 wt% prepolymer, which will substantially increase the local viscosity and suppress autoacceleration, resulting in a slower local polymerization rate. At the early stages of the reaction, observed volumetric shrinkage and polymerization stress is at a minimum, as shrinkage that occurs due to conversion can be compensated for by network rearrangement since the system, and specifically the prepolymer-rich phase, has not yet gelled. The network

rearrangement pre-gelation is accomplished by thermodynamically driven monomer diffusion out of the prepolymer-rich domains.

At moderate degrees of conversion (25-50 %), the volume change associated with converting monomer to polymer results in an increase in observed volumetric shrinkage and polymerization stress, since the network has gelled and cannot compensate for TEGDMA shrinkage as effectively. Although the prepolymer-rich phase will have a decreased cross-link density, the linear prepolymer reinforces these domains through physical entanglements promoted by the concentration effects, causing the bulk modulus to remain equivalent to or greater than that of a non-phase-separated network. The efficiency of this dynamic mechanism at stress reduction during polymerization depends on the domain size, interfacial surface area between different phases and most importantly, the local differential between phases in properties such as reaction rate, viscosity, and T_g .

4.4 Conclusions

Here, we have investigated stress reduction via PIPS in a dimethacrylate photopolymerization modified by the addition of thermoplastic prepolymers. TEGDMA polymerizations modified with PEMA or PBMA had reduced polymerization stress, while maintaining equivalent or enhanced bulk final modulus at loading levels greater than 10 wt%. PMMA-modified polymerizations also exhibited a reduction in overall polymerization stress, but this only occurred at a loading level of 20 wt%.

By imaging phase structure as a function of prepolymer loading level, it was found that an irregular continuous domain of TEGDMA/prepolymer is established when the prepolymer loading is greater than \sim 3 wt%. Co-continuous phase structure that is regular in domain size and shape is observed when the prepolymer loading is \sim 20 wt%. At early stages of conversion,

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volumetric shrinkage and polymerization stress is at a minimum because any changes in density that occur from TEGDMA-conversion are compensated for by network re-arrangement.

For effective stress reduction the following are necessary: a sufficient level of prepolymer to form a continuous phase of TEGDMA/prepolymer, sufficient time between phase separation and gelation to allow for diffusion of incompatible phases, and finally a polymerization rate that leads to a high final degree of conversion across the entire network. The differences that arise between the prepolymers in use here is due to a combination of differences in molecular weight and T_g Future work will involve systematic studies to understand the impact of these physical properties on PIPS.

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CHAPTER 5

MODIFICATION OF LINEAR PREPOLYMERS TO TAILOR HETEROGENEOUS NETWORK FORMATION THROUGH PHOTOINITIATED POLYMERIZATION-INDUCED PHASE SEPARATION

Polymerization-induced separation (PIPS) phase was studied in ambient photopolymerizations of TEGDMA modified by PMMA. The molecular weight of PMMA and the rate of network formation (through incident UV-irradiation) were varied to influence both the promotion of phase separation through increases in overall free energy, as well as the extent to which phase development occurs during polymerization through diffusion prior to network gelation. The overall free energy of the polymerizing system increases with PMMA molecular weight, such that PIPS is promoted thermodynamically at very low loading levels (5 wt%) of a higher molecular weight PMMA (120 kDa), while a higher loading level (20 wt%) is needed to induce PIPS with lower PMMA molecular weight (11kDa), and phase separation was not promoted at any loading level tested of the lowest molecular weight PMMA (1kDa). Due to these differences in overall free energy, systems modified by PMMA (11kDa) underwent phase separation via Nucleation and Growth, and systems modified by PMMA (120kDa), followed the Spinodal Decomposition mechanism. Despite differences in phase structure, all materials form a continuous phase rich in TEGDMA homopolymer. At high irradiation intensity ($I_0=20$ mW/cm²), the rate of network formation prohibited significant phase separation, even when thermodynamically preferred. A staged curing approach, which utilizes low intensity irradiation $(I_0=300 \mu W/cm^2)$ for the first ~50% of reaction to allow phase separation via diffusion, followed by a high intensity flood-cure to achieve a high degree of conversion, was employed to form phase-separated networks with reduced polymerization stress yet equivalent modulus.

5.1 Introduction

The formation and design of heterogeneous polymer networks is a widely studied and growing topic in materials science with applications in many fields including biomaterials, liquid crystals and optical displays, membranes, adhesives, and composites.¹⁻⁹ For these applications, the ability to design a network with local property differentials, while maintaining critical bulk performance is highly desirable. Towards this design, two different approaches have been used most widely: the blending of two different polymers, or the formation of block copolymers.⁹⁻¹¹ With blending, heterogeneous morphology is controlled by the type of apparatus used to mix the two components, the rate or extent of time they are mixed, as well as the relative viscosities of each component.^{10, 12, 13} This approach to heterogeneity requires a large physical input to effectively blend the components, and often needs to be performed at elevated temperatures.^{10, 12} With the block copolymer method precise initial preparation of monomers is necessary, as well as exact processing conditions (temperature, composition) to achieve the desired phase structure.¹¹ The ability to develop heterogeneous networks without these processing and synthetic constraints is desirable for many *in-situ* applications.

An alternate method to achieve network heterogeneity is through well-controlled polymerization-induced phase separation (PIPS). In this approach, a phase-separated, heterogeneous network is formed from an initially homogenous and stable multi-component monomer formulation. The reaction of monomer into polymer leads to limited miscibility of the different components in the formulation. If diffusion is possible, phase separation will occur to minimize the free energy of the system, resulting in a network composed of phases with limited miscibility. Since the phase separation occurs coincidentally with network formation, the extent to which partially or fully immiscible phases diffuse from one another depends on the rate of network formation, the onset of gelation and the degree of cross-linking at any given point during the reaction as well as any attractive or repulsive interactions between the components.¹⁴ The dynamic interplay between the kinetics of network formation and thermodynamics of the polymerizing system is crucial to understanding and controlling the PIPS process.¹⁵ This approach has already shown promise for numerous applications including the development of polymer-dispersed liquid crystals,^{1-3, 5, 6, 8} poly-electrolyte membranes⁷ as well as thermosets and composites.⁴

Since PIPS depends heavily on the relationship between rate of network formation and the overall free energy of the system, being able to easily control either of these effects will allow for precise design of the final phase structure. Utilizing a photoinitiator to initiate the polymerization process is an elegant approach to easily modulate the network kinetics and thus the rate of network formation. The relationship between polymerization kinetics and the photoinitiator type, loading, incident irradiation intensity and wavelength has been well studied and characterized.¹⁶ Additionally, the use of light as the initiating mechanism allows for spatial and temporal control over the polymerization, which is advantageous for *in situ* applications.

Little work has been done to explore the additional control found when utilizing photoinitiation in PIPS. One study suggests that with increasing irradiation intensity, and rate of polymerization, the characteristic length scale of morphology increases.¹⁷ It has also been demonstrated that by decreasing the irradiation intensity, the mechanism of phase separation will transition from Spinodal Decomposition at higher polymerization rates to Nucleation and Growth.¹⁸ The effect of material thickness and temperature has been explored in heterogeneous networks formed through photo-induced PIPS.^{19, 20} A number of studies have looked at the resulting phase structure from photo-PIPS in polymer-dispersed liquid crystals.^{2, 3, 8} In the

examples listed, if a di-functional monomer is used, it is at a very low volume fraction and results in a loosely cross-linked network. Additionally, in many of these studies temperature is often still utilized as a significant control parameter to vary phase structure in addition to the rate of network formation. Little work has been towards designing heterogeneous structures with photo-PIPS in highly cross-linked networks formed under ambient polymerization conditions. While the presence of increased cross-linking will elevate the resulting modulus and glass transition temperature of the network, it does impose additional limitations to phase separation during polymerization. Therefore, it is crucial to understand what aspects of the polymerization can be addressed to promote PIPS and allow for phase development in an ambient, cross-linking photopolymerizations.

Our initial studies into heterogeneous network formation have shown that photoinitiated PIPS is a facile approach to develop phase-separated structure in a dimethacrylate homopolymer matrix modified by linear, non-reactive prepolymers.²¹ Additionally, we have found that distinctly phase-separated network formation relies heavily on the amount of time for partially immiscible phases to develop prior to network gelation.²² Liquid-gel de-mixing has been cited during phase separation post-network gelation in other studies.¹⁻³ However when forming heterogeneous networks in densely cross-linked systems, phase development is restricted post-gelation and cannot proceed via liquid-gel de-mixing. Therefore, systems that maximize the amount of phase development prior to network gelation can result in fully-developed phase structure.⁴

In this work, we explore the impact of prepolymer molecular weight on heterogeneous network formation via PIPS. First, we will study how adjustments in the prepolymer chainlength directly impact the free energy of the polymerizing system through entropic contributions. We will also demonstrate that by tailoring the prepolymer molecular weight while directly controlling the rate of network formation via photoirradiation, varying network morphologies can be formed. Limited work has been done to understand how both of these controls can be used in conjunction. Previous work into the impact of prepolymer or additive size in heterogeneous networks formed via PIPS has focused on thermally cured epoxy-based resins.²³ Here, we show that using both prepolymer molecular weight and the rate of network formation we can define the limits where PIPS is restricted from physical and energetic limitations in an ambient-cured photopolymerization.

5.2 Experimental

Materials - Triethylene glycol dimethacrylate (TEGDMA, Esstech) was utilized as the bulk homopolymer matrix in this study. The matrix was modified by the addition of three different non-reactive, linear prepolymers. The prepolymers have the same repeat unit ((polymethyl methacrylate); PMMA) but differ by an order of magnitude in molecular weight (discussed below). The photoinitiator in all studies was 2-2-dimethoxy-2-phenyl acetophenone (DMPA), which absorbs in the UV-region. The loading of photoinitiator was kept at 0.5 wt% relative to the monomer/prepolymer mass. The irradiation source in all photopolymerizations was 365 (±10) nm.

Prepolymer Synthesis - Three different prepolymers of varying molecular weight, based on a methyl methacrylate repeat unit were developed to modify the homopolymer matrix. The highest molecular weight prepolymer utilized was commercially obtained (Aldrich; reported to have a weight average molecular weight (M_w) of 120kDa and a polydispersity index (PDI) of 2.0). The remaining two prepolymers were prepared by a bulk thermal polymerization of methyl methacrylate in toluene, conducted at 65°C for 3 hours after which the temperature was elevated to 80°C until reaching 95% conversion. The thermal initiator used was azobisisobutyronitrile (AIBN) at a loading level of 0.5 wt% relative to the initial monomer mass. Conversion was monitored through the change in methacrylate peak area in the mid-IR (1635 cm⁻¹) with the carbonyl absorption used as an internal reference (1720 cm⁻¹). To modulate the resulting molecular weight, a chain transfer agent (dodecanethiol) was added to the bulk reaction medium. The molar ratio of chain transfer agent to monomer was calculated based on the desired final molecular weight utilizing the Mayo Equation.²⁴ The final product was isolated by precipitation in hexanes. The molecular weight (determined by gel permeation chromatography (Viscotek triple detector) with tetrahydrofuran as eluent), glass transition temperature (T_{g:} determined by dynamic mechanical analysis (Perkin Elmer 8000) using 10 mg of the powdered prepolymer in thin aluminum pockets subjected to deflection of 50 μ m at 1 Hz in air with heating at 2 °C/min), and refractive index (n_D^{22}) (based on extrapolation from increasing concentrations of prepolymer in TEGDMA with a refractometer (Atago T2)) of the three different prepolymers are listed in Table 5.1.

Table 5.1 – Prepolymer Properties			
PMMA (1kDa)	PMMA (11kDa)	PMMA (120kDa)	
M _W ~1,600 Da	M _W ~11,700 Da	M _W ~120,000 Da	
PDI ~1.2	PDI ~1.5	PDI ~1.8	
T _g ~45 °C	T _g ∼74 °C	T _g ~117 °C	
$n_D^{25}=1.510 (\pm 4 \text{ E-4})$	$n_D^{25}=1.501 \ (\pm 4 \text{ E-4})$	n_D^{25} =1.491 (± 7 E-4)	

Dynamic Mechanical Analysis - A dynamic mechanical analyzer (DMA, TA Q800) was used to characterize the thermal properties of networks post-cure. Samples had approximate dimensions (*length* x *width* x *thickness*) of 8 x 5 x 1 mm and were analyzed using a temperature sweep under 0.01% strain. After allowing the sample to equilibrate at -50 °C for 20 min, the samples were brought to a temperature of 200 °C at a rate of 3 °C/min, held isothermally at 200 °C for 20 min, and then cooled back to -50 °C at a rate of 3 °C/min. All samples were photopolymerized and then thermally post-cured at 180 °C to a conversion greater than 90% before DMA analysis so that no additional cure occurred as a result of the thermal scan. In select materials, conversion was monitored before and after the thermal scan in the DMA to further ensure no significant curing during the analysis. It was found that degree of methacrylate conversion might increase by 1-2% during the DMA scan, if at all. Since there already exists an error of \pm 0.5 % in the final conversion measurements, any additional cure is minimal and should not change the DMA data. Results presented here are from the initial scan (increase) in temperature.

Optical Density during Polymerization - To measure optical properties during polymerization a UV/Vis portable spectrometer (Ocean Optics, USB2000) was used. A disc-shaped sample (thickness = 240 μ m, diameter =20 mm) was secured so that a near-IR source, visible light source, and UV curing light source could transmit simultaneously through the material. A Fourier transform infrared spectrometer (FTIR) with near-IR fiber optic cables (Thermo scientific, Nicolet 6700) was used as the near-IR source to simultaneously monitor methacrylate conversion. The degree of conversion was measured by monitoring the dynamic change in methacrylate peak area (=CH₂, first overtone at 6165cm⁻¹). To follow the changes in optical density of the polymerizing sample, the UV/Vis spectrometer was employed. A visible light source that emits broadband 400-800 nm wavelength light as a photo probe independent of the photoinitiator was used with the intensity of the 600 nm wavelength transmitted through the sample monitored in real time. The photoinitiator in this study (DMPA) does not absorb above 380nm,²⁵ so the visible light source did not alter the photopolymerization kinetics.

Viscosity - Monomer/prepolymer solution viscosities were measured using a parallel plate rheometer (TA Ares). To accomplish this, a steady rate sweep test (strain controlled) was done under ambient conditions. Sample dimensions were 0.200 mm thickness and 20 mm diameter. The initial rate was 0.1 and the final rate was 1000 (s^{-1}).

Tensometer - Real-time polymerization stress was measured under ambient photopolymerization conditions using a cantilever beam tensometer (Volpe Research Center, American Dental Association Health Foundation, Gaithersburg, MD). The tensometer was coupled with a Fourier transform infrared spectrometer (FTIR) with near-IR fiber optic cables (Thermo Scientific, Nicolet 6700) so methacrylate conversion could be observed simultaneously using the same conditions as described in the optical density experiments. This set-up was used to collect all kinetic data presented throughout this manuscript. All samples were disc shaped with 6mm diameter and 1mm thickness. The details of this instrument and its operation are described more thoroughly in other publications.²⁶

Three-point Bending - Bar-shaped specimens of approximate dimension (*length* x *width* x *thickness*) 20 x 2 x 2 mm formed via ambient photopolymerization were tested in a universal testing machine (Mini Bionix 858, MTS). The machine was equipped with a 5 kN load cell for flexural strength and elastic modulus (n=3). All samples were tested with a crosshead speed of 1mm/min and a span of 15 mm between supporting rollers. The flexural modulus was calculated by extracting data from the initial linear portion of the load vs. displacement curve, and applying the formula:

$$E = \frac{CL^3}{4bh^3d} \times 10^{-3}$$

Where: C=load at fracture (N) d=displacement (mm) L= distance between the supports (mm) b= width of specimen (mm) h= height of specimen (mm).

AFM Imaging - Heterogeneous networks were imaged using atomic force microscopy (AFM) in phase contrast imaging mode using an Easy Scan 2 (Nanosurf) AFM. Imaging was done under tapping mode using conical tapping mode AFM probes (Aspire CT-170), which have a spring constant of 50 N/m. Samples were prepared via ambient photopolymerization at various irradiance levels between glass slides (sample thickness ~ 1mm).

5.3 Results & Discussion

The promotion of phase separation during polymerization is dictated by changes in overall free energy. In a multi-component polymerizing resin such as the one studied here, this thermodynamic property is described through the Gibbs free energy of mixing:

$$\Delta G^{mix} = \Delta H^{mix} - T \Delta S^{mix}$$

When $\Delta G^{mix} > 0$, a system will phase separate or de-mix, if possible, to achieve a lower overall free energy. In the phase-separating polymerizations studied here, changes in ΔG^{mix} are anticipated with changes in linear prepolymer chain length, as the entropy of mixing ΔS^{mix} will vary with this modification.

The entropy of mixing, ΔS^{mix} , depends directly on the degrees of freedom and number of conformations available for the different molecules in the polymerizing system. There are two main factors that contribute to the entropic term during PIPS, the first being the initial number of components in the system. To achieve an equivalent mass fraction loading level of prepolymer at different molecular weights, the number of prepolymer molecules introduced into the TEGDMA resin will have the following relationship:

$$n^{PMMA-120K} < n^{PMMA-11K} < n^{PMMA-1K}$$

The value for the entropy of mixing of each TEGDMA/PMMA formulation will follow this trend, as an increased number of molecules in the resin will increase the degrees of freedom. Thus, at any given loading level, in the monomeric state:

$$\Delta S_{PMMA-120K}^{mix} < \Delta S_{PMMA-11K}^{mix} < \Delta S_{PMMA-1K}^{mix}$$

Since the entropy of mixing is significantly lower with the higher molecular weight prepolymer, it will increase the overall free energy to a value higher than systems modified by PMMA-11K and PMMA-1K. Therefore, phase separation will be more favored in TEGDMA matrices modified by PMMA-120K. Another factor influencing the system entropy is the extent of conversion. As the polymerization proceeds and more TEGDMA monomer molecules become part of the cross-linked network (which approaches a single molecule with infinite molecular weight), the entropy of mixing will decrease, making phase separation more favorable throughout the entire reaction. The decrease in entropy with methacrylate conversion will occur in systems modified by all three different prepolymers.

It should be noted that changes in entropy are not the only factor influencing overall free energy during PIPS. During polymerization, the chemical potential of the mixture, characterized by the Flory-Huggins interaction parameter will also change.^{27, 28} Since this work focuses on TEGDMA matrices modified by PMMA of varying molecular weights, there should not be significant differences in interaction parameter between monomer and prepolymer since the prepolymer repeat unit is constant in all studies. However, as the molecular weight changes, the conformation of the prepolymer chains in the matrix change as well. At higher molecular weights, the chain end concentration will decrease, which will impact how PMMA interacts both intra- and inter-molecularly with other PMMA chains and TEGDMA. These interactions can contribute to the overall free energy of the polymerizing material. The effect of prepolymer

conformation will not be a focus of this study. To probe whether the anticipated changes in entropy and free energy with PMMA molecular weight described above significantly influence PIPS, dynamic mechanical analysis (DMA) was utilized to probe multi-phase structure postpolymerization, in TEGDMA matrices modified by the three different PMMA prepolymers.

Dynamic Mechanical Analysis - DMA was utilized after polymerization to evaluate thermal properties of the formed networks and to probe whether phase-separated domains formed. In these experiments all networks were thermally post-cured after the ambient photopolymerization, at 180 °C for approximately 1 h to achieve a final conversion greater than 90% so that no additional cure occurs during the thermal scan (limiting conversion via ambient photopolymerization ranges from 70-85% methacrylate conversion depending on the formulation). All materials analyzed via DMA were cured for 10 min at $I_0=5mW/cm^2$.

Tan delta profiles for materials modified by the highest molecular weight prepolymer, PMMA-120K are shown in Figure 5.1. The control matrix, poly(TEGDMA) displays one broad transition in the tan delta profile centered about 161 °C, indicating single-phase structure with a degree of structural heterogeneity, typical of dimethacrylate networks. When PMMA is added to the matrix, secondary peak formation is observed at 135 °C, corresponding to the formation of a secondary phase rich in a combination of poly(TEGDMA) and PMMA-120K since the T_g has shifted to a value between that of poly(TEGDMA) and PMMA-120K (Table 5.1).²⁹ In all PMMA-120K modified samples, a shoulder is still observed at ~161 °C indicating that a phase rich in poly(TEGDMA) remains. As seen in Figure 5.1, two peaks are observed at all loading levels of PMMA-120K greater than 5 wt%. With this prepolymer, even small additions can significantly increase the overall free energy to promote phase separation.



Figure 5.1 – Tan delta profile of post-cured poly(TEGDMA) networks modified by PMMA-120K. All networks were photopolymerized under ambient conditions (I_o=5mW/cm²) and postthermally cured for 1 h at 180°C to reach a final conversion >90%.

When the same analysis is done for poly(TEGDMA) matrices modified by PMMA-11K or PMMA-1K, the results differ (Figures 5.2-5.3). In the matrices modified by PMMA-11K (Figure 5.2), secondary peak formation, indicating phase-separated structure, is only observed at the highest loading level of prepolymer tested (20 wt%). At lower loading levels (5 - 10 wt%), a single T_g is observed that has shifted to slightly lower temperatures than the poly(TEGDMA) control. This indicates that the system has not undergone phase separation, but instead the prepolymer remains uniformly dispersed throughout the matrix. The tan delta peak is also broadened at lower loading levels, indicating a slightly larger degree of heterogeneity compared to poly(TEGDMA) caused by the addition of prepolymer.



Figure 5.2 – Tan delta profile post-cure of poly(TEGDMA) networks modified by PMMA-11K. All networks were photopolymerized under ambient conditions (I_o=5mW/cm²) and post-thermally cured for 1 h at 180°C to reach a final conversion >90%.

In the matrices modified by PMMA-1K, no visible secondary peak formation is observed at any loading level up to 20 wt% (Figure 5.3). However, there again is broadening of the tan delta peak with increasing prepolymer loading, and there is a slight shoulder in the 10 and 20 wt% modified samples. There are a couple different explanations to be offered for this behavior. The first is that phase-separated networks form at these higher loading levels but the two phases formed have similar T_g's, so only a slight shoulder is observed in the tan delta profile. Another explanation could be that the shoulder is an artifact of forming a more heterogeneous network than the poly(TEGDMA) control, and that no distinct phase structure is formed during polymerization. Additional characterization discussed throughout this study will demonstrate that the lack of secondary peak formation indicates that these networks do not undergo distinct PIPS and instead form broadly heterogeneous networks.



Figure 5.3 – Tan delta profile post-cure of poly(TEGDMA) networks modified by PMMA-1K. All networks were photopolymerized under ambient conditions ($I_0=5mW/cm^2$) and post-thermally cured for 1 h at 180°C to reach a final conversion >90%.

In the materials that display two transitions in the tan delta profile, the shift in T_g observed after polymerization can be used to estimate the composition of each phase formed. Since in all phase-separated materials studied here, one transition falls very close to that observed in bulk poly(TEGDMA), and the other falls between the T_g of poly(TEGDMA) and the T_g of the modifying PMMA (Table 5.1), the two phases formed will be rich in TEGDMA and rich in TEGMDA/PMMA, respectively. The phase compositions were estimated by applying a modified version of the Fox Equation, displayed below.²⁹

$$TEGDMA\ Fraction = 1 - \left(\frac{\left(T_g^{poly(TEGDMA)} - T_g^{NewPhase}\right)}{\left(T_g^{poly(TEGDMA)} - T_g^{PMMA}\right)}\right)$$

The weight fraction of poly(TEGDMA) in each phase has been estimated for the TEGDMA polymerizations modified by 20 wt% PMMA-11K and 20 wt% PMMA-120K, as they both displayed distinct secondary peak formation (Figures 5.1-5.2) and the results are displayed in Table 5.2. It should be noted that the experimentally observed poly(TEGDMA) T_g is utilized in the Fox equation. Therefore, it is possible to calculate a phase composition greater than 1, if a sample has a higher T_g than the poly(TEGDMA) average. All T_g 's associated with a TEGDMA-rich domain fell within error of that observed in bulk poly(TEGDMA).

Table 5.2 – Average TEGDMA fraction in phase-separated materials (n=3)			
	TEGDMA/ 20 wt% PMMA-11K	TEGDMA/ 20 wt% PMMA- 120K	
TEGDMA-rich	0.97 (± 1 E-1)	1.0 (± 2 E-1)	
TEGDMA/ PMMA-rich	0.60 (± 4 E-2)	0.35 (± 4 E-2)	

In both phase-separated networks, a phase that is essentially pure TEGDMA forms. This phase is expected to be a continuous domain in both materials probed, as TEGDMA is the major component in the initial resin. Also observed in Table 5.2, is that the TEGDMA/PMMA-rich phase varies in composition depending on the prepolymer molecular weight. The highest molecular weight prepolymer, PMMA-120K forms a secondary phase that is much more concentrated in PMMA. This finding, along with the observation that a lower loading of PMMA-120K is necessary to induce phase separation, indicates that the thermodynamic instability encountered during polymerization varies based on prepolymer molecular weight. Additionally, the differences in phase composition indicate that there should be an observed difference in volume fraction of the TEGDMA/PMMA-rich phase, which will be validated by phase morphology characterization later in this study.

Thus far, these studies have identified how PMMA molecular weight influences the overall free energy of a polymerizing resin, affecting whether PIPS is promoted. However, analysis of the resulting phase compositions indicates that even in two materials where the overall free energy is sufficiently high and PIPS is promoted, the resulting phase structure and composition varies. To begin to probe the differentials in the phase separation process amongst these systems with sufficiently high free energy, light transmission behavior was observed during polymerization.

Turbidity measurements during polymerization - An additional measure to probe phase separation is to monitor the changes in light transmission through the material during polymerization. To accomplish this, the transmission of visible light ($\lambda = 600$ nm) was monitored during ambient photopolymerizations. Since the irradiation source used to cleave the photoinitiator and initiate the polymerization has $\lambda = 365 \pm 10$ nm, there will be no interference on the reaction kinetics by introducing this visible light source and the UV source does not perturb the optical density measurements. All TEGDMA/PMMA samples begin as optically clear monomer formulations with essentially equivalent light transmission values. The decrease in prepolymer refractive index (Table 5.1) with increasing PMMA size was unexpected since density and presumably refractive index typically increase with polymer molecular weight.³⁰ Figure 5.4 displays visible light transmission as a function of conversion through TEGDMAmodified networks during polymerization (I_o=5mW/cm²).

During the photocure of TEGDMA/20 wt% PMMA-1K, there is very little change observed in light transmission, indicating that no significant difference in refractive index is observed across the material during polymerization. This behavior is identical to the visible light transmission during a poly(TEGDMA) polymerization, which is also displayed in Figure 5.4.

There are slight deviations from $I/I_0=1$ during the reaction, which is likely due to microgel formation and small heterogeneities associated with a poly(TEGDMA) bulk polymerization, as well as noise in the measurement process. The lack of any significant change in optical density in the formulations modified by PMMA-1K is an additional indication that phase separation does not occur in these formulations.



Figure 5.4 –Visible light transmission behavior during polymerization. Samples cured with UVirradiation, $I_0=5$ mW/cm², $\lambda=365$ (±10nm). Visible light transmission probed by monitoring $\lambda=600$ nm.

When TEGDMA is modified with 10 wt% PMMA-120K or 20 wt% PMMA-11K, both materials which display multiple peaks in their tan delta profiles (Figures 5.1 & 5.2), there is an observed decrease in visible light transmission at very early stages of the polymerization. This occurs between 1-7 % methacrylate conversion, depending on the specific formulation, and is attributed to the onset of phase separation with the formation of partially immiscible phases; one rich in TEGDMA and one rich in TEGDMA/PMMA with differing refractive indices. The phase

enriched with PMMA will initially have a higher refractive because of the relatively high prepolymer content compared to the TEGDMA-rich phases.

The visible light transmission in the TEGDMA/10wt% PMMA-120K sample decreases until approximately 20% methacrylate conversion. During this period, the refractive index difference between compositionally different phases increases, as one phase polymerizes more rapidly and reaches a higher local extent of conversion, as conversion of monomer into polymer will increase refractive index in a linear manner.³¹ Specifically, the TEGDMA-rich phase, which has a lower local viscosity and higher local double bond concentration will initially polymerize more rapidly. The PMMA-rich phase, with a higher viscosity will develop at a slower rate.²¹ For comparison, the refractive index of TEGDMA begins at about 1.460 and approaches a limiting value of ~ 1.53 during ambient condition photopolymerization,³² which is higher than that of the pure prepolymers (Table 5.1). An additional effect that may be enhancing the decrease in light transmission is further changes in the composition of each phase through continued diffusion of monomer or prepolymer, although this effect will be minimized by gelation, which is delayed significantly to 10-20% methacrylate conversion in the bulk.²² This delayed gelation is again a result of the formation of two co-continuous domains, polymerizing at nonequivalent rates. Bulk gelation is not observed until one of the continuous domains gels, which can occur at a much higher degree of overall methacrylate conversion.

After the light transmission minimum at about 20% methacrylate conversion, a recovery to ~95% of the initial visible light transmission is observed in the TEGDMA/10wt% PMMA-120K polymerization. This occurs as the TEGDMA/PMMA-enriched phase, which polymerizes more slowly, approaches a level of network development closer to that of the TEGDMA-enriched domains which polymerized more rapidly at the early stage of the polymerization, thus

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minimizing the refractive index differential between the two phases caused by differences in local extent of conversion.^{31, 32} At the end of polymerization when both phases have reached limiting conversion, there will be compositional differences between the domains, which has already been probed through shifts in T_g (Table 5.2), and this causes a modest refractive index mismatch, and a slight decrease in light transmission compared to the monomeric resin.

In the TEGDMA/20wt% PMMA-11K sample, reduction in visible light transmission begins early in the polymerization, however the visible light reduction continues throughout much more of the reaction, and there is a less significant recovery period at the end of the ambient cure. This could indicate differences in domain size between the two samples. The formation of larger domains could increase light scattering resulting in a more dramatic decrease in light transmission observed in the TEGDMA / 20wt% PMMA-11K polymerization. In this sample, the more gradual and constant rate of change in visible light transmission could also indicate that phase separation is occurring through the Nucleation and Growth mechanism.

Thus far, our analysis has focused on how modulations in overall free energy of mixing can influence phase separation behavior during polymerization. Specifically, the changes in free energy due to modification of prepolymer molecular weight in a TEGDMA/PMMA polymerization have been studied. At lower loading levels of prepolymer (5-10 wt%), phase-separated networks are only observed in the TEGDMA/ PMMA-120K networks (Figure 5.1). This is the only material with entropy of mixing sufficiently low at these PMMA loading levels to promote phase separation. However, at higher prepolymer loadings (20 wt%) the combined effects of high prepolymer content and decreased TEGDMA concentration makes PIPS favorable in the formulations modified by PMMA-11K as well as PMMA-120K. The entropic contributions to the overall free energy in these two systems are non-equivalent since the light
transmission behavior (Figure 5.4) and resulting phase compositions differ (Table 5.2). The polymerizations modified by PMMA-120K produce a highly PMMA-enriched phase, which increases the initial mismatch in refractive index observed early on in the polymerization, despite PMMA-120K having the lowest prepolymer refractive index (Table 5.1). The lowest molecular weight prepolymer, PMMA-1K does not undergo phase separation at any of the loading levels tested here, as it has the highest entropy of mixing.

Beyond the thermodynamics of the polymerizing solution, as influenced by the overall free energy, an effect that must be considered when studying PIPS is that the kinetic and physical parameters are changing throughout the polymerization process. Increases in solution viscosity, formation of cross-links, gelation, and vitrification can significantly limit the extent to which phase separation can occur through diffusion during polymerization. For instance, two material systems undergoing PIPS that both have a sufficiently high free energy of mixing, promoting phase separation, may achieve drastically different phase structures and compositions based on the rate of network formation. If network formation is very rapid, the period allowed for phase separation through diffusion before the network gels (and presumably locks network structure into place) will be limited and will restrict the domain size and composition that can form. In this scenario, the material may never achieve thermodynamic equilibrium as the phase separation process is suppressed very early during the polymerization. However, if network formation is much slower, and the time available for diffusion of immiscible phases after the onset of phase separation is much greater, a material may form well-developed, regular phase structure through diffusion prior to network gelation. Our previous work into PIPS in a TEGDMA-based matrix has shown that the type of phase structure formed from PIPS relies heavily on the average polymerization rate and the amount of time between the onset of phase separation and the onset of network gelation.²² Therefore, the remainder of this study will focus on how the modification to PMMA molecular weight will influence the kinetic development of phase-separated networks, and the extent to which phase separation can occur during polymerization through diffusion processes. To probe this, a constant PMMA-loading level (20 wt%) was chosen for analysis.

Kinetics of Polymerization during PIPS - The polymerization rate behavior during the reaction is greatly affected by the viscosity of the initial monomer solutions in addition to the heterogeneous phase compositions that ensue. The viscosity of each TEGDMA/PMMA solution was measured in the monomeric state, and the results are displayed in Table 5.3.

Table 5.3 – Monomer/Prepolymer Solution Viscosities (n=3)		
Sample	Viscosity (Pa*s) (E-02)	
TEGDMA	1.09 (±0.05)	
TEGDMA / 20 wt% PMMA-1K	1.79 (±0.17)	
TEGDMA / 20 wt% PMMA-11K	5.75 (±1.2)	
TEGDMA / 20 wt% PMMA-120K	283 (±6.0)	

As is expected, the viscosity increases with the molecular weight of prepolymer. The most significant increase occurs between the PMMA-11K and 120K, as the viscosity increases by a factor of ~40 as opposed to 1.6 and 5-fold increases, respectively. This indicates that in the TEGDMA /20wt% PMMA-120K, despite the reduced polymer chain number, there is significant increased prepolymer/prepolymer entanglement affecting viscosity. These differences in viscosity of the initial formulations also influence the polymerization kinetic behavior. Figures 5.5-5.6 display the polymerization rate as a function of conversion for the three prepolymer-modified formulations polymerized for 10 min at $I_0=20$ mW/cm² (Figure 5.5) or $I_0=300\mu$ W/cm² (Figure 5.6).



Figure 5.5 – Rate of polymerization (R_p) development during reaction of PMMA-modified matrices, $I_0=20$ mW/cm². All series are normalized by initial double bond concentration [=]₀ to eliminate rate concentration differences between prepolymer modified and un-modified systems.

When the irradiation intensity is sufficiently high ($I_o=20$ mW/cm²), no difference is observed in polymerization rate behavior across the three different modifying prepolymers (Figure 5.5). All three have a nearly instantaneous increase in polymerization rate, and this increase is more rapid than in the control poly(TEGDMA) polymerization. This autoacceleration behavior at early stages of the reaction is typical in cross-linked polymerizations. The increased viscosity of PMMA-modified monomer solutions (Table 5.3) favors autoacceleration and diffusion-limited termination early on in the reaction, leading to a relatively higher overall rate of polymerization compared to bulk poly(TEGDMA). All materials achieve a similar final methacrylate conversion of 80%.

The overall polymerization rates decrease, as expected, in the $I_0=300\mu$ W/cm² polymerizations (Figure 5.6). It should be noted, that the observed decrease in polymerization

rate of the control matrix poly(TEGDMA), was not as significant as expected. A half order dependence of incident irradiation intensity (I_0) on the resulting polymerization rate (R_p) has been characterized for bulk, cross-linking free radical polymerizations.³³ With the intensities tested here, which vary by a factor of 66, an 8-fold differential is expected in the polymerization rate of poly(TEGDMA). With closer evaluation of the poly(TEGDMA) kinetics presented here, it is found that the scaling factor (which, as stated, is expected to be ~ 0.5) between I₀ and R_p varies during the polymerization. Up to $\sim 40\%$ conversion, the scaling factor is roughly 0.3, but then steadily increases with further methacrylate conversion, reaching a value of 0.4 at 80% methacrylate conversion. Both the variation in the scaling factor with conversion, as well as the dependence on initiation rate that scales less than the traditional value of 0.5 at early stages of the reaction, have been characterized during the polymerization of multi-functional methacrylates.³⁴⁻ ³⁶ The deviation from the half order scaling law at early stages of the reaction is due to chainlength dependent termination kinetics,³⁴ while the portion of the reaction where the scaling factor varies with conversion (encountered after 40% methacrylate conversion) indicates that the polymerization is transitioning to a regime where termination is controlled by reaction diffusion.35

Moving the focus to the phase separating polymerizations, at the lower irradiation intensity (I_0 =300 μ W/cm²), differences are observed in the bulk polymerization rate as a function of modifying prepolymer molecular weight. All three materials still undergo the typical autoacceleration and autodeceleration behavior, and the TEGDMA/20 wt% PMMA-1K and TEGDMA/20 wt% PMMA-11K polymerizations have identical rate profiles with slightly lower rates of polymerization compared to the control, poly(TEGDMA). However, the TEGDMA/20 wt% PMMA-120K polymerization has an enhanced autoacceleration behavior, reaching a higher

maximum rate of polymerization (R_p^{max}) at a later stage of the reaction and having a higher limiting methacrylate conversion compared to the other PMMA-modified systems. All three PMMA-modified matrices have limiting conversions lower than that of poly(TEGDMA). Since the irradiation intensity and rate of radical generation is so low, and the viscosity of PMMAmodified systems is higher, the limiting conversion decreases due to diffusion constraints.



Figure 5.6 – Rate of polymerization rate (R_p), development in PMMA-modified matrices, $I_0=300\mu$ W/cm². All series are normalized by initial double bond concentration [=]_o to eliminate rate concentration differences between prepolymer modified and un-modified systems.

We suspect that the lower polymerization rate when the irradiation intensity is decreased allows for more distinct phase-separated structure to form, especially compared to the polymerizations conducted at much higher irradiation intensities, since there is more time for diffusion of immiscible phases prior to the onset of viscous effects such as gelation that prohibit further phase development. Additionally, the observed differences in polymerization rate with PMMA molecular weight during this slow kinetic regime indicate that physical factors affecting PIPS such as viscosity and gel fraction develop differently based on the PMMA molecular weight. These varying kinetic rate profiles are likely related both to differentials in phase morphology (which will be addressed shortly), as well as phase composition (Table 5.2) which will influence the bulk polymerization rate which is measured across all domains formed. The remainder of this study will focus on demonstrating how both these kinetic variations as well as changes in overall free energy discussed previously must be addressed and understood to design and engineer phase-separated networks.

Stress Reduction through PIPS - To demonstrate the influences of both polymerization kinetics and overall free energy on designing networks via PIPS, we evaluated the polymerization stress development in TEGDMA/PMMA matrices while varying the PMMA molecular weight, as well as the rate of network formation (through incident UV-irradiation intensity).

Formation of phase-separated networks has been explored as an approach to reduce polymerization stress.^{4, 37, 38} In a TEGDMA-based polymerization, we have found that networks formed via photo-PIPS often display a reduction in polymerization stress while maintaining an equivalent modulus to a control homopolymer matrix post-ambient cure. For effective stress reduction, it is necessary that there is an ample amount of pre-gel network development between the onset of phase separation and the onset of network gelation to allow for development of two co-continuous phases.^{4, 22} Polymerizations where the degree of network development, and thus the time, between phase separation and gelation is limited results in minimal polymerization stress reduction. In the studies here, the variation of prepolymer molecular weight significantly alters the ability of the prepolymer to diffuse throughout the reaction medium. Additionally, since the prepolymer molecular weight also impacts the solution viscosity (Table 5.3), this

property also has an effect on monomer diffusion, which is equally if not more important and more likely than prepolymer diffusion. These changes in diffusivity throughout the reaction medium during polymerization may impact the extent to which phase structure develops in the TEGDMA/PMMA networks based on PMMA molecular weight. To probe the efficiency of the varying prepolymers at this diffusion process, the development of polymerization stress was monitored at different rates of network formation.

By varying the rate of network formation, the amount of time between phase separation and gelation can be shortened or extended based on the curing intensity employed. At high irradiation intensities, the network formation may occur so rapidly that minimal diffusion of partially miscible phases is possible, and there is likely insufficient time to form distinctly phaseseparated structure prior to network gelation. In the TEGDMA/PMMA polymerizations studied here, suppression of phase separation is encountered when polymerizations are conducted at high incident irradiation intensity ($I_0=20$ mW/cm²). At this rate of network formation, the control homopolymer network, poly(TEGDMA), experiences ~2.0 MPa stress at the end of ambient photopolymerization. When the TEGDMA matrix is modified at a loading level of 20 wt% by the PMMA prepolymers the final polymerization stress is 1.55 MPa (Supplemental Figure S5.1), and this result does not vary with the prepolymer molecular weight. The reduction in polymerization stress with PMMA modification scales with the loading level of prepolymer. This reduction in polymerization stress is an artifact of the decrease in double bond concentration, which for a fixed level of conversion will produce less shrinkage strain. Since diffusion is limited at this high rate of network formation, distinct phase structures that provide interfaces that compensate for polymerization stress reduction through internal volume rearrangement do not

form. This result is expected, as kinetic analysis of PMMA-modified resins at this irradiation regime (Figure 5.5) displayed no differences as a function of PMMA molecular weight.

If the rate of network formation is slowed down, thus allowing for more diffusion of partially miscible phases, the stress reduction should go beyond the effect of decreased double bond concentration. To probe this, the polymerization stress development was evaluated during a 'staged curing' ambient photopolymerization (Figure 5.7). The initial irradiation intensity was set to 300 μ W/cm² until 50% methacrylate conversion was achieved. This was monitored using FTIR spectroscopy simultaneously with the tensometer used to measure polymerization stress. After this point, the irradiation intensity was increased to I_o=20mW/cm² for the remainder of the polymerization, to achieve a sufficiently high final degree of conversion. This benchmark (50% methacrylate conversion) was chosen as the point to switch between low and high irradiation intensity since it is well beyond the gel point, and thus network structure can reasonably be assumed to be locked in place by this stage. The initial low intensity cure was chosen, as it has already been demonstrated to lead to differentials in kinetic behavior based on the modifying PMMA and likely variations in phase separation behavior (Figure 5.6).

As seen in Figure 5.7, using this staged curing approach there is an observed difference between polymerization stress reduction based on the molecular weight of the modifying prepolymer. As in the completely high irradiation polymerization (Supplemental Figure S5.1), the poly(TEGDMA) control has a final polymerization stress of 2.0 MPa. The TEGDMA/ 20 wt% PMMA-1K experiences ~1.6 MPa of stress, a value that scales with the loading level of prepolymer. This further supports that as the molecular weight of the prepolymer becomes sufficiently low, it does not impose any thermodynamic instability during polymerization and thus behaves like inert filler in the matrix. The networks modified with PMMA-11K and

PMMA-120K have ~35-45% reduction in polymerization stress compared to the poly(TEGDMA) matrix. In these networks, the combination of higher overall free energy promoting PIPS and sufficient time prior to network gelation allow for the formation of phase-separated structure. This structure formation allows for more efficient compensation of volumetric shrinkage and polymerization stress, which has been characterized in detail.²²



Figure 5.7 – Real-time polymerization stress of TEGDMA matrices modified by PMMA of varying molecular weights. Irradiation begins at 70 s, I_0 = 300 μ W/cm² until ~50% methacrylate conversion, and then I_0 =20mW/cm² for the remainder of the reaction.

A benefit of utilizing this staged curing approach is that we can develop phase-separated networks utilizing the low intensity initial cure, but by employing the late stage flood cure the materials can achieve certain critical bulk properties (such as degree of conversion and modulus) at the end of the polymerization. To confirm this, the bulk elastic modulus of poly(TEGDMA) and TEGDMA/PMMA matrices cured under varying light intensities, was evaluated post-ambient photopolymerization (Figure 5.8).



Figure 5.8 – Bulk elastic modulus of networks post-ambient photopolymerization at varying irradiation intensities and patterns. Average limiting fractional methacrylate conversion is denoted above each data set (n=3).

In some cases, there is a modest difference in final modulus between materials formed using a high intensity irradiation ($I_0=20$ mW/cm²) for the entire polymerization or employing the staged curing (20 wt% PMMA-11K, 20 wt% PMMA-120K). This is due to the differences in reaction exotherm from the different curing methods. In all materials, when the networks are formed under low irradiation intensity, ($I_0=300 \mu$ W/cm²) the resulting bulk modulus is decreased significantly, mostly because these materials do not achieve an equivalent final degree of conversion. Again, this shows that by understanding the limitations to diffusion of incompatible or partially miscible phases, processing procedures can be designed that allow for distinct phase-separated network formation via PIPS without compromise in desired final properties such as bulk modulus.

The last point to be addressed in this study are the differences observed in the phase separation process, and how PIPS influences bulk property development in the 11K and 120K modified networks. When TEGDMA is modified by 20wt% of either of these PMMA prepolymers, the free energy is sufficiently high to promote PIPS as validated in Figures 5.1-5.2. However, many differentials in the phase behavior and bulk network development are observed between these polymerizations. Under low irradiation conditions, the initial rates of network formation vary significantly (Figure 5.6). Since TEGDMA / 20 wt% PMMA-120K has a higher viscosity, and an extended autoacceleration period, this serves as a first indication that a greater extent of phase development can occur prior to viscous effects prohibiting further phase evolution. Additionally, the visible light transmission behavior through the PMMA-11K modified networks is quite different from that of the PMMA-120K networks (Figure 5.4). Lastly, the absolute degree of stress reduction at the completion of ambient photopolymerization varies between 35% for TEGDMA/20wt% PMMA-11K, and 45% for TEGDMA/20wt% PMMA-120K (Figure 5.7). This could result from differences in domain size or the mechanism of phase separation that is occurring during polymerization. It has been cited that co-continuous structure is more effective at shrinkage reduction.⁴ We anticipate that the differences in stress reduction behavior are attributed to differences in the phase structure formed, which will be evaluated next.

Phase structure imaging through atomic force microscopy (AFM) - To ensure that the observed differences in bulk properties (polymerization stress) were in fact a result of different types of heterogeneous network formation, AFM was utilized to image materials cured at different irradiation intensities post-polymerization. When poly(TEGDMA) homopolymer was analyzed, no distinct phase structure on the micron length scale was observed, as is expected with the control, which may display some degree of structural heterogeneity but is

compositionally homogeneous (Supplemental Figure S5.2). When the materials modified by PMMA-1K were imaged post-cure, they appeared identical to that of the poly(TEGDMA) control (Supplemental Figure S5.3), which further supports our claim that with a sufficiently low prepolymer molecular weight, PIPS is not favored during the photopolymerization.

If the modifying prepolymer molecular weight is increased to 11K, phase-separated structure is observed, as expected and this is displayed in Figure 5.9. When the network is formed rapidly (I_0 =20mW/cm²), as in Figure 5.9A, there are very small spherical domains on the order of 100 nm in diameter, and the material remains transparent during polymerization. However, these spherical domains are dispersed within a continuous matrix. When the material is polymerized at a slower rate, as in 5.9B and 5.9C, much larger spherical domains are present throughout the entire matrix. Now, instead of having diameters on the scale of nanometers, the domains have diameters varying from 0.5-1 μ m. In both kinetic regimes, phase structure characteristic of the Nucleation and Growth phase separation mechanism, results. It is not surprising that in the slower polymerization, the spherical domains increase in size, as the decrease in rate of network formation will allow for coalescence and growth prior to network gelation. This does not happen in the rapidly cured material, which is why such small, spherical domains result.

The composition of the two phases formed through PIPS in TEGDMA/20wt% PMMA-11K has been estimated (Table 5.2): one being TEGDMA-rich and one being TEGDMA/PMMA-rich. In the images presented below, we anticipate that the TEGDMA-rich domains are the continuous phase, as there is a much more significant volume fraction of TEGDMA monomer in the initial resin. Additionally, we expect that the TEGDMA-rich domains polymerize more rapidly, and therefore can form an interconnected, continuous domain readily. However, when this continuous network forms more slowly there is more time for diffusion and coalescence of the dispersed TEGDMA/PMMA rich domains, which accounts for the increase in domain size as the irradiation intensity decreases. This result also shows promising evidence that phase morphology can be manipulated with the rate of network formation. It is unlikely that a phase inversion could be achieved with further decrease of the polymerization rate, as the reaction in the TEGDMA-rich domains will still proceed more rapidly compared to the TEGDMA/PMMA-rich domains, promoting the formation of a TEGDMA continuous phase.



Figure 5.9- AFM images, poly(TEGDMA) / 20 wt% PMMA-11K , post ambient photopolymerization. (A) $I_0=20mW/cm^2$ (B) $I_0=300\mu W/cm^2$ until ~50% methacrylate conversion, then $I_0=20mW/cm^2$ for the remainder of the reaction (C) $I_0=300\mu W/cm^2$ until ~50% methacrylate conversion, then $I_0=20mW/cm^2$ for the remainder of the

With the highest prepolymer molecular weight modification (TEGDMA/20wt% PMMA-120K), phase morphology also varies with rate of network formation (Figure 5.10). When the network is formed rapidly, there is no observable distinct phase structure. Broad, structural heterogeneities are observed when the sample is scanned over an area of 20 µm or more. However these irregularities are not regular in size or shape (Figure 5.10A). When the sample is scanned over an area smaller than 20 µm, no heterogeneity is observed (Figure 5.10B). In this case, phase separation is limited by the rapid rate of network formation, and the broad structural heterogeneities observed in Figure 5.10A are a result of incomplete phase separation as there is insufficient time available for diffusion of immiscible phases. When the initial rate of network formation is slower, as permitted by employing staged curing, phase-separated structure is observed (Figure 5.10C-D). In the networks modified by PMMA-120K, the domains appear to be more co-continuous, indicative of the Spinodal Decomposition mechanism.^{4, 39} In this polymerization a TEGDMA-rich and TEGDMA/PMMA-rich phase also develops (Table 5.2). Again, the TEGDMA-rich domain is expected to develop more rapidly. It may grow in size, as free TEGDMA monomer will diffuse to these regions during initial stages of the reaction. After the onset of network gelation (at 10-20% bulk conversion), the phase morphology will not vary significantly, as diffusion is significantly limited.



Figure 5.10 - AFM images, poly(TEGDMA) / 20 wt% PMMA-120K, post-ambient photopolymerization. (A) $I_0=20mW/cm^2$ (B) $I_0=20mW/cm^2$ (C) $I_0=300\mu W/cm^2$ until ~50% methacrylate conversion, then $I_0=20mW/cm^2$ for the remainder of the reaction (D) $I_0=300\mu W/cm^2$ until ~50% methacrylate conversion, then $I_0=20mW/cm^2$ for the remainder of the reaction.

The differences in resulting phase structure between materials modified with PMMA-11K and PMMA-120K are not unexpected based on the studies presented here. With PMMA-120K as a modifier, the entropy of the polymerizing system is lowest. This leads to the material system with the highest free energy tested, and could promote a highly unstable thermodynamic state during polymerization, resulting in the Spinodal Decomposition mechanism. In the system modified by PMMA-11K, the higher degree of entropy results in the system only becoming metastable during polymerization, forming a dispersed phase structure typical of Nucleation and Growth, as seen in Figure 5.9.³⁹ The much larger domain sizes that form in TEGDMA/ 20wt% PMMA-11K materials indicate that coalescence, and diffusion of incompatible phases is less hindered in this polymerization as the viscosity is lower (Table 5.3), and also reflects the difference in phase composition of the TEGDMA/PMMA-rich phase, calculated earlier (Table 5.2). Lastly, the polymerization stress is reduced less significantly in the TEGDMA / 20wt% PMMA-11K material, which supports the previously proposed claim that phase structure resulting from the Nucleation and Growth mechanism is less efficient at stress reduction.⁴⁰ This is supported by the co-continuous network structure and higher degree of stress reduction observed in the network modified by PMMA-120K.

5.4 Conclusions

Here we have demonstrated the ability to use prepolymer molecular weight to adjust the overall free energy of a TEGDMA polymerization modified by linear PMMA prepolymer, to either promote or suppress polymerization-induced phase separation (PIPS). When the modifying prepolymer has a very low molecular weight (1,000 Da, PMMA-1K), phase separation is never favored during the polymerization, as indicated by tan delta behavior post-cure, even when the loading level of prepolymer is as great as 20 wt%. At intermediate

prepolymer molecular weights (11,000 Da, PMMA-11K), PIPS is observed at loading levels of 20 wt%, and when the prepolymer molecular weight is further increased to 120,000 Da, PIPS is observed at all loading levels. As the prepolymer molecular weight increases, the overall system entropy decreases, promoting PIPS since the overall free energy is much higher and closer to the instability threshold throughout the reaction.

Understanding the impact of prepolymer molecular weight on the overall free energy from these results, we explored how the network design could be more precise by controlling the rate of network formation through photoirradiation. When the rate of network formation is sufficiently high ($I_0=20$ mW/cm²), PIPS is suppressed significantly. No enhanced stress reduction is observed in these polymerizations. Imaging of samples cured under these conditions shows slight and small structural heterogeneities; but no distinct phase structure. When a staged curing approach is taken, where the sample is first initiated under low light intensities ($I_0=300 \mu W/cm^2$) until 50% methacrylate conversion, followed by high-intensity curing ($I_0=20$ mW/cm²) for the remainder of the reaction, PIPS occurs in the systems modified by PMMA-11K and PMMA-120K. When modified by PMMA-11K, the resulting phase structure is dispersed with a TEGDMA continuous network and a TEGDMA/PMMA dispersed domain, indicative of the Nucleation and Growth mechanism. The size of the resulting phase structure can be tailored with the irradiation intensity employed, as a lower intensity and thus a slower rate of reaction will allow for a greater extent of diffusion pre-gelation and the formation of larger dispersed domains. In materials modified by PMMA-11K there is an observed reduction in polymerization stress of 35% compared to the poly(TEGDMA) control. When PMMA-120K is the modifying prepolymer, the phase structure is co-continuous, indicative of the Spinodal Decomposition mechanism of phase separation, and the observed stress reduction is 45% with no significant decrease in bulk modulus.

This study demonstrates that the combined effects of preoplymer molecular weight and rate of network formation can be used to precisely design heterogeneous networks formed via PIPS. Even though a di-functional monomer that forms a densely cross-linked network is used as the bulk material, differing phase structures and domain sizes can form. The formation of these differing heterogeneities depends on both the rate of network formation, or the kinetics of network formation, as well as the overall free energy of the polymerizing system.

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5.6 References

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5.7. Supplemental Material



Figure S5.1 – Real-time polymerization stress of TEGDMA matrices modified by PMMA of varying molecular weights. Irradiation begins at 70 s, I_o=20mW/cm² for the entire polymerization.



Figure S5.2 – AFM image, poly(TEGDMA), post-ambient photopolymerization (I₀=20mW/cm²).



Figure S5.3 – AFM images, poly(TEGDMA) / 20 wt% PMMA-1K post ambient photopolymerization. (A) $I_0=20$ mW/cm² (B) $I_0=300$ µW/cm² until ~50% methacrylate conversion, then $I_0=20$ mW/cm² for the remainder of the reaction.

CHAPTER 6

UTILIZING THERMAL PROPERTY EVOLUTION DURING POLYMERIZATION TO ESTIMATE LOCAL PROPERTY DIFFERENTIAL IN PHASE-SEPARATING POLYMERIZATIONS

Phase-separating polymerizations that utilized both a classical photoinitiator (DMPA) and a photo-iniferter (XDT) were analyzed at varying extents of reaction to probe the conversion-dependent evolution of glass transition temperature (T_o) of both phases as a consequence of polymerization. The analysis was first conducted on the development of T_g in triethylene glycol dimethacrylate (TEGDMA) homopolymer, and it was found that the Tg developed following a second order relationship with degree of methacrylate conversion. Two non-reactive, methacrylate-based linear prepolymers (poly-methyl methacrylate PMMA, and poly-butyl methacrylate PBMA) with varying T_g's (PMMA - 117 °C, PBMA - 22 °C) were introduced into the TEGDMA monomer formulation to induce phase separation upon polymerization. When the Tg development of the TEGDMA-rich domains formed during phase separation were compared to that of a TEGDMA homopolymer, it was found that in the phaseseparating resins the TEGDMA Tg development was accelerated, indicating a differential in local extent of conversion. This difference was estimated using the homopolymer $T_{\rm g}\mbox{-}conversion$ relationship, and it was found that in PBMA-modified polymerizations, the local differential in conversion was most significant, leading to the largest differential in Tg between TEGDMA-rich and prepolymer-rich domains during polymerization. This finding was supported by observed differences in optical properties during polymerization. The differential in local conversion and Tg was studied in the context of polymerization stress development. When the more slowly polymerizing prepolymer-rich phase has a significantly lower local Tg than the matrix, significant increases in polymerization stress were delayed to much higher extents of bulk conversion.

6.1 Introduction

Polymerization induced phase separation (PIPS) is a powerful tool to utilize in the development of heterogeneous polymer networks, especially since it permits *in situ* formation of phase-separated materials, often under ambient conditions. However, heterogeneous network development through this approach is a complex and dynamic process as it relies heavily on the interplay between thermodynamic and kinetic factors, which, depending on the material system in use can either hinder or promote the formation of distinct phase structure. Therefore, to precisely design and engineer materials for a desired application, careful consideration must be taken to understand how critical factors such as the polymerization kinetics, phase morphology, as well as the structure of the reactive and non-reactive components influence the phase separation process.

PIPS has been studied, in detail, for certain applications where precise control over the dispersion of one component in the network is necessary, such as the development of polymer dispersed liquid crystals used for optical displays.^{1.5} Here, the influence of phase separation on switching properties, refractive index, and contrast ratio has been studied most often in linear polymerizations modified by a significant liquid crystal fraction. Other studies into heterogeneous networks formed through PIPS have focused on totally polymeric resins tailored for a variety of applications and design of bulk properties, one popular example being the development of networks with reduced interfacial polymerization stress.⁶⁻¹¹ Many of these approaches have been successful at controlling phase structure and network properties through a variety of techniques including dual-cure networks,¹²⁻¹⁴ thermally initiated resins,¹⁵ as well as composite polymerizations.¹⁶

Recently we have investigated PIPS as an approach to heterogeneous network formation in photoinitiated, ambient cross-linking bulk polymerizations.¹⁷⁻¹⁹ The model system we have studied is composed of a bulk methacrylate polymer network modified by linear, nonreactive prepolymers. The resulting phase-separated networks have a much higher degree of cross-linking and T_g than networks previously formed through PIPS. Through these studies, we have isolated the impact of key factors on the phase separation process such as rate of network formation modulated through irradiation intensity, chain length of modifying prepolymer, and degree of cross-link density, and have identified how these factors can influence the resulting phase morphology and bulk properties (such as modulus, thermal stability, resulting degree of interfacial polymerization stress). However, a critical factor that remains to be studied in this system is the differential in the dynamic thermomechanical properties of the phases as they form and develop under ambient polymerization conditions. Previous work into networks formed via PIPS have pointed to the formation of phases of differing thermal expansion coefficients as being critical to tailor bulk properties such as volumetric shrinkage during polymerization.^{6, 7} Here, we investigate the influence on phase separation of the thermal properties (mainly T_g) of phases formed during PIPS.

In this study the T_g development in phase-separating polymer networks was monitored as a function of conversion. To achieve this, a photo-iniferter was introduced into the polymerization to cap active radicals in partially-cured networks that have not achieved their limiting conversion.²⁰ This permits thermal analysis without the risk of additional reaction occurring in networks being probed by thermal analysis techniques. With this approach, the local property differential between phases formed was estimated during the polymerization. Even though the model system studied here relies only on the homopolymerization of a single monomer modified with an inert prepolymer to promote phase separation, it is still very difficult to probe the relative kinetic rate and extent to which different phases develop during the polymerization, as bulk conversion measurements average the methacrylate reaction in both phases. The approach studied here allows us to make conclusions about the order of phase formation and relative reaction rate differential during polymerization, and the significant impact they have on bulk property development. Previous work into T_g development during varying stages of reaction has focused on the impact of reaction conditions on the thermal property development, such as the temperature at which the polymerization is conducted,²¹⁻²⁴ and there have also been studies that propose theoretical relationships between T_g and extent of reaction²⁵ but are often only applicable in linear systems.²⁶ This study will highlight, for the first time, how phase separation can impact the development of the glass transition in a cross-linked network where compositionally different domains form.

6.2 Experimental

Materials - Two different bulk homopolymer matrices were utilized in this study. The first being triethylene glycol dimethacrylate (TEGDMA, Esstech), which, when homopolymerized forms a densely cross-linked, high T_g material with conversion limited by vitrification. The second homopolymer matrix utilized was poly(ethylene glycol dimethacrylate), with an average $M_n \sim 550$ (PEGDMA, Sigma-Aldrich), which when homopolymerized provides a rubbery matrix that effectively reaches complete conversion during ambient photopolymerization.

Two methacrylate-based, commercially obtained prepolymers were utilized to modify either bulk homopolymer matrix: poly(methyl methacrylate) and poly(butyl methacrylate) (PMMA and PBMA, respectively). The prepolymers utilized vary in molecular weight, density, and glass transition temperature (T_g) as indicated in Table 6.1. These prepolymers were chosen, as they have distinctly different T_g 's especially compared to the TEGDMA-matrix that will be utilized throughout the majority of this study. When PMMA is the modifying prepolymer, the matrix T_g will be below that of the prepolymer for the majority of the polymerization. However when the modifier is PBMA, the opposite will occur and the prepolymer T_g will be below that of the bulk matrix throughout the majority of the reaction. In all studies presented here, the loading level of prepolymer was maintained at 10 wt% to induce phase separation.

Table 6.1 – Prepolymer Properties		
Poly (methyl methacrylate) (PMMA)	Poly (butyl methacrylate) (PBMA)	
M _W ~120,000 Da	M _W ~337,000 Da	
T _g ~117(±6.0) °C	T _g ~22.4(±2.5) °C	
n_D^{25} =1.4906 (± 4 E-4)	$n_D^{25}=1.4804 \ (\pm 6 \text{ E-4})$	
$\rho = 1.19 \text{ g mL}^{-1}$	$\rho = 1.07 \text{ g mL}^{-1}$	

All material formulations included 0.5 wt% of a photoinitiator: 2,2-dimethoxy-2phenylacetophenone (DMPA). A photo-iniferter (*p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate; XDT) was also added to the monomer formulations at 0.5 wt%. The efficiency of this molecule at both initiating and capping active centers in a free-radical polymerization has been studied previously.^{20, 25, 27} With this work, the iniferter is included to promote radical capping in partial cure polymerizations so that networks that have not reached their limiting conversion can still be analyzed thermally without additional cure during analysis. A UV-irradiation source ($\lambda = 365 \pm 10$ nm) was utilized in all polymerizations since both XDT and DMPA absorb in the UV-region. The irradiation intensity was maintained at I₀=5mW/cm² for all studies to eliminate differences in phase separation as a result of the kinetics of polymerization, which has been shown to significantly impact the resulting domain size and morphology.

Kinetics of Polymerization and Conversion Analysis – To develop partially cured networks for thermal analysis, bar-shaped specimens of dimensions 8.0 x 5.5 x 1.0 mm (*length* x *width* x *thickness*) sandwiched between glass slides were photopolymerized for varying periods

of UV-exposure. The photopolymerization was conducted *in situ* to probe reaction rate and conversion development during polymerization. To measure the reaction rate, a FTIR spectrometer was utilized (Thermo Scientific, Nicolet 6700). The dynamic change in methacrylate peak area in the near-IR (=CH₂ first overtone at 6165 cm⁻¹) was used to calculate degree of conversion and reaction rate. All experiments were conducted with 2 cm⁻¹ resolution. In all experiments, kinetic data was collected for at least one minute after the UV-exposure was completed to ensure that the true extent of conversion was calculated.

Differential Scanning Calorimetry to Probe Monomeric T_g – A differential scanning calorimeter (DSC, Perkin Elmer Pyris Series Diamond) was utilized to measure the glass transition temperature of liquid monomer formulations. A sample of mass 10-15 mg was placed in a 50µL, thin-walled aluminum pan, and an empty pan of the same dimension was utilized as a reference. The sample was allowed to equilibrate at -120°C and then brought to a temperature of 150°C at a rate of 10°C/min. It was then cooled back down to -120°C and the procedure was repeated.

Dynamic Mechanical Analysis – A dynamic mechanical analyzer (DMA, TA Q800) was utilized to evaluate the thermal properties of partially cured networks. The specimens were prepared as described in the kinetic analysis section (above) with approximate dimensions of: 8.0 x $5.5 \times 1.0 \text{ mm}$ (*length* x *width* x *thickness*). The DMA was used in tension mode under 0.01% strain with a frequency of 1 Hz. After allowing the sample to equilibrate at -115°C for 20 min, the chamber temperature was raised to 115°C, which was determined to be the practical limit to maintain the stability of XDT-capped radicals, at a rate of 3°C/min and then held isothermally for 20 min. The temperature was then brought back to -115°C at the same rate to verify

consistency in the heating and cooling tan δ data. Results presented here are from the initial ramp in temperature.

UV-Vis Optical Transmission - Disc-shaped samples were mounted on an optical bench used to align the UV curing light, a visible light probe, the near-IR transmitted signal and a UV-Vis detector to monitor dynamic changes in optical properties during polymerization. The samples, which were sandwiched between a glass slide and coverslip, had dimensions of 20 mm diameter and 240 μ m thickness. The samples were irradiated with a UV-curing light source (λ =365 ± 10nm), to initiate the polymerization. Near-IR fiber optic cables were used to measure methacrylate conversion during polymerization under the same conditions as described in the kinetic analysis section. A broadband light source that emits visible light (λ =400-800nm) was transmitted through the material during polymerization, and a UV/Vis portable spectrometer (Ocean Optics, USB 2000) was used to monitor dynamic changes in visible light transmission. Specifically, the intensity of 600nm light transmitted through polymerizing material was monitored. Since neither the photoinitiator (DMPA) nor the photo-iniferter (XDT) absorb above 380nm,²⁸ the visible light source acts as an independent probe without affecting the reaction kinetics.

Tensometer - Real-time polymerization stress was measured under ambient photopolymerization conditions using a cantilever beam tensometer (Volpe Research Center, American Dental Association Health Foundation, Gaithersburg, MD). The tensometer was coupled with a Fourier transform infrared spectrometer (FTIR) with near-IR fiber optic cables (Thermo Scientific, Nicolet 6700) so methacrylate conversion could be observed simultaneously using the same conditions as described in the kinetic analysis. All samples were disc shaped with

6mm diameter and 1mm thickness. The details of this instrument and its operation are described more thoroughly in other publications.^{29, 30}

6.3 Results and Discussion

Kinetic Impact of Introducing Iniferter into the Polymerization – Prior to utilizing the photo-iniferter to probe network properties at vary extents of reaction, the changes in polymerization kinetics as a result of iniferter introduction must be understood, as the rate of reaction can significantly impact the extent to which phase separation can occur.³¹⁻³³ To determine the impact of the photo-iniferter on the reaction kinetics, the polymerization rate of TEGDMA-homopolymer, without prepolymer modification was determined at varying photoinitiator and photo-iniferter contents (Figure 6.1).



Figure 6.1 – Conversion as a function of time for TEGDMA homopolymerizations with varying photo-iniferter (XDT) and photoinitiator (DMPA) content, I_o=5mW/cm², total exposure time is 600s in all experiments, irradiation begins at t=30s.

When the photoinitiator (DMPA) is omitted from the material formulation and the only source of free radicals is from the photo-iniferter (XDT), the reaction rate is severely depressed. Even after 600s of observation, the polymerization has not reached the limiting conversion. This is expected, and has been observed in the polymerization of both mono- and di-methacrylate monomers.²⁰ The dithio-carbamyl (DTC) radical produced upon cleavage of XDT has been shown to be significantly less reactive and does not participate significantly in propagation,²⁰ unlike the radicals produced upon photo-cleavage of DMPA. In the polymerizations with only XDT producing free radicals, there is an initial induction period followed by a gradual polymerization that progresses without any significant autoacceleration behavior. However, at later stages of the reaction where termination between carbon based radicals is limited due to diffusional constraints, the termination that occurs between the DTC and a carbon-based radical becomes much more significant.²⁵ When a conventional photoinitiator such as DMPA, is present in the formulation the reaction kinetics proceed much more rapidly and a limiting conversion is achieved under the same irradiation and exposure conditions.

In this study, both the conventional photoinitiator and the photo-iniferter are utilized in the monomer formulation, so that a rapid initial rate and autoacceleration behavior are observed in the polymerization, while still getting sufficient termination or "radical-capping" at the end of the polymerization to create thermally stable networks prior to analysis. Our previous work into phase-separating polymerizations has shown that the rate of reaction and the time prior to gelation significantly alters the extent to which phase separation occurs.¹⁸ Here, with both the photoinitiator and the photo-iniferter, phase separation kinetics are expected to be similar to that observed in our previous studies.

The extent of conversion was monitored as a function of time for partially cured materials to show the efficiency of XDT at capping active radicals, and the kinetic stability of the partially cured networks. All materials were exposed to a series of UV-exposure intervals to reach varying extents of final conversion. The resulting kinetic profiles for TEGDMA homopolymerizations in the presence of both XDT and DMPA show that depending on the exposure time, the conversion attained varies (Figure 6.2). It should be noted, that after shuttering the UV lamp, the conversion level was stable for the remainder of the extended measurement time as a first indication that no post-cure reaction is occurring and the partially cured samples can be considered kinetically stable below the limiting final conversion.



Figure 6.2 – TEGDMA / 0.5wt% DMPA / 0.5wt% XDT conversion profiles for varying periods of UV-irradiation, I_o=5mW/cm², in all series UV-irradiation begins at t=30s.

In addition to the degree of conversion, the development of the polymerization rate was also monitored based on the exposure time for TEGDMA polymerizations in the presence of XDT and DMPA (Figure 6.3). All materials undergo the autoacceleration and autodeceleration periods typical of free-radical dimethacrylate polymerizations. However, the maximum rate of polymerization and limiting conversion varies, as expected with the exposure time. Despite these differences, it is clear that the initial rate of polymerization is relatively consistent across the varying exposure periods. This is critical, since the most significant phase development via diffusion will occur prior to network macrogelation, which occurs anywhere from 5% methacrylate conversion (TEGDMA homopolymer) to 20% conversion (phase-separating TEGDMA/PBMA matrix).^{17, 18} The same kinetic analysis has also been done on the prepolymer-modified phase-separating resins, and again a consistent initial rate and stable intermediate conversion levels were observed with the varied exposure times (Supplemental Figures S6.1-S6.4).



Figure 6.3 – TEGDMA / 0.5wt% DMPA / 0.5wt% XDT reaction rate profiles for varying periods of UV-irradiation exposure, I_o=5mW/cm².

Monomeric Glass Transition Analysis – The glass transition temperature of TEGDMA and TEGDMA/prepolymer monomer resins was probed utilizing differential scanning calorimetry with the results displayed in Table 6.2. The glass transition of TEGDMA monomer

falls roughly around -88 °C, which is consistent with previously reported results.³⁴ When prepolymer is introduced into the formulations, there is a slight increase in the monomeric T_g . This increase, while small, is expected due to the uniform presence of a prepolymer with much higher T_g in the monomer solution. When the loading level of prepolymer is increased above 10 wt%, multiple glass transitions are observed in the monomeric state, and the exact loading level at which this occurs varies based on the modifying prepolymer. For this reason, the loading level was maintained at 10 wt% in all studies presented here.

Table 6.2 – Glass Transition Temperature (Tg) of TEGDMA-based monomer solutionsmodified with varying prepolymers (*n=3)		
Sample	Monomeric T _g (°C)	
TEGDMA*	-88.3 (±1.1)°C	
TEGDMA / 10 wt% PMMA	-86.6 °C	
TEGDMA / 10 wt% PBMA	-86.8°C	

Monitoring Glass Transition Temperature with Respect to Conversion – The partially cured polymer networks, that reached varying degrees of bulk methacrylate conversion were analyzed utilizing dynamic mechanical analysis (DMA) to probe the evolution of glass transition temperature (T_g) during polymerization. The DMA measurements do require that the sample be exposed to elevated temperatures. Since the temperature ramp used goes up to 115 °C, there is potential for additional cure during the thermal analysis, but that is avoided here by use of the photo-iniferter.²⁵ This thermal stability was verified by monitoring the bulk conversion by FT-IR spectroscopy of select samples prior to and after the thermal analysis. It was found that, within the error of the spectroscopic method employed, no significant additional conversion occurred during the experiment.

The tan delta profile at varying extents of conversion, for TEGDMA-homopolymer is plotted in Figure 6.4. Even though the development of a single homopolymer is being displayed here, it is obvious that there are structural heterogeneities associated with this polymerization, especially at earlier stages of the reaction. Heterogeneous structures associated with free-radical, cross-linking polymerizations have been described in detail.³⁵⁻³⁷ It has been well characterized that in photoinitiated free-radical polymerizations during the early stages of the reaction polymerization is mostly isolated in relatively densely cross-linked microgels dispersed in a matrix that is loosely cross-linked and mostly monomer, causing the observed heterogeneity. The polymerization progresses to eventually connect the microgels into a continuous network. This is why, at early stages of conversion there are two local maxima observed in the tan delta profile for a TEGDMA homopolymerization (Bulk Conversion, as denoted by χ , =0.28 and χ =0.50 trends, Figure 6.4). The lower temperature transition is centered about -50°C, and is assumed to be a phase rich in monomer and loosely cross-linked or converted methacrylate functionalities, which is why the T_g is higher than that of the pure monomer T_g measured via DSC (Table 6.2). The tan delta maxima that occurs at a higher temperature (-16 °C and 6 °C for χ =0.28 and 0.50, respectively) in these trends are attributed to the spatially isolated microgels that form with a higher degree of cross-linking.


Figure 6.4 – Tan delta profiles of TEGDMA homopolymer at varying extents of conversion. The high conversion profile (χ =0.95) was polymerized only with conventional photoinitiator (DMPA) and was post-cured thermally after ambient photopolymerization to reach this high extent of conversion, and to allow for thermal analysis at the matrix T_g.

At higher degrees of conversion, the two distinct peaks in the profile eventually merge to form a profile with a single, broad transition. In the χ =0.61 trend, there is a shoulder observed at lower temperatures than that of the tan delta maxima (33 °C), which is again attributed to the process of connecting the isolated microgels into one continuous matrix, and this shoulder is due to small domains or regions that have not achieved as significant a degree of cross-linking as the rest of the matrix. At higher degrees of conversion (χ =0.75, χ =0.95 trends) there is one distinct tan delta maxima. The peak is asymmetric and has a large breadth, which is typical of dimethacrylate polymerizations. A factor that leads to this large T_g breadth throughout the entire polymerization is the formation of cycles that do not contribute to the bulk network structure. It should be noted that to analyze the sample with the highest extent of conversion here (χ =0.95), no photo-iniferter was included with the conventional photoinitiator (DMPA). This sample was thermally post-cured at 180 °C for one hour prior to analysis to ensure conversion of 95%, which

is not attainable from an ambient photocure of this glass-forming polymer. This high level of conversion makes the iniferter-free sample thermally stable under the testing conditions applied here.

The progression of the TEGDMA homopolymer T_g can be plotted as a function of conversion (Figure 6.5). In low conversion samples, where multiple transitions are observed, the bulk T_g was taken as the average of the two distinct transitions, as this approximation had the best agreement with that predicted with theory, discussed next. The shape of the T_g development as a function of conversion is in good agreement with other studies into this phenomenon.^{21, 24, 25} In previous studies,^{21, 25} this relationship has been found to fit well with that predicted by the free volume theory, which relates the T_g to degree of conversion (*x*) using the following equation:

$$T_g = \frac{(\alpha_m T_{gm} + (\alpha_p T_{gp}\nu_p - \alpha_m T_{gm})x)}{(\alpha_m \nu_m + (\alpha_p \nu_p - \alpha_m \nu_p)x)}$$

Here, α_m and α_p are expansion coefficients of the monomer and polymer, respectively (taken to be 5.0 E-4 and 1.1 E -4 / °C ^{21, 25, 38}); v_m and v_p are specific volumes of the monomer and polymer (taken as 0.92 cm³/g from the manufacturer for the monomer and estimated experimentally as 0.82 cm³/g for the polymer), T_{gm} and T_{gp} are the extrapolated glass transition temperature of the monomer and the polymer at 100% conversion, respectively. The extrapolation of both the monomeric and polymeric transitions were done to reduce the error between the experimentally observed and theoretically predicted values of the glass transition temperature. It should be noted, that the extrapolated value of T_{gp} may not be readily attainable, as this T_g value has practical and physical limitations, since the depolymerization of normal methacrylates is observed at temperatures as low as 180-200 °C.³⁹ The extrapolated value of T_{gm} (-51°C) is higher than what is observed experimentally (Table 6.2) via DSC analysis. The T_g of TEGDMA homopolymer as a function of conversion, based on the relationship predicted by free volume theory is also plotted in Figure 6.5.





While this theoretical relationship agrees reasonably well with the observed trends at lower values of bulk conversion, there is significant deviation at higher extents of reaction. This deviation is likely due to the fact that the free volume theory treats pendant double bonds as monomer fraction, which is not applicable in a system like this. In a TEGDMA homopolymerization with a high degree of cross-linking, the mobility of the pendant double bonds that are attached to the bulk network are much different than the free monomer molecules. This effect will become more significant as the degree of cross-linking increases, and especially once the system vitrifies at later stages of the polymerization. Additionally, to the best of our knowledge, previous applications of this theory to cross-linked networks have extrapolated much of the T_g behavior at very early and late stages of the polymerization.^{21, 25} In this study, we have observed T_g 's at extents of conversion much closer to both 0 and 100%, which when applied to this theory show more significant deviations at the very early and late stages of reaction, which had not been explored through experiments previously. It should be noted that to analyze the TEGDMA homopolymer T_g at 95% conversion, a thermal cure is applied to the network prior to thermomechanical analysis, which may alter the network development and contribute to the deviation from free volume theory at late stages of the polymerization.

Despite the disagreement between the observed relationship and that predicted by the free volume theory, both series follow second order behavior with respect to conversion. The second order equation that was fit to our observed data has reasonably good agreement (Trend line Figure 6.5, R^2 =0.940), and assumes T_{gm} =-88 °C. For the remainder of this study, this experimentally derived relationship will be utilized to estimate the T_g in TEGDMA homopolymer.

Monitoring the T_g Development in Phase-Separated Resins – As mentioned, the purpose of this study is to evaluate the glass transition development in phase-separated networks that form compositionally different domains during polymerization. The work up to this point has served to provide a reference and control relationship for T_g development in a dimethacrylate bulk network. Now, this information will be applied to examine how the T_g development deviates from that of neat TEGDMA when phase separation occurs during the polymerization. With the knowledge of the resulting phase composition, as well as expected differences in local reaction rate, we are able to assign the peaks in the tan delta profile of the heterogeneous materials. A description of this process follows.

We have already established that the starting formulations of TEGDMA/prepolymer in this study are homogeneous and display one T_{gm} . The ultimate T_g of these networks after undergoing phase separation during polymerization was monitored initially by the analysis of the fully-cured networks with a thermal scan in the DMA from -50-200°C, so as to capture the full tan delta profile. In these samples, there was no need to include the photo-iniferter since the highly converted networks are thermally stable under the thermal analysis conditions used. These full-cure samples were photocured under ambient conditions (I_0 =5mW/cm²) and then held at 180°C in an oven for an hour after the photocure to reach a conversion greater than 90% prior to DMA analysis. Since the prepolymers in use are non-reactive, the shift in T_g in the fully-cured networks can be used to estimate the resulting phase compositions by applying a modified version of the Fox Equation⁴⁰:

$$\% TEGDMA = \left(1 - \frac{\left(T_g^{TEGDMA} - T_g^{NewPhase}\right)}{\left(T_g^{TEGDMA} - T_g^{Prepolymer}\right)}\right) * 100$$

The resulting T_g 's in different phases, as well as phase compositions are displayed in Table 6.3. As has been described in other work previously, upon phase separation, two phases form, one rich in TEGDMA and the other rich in TEGDMA/prepolymer.

Table 6.3 – Glass Transition Temperature (T_g) and phase compositions of TEGDMA/prepolymer phase-separated networks at >90% conversion (n=3)								
Sample	TEGDMA- rich Phase T _g (°C)	TEGDMA fraction (wt%) in TEGDMA- rich phase	TEGDMA/ prepolymer-rich Phase T _g (°C)	TEGDMA fraction (wt%) in TEGDMA/ prepolymer-rich phase				
TEGDMA / 10 wt% PMMA	167 (±2.1) °C	1.1 (±0.05)	133 (±1.8) °C	0.37 (±0.04)				
TEGDMA / 10 wt% PBMA	156 (±5.4) °C	0.97 (±0.04)	82 (±6.7) °C	0.43 (±0.04)				

This table points to some key similarities in the final properties of these networks. One being that in both systems very similar phase compositions form. The prepolymer-deficient phase achieves a T_g close to that of the bulk homopolymer with either of the prepolymer-modified materials. Additionally, despite the large differential in T_g and side-chain structure associated with the modifying prepolymers, the compositions of the respective prepolymer-rich phases (wt%) are also similar.

With this understanding of the initial and ultimate phase composition in TEGDMAmodified resins undergoing phase separation, the T_g of the two phases formed were analyzed as a function of conversion. As mentioned, the analysis of the tan delta profiles is complicated based on multiple transitions detected, especially at earlier stages of conversion. To accomplish this, the tan delta profiles of neat TEGDMA and the prepolymer-modified systems were compared at reasonably similar degrees of conversion. Two such comparisons are shown in Figures 6.6-6.7 for TEGDMA/10 wt% PBMA and TEGDMA/10wt% PMMA at $\chi \approx 0.30$.



Figure 6.6 – Comparison of tan delta profiles of poly(TEGDMA) homopolymer and TEGDMA/10 wt% PBMA phase-separating network at χ≈0.30. Local maxima are detected at: -52 °C and -16 °C (TEGDMA), -66 °C and -46 °C and 38 °C (TEGDMA/10wt% PBMA).

In both examples, three local maxima in the tan delta profile are observed in the phaseseparating materials. Based on the final phase compositions, we expect that two of the transitions are a result of the two phases formed, one rich in TEGDMA and another enriched in the modifying prepolymer. Finally, the third transition is likely again a monomer-rich fraction, as the bulk conversion is still very low at this stage of analysis.



Figure 6.7 – Comparison of tan delta profiles of poly(TEGDMA) homopolymer and TEGDMA / 10 wt% PMMA phase-separating network at χ≈0.30. Local maxima are detected at: -52 °C and - 16 °C (TEGDMA), -63 °C and -39 °C and 10 °C (TEGDMA/10wt% PMMA).

Both prepolymer-modified resins were de-convoluted into three peaks that contribute to the overall shape of the tan delta profile. When doing this, there are some key differences between the TEGDMA control and the phase-separating prepolymer-modified systems. The first is the presence of a local maximum that appears as a shoulder at temperatures above 0oC. Specifically, this transition occurs at 38oC and 10oC for the PBMA and PMMA modified resins respectively. In both these polymerizations, this peak is assigned as the transition from the more rapidly forming TEGDMA-rich phase. The other two transitions observed are assigned as a monomer-rich fraction (transition observed at lowest temperature) and a TEGDMA/prepolymerrich fraction.

It has already been determined that a phase rich in TEGDMA homopolymer forms as a result of the phase separation process. Additionally, it is known that the prepolymer-rich phase formed has between 50-60wt% of prepolymer present, depending on the modifying prepolymer (Table 6.3). Based on these compositions, we expect that initially polymerization will proceed in the TEGDMA-rich domains. One reason for this is that the TEGDMA-rich domains will have a much higher local double bond concentration. A second, and likely more significant reasoning for this is that the local viscosity in the TEGDMA-rich domains will be substantially lower. In previous studies we have observed an overall decrease in bulk polymerization rate from the increase in viscosity caused by introduction of prepolymer, above a certain threshold limit. In PBMA and PMMA modified resins, this decrease in reaction rate occurred between 15-20wt% prepolymer modification.¹⁷ Considering that the prepolymer-rich phases that form here have a much more significant prepolymer fraction, it is likely that the local reaction rate is suppressed, especially when compared to that of the TEGDMA-rich domains. While the TEGDMA-rich domains have a small prepolymer fraction, it is below the threshold for inhibiting the bulk rate and likely contributes to a slightly enhanced autoacceleration behavior. With these combined observations, it seems reasonable that the highest temperature transitions observed in the phaseseparating polymerizations be assigned as TEGDMA-rich domains, as it is unlikely that a TEGDMA/prepolymer-rich domains would have a much higher Tg than the rest of the matrix at this point of the reaction.

There is also an observable difference in the maximum tan delta values observed below 0° C. When PMMA is the modifying prepolymer, these values are significantly higher than that

of neat TEGDMA, but when PBMA is the modifying prepolymer, the opposite is observed. This behavior is quite complex and it is difficult to identify and isolate a single mechanism that leads to this observation. In general, as extent of cross-linking increases, so will the absolute value of tan delta,⁴¹ which has been observed clearly in Figure 6.4. However, at these low temperature transitions, we predict that these peaks are a result of domains rich in TEGDMA-monomer and a mixture of TEGDMA-monomer and prepolymer. Therefore, the absolute value of tan delta varies based on numerous factors including: the extent of local conversion in these domains, the physical properties of the prepolymer, and any covalent interactions between the prepolymer and monomer and loosely cross-linked TEGDMA homopolymer.

Much of the argument for peak assignment up to this point has been based on the knowledge that a phase rich in TEGDMA, and a phase rich in TEGDMA/prepolymer form as a result of this process, which has been validated. However, the exact composition at varying stages of conversion is not something we can easily probe since not only is there prepolymer affecting the T_g but also partially cured domains that include polymer, monomer and prepolymer. There are some assumptions that can be reasonably made, since all DMA analyses are conducted on materials that have achieved macrogelation. Mainly, diffusion is significantly limited post macrogelation, so it is highly unlikely that any significant diffusion of long prepolymer chains occurs between phase boundaries in the samples analyzed here. Since phase separation in the TEGDMA/prepolymer systems tested here has been characterized to occur very early on in the reaction (1-4% bulk methacrylate conversion),¹⁷ we can assume that the prepolymer-rich domains have been isolated prior to gelation. Based on concentration differences, this would occur from prepolymer-rich domains (lower TEGDMA concentration) to the TEGDMA-

rich domains, so a phase more enriched in prepolymer can form through phase separation. This means that while the composition of the TEGDMA-rich fractions will not be changing as a result of any late stage diffusion, the local double bond concentration and volume fraction may undergo modest changes.

Beyond ~40% bulk methacrylate conversion, the analysis and assignment of tan delta maxima to either prepolymer- or TEGDMA-rich domains becomes simpler, as only two maxima are observed in the tan delta profile. Additionally, the shape of the tan delta profile mimics closely that observed in the fully-cured network except with the transitions shifted to lower temperatures, so it can be reasonably assumed that the lower temperature transition is attributed to the prepolymer-rich phase and the higher temperature transition to the TEGDMA-rich phase. To illustrate this similarity, two tan delta profiles of TEGDMA/10 wt% PBMA networks, one at moderate and one at full conversion, are displayed in Figure 6.8. Again, it should be noted that the fully cured network did not utilize the photo-iniferter, but only DMPA in the formulation so thermal analysis above 115 °C could be conducted.



Figure 6.8 - Comparison of tan delta profiles of TEGDMA / 10 wt% PBMA phase-separating networks at 62% and 93% bulk methacrylate conversion. Local maxima are detected at: 7 °C and 69°C (χ =0.62), 88 °C and 164 °C (χ =0.93).

After collecting tan delta profiles for both phase-separating resins at varying extent of conversion, the development of both the TEGDMA-rich and prepolymer-rich phases were plotted as a function of conversion. Again, as in the TEGDMA-homopolymer example, the data obtained for networks at bulk conversion greater than 90% were obtained from resins that only contained DMPA photoinitiator and were exposed to thermal post-cure after the ambient photopolymerization reaction. At early stages of conversion, the monomer-rich peak seen at roughly -65 °C (such as in Figures 6.6-6.7) is not included in the either of these trends. We hypothesize that this monomer fraction is isolated in the prepolymer-rich domains that are polymerizing more slowly, and would actually depress the observed prepolymer-fraction T_g from what is reported in Figures 6.9-6.10.

In the TEGDMA/10wt% PBMA networks (Figure 6.9), the TEGDMA-rich phase develops in a similar manner as in the homopolymer, however the trend line added here is to aid the reader visually, and does not imply any physical or theoretical relationship. A significant increase in the T_g of the PBMA-rich phase is not observed until greater than 50% bulk conversion. Interestingly, the ultimate T_g of the prepolymer-rich phase is achieved at roughly 80% bulk methacrylate conversion, and remains constant throughout any additional conversion. It should be noted that 80% is the limiting conversion for this network when formed under ambient conditions, so this plateau indicates that in the PBMA-enriched domains, the maximum conversion is achieved during the ambient cure, and further cross-linking does not occur in these regions when the sample is exposed to the thermal post-cure. With this non-continuous manner, no fit was applied to the T_g versus conversion development in PBMA-enriched domains, and instead a trend line was applied to guide the eye through the general development up to 80% bulk conversion.



Figure 6.9 – Glass transition temperature development in TEGDMA/10 wt% PBMA phaseseparating network at varying extents of conversion.

In the TEGDMA/10wt% PMMA polymerization (Figure 6.10) both T_g 's develop in a similar manner with respect to conversion throughout the entire reaction, as indicated by trend lines applied to each curve (again these are added for visual assistance and are not a result of a theoretical relationship). In this system there is no obvious difference between the rates at which the two different phases develop. Meaning, there is no delay compared to the TEGDMA-rich domains in significant increase in T_g of the PMMA-rich domains. Here, the limiting conversion from the ambient photocure is ~70%, and both phases experience notable increases in T_g when exposed to the post-ambient thermal cure. In the PBMA-modified materials, full conversion is achieved in the PBMA-rich domains during ambient photocure since the ultimate local T_g is closest to the temperature at which the polymerizations are conducted (22-25 °C), and this relationship has been cited to be critical to achieve the maximum T_g during cross-linking

polymerizations. However, in domains with a high fraction of the high- T_g prepolymer, PMMA, full conversion is not achievable under ambient conditions.²¹



Figure 6.10 – Glass transition temperature development in TEGDMA/10 wt% PMMA phaseseparating network at varying extents of conversion.

TEGDMA-Rich Phases – The observed T_g development in TEGDMA-rich domains (Figures 6.6-6.7, 6.9-6.10) compared to the TEGDMA bulk homopolymer (Figure 6.5) all support the proposed hypothesis that in phase-separating resins, the TEGDMA-rich domains polymerize more rapidly at the beginning of the polymerization, since the T_g observed in these regions is consistently greater than that observed in neat-TEGDMA (Figures 6.6-6.7) at a similar degree of bulk conversion. This indicates that local conversion in these regions must be greater than that measured as the bulk value, and that the degree of conversion in prepolymer-rich domains is lower than the measured bulk value, since bulk conversion will average the conversion across both phases that are forming. A second order equation was fit to the relationship between observed neat TEGDMA T_g development and the extent of bulk methacrylate conversion (Figure 6.5). Since our phaseseparating resins form a phase rich in poly(TEGDMA) with minimal prepolymer present (Table 6.2), we can use this relationship to reasonably estimate the local extent of conversion in the TEGDMA-rich domains at varying measured bulk conversions. Meaning, that when we measure in a TEGDMA/10wt% PBMA resin that the TEGDMA-rich domain has a T_g of 38 °C at 30% bulk methacrylate conversion, we can estimate the local TEGDMA conversion based on the observed relationship between T_g and conversion in TEGDMA homopolymer. This was done on both the PBMA and PMMA modified resins, and the resulting plot of estimated local TEGDMA-rich conversion versus measured bulk conversion is shown below (Figure 6.11). For reference, the TEGDMA-control is plotted as the straight diagonal line in the center of the plot, denoting a relationship where bulk TEGDMA conversion is the same as local TEGDMA conversion, since the system is a homopolymer.



Figure 6.11 – Extent of methacrylate conversion estimated in TEGDMA-rich domains compared with bulk, measured methacrylate conversion.

Two things are apparent from this representation. The first is that both prepolymer modified resins have accelerated development of TEGDMA-rich domains compared to a bulk TEGDMA homopolymerization, and this effect is most dramatic at the beginning of the polymerization. This observation also minimizes the probability of TEGDMA monomer diffusion that was hypothesized to occur from prepolymer-rich to TEGDMA-rich domains. This process is limited from the beginning of the reaction, since such a high local extent of conversion and cross-linking is estimated in the TEGDMA-rich regions at early stages of bulk conversion. At the end of the polymerization the T_g development in all three systems follow the same trajectory. Additionally, it is clear that the differential between the bulk TEGDMA development and the local TEGDMA development is most dramatic in the PBMA-modified resins.

The bulk reaction rate was measured in both phase-separating resins (Figure 6.12). The rate profiles are quite similar, especially at early stages of the bulk reaction. This implies that in the PBMA-modified resins the rate differential between the PBMA-rich and TEGDMA-rich phases must be greater than in PMMA-modified resins, as the bulk conversion is an average value across both domains formed. The exact cause of this difference in local rate based on modifying prepolymer has not yet been probed. We suspect it may be related to differences in local viscosity or conformation of long prepolymer chains in the prepolymer-rich domains, which could influence the ability of initiating radicals or short radical chains to diffuse to the TEGDMA-rich domains at early stages of the polymerization.





The difference in local polymerization rate of the TEGDMA-rich domains with varying prepolymer modification correlates very well with other observations we have made, the first being the delay in significant increases in the PBMA-rich T_g (Figure 6.9). If the development of TEGDMA-domains is accelerated compared to the bulk conversion observed, it is likely that significant development of the secondary phase will not occur until this phase approaches a limiting conversion and it's local rate decelerates. Additionally, these findings correlate well with differences we have observed in the refractive index differential development during polymerization (Figure 6.13).

While both phase-separating polymerizations display an initial reduction in light transmission, followed by a recovery period to near-transparency, the extent to which light transmission is reduced as a function of conversion varies significantly based on the modifying prepolymer. This initial loss in transmission is attributed to the formation of compositionally different phases via phase separation with differing refractive indices, which depends directly on the individual refractive index (Table 6.1). This is why, for instance, at the end of the polymerization that the PMMA and PBMA modified resins have differing degrees of light transmission despite having similar compositions of phases formed. The native refractive index of the prepolymer will influence this value, and at the end of the polymerization this causes a 10% differential in final degree of light transmission between the PMMA and PBMA modified systems.



Figure 6.13 – Measure of relative visible (λ =600nm) light transmission reduction during photopolymerization (I_o=5mW/cm²) in TEGDMA homopolymerization and TEGDMA/10wt% PBMA and TEGDMA/10wt% PMMA phase-separating polymerizations.

However, during the polymerization, differences in local conversion as well as local composition will impact the extent to which relative light transmission is reduced. For instance, in Figure 6.13, at $\chi = 0.35$, the transmission reduction is either 10% or 60% for the PMMA and PBMA modified polymerizations, respectively, which is a much larger differential between the prepolymers than that observed at the completion of the polymerization. Since both systems are beyond macrogelation by this extent of reaction, it is likely that both resins will have similar phase compositions as no more significant diffusion should be occurring and both materials end

the reaction with relatively similar phase compositions. However, the degree of light transmission reduction changes based on the difference in extent of conversion between phases formed, as refractive index increases linearly with degree of conversion.⁴² While this effect is not directly probed through this experimental technique, it does support our findings up to this point.

Stress Development During Polymerization – Thus far, we have identified how the modifying prepolymer can impact the T_g development during the polymerization, but another aim of this study is to identify how that differential impacts the development of key bulk properties. Previous work into stress reduction in a phase-separating polymerization such as this has shown that the formation of co-continuous network structure, allowed for by a delay in network gelation, leads to a reduction in polymerization stress beyond that of the volumetric effect of introducing prepolymer into the resin.¹⁸ However, based on the modifying prepolymer, the formation of co-continuous network structure resulted in varying degrees of stress reduction.

Similar work into phase-separated polymer networks has attributed stress reduction to micro-void formation or cavitation along interfaces of phases with different thermal expansion coefficients, which is highlighted when a system polymerized at an elevated temperature is brought back to an ambient temperature.^{6, 7} While our materials do not undergo a severe temperature change from processing to storage (besides the modest exotherm that results from the conversion of methacrylate functionalities), we anticipate that a system which forms phases of significantly varied T_g, both during the polymerization and in the final state, will be more efficient at compensating for volume changes as a result of polymerization along the interfaces formed between phases.

To test this hypothesis, the development of polymerization stress was monitored in realtime for the phase-separating systems tested thus far. As displayed in Figure 6.14, stress

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reduction, as well as a significant delay in the onset of stress development was observed in the PBMA modified resins compared to the TEGDMA-control. Similar behavior, both in delay of stress development as well as reduction in stress has been observed in similar materials that are formed in the presence of only a conventional photoinitiator.¹⁸ Interestingly, the onset of stress development in the TEGDMA/10wt% PBMA series corresponds well with the onset of significant increase in the prepolymer-rich phase T_g. However, in the TEGDMA/10 wt% PMMA stress profile, the build-up of stress occurs very similarly to the TEGDMA-control. There are observed differences between the magnitude of stress reduction in the phase-separating samples, however that will not be a focus of this study, as it will depend on the resulting domain size and structure that is not evaluated here.



Figure 6.14 – Measure of interfacial stress during photopolymerization (I_o=5mW/cm²) in TEGDMA hompolymerization and TEGDMA/10wt% PBMA and TEGDMA/10wt% PMMA phase-separating polymerizations.

This data does indicate that significant differences in the stress development as a function of conversion are observed in the phase–separating resins based on the modifying prepolymer. When the Tg differential between TEGDMA-rich and prepolymer-rich domains is maximized, as in the case of PBMA modification, significant development of bulk stress is delayed until a much later point in the reaction. This is a result of the prepolymer-rich domains remaining loosely cross-linked and therefore able to compensate for volumetric changes occurring in the TEGDMA-rich domains throughout a much greater extent of the reaction. In the PMMA modified resins, since there is a less significant differential in local conversion as well as thermal properties between TEGDMA and PMMA-enriched domains, this effect is lessened. The combined effects of bulk modulus and shrinkage strain contribute to the magnitude of polymerization stress experienced by a network. Our previous work has shown that the final resulting bulk modulus is equivalent between the TEGDMA-homopolymer and phase-separating systems.¹⁸ Therefore, much of the stress reduction during polymerization, especially compared to the TEGDMA homopolymer, is attributed to the efficiency at the prepolymer-rich domains to compensate for volumetric shrinkage.

Investigation in Low T_g **Matrix** – The same approach as detailed throughout this study was used to infer the glass transition temperature development in a low T_g homopolymer modified with a high T_g prepolymer, specifically PMMA. This was done as a quick test to probe whether the resulting matrix T_g is a significant influence towards the order of phase formation during PIPS. For these experiments, a poly(ethylene glycol) dimethacrylate (PEGDMA) matrix was modified by 10 wt% PMMA. The monomeric T_g, as well as the resulting phase compositions obtained after PIPS are displayed in Table 6.4. Again, a phase that is rich in neathomopolymer (PEGDMA) and a phase that is enriched in prepolymer (PMMA), form. Here, the relative composition of prepolymer in the PMMA-rich domains is higher than in the TEGDMA analog.

Table 6.4 – Glass Transition Temperature (T _g) and phase-compositions of PEGDMA homopolymer and PEGDMA/10wt% PMMA phase-separated networks at >90% conversion								
Sample	Monomeric T _g (°C)	PEGDMA-rich Phase T _g (°C)	PEGDMA fraction (wt%) in PEGDMA-rich phase	PEGDMA / PMMA-rich Phase T _g (°C)	PEGDMA fraction (wt%) in PEGDMA / PMMA-rich phase			
PEGDMA	-74 (±1.1) °C	24 °C	n/a	n/a	n/a			
PEGDMA / 10 wt% PMMA	-74 (±1.6) °C	22 °C	1.0	105 °C	0.23			

The Tg development in both the PEGDMA-homopolymer and PEGDMA/10wt% PMMA resin were monitored at varying extents of conversion. The combined results of these studies are shown in Figure 6.15. Like the TEGDMA homopolymer, the Tg development of the PEGDMA homopolymer follows second order behavior. Again, the PEGDMA-rich fraction in the phaseseparating example has a higher measured Tg than the PEGDMA-homopolymer at an equivalent of bulk methacrylate conversion. This supports claim that extent our in а homopolymer/prepolymer phase-separating polymerization, the reaction is initially preferred in double-bond rich, lower viscosity domains (typically, the homopolymer rich regions). This order of phase formation does not vary when the differential between bulk matrix and prepolymer is altered. However, as indicated previously, the extent to which polymerization is accelerated in the homopolymer rich domains may vary. There is an observed steady increase of the $T_{\rm g}$ in the PMMA-rich domains. The combined factors of increasing degree of local conversion as well as free monomer diffusion out of PMMA-rich regions to the homopolymer-rich domains contributes to this behavior.



Figure 6.15 – Glass transition development in PEGDMA homopolymer and PEGDMA/10wt% PMMA phase-separating polymerization, ($I_0=5mW/cm^2$). PEGDMA homopolymer T_g development fit with second order polynomial ($R^2=0.999$).

The development of interfacial polymerization stress was also monitored in the PEGDMA based polymerizations (Figure 6.16). In this case, the stress development is accelerated in the phase-separating resin. Here, the phase-separated domains formed have a much higher T_g and local modulus. Since in the PEGDMA homopolymer, the entire material is a low T_g , rubbery matrix, volumetric shrinkage is compensated for by viscous flow of the residual monomer in the matrix. However, in the phase-separating example, where domains rich in the high T_g prepolymer form, this effect is lessened, and the stress development occurs more rapidly as a function of conversion.



Figure 6.16 – Interfacial polymerization stress development in PEGDMA homopolymer and PEGDMA/10wt% PMMA phase-separating polymerization, (I_o=5mW/cm²).

6.4 Conclusions

In this work, we have identified an approach to estimate differential in local properties during a phase-separating polymerization. A photo-iniferter was introduced into the polymerization, so thermal analysis of partially cured photopolymers could be conducted. The T_g development in a bulk dimethacrylate homopolymer, TEGDMA, was characterized as degree of conversion. It was found that this development followed a second order relationship with extent of conversion.

The T_g development was also followed in phase-separating photopolymerizations where domains of varying compositions form. Two different prepolymers, PMMA and PBMA, with ~100 °C differential in T_g were added to the bulk matrix to induce phase separation. In both systems, the resulting phases formed were equivalent in composition. Both phases formed a phase very rich in TEGDMA-homopolymer. When the T_g development of this was compared to that of neat-TEGDMA at equivalent bulk conversion, it was found that the TEGDMA-rich domains have a higher T_g . This indicates that these domains develop at an accelerated rate, and the difference in estimated local conversion versus bulk, measured conversion was estimated, and the differential was most significant in the PBMA-modified resins. This finding was also supported by observed differences in light transmission during polymerization of PMMA and PBMA modified resins.

The differential in local conversion, as well as local T_g was studied in the context of polymerization stress development. When the more slowly polymerizing prepolymer-rich phase has a significantly lower local T_g than the matrix, significant increases in polymerization stress are delayed to much higher extents of bulk conversion. When the opposite relationship is tested, a lower T_g matrix with a higher T_g prepolymer-rich domain, the stress development is actually accelerated. This shows that in phase-separating polymerizations, the physical and thermal property differential between phases can significantly impact the bulk property formation.

6.5 Acknowledgements

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6.7 Supplemental Material



Figure 6S.1 – TEGDMA / 10 wt% PBMA / 0.5wt% DMPA / 0.5wt% XDT conversion profiles for varying periods of UV-irradiation exposure, I_o=5mW/cm².



Figure 6S.2 – TEGDMA / 10 wt% PBMA / 0.5wt% DMPA / 0.5wt% XDT reaction rate profiles for varying periods of UV-irradiation exposure, I_o=5mW/cm².



Figure 6S.3 – TEGDMA / 10 wt% PMMA / 0.5wt% DMPA / 0.5wt% XDT conversion profiles for varying periods of UV-irradiation exposure, I_o=5mW/cm².



Figure 6S.4 – TEGDMA / 10 wt% PMMA / 0.5wt% DMPA / 0.5wt% XDT reaction rate profiles for varying periods of UV-irradiation exposure, I_o=5mW/cm².

CHAPTER 7

ACCESSING PHOTO-BASED MORPHOLOGICAL CONTROL IN PHASE-SEPARATED, CROSS-LINKED NETWORKS THROUGH DELAYED GELATION

We present an approach to extend the period for phase separation, independent of temperature, in ambient photopolymerizations based on the copolymerization of structurally similar mono- and di-vinyl monomers. Copolymer resins composed of triethylene glycol dimethacrylate (TEGDMA) and ethelyene glycol methyl ether methacrylate (EGMEMA) were modified with a thermoplastic prepolymer, poly(butyl methacrylate). With increasing EGMEMA modification into the bulk TEGDMA resin, there is a decrease in the initial reaction rate, which increases the time for development of compositionally different phases prior to network gelation. The period between phase separation and gelation was probed through optical and rheological measurements, and it was extended from 22 s in a TEGDMA resin to 69 s in a TEGDMA:EGMEMA copolymer, allowing these materials to be processed under a wide range of UV-irradiation intensities (300 μ W/cm² – 100mW/cm²). Furthermore, the irradiation intensity can be utilized to tailor the resulting domain size and morphology.

7.1 Introduction

The application of heterogeneous polymer networks has been explored extensively in materials science, in fields ranging from membrane development, holographic polymers, biomaterials and liquid crystal-based displays.¹⁻⁵ In these applications, heterogeneous networks are necessary since the desired bulk properties cannot be achieved from a single polymeric network or precursor.⁶ However, the level of dispersion and morphology of these materials can significantly alter critical properties such as strength and appearance. Therefore it is necessary to design approaches to develop heterogeneous networks where morphology of the different components is easily tunable. Traditional approaches to forming these networks include blending two different polymeric components, which typically involves a large mechanical and thermal input to effectively create defined heterogeneous structure.^{6, 7}

Polymerization induced phase separation (PIPS) has been explored as a more elegant approach to develop network heterogeneity.⁸⁻¹⁶ With PIPS, a phase-separated structure is formed from an initially homogeneous state by the diffusion of partially or totally immiscible components during a polymerization. Since the polymerization reaction is promoting the onset and development of heterogeneity, this approach eliminates the need for external apparatus to form the heterogeneous structure. The relative composition and morphology of phases formed depends on the thermodynamics of the polymerizing system, as well as the kinetic factors limiting morphological development. Understanding this balance between thermodynamic and kinetic constraints, or more simply put, the competition between phase separation and the polymerization, is essential if precise design of heterogeneous networks is desired.¹⁷ Thermodynamic factors influencing PIPS include miscibility between components, temperature at which the polymerization is conducted, and the overall entropy, which is influenced by

molecular weight and number of components in the resin.¹⁸ Kinetic constraints on phase separation include physical properties such as viscosity that may limit the diffusion and demixing of partially or fully immiscible phases. Using photoirradiation as the mechanism of initiation in a phase-separating polymerization adds a level of control over the kinetics of phase separation. Not only can the rate of initiation, and thus the rate at which the polymer network forms be controlled precisely through selection of photoinitiator and irradiation intensity but also there is enhanced spatial and temporal control over the polymerization. Additionally, photoirradiation allows the temperature at which the polymerization is conducted to be varied independent of the reaction rate. These benefits make photo-induced PIPS an attractive route to network heterogeneity for *in situ* applications. It should be noted, that there is often an observed decrease in optical clarity of polymeric materials that undergo PIPS, which could limit the application of photoirradiation and cause a gradient in material properties based on the sample geometry, transparency and penetration depth of the light source.

Morphological control through photo-induced PIPS has been demonstrated in the development of polymer-dispersed liquid crystal (PDLC) materials,^{2-4, 19-21} and is useful in tailoring properties such as transmittance, driving voltage and contrast ratio. Traditionally, these studies have utilized linear based polymeric systems. Furthermore, the fraction of the resulting material that is composed of the liquid crystal is quite high, ranging from 60-80wt%, meaning there is a low polymer fraction in the PDLC. These materials are often cited as being elastically weak or that the liquid crystal fraction acts similar to a solvent.^{2-4, 20, 21}

When utilizing photo-PIPS to form an entirely polymeric material, the physical limitations on phase separation are significantly larger than in the PDLC examples. Success has been demonstrated in controlling phase domains in polymeric resins based on linear prepolymer

precursors.^{8, 11, 22} Use of photo-PIPS to control morphology becomes increasingly more difficult when multi-functional monomers are utilized to form a cross-linked network, such as in thermoset/thermoplastic blends, since the thermoset alone has a degree of heterogeneity associated with it.⁹ However, the resulting cross-linked network has much higher strength and moisture resistance compared to linear counterparts, which is advantageous for many applications. In both linear and cross-linked phase-separating polymerizations, the viscosity of the material will become so high during reaction that morphological development of different phases is halted, and structure is locked into place, even if not at thermodynamic equilibrium. In systems with linear precursors, this typically coincides with the onset of autodeceleration,^{8, 10} but in cross-linked resins this limit is observed earlier in the reaction at the onset of network gelation.^{16, 23} In some cross-linked PDLC materials there have been examples of phase development that proceeds via liquid-gel de-mixing post-network gelation.^{3, 21} However, in cross-linked networks with a higher polymer fraction, it has been well studied that the amount of network development prior to gelation impacts the limiting domain size and morphology.^{8, 12, 24-27} A very common approach to minimize this limitation is to use elevated temperature to enhance the diffusion of phases by reducing viscous effects in the matrix.^{10, 12, 16, 22, 24-26} However this approach is unavailable in applications where ambient, in situ polymerization is necessary. Another approach to delay gelation is to introduce thiol compounds that will act as chain transfer agents during the reaction.²⁸ While effective, the structure of the thiol utilized may change the relative miscibility in a heterogeneous system, and thus further complicate the analysis of phase separation.

Here, we demonstrate an approach to adjust the time between phase separation and gelation independent of temperature in a phase-separating polymerization, and exploit the ability

to develop varying morphology by adjusting the irradiation intensity of a single bulk precursor. A dimethacrylate resin modified with thermoplastic prepolymer, utilized in previous studies in photo-based PIPS,^{29, 30} is modified by the addition of a structurally similar monomethacrylate comonomer. The addition of the mono-vinyl decreases the viscosity as well as the conversion-dependent physical limitations to diffusion of partially miscible phases during polymerization. This is different from other approaches that utilize the polymerization of co-monomers to create limited miscibility during the reaction to promote phase separation,^{13, 14, 31} as we use the presence of a co-monomer to simply enhance the time between phase separation and gelation, but not to alter the miscibility during polymerization. This permits a broader range of phase morphologies and processing conditions that can be utilized to form cross-linked, phase-separated networks.

7.2 Experimental

Materials - Ethylene glycol methyl ether methacrylate (EGMEMA, Aldrich) was added to tri-ethylene glycol dimethacrylate (TEGDMA, Esstech) to form the bulk comonomer matrix. The amount of EGMEMA added was varied to increase the fractional contribution of double bonds present in the matrix from EGMEMA. For example, the 50:50 TEGDMA:EGMEMA designation indicates that half of the double bonds in the resin originate from each monomer; it does not indicate a molar ratio of the two monomers.

To induce phase separation, 20 wt% of poly(butyl methacrylate) (PBMA, Aldrich) was added to the comonomer matrices. This prepolymer has $M_w \sim 337,000$ Da and $T_g \sim 22.4$ (± 2.5 °C). The photoinitiator utilized in all studies was 2,2-dimethoxy-2-phenylacetophenone (DMPA), which absorbs in the UV-region. The photoinitiator loading was maintained at 0.5 wt% (relative to the comonomer/prepolymer mass). A UV irradiation source was utilized in all studies to
initiate polymerization (λ =365 ± 10nm). All polymerizations were conducted at ambient temperature (22-25 °C).

Dynamic Mechanical Analysis - All samples (8.0 x 5.5 x 1.0 mm; n=3) were photopolymerized under ambient conditions and then post-cured at 180°C to ensure a total methacrylate conversion greater than 90%, and eliminate any possibility of additional cure occurring during the thermal analysis. A dynamic mechanical analyzer (DMA, TA Q800) was used in tension mode under 0.01% strain with a frequency of 1 Hz. After allowing the sample to equilibrate at -50°C for 20 min, the chamber temperature was raised to 200°C at a rate of 3°C/min, and then held isothermally for 20 min. The temperature was then brought back to -50°C at the same rate to verify consistency in the tan δ data. Results presented here are from the initial ramp in temperature.

Differential Scanning Calorimetry - A differential scanning calorimeter (DSC, Perkin Elmer Pyris Series Diamond) was utilized to measure the glass transition temperature of linear poly(EGMEMA), post-ambient cure, which cannot be analyzed via DMA. A disc-shaped sample (6.5 mm diameter, 0.80 mm thickness) with mass of ~15 mg was photocured (I_0 =5mW/cm²) prior to DSC analysis. The sample was placed in a 50 µL, thin-walled aluminum pan, and an empty pan of the same dimension was utilized as a reference. The sample was allowed to equilibrate at -120°C and then brought to a temperature of 50°C at a rate of 10°C/min. It was then cooled back down to -120°C and the procedure was repeated.

Kinetic Analysis - Bar-shaped specimens of dimensions 8.0 x 5.5 x 1.0 mm (*length* x *width* x *thickness*) sandwiched between glass slides were photopolymerized *in situ* to probe reaction rate development during polymerization. To measure the reaction rate, a FTIR spectrometer was utilized (Thermo Scientific, Nicolet 6700). The dynamic change in

methacrylate peak area in the near-IR (= CH_2 first overtone at 6165 cm⁻¹) was used to calculate degree of conversion and reaction rate. All experiments were conducted with 2 cm⁻¹ resolution.

Photo-Rheometry - A parallel-plate rheometer (TA Ares) was coupled to an in-house designed optical attachment that allowed for simultaneous measurement modulus development and methacrylate conversion, which has been described in detail in other work.^{28, 32} The gel point was assigned as the G'/G'' crossover point.³³ Methacrylate conversion was measured utilizing a FTIR spectrometer (Thermo Scientific, Nicolet 6700) equipped with near-IR fiber optic cables. The near-IR source was directed through the center of the sample, and conversion was calculated using the same approach as in the kinetic analyses. This attachment also allowed for *in-situ*, uniform UV-irradiation of the sample. The samples were sandwiched between two quartz plates (22 mm diameter) and thickness was maintained at 300 μ m. A chamber was constructed for nitrogen purging, and each sample was purged while the quartz plates were separated by 1.5 mm for 1 h. This was done to remove all dissolved oxygen and avoid any oxygen-inhibited edge effects, which would confound the rheological data.

Viscosity - The same rheometer utilized for gel-point determination was used to measure viscosity of comonomer/prepolymer solutions. To measure viscosity, a steady rate sweep test (strain-controlled) was performed on samples with 0.200 mm thickness and 22 mm diameter. The initial rate in the tests was 0.1 and the final rate was 1000 (s^{-1}).

Optical Property Development During Polymerization - Disc-shaped samples were fixed to an optical bench used to monitor dynamic changes in optical properties during polymerization. The samples, which were sandwiched between a glass slide and coverslip, had dimensions of 20 mm diameter and 240 μ m thickness. The samples were irradiated with a UVcuring light source (λ =365 ± 10nm), to initiate the polymerization. Near-IR fiber optic cables were used to measure methacrylate conversion during polymerization under the same conditions as noted previously with a FTIR spectrometer (Thermo Scientific, Nicolet 6700). A broadband light source that emits visible light (λ =400-800nm) was transmitted through the material during polymerization, and a UV/Vis portable spectrometer (Ocean Optics, USB 2000) was used to monitor dynamic changes in visible light transmission, specifically the intensity of 600nm light transmitted through forming material. Since DMPA does not absorb above 380nm³⁴ the visible light source acts as a probe independent of the photoinitiator and does not affect the reaction kinetics.

Atomic Force Microscopy - Atomic force microscopy (AFM, Easy Scan 2 Nanosurf) was used to image heterogeneous networks post ambient photopolymerization. All images were collected in tapping mode using conical tapping mode AFM probes with a spring constant of 50 N/m (Aspire CT-170). The images presented in this manuscript are phase contrast maps.

7.3 Results and Discussion

Dynamic Mechanical Analysis - To detect multi-phase structure post-cure, the tan delta profile of different networks was evaluated with Dynamic Mechanical Analysis (DMA). This was first done on the copolymer networks without prepolymer additive to ensure no phase separation occurred from the bulk copolymerization. When EGMEMA is introduced as a comonomer, up to 50:50 modification, the main peak in the tan delta profile shifts to lower temperatures (Supplemental Figure S7.1), from 161°C for bulk poly(TEGDMA) to 139°C and 105°C in 75:25 and 50:50 TEGDMA:EGMEMA resins, respectively. This is expected, as the decrease in overall cross-linking will decrease the T_g . All profiles display one broad, asymmetric peak in the tan delta profile, indicating single-phase network structure since there is only one transition region where the tan delta value goes through a local maximum. The peak breadth and

presence of a slight shoulder at lower temperatures are attributed to the heterogeneous nature of methacrylate based cross-linking polymerizations, and specifically the formation of cycles.³⁵ This is supported by the fact that the contribution of the shoulder to the total area underneath the tan delta curve is equivalent independent of the degree of EGMEMA modification. The linear poly(EGMEMA) in bulk was found to have a broad T_g from 0-20°C. While this does correlate with observed shoulders, and could indicate a degree of separation between the mono- and dimethacrylate components, other experiments presented in this study indicate that no distinct phase separation occurs without the introduction of prepolymer.

When prepolymer is introduced into the comonomer matrix multi-phase structure, as detected by multiple peaks in the tan delta profile, is observed (Figure 7.1), indicating the formation of compositionally different phase-separated structures. A loading level of 20 wt% PBMA was utilized in the resins to induce phase separation. This loading level was chosen as in previous studies based in totally dimethacrylate-based resins it was significantly large enough to induce phase separation during polymerization.^{29, 30}

In all matrices, the first peak in the tan delta profile lies between the T_g of the pure prepolymer (22.4°C) and the pure copolymer. The second peak, which occurs at a higher temperature, falls very close to the pure copolymer T_g . Table 7.1 displays the comparison between the T_g of the totally copolymeric resins and the T_g assigned as the copolymer-rich domains in phase-separated materials. The difference in the copolymer-rich T_g compared to the bulk copolymer is not significant, as determined by a paired t-test with a 95% confidence interval. This indicates that a structurally similar network forms in the copolymer-rich regions of the phase-separated networks as in the bulk copolymers, and that the phase separation does not lead to significant differentials in diffusion of either monomer present in the resin.



Figure 7.1 - Tan delta profiles, post-cure of TEGDMA:EGMEMA copolymer resins modified by 20 wt% PBMA. All samples were photopolymerized (I_o=5mW/cm²) under ambient conditions and thermally post-cured at 180°C prior to analysis.

Table 7.1 - Copolymer T_g in Control Networks and Phase-Separated Networks $(I_o=5mW/cm^2, n=3)$					
Sample	Copolymer T _g	Copolymer-Rich T _g in Phase- Separated Network			
50:50 TEGDMA:EGMEMA	105 (± 7.3) °C	112 (± 1.7) °C			
75:25 TEGDMA:EGMEMA	139 (± 5.4) °C	131 (± 2.7) °C			
100:0 TEGDMA:EGMEMA	161 (± 4.0) °C	150 (± 10) °C			

With this observation, it is expected that a phase rich in copolymer and a phase rich in copolymer/prepolymer form during PIPS. To estimate the composition of each phase, a modified version of the Fox equation ³⁶ was utilized (Equation 1).

$$\% PBMA = \left(\frac{(T_g^{Comonomer} - T_g^{NewPhase})}{(T_g^{Comonomer} - T_g^{PBMA})}\right) * 100 \tag{1}$$

Using this relationship, the relative composition (wt%) of PBMA in the copolymer rich phase and the prepolymer rich phase was found for phase-separating matrices at varying levels of EGMEMA modification. In all cases, the TEGDMA:EGMEMA rich phase had minimal PBMA present, consistently at a level of 10 wt% or less. However, the composition of PBMA in the prepolymer-rich phase varied based on the degree of EGMEMA modification (Figure 7.2).



Figure 7.2 - Weight fraction of PBMA in copolymer/prepolymer rich phase post-polymerization (n=3). Weight fraction calculated using shift in T_g as measured by DMA and applying a modified version of the Fox equation. All samples were photocured under ambient polymerization conditions (I_o=5mW/cm²) and thermally post cured at 180°C prior to analysis.

Based on the comonomers selected here, the modification by EGMEMA in the TEGDMA matrix alters the potential crosslink density but with negligible variation in the initial reactive group concentration. As the degree of cross-linking decreases, the PBMA mass fraction in the copolymer/prepolymer rich phase increases. This is the first indication that the diffusion of small molecules during PIPS differs based on the degree of cross-linking present in the matrix. Similar trends of PBMA weight fraction increasing in prepolymer-rich domains with EGMEMA modification is observed when the materials are formed under more rapid or slower

polymerization conditions ($I_0=20 \text{ mW/cm}^2 \text{ or } 300 \text{ }\mu\text{W/cm}^2$ – Supplemental Figures S7.2 and S7.3). At the lowest irradiation conditions tested, there is only a significant difference in the PBMA mass fraction in the 100:0 modified matrix, which is lower than that of the 50:50 and 75:25 modified systems. At such a low rate of network formation, only the most densely cross-linked system imposes significant limitations to diffusion of immiscible phases. This point will be supported further in this study through morphology studies.

Viscosity and Kinetics of Reaction - The viscosity of each comonomer/prepolymer solution, prior to polymerization was measured using a parallel plate viscometer (Table 7.2). As expected, based on the individual monomer viscosities, with increasing dimethacrylate fraction in the bulk comonomer resin, there is a gradual associated increase in viscosity. The addition of prepolymer significantly increases resin viscosity as compared to the control matrices.

Table 7.2 - Viscosity of Initial Comonomer/PBMA Formulations (n=3)					
Sample	Copolymer Viscosity (Pa*s)	Copolymer modified with 20 wt% PBMA Viscosity (Pa*s)			
50:50 TEGDMA:EGMEMA	1.9 E-3 (± 2.1E-4)	0.23 (± 3.2E-3)			
75:25 TEGDMA:EGMEMA	3.1 E-3 (± 1.5E-4)	0.51 (± 8.9E-3)			
100:0 TEGDMA:EGMEMA	5.3 E-3 (± 1.5E-4)	0.99 (± 2.3E-2)			

The kinetics of polymerization were analyzed utilizing FTIR spectroscopy. The dynamic change in rate of polymerization (R_p) was calculated from the obtained conversion data. The kinetic rate profiles were collected at varying rates of initiation, varied by incident UV irradiation. The rate profiles for polymerizations conducted at $I_o=5mW/cm^2$ are shown for the control copolymer resins (Figure 7.3) and the phase separating resins (Figure 7.4).



Figure 7.3 - Polymerization rate development in TEGDMA:EGMEMA matrices ($I_0=5mW/cm^2$). R_p^{max} is observed in the reaction approximately 42, 63 or 116 s after initiation for the 100:0, 75:25 and 50:50 resins, respectively.

All reaction rate profiles, regardless of degree of EGMEMA or PBMA modification display an autoacceleration period typical of a cross-linking polymerization.^{37, 38} In the control materials this autoacceleration period persists to a significantly higher degree of methacrylate conversion with increasing EGMEMA modification. This result is not unexpected based on the initial differences in viscosity. The initial rate in the 100:0 matrix is larger than the 75:25 and 50:50 matrices, as it has a higher initial viscosity that favors diffusion limited termination earlier in the reaction and allows for a greater polymerization rate. Since the resin viscosity decreases with EGMEMA modification (Table 7.2), it is not until a higher degree of conversion and extent of polymerization rate. This is why with increasing EGMEMA modification, the maximum rate of polymerization (R_p^{max}) is delayed in the reaction occurring approximately 42, 63 or 116 s after initiation for the 100:0, 75:25 and 50:50 resins respectively. The delay in R_p^{max} and the

onset of vitrification³⁹ leads to an increase in final degree of methacrylate conversion with increasing EGMEMA modification.



Figure 7.4 - Polymerization rate development in TEGDMA:EGMEMA matrices modified by 20 wt% PBMA (I_o=5mW/cm²). R_p^{max} is observed in the reaction approximately 51, 51 or 78 s after initiation for the 100:0, 75:25 and 50:50 modified resins, respectively.

In the phase-separating matrices (Figure 7.4), the same trend of decreasing initial rate of reaction and final degree of conversion with increasing EGMEMA modification is observed. However, other aspects of the polymerization kinetics are altered significantly by the phase separation. First of all, in the phase-separating reactions, at all levels of EGMEMA modification, R_p is reduced from the control polymerizations, likely due to the significant increase in viscosity by introducing the high molecular weight prepolymer into the matrix, thus limiting diffusion of all species in the reaction medium. This leads to a smaller time interval prior to R_p^{max} , which occurs at 51, 51, or 78 s after initiation for the 100:0, 75:25 and 50:50 modified matrices. However despite this rate depression, in all phase-separating reactions the autoacceleration period is expanded compared to the control reaction. Meaning, the period during which a

relatively high R_p is observed extends for a much larger portion of the reaction, and results in a higher limiting conversion than in the non-phase-separating counterparts. This is expected, based on the delayed vitrification in the prepolymer-rich phase as a consequence of the relatively low prepolymer T_g . This expanded period is likely a result of the formation of compositionally different domains, which will undergo local autoacceleration behavior at different points of the polymerization, and thus enhance the observed bulk autoacceleration behavior. The same kinetic trends amongst varying degrees of EGMEMA modification were observed at lower (I_o =300 μ W/cm²) and higher (I_o =20mW/cm²) irradiation intensities tested (Supplemental Figures S7.4, S7.5).

The kinetic profiles support the phase composition findings (Figure 7.2). With a delayed autoacceleration period, the 50:50 modified matrices have an extended opportunity for diffusion of small molecules (i.e. small radicals and monomer, though likely not prepolymer to any significant degree) to a much later extent of reaction. This allows for thermodynamic diffusion of TEGDMA and EGMEMA monomer out of the prepolymer rich domains, to form a phase more concentrated in PBMA. Since the mono- and di-vinyl monomers used in this study were intentionally selected to have structural similarity, we do not expect selective diffusion of either monomer out of the prepolymer-rich domains based on affinity. However, since only free monomer can diffuse, there is likely more of the monomethacrylate that diffuses into copolymer-rich domains prior to gelation. This variation in diffusion, however, does not make a significant impact on the composition of copolymer rich domains as the pure copolymer T_g and copolymer-rich T_g 's in phase-separated networks are equivalent at varying levels of monomethacrylate modification (Table 7.1).

The experiments presented up to this point have provided general ideas of how the final phase-separated structure varies with di:mono-methacrylate ratio; however, the remainder of the experiments will more closely monitor the real-time phase separation process to understand distinct differences and advantages associated with PIPS in mono-vinyl modified comonomer resins.

Onset of Phase Separation/Gelation Measurement - The period of time and network development that occurs between phase separation and gelation is critical in a system that undergoes PIPS. Previously, we have shown that in a purely dimethacrylate based phase-separating polymerization, maximizing the extent of network development between phase separation and network gelation is highly favorable.³⁰ It allows for the formation and development of purely co-continuous network structure, as well as maximizes the level of internal polymerization stress reduction. When this period is minimized, there may be insufficient time for diffusion of partially immiscible phases prior to gelation. Once gelation is encountered, there is a large decrease in diffusivity throughout the reaction medium, and it is assumed that no significant changes in phase structure can occur beyond that point.

The onset of network gelation and the onset of phase separation were measured in prepolymer modified comonomer matrices utilizing photo-rheometry and changes in optical density, respectively. The onset of network gelation was assigned as the G'/G'' crossover point,³³ measured coincidentally with conversion with photo-rheometry. The onset of phase separation during polymerization was taken as the point at which a decrease in the visible light transmission (λ =600nm), or more simply stated the onset of turbidity, was observed during polymerization as measured by UV/Vis analysis with the optical bench set-up. Although these two points were measured independently and in different apparatuses, the irradiation conditions

and sample geometry were nearly identical so reasonable comparisons can be made between the two. The measured degree of conversion at these two different reaction benchmarks is shown in Table 7.3.

Table 7.3 - Onset of PIPS and onset of Gelation Conversion Data (n=3, $I_0=300 \ \mu W/cm^2$)					
Sample	Conversion at onset of PIPS	Conversion at onset of network gelation	Average Elapsed time (s)		
50:50					
TEGDMA:EGMEMA	$1.40 (\pm 2.50)$	16.1 (± 4.1)	65 (± 2.0E-3)		
20 wt% PBMA					
75:25					
TEGDMA:EGMEMA	2.70 (± 3.60)	24.6 (± 2.1)	39 (± 1.5)		
20 wt% PBMA					
100:0					
TEGDMA:EGMEMA	$4.10 (\pm 0.80)$	$14.5 (\pm 0.6)$	22 (± 7.8)		
20 wt% PBMA					

The onset of PIPS is nearly instantaneous with the polymerization, occurring at roughly 1-4% methacrylate conversion independent of the level of mono-methacrylate modification. This indicates that despite the mono-methacrylate modification, the polymerization reaction does lead to limited miscibility early on in the reaction. The gelation behavior, however, varies with the degree of methacrylate modification. In the 100:0 modified matrix there is roughly 10%, in the 50:50 15% conversion, and in the 75:25 case 20% methacrylate conversion between the onset of phase separation and the onset of gelation. For reference, the gel point conversion for the three different control copolymer resins, 100:0, 75:25, and 50:50 TEGDMA:EGMEMA, occurred very early in the reaction, at 3.4, 4.5 and 6.3% methacrylate conversion respectively. This is expected, as the mono-vinyl modification is known to modestly delay network gelation to higher degrees of conversion. However, when PIPS occurs in the matrix, gelation is delayed significantly from that of the control, and that delay corresponds to an additional 10-20% overall methacrylate conversion occurring in the pre-gel state.

It is difficult to probe the exact origin of the substantial and reproducible delay in gelation observed in the 75:25 TEGDMA:EGMEMA network when compared to the 50:50 TEGDMA:EGMEMA composition. However, this is likely due to the nature of the phase-separated domains formed as well as the local differentials in the polymerization kinetics. If a dispersed phase structure forms, the network formation in the continuous domain determines the bulk gel point. If the volume fraction of dispersed domains is small, then the polymerization proceeds mostly in the continuous phase, and gelation is observed earlier in the reaction. However, if a fully co-continuous domain structure is formed, gelation will be delayed substantially until one of the continuous domains gels, which has been shown experimentally.³⁰ In these experiments, we expect co-continuous structure to form based on the loading level of PBMA added to the resins. Depending on the kinetic rate differential between the two phases formed, as well as any additional diffusion of monomer that occurs early on in the reaction, the delay in gelation may vary substantially between the different copolymer-based resins.

While the extent of conversion that occurs between phase separation and gelation is important, it is again helpful to relate the extent of conversion between these reaction benchmarks to time intervals, since both the reaction kinetics (Figures 7.3-7.4) and the resulting phase compositions (Figure 7.2) vary significantly with extent of mono-methacrylate modification. The amount of time between these two reaction benchmarks was calculated based on the kinetics of the reaction, and are also presented in Table 7.3.

With increasing monomethacrylate modification, there is increasing elapsed time between phase separation and gelation, and this increase is most significant when increasing the modification from the 75:25 to the 50:50 matrix, which should allow for more extensive phase development prior to network gelation. This again supports the previous results on purity of phases formed, and likely indicates differences in resulting phase structure, which will be discussed shortly. The error in these measurements becomes larger with increasing degree of cross-linking, which is again a consequence of the heterogeneous nature and kinetic anomalies that occur in dimethacrylate-based polymerizations that become more significant in a purely TEGDMA resin.^{37, 38} The extended period between phase separation and gelation in the EGMEMA-modified systems is very promising as it presents an approach, independent of temperature or irradiance, to extend the time for diffusion of partially miscible components during PIPS. In the matrices (i.e. 50:50 TEGDMA:EGMEMA) where this time period is increased significantly, it is likely that even under high intensity curing conditions, phase-separated structure will still form. Previous approaches to phase-structure control with photo-irradiation in PIPS have only explored UV curing intensities less than 1 mW/cm^{2 3, 10} and visible light intensities less 4 mW/cm^{2 8, 11} so as not to suppress the phase separation. With our approach, we likely can access distinct phase-separated structure formed under much more rapid polymerization conditions, as discussed next.

Monitoring phase separation during polymerization and corresponding phase structure post-cure - To understand dynamic differences in phase separation at different ratios of di:mono-methacrylate, a dynamic light scattering technique was utilized. With this, the development of turbidity, or haziness in the materials could be monitored in real-time during the polymerization reaction. An additional control variable was utilized in these reactions, irradiation intensity. The phase separating polymerizations were conducted at 3 different intensities: $I_o = 20$ mW/cm² (high), 5 mW/cm² (intermediate) and 300 μ W/cm² (low).

The onset of turbidity is typically used as a sign of phase separation during polymerization, as it can indicate whether or not a system has domains of differing refractive indices.⁹ During a phase separating polymerization, two main factors will lead to differences in refractive index. The first will be the difference in relative methacrylate conversion between the two different phases. In a pure comonomer resin, as methacrylate conversion increases, the refractive index will increase in a linear manner.⁴⁰ This means that domains polymerizing at non-equivalent rates, and with different degrees of local conversion will have disparity in refractive index. For reference, the refractive indices of initial monomeric state and fully cured samples for the different pure comonomer resins are included in the Supplemental Information (Table S7.1). There is a slight decrease in refractive index both in the monomeric and polymeric states associated with increasing mono-methacrylate modification.

The second factor that also contributes to local disparity in refractive index is the compositional differences between different domains. We have characterized that two phases form during the polymerization; one highly rich in comonomer and the other composed of a varied mixture of comonomer and PBMA. The pure prepolymer, PBMA, has a refractive index of \sim 1.4804 (± 6E-4), which will either increase or decrease the local refractive index depending on the relative mass fraction of PBMA and extent of methacrylate conversion. The formation of micro-sized domains may also lead to an increase in the level of scattering observed during polymerization. Post network gelation, due to diffusion constraints there should be no significant changes in morphology shape or size. Therefore, significant changes in light scattering behavior after macro-gelation are likely due changes in the refractive index differential between phases. Taking these factors into account, the dynamic changes in light transmission was monitored in phase-separating comonomer/prepolymer resins at varying UV irradiation intensities.

The results of these experiments for 100:0 modified polymerizations are displayed in Figure 7.5. The control, poly(TEGDMA) does not experience any significant change in visible

light transmission during polymerization, which is consistent across all irradiation intensities (only one control polymerization is shown here for clarity). The optical development during polymerization in phase separating materials does not vary significantly as a result of irradiation intensity, but they all display similar profiles in that there is an initial decrease in light transmission (observed turbidity of the sample) up to moderate degrees of conversion (30-40%). This results from two phases of differing refractive indices at the onset of phase separation, early in the reaction. The degree of light transmission continues to decrease as diffusion of partially miscible components, as well as the kinetic development of the two phases occurs at nonequivalent rates, increasing the refractive index disparity. This is followed by a period where the intensity of light transmission is recovered, and the sample approaches near-transparency. Here, polymerization approaches limiting conversion in both phases and differences in refractive index based on extent of reaction are minimized. Since the network is highly cross-linked and has already gelled this increase in visible light transmittance is not due to significant changes in domain shape or size. The final degree of clarity is based on compositional and extent of conversion differences between the two phases formed. This type of behavior has been observed in TEGDMA/prepolymer systems undergoing photo-PIPS.²⁹ The 100.0previously TEGDMA:EGMEMA polymerization conducted at $I_0=20$ mW/cm² has a slightly extended period prior to light transmission recovery, as well as a total optical clarity at the end of the reaction. This is likely due to the higher exotherm experienced from utilizing higher irradiation intensity. This thermal effect will allow more diffusion during polymerization, which will lead to a higher degree of methacrylate conversion obtained during an ambient polymerization.



Figure 7.5 - Dynamic changes in visible light transmission during polymerization at varying light intensities for 100:0 TEGDMA:EGMEMA, 20 wt% PBMA polymerizations.
Polymerization initiated via UV-irradiation at varying intensities λ=365nm. Visible light transmission monitored at λ=600nm, which acts independent of the photoinitiating light source.



Figure 7.6 - Phase morphology of 100:0 TEGDMA:EGMEMA, 20 wt% PBMA networks cured at varying light intensities, post-polymerization. (A) $I_0=300 \ \mu\text{W/cm}^2$ (B) $I_0=5 \ \text{mW/cm}^2$ (C) $I_0=20 \ \text{mW/cm}^2$. Scale bar = 10 μ m.

The resulting phase structure, as characterized with AFM, is also constant across the three different polymerization rates in the 100:0 TEGDMA:EGMEMA polymerization (Figure 7.6). In all cases, co-continuous phase structure, typical of the Spinodal Decomposition mechanism of phase separation, results. The average domain size, calculated by taking a weighted average of segments in both the x and y-direction with similar phase angles, stays between 0.5 - 1 μ m at all three irradiation intensities. It is slightly larger both at the low (I_o=300

 μ W/cm², domain size ~ 0.82 ± 0.57 μ m) and intermediate (I_o=5mW/cm², domain size ~ 1.28 ± 0.92 μ m) intensities compared to the most rapidly formed network (I_o=20mW/cm², domain size ~ 0.66 ± 0.50 μ m)

When monomethacrylate modification is introduced into the bulk matrix, at the 75:25 ratio, the optical behavior and phase morphology varies with the irradiation intensity employed (Figures 7.7-7.8). While in all cases, turbidity is observed very early in the reaction, at less than 5% methacrylate conversion, there is a strong correlation between the degree of turbidity observed during polymerization (minimum value of light transmission) and the irradiation intensity. At higher light intensities, there is a less dramatic decrease in light intensity than at slower rates of network formation. Additionally, the rate at which turbidity develops within the material is slower at higher irradiation intensities (i.e. the minimum light transmission is not observed until later stages in the reaction).



Degree of Conversion

Figure 7.7 - Dynamic changes in visible light transmission during polymerization at varying light intensities for 75:25 TEGDMA:EGMEMA, 20 wt% PBMA polymerizations.
Polymerization initiated via UV-irradiation at varying intensities λ=365nm. Visible light transmission monitored at λ=600nm, which acts independent of the photoinitiating light source.

When this is coupled with the network morphology post-polymerization (Figure 7.8), there is a decrease in the size of phase-separated domains as a function of irradiation intensity. All materials display co-continuous morphology, which is expected given the loading level of prepolymer. Since phase separation in the monomethacrylate modified resins still occurs at early stages of conversion, the polymerization likely still enters a highly unstable energy state. At low and intermediate irradiation intensities, the resulting domain sizes are relatively similar ($2.2 \pm 1.6 \mu$ m or $2.7 \pm 1.9 \mu$ m for I₀= 300 μ W/cm² or 5mW/cm² respectively). In the intermediate irradiance sample, the contrast between phases is less, a result of less complete phase separation and a prepolymer-rich phase less concentrated in PBMA, as the increased reaction rate limits diffusion. The relative size of phase-separated domains decreases ($0.60 \pm 0.45 \mu$ m) significantly at the highest irradiation intensity, I₀=20mW/cm². This is to be expected, as with increasing light intensity, the time for diffusion and morphological development decreases. Therefore, at higher irradiances there is minimal time for coalescence of phase-separated domains, making them smaller.



Figure 7.8 - Phase morphology of 75:25 TEGDMA:EGMEMA, 20 wt% PBMA networks cured at varying light intensities, post-polymerization. (A) $I_0=300 \ \mu\text{W/cm}^2$ (B) $I_0=5 \ \text{mW/cm}^2$ (C) $I_0=20 \ \text{mW/cm}^2$. Scale bar = 10 μ m.

In the 50:50 modified polymerizations, similar differences in light transmission during polymerization (Figure 7.9) and domain size (Figure 7.10) are observed as in the 75:25 modified matrices. In this material with increasing irradiation intensity, the resulting domain size

decreases steadily from $3.3 \pm 2.5 \mu m$, $2.5 \pm 1.5 \mu m$, to $0.81 \pm 0.62 \mu m$ for low, intermediate and high irradiation intensities, respectively. Again, the degree of turbidity also decreases steadily with irradiation intensity.







Figure 7.10 - Phase morphology of 50:50 TEGDMA:EGMEMA, 20 wt% PBMA networks cured at varying light intensities, post-polymerization. (A) $I_0=300 \ \mu\text{W/cm}^2$ (B) $I_0=5 \ \text{mW/cm}^2$ (C) $I_0=20 \ \text{mW/cm}^2$. Scale bar = 10 μ m.

When compared to the 75:25 resins, the 50:50 modified matrices have a more dramatic loss of light transmission during polymerization at the three irradiation intensities tested. This

correlates nicely with the final phase composition results presented earlier (Figure 7.2). Since in the 50:50 modified matrices, a more concentrated PBMA-rich phase is formed than in the 75:25 and 100:0 counterparts, there will be a more significant disparity in refractive index between the comonomer-rich and comonomer/PBMA-rich phase. While the reduction in transmitted visible light (λ =600nm) is as great as 50% in some polymerizations, since the materials in these experiments are optically thin, there is no significant decrease in the degree of conversion through the material thickness. However, if applying these reactions to optically thick materials, the decrease in light transmission could create issues in obtaining uniform bulk properties.

We suspect that the observed differences in light transmission behavior as a function of irradiation intensity in the 50:50 and 75:25 modified matrices points to some key differences in these phase-separating polymerizations. The first, as indicated earlier, is that in these matrices irradiation intensity can be utilized as a key parameter to control and vary phase structure at the levels tested here. The decrease in minimum light transmission at slower reaction rates correlates with the formation of larger domains as well as larger compositional differential between phases, which will increase the degree of light scattering. Under slower reaction conditions, diffusion of partially miscible components is hindered the least, which allows for diffusion and coalescence of domains as well as formation of a phase more concentrated in PBMA prior to network gelation. With increasing irradiation intensity, this time period decreases, and thus less coalescence is observed and smaller phase domains result, additionally there is a slight decrease in the local concentration of PBMA in the prepolymer rich domains.

Additionally, it is possible that the differential in reaction rate between the two phases formed varies with irradiation intensity, which would also contribute to the increased scattering. In the lower irradiance polymerizations, primary radical diffusion is not limited in initial stages

of the reaction, so the polymerization can proceed primarily in the copolymer rich regions that effectively have a much higher double bond concentration and will be thermodynamically preferred. This is difficult to show experimentally, since both phases rely on the conversion of methacrylate functional groups so their individual conversions cannot be monitored separately. In some phase-separating reactions, two distinct kinetic regimes have been observed during polymerization, one example being based in the copolymerization of a monomethacrylate and a dimethacrylate with limited miscibility.³¹ These distinct and separate regimes make it much simpler to assign the order of polymerization of the two phases formed. However, we do no observe two distinct kinetic regimes so we cannot easily de-convolute this type of data and it is likely that our phases polymerize simultaneously but at differing rates. Further complicating this analysis is that each phase has some extent of cross-linking, which even in a non-phase separating system already displays kinetic and structural anomalies that are complex to analyze as a function of conversion.^{37, 41} Since our current kinetic approaches can only monitor bulk methacrylate conversion as a function of time, future studies in this area should probe the difference in local methacrylate conversion.

As stated, phase structure control through photo-PIPS has only been demonstrated over a limited range of irradiation intensities, and not at all at UV-irradiation intensities above 1 mW/cm². At higher irradiation intensities, the polymerization reaction was sufficiently high that diffusion of immiscible components was too slow compared to the polymerization reaction, and phase separation became totally suppressed. With the system we study here, we have already demonstrated that we can apply photoinitiated PIPS in higher intensity ($20mW/cm^2$) UV photopolymerizations. To further demonstrate the robustness of this system, we photocured the 50:50 TEGDMA:EGMEMA, 20 wt% PBMA resin under ambient conditions at I_o=100mW/cm².

The phase structure post-ambient cure is displayed in Figure 7.11. Phase separation is not suppressed, and the resulting phase structure appears dispersed, and has domains on the order of $0.98 \pm 0.62 \ \mu\text{m}$ in size, similar to what is observed for the same resin cured at I_o=20mW/cm² (Figure 10C). Although this indicates that a limit in the size and shape of domains formed has been reached (i.e. the size scale cannot be pushed to nanoscale domains by further increasing the irradiation intensity), this shows that this material system can be applied to create phase-separated networks cured under much more rapid conditions than have been explored previously.



Figure 7.11 - Phase morphology of 50:50 TEGDMA:EGMEMA, 20 wt% PBMA network cured at $I_0=100 \text{ mW/cm}^2\text{post-polymerization}$. Scale bar = 5µm.

7.4 Conclusions

These results highlight some of the advantages and control that can be exploited by introducing monomethacrylate modification into a phase-separating, dimethacrylate-based polymerization. In an exclusively dimethacrylate resin, there is little control offered by adjusting the irradiation intensity. The formation of cross-linked microgels from an early stage of the reaction prohibits significant diffusion during the phase-separation process,^{41, 42} meaning little control is offered by changing the reaction conditions.

In the mono-methacrylate modified resins, the decrease in initial reaction rate (Figure 7.4) increases the time for diffusion prior to gelation (Table 7.3) such that distinctly phaseseparated structure forms much more readily and larger domains, which are also more concentrated in prepolymer can form. This effect becomes exaggerated in the lowest intensity polymerizations, where there is a significant loss of light transmission in the materials. This extended period prior to gelation allows processing of bulk, cross-linked, phase-separated networks to be conducted at a much wider range of irradiation intensities. Previous work has been limited to UV processing at or below 1mW/cm², whereas the current materials still produce phase-separated morphologies at intensities as high as 100mW/cm².

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7.7 Supplemental Material



Figure S7.1 - Tan delta profiles, post-cure of copolymer resins, formed of EGMEMA and TEGDMA. The ratios (i.e. 50:50, 75:25) correspond to the percentage of double bonds coming from TEGDMA or EGMEMA respectively. All samples were photopolymerized (I_o=5mW/cm²) under ambient conditions and thermally post-cured at 180°C prior to analysis.



Figure S7.2 - Weight fraction of PBMA in copolymer/prepolymer rich phase postpolymerization (n=3). Weight fraction calculated using shift in T_g as measured by DMA and applying a modified version of the Fox equation. All samples were photocured under ambient polymerization conditions ($I_o=20$ mW/cm²) and thermally post cured at 180°C prior to analysis.



Figure S7.3 - Weight fraction of PBMA in copolymer/prepolymer rich phase postpolymerization (n=3). Weight fraction calculated using shift in T_g as measured by DMA and applying a modified version of the Fox equation. All samples were photocured under ambient polymerization conditions ($I_o=300\mu$ W/cm²) and thermally post cured at 180°C prior to analysis.



Figure S7.4 – Polymerization rate development in TEGDMA:EGMEMA matrices modified by 20 wt% PBMA (I_o=300μW/cm²). R_p^{max} is observed in the reaction approximately 229, 247 or 287 s after initiation for the 100:0, 75:25 and 50:50 modified resins, respectively.



Figure S7.5 – Polymerization rate development in TEGDMA:EGMEMA matrices modified by 20 wt% PBMA (I_o=20mW/cm²). R_p^{max} is observed in the reaction approximately 25, 29 or 64 s after initiation for the 100:0, 75:25 and 50:50 modified resins, respectively.

Refractive Index - The refractive index (n_D^{22}) of each comonomer/prepolymer resin was measured with a refractometer (Atago T2). Fully cured refractive indices were found by extrapolation of the copolymer/prepolymer refractive indices measured at varying extents of conversion. The refractive index of PBMA was found by extrapolation from increasing concentrations of PBMA in TEGDMA monomer (Table S7.1).

Table S7.1 - Refractive Index of Copolymer Resins in the Monomer and Fully Cured State					
Sample	Monomer Refractive Index	Fully Cured Copolymer Refractive Index			
50:50 TEGDMA:EGMEMA	1.453	1.500			
75:25 TEGDMA:EGMEMA	1.457	1.509			
100:0 TEGDMA:EGMEMA	1.460	1.530			

CHAPTER 8

POLYMERIZATION INDUCED PHASE SEPARATION IN FILLED RESINS: INFLUENCE OF SPATIAL CONSTRICTION ON THE DIFFUSION AND FORMATION OF COMPOSITIONALLY DIFFERENT DOMAINS

Inert, non-functionalized barium aluminosilicate glass filler was introduced into a TEGDMA-based matrix modified with non-reactive prepolymers to study polymerization induced phase separation in spatially constricted composite-based materials formed by ambient photopolymerizations. When the particulate filler was introduced into a neat TEGDMA-matrix, the viscosity of the monomer formulation increased exponentially with increasing filler content, due to a decrease in the interparticle spacing. At 60wt% loading, the decrease in interparticle spacing significantly impacted the TEGDMA continuous network development, as the tan delta behavior showed a decrease in T_g as well as significant broadening of the transition profile.

Two prepolymers (poly-ethyl and poly-butyl methacrylate, PEMA and PBMA) were introduced into filled TEGDMA-resins to induce phase separation in the resin matrix. The modification by prepolymer was kept constant at a loading of 10 wt%, while the amount of filler in the resin was steadily increased. The addition of prepolymer increased the solution viscosity above that in the neat TEGDMA-filler resins, and this increase was more significant with PEMA modification. A threshold, in terms of filler content, above which phase separation is suppressed, was observed in PEMA-modified resins (at a loading of TEGDMA/10wt% PEMA/30wt% Filler). This is likely due to viscous and physical limitations of diffusion within the resin, as well as limitations to the size of phase morphology formed based on the interparticle spacing in which the continuous matrix can form. With the lower viscosity prepolymer, PBMA, phase separation is observed at as high loadings as TEGDMA/10 wt% PBMA/40wt% filler.

8.1. Introduction

Heterogeneous polymer networks have been explored widely as an approach to develop materials with a combination of properties that cannot be accessed from a single bulk precursor.¹ This is often achieved through the blending of at least two thermoplastic polymeric components. One such example is the combination of polystyrene and polyethylene, which not only improves material properties such as moisture resistance, toughness and strength but also decreases processing limitations of the final material.² Another approach to the development of polymer networks with varying degrees of heterogeneity is through polymerization-induced phase separation (PIPS).³⁻¹⁶ This approach exploits changes in the overall free energy during polymerization to promote the formation of compositionally distinct phases through reactionpromoted diffusion. The advantage to using PIPS, as opposed to more traditional approaches such as blending, is that the formation of network heterogeneity occurs as a result of a bulk polymerization reaction, so there is no need for additional processing. The heterogeneous network can be developed from a single reactive precursor, and can also be formed *in situ*. While PIPS does have the advantage of being a 'one-step' approach to heterogeneity, it does require understanding the competing factors during polymerization that can either enhance the phase development, or suppress the phase separation process. In a cross-linking polymerization, PIPS may be physically suppressed by the formation of chemical cross-links and a significant increase in viscosity with conversion that will drastically reduce the ability of partially miscible components to diffuse from one another.^{1,6,10,17}

Another common approach to enhance the properties of polymer networks has been through the addition of inorganic filler as either fibers or particles, most commonly used to adjust the resulting modulus of the network formed. The majority of *in situ* curable composite materials

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involve the introduction of filler in particulate form to simplify processing. Additionally, filler particles impact the overall appearance, volumetric shrinkage, and interfacial stress experienced by the resin, and may be introduced to influence any of these properties.¹⁸⁻²² The size of these particles can vary from nano- to micro-scale, and the impact of changing the diameter of filler particles in resin polymerizations has been studied previously, but will not be a focus here.²³ Surface functionalization of filler particles in resin polymerizations has also been explored.²⁴ With surface functionalization, a main goal is to provide avenues for covalent attachment between the resin matrix and the filler surface, which has been shown to provide interfaces that can also compensate for volume changes during polymerization as a result of volumetric shrinkage.

This study will explore the possibility of creating phase-separated domains in a polymer network that is spatially confined by the introduction of filler particles. As mentioned, significant limitations that develop during a polymerization can suppress the energetically favored phase separation during PIPS. This idea has been demonstrated and studied, especially in the context of rate of network development.^{14,25} If the formation of cross-links occurs too rapidly, then the phase separation may not proceed due to insufficient time for diffusion, even if it is thermodynamically favorable. In this work, since the filler utilized is both non-reactive and non-functionalized it will not increase the density of cross-links in the continuous matrix. However, it will increase the solution viscosity, which will influence the extent and rate at which immiscible components can diffuse. Additionally, depending on the loading level of filler particulate in the resin, the interparticle spacing between inorganic filler will vary, and thus the domains in which phase separation can occur is physically constrained.^{21,26} Similar studies into thermally-initiated epoxy based systems modified with thermoplastics has shown that both increased filler content

and size will eventually suppress the phase separation process.²³ However, this particular study only investigated filler contents up to \sim 5 wt%, here we will investigate resins with a significantly broader filler range that will include materials closer to that used in dental composite restorative applications. The purpose of this study is to identify whether PIPS during ambient photopolymerizations is still a viable approach to create heterogeneous polymer networks when filler particles are introduced into the material formulation, thus reducing spatially the regions in which phase separation can proceed through diffusion, and potentially decreasing the size of domains formed from the phase separation process.

8.2 Experimental

Materials – The bulk, reactive homopolymer matrix utilized in all studies was triethylene glycol dimethacrylate (TEGDMA, Esstech, Inc.), which has been utilized in many of the studies detailed in this thesis. It is a relatively low viscosity, divinyl monomer, that when homopolymerized, will form a high conversion, densely cross-linked network with a degree of structural heterogeneity typical of a dimethacrylate polymerization. At full conversion, the TEGDMA homopolymer has a limiting glass transition temperature of ~161 °C. A nonfunctionalized, barium aluminosilicate glass filler (mean particle diameter 0.74 μ m) was introduced into the TEGDMA-based resin. The filler was used as received, and was donated by Septodont-Confi-Dental Products Division (Louisville, Colorado, USA).

Non-reactive, linear prepolymers were added to the filled and unfilled formulations to induced phase separation during polymerization. The two prepolymers tested are: poly(ethyl methacrylate) and poly(butyl methacrylate). They are commercially obtained (Aldrich) and have differing physical properties, including molecular weight, glass transition temperature (T_g) and refractive index. This data has been presented previously, but for convenience these properties
are reproduced below in Table 8.1. The two prepolymers utilized in this study were chosen as they have glass transition temperatures (T_g) significantly below that of bulk poly(TEGDMA) at full conversion but PEMA contributes a T_g similar to that of ambient photocured poly(TEDGDMA). Since this study relies on utilizing the presence of multiple T_g's as well as shifts in T_g from the bulk homopolymer matrix in fully cured networks as a way to monitor the presence of multi-phase structure, it is necessary utilize components with a significantly large T_g differential. The photo-initiator utilized in all studies was 2,2-dimethoxy-2-phenylacetophenone (DMPA), which absorbs in the UV region. For all photopolymerizations, the curing conditions were as follows: I_o=5mW/cm², λ =365 (±10nm).

Table 8.1 – Prepolymer Properties		
Poly (ethyl methacrylate) (PEMA)	Poly (butyl methacrylate) (PBMA)	
M _W ~515,000 Da	M _W ~337,000 Da	
$T_{g} \sim 72.5(\pm 1.1)$ °C	T _g ~22.4(±2.5) °C	
$\rho = 1.11 \text{ g mL}^{-1}$	$\rho = 1.07 \text{ g mL}^{-1}$	

Sample Formulation – For all samples, the required mass of TEGDMA monomer and photoinitiator DMPA were initially weighed out and mixed until the DMPA was fully incorporated into the monomer. For phase-separating resins, both the appropriate mass of prepolymer and filler were then added to the monomer formulation. In all phase-separating resins the prepolymer loading level remained constant at 10 wt% and the filler content was varied from 10-50 wt%. Therefore, the total modification of the TEGDMA resin was the combined loading of both filler and prepolymer (i.e. 30wt% total modification indicates a resin with 10 wt% prepolymer and 20 wt% filler). When the combined loading level of prepolymer and filler were sufficiently low (i.e. less than 20 wt%), these constituents were incorporated under light stirring.

In formulations where the filler and prepolymer mass content exceeded 20 wt%, a speed-mixer (Flack Tek Inc., DAC 150.1 FVZ-K) was utilized to incorporate all components into a homogeneous formulation. Samples were mixed at 2500 RPM for 3 min. If the sample was not fully incorporated after one cycle of mixing (based on visual inspection), it was repeated until homogeneous formulations resulted. In non-phase separating resins, the same procedure was followed except the prepolymer addition was omitted.

Viscosity Measurements – A parallel-plate rheometer was used to measure viscosity of filled resins in the monomeric state. To measure viscosity, a steady rate sweep test (strain-controlled) was performed on samples with 0.200 mm thickness and 22 mm diameter. The initial rate in the tests was 0.1 and the final rate was 1000 (s^{-1}).

Dynamic Mechanical Analysis – To evaluate thermal properties of fully cured materials, Dynamic Mechanical Analysis was utilized. All samples ($l \ge w \ge t$, 8.0 $\ge 5.5 \ge 1.0$ mm) were photopolymerized under ambient conditions and then post-cured at 180°C to ensure a total methacrylate conversion greater than 90%, and eliminate any possibility of additional cure occurring during the thermal analysis. A dynamic mechanical analyzer (DMA, TA Q800) was used in tension mode under 0.01% strain with a frequency of 1 Hz. After allowing the sample to equilibrate at -50°C for 20 min, the chamber temperature was raised to 200°C at a rate of 3°C/min, and then held isothermally for 20 min. The temperature was then brought back to -50°C at the same rate to verify consistency in the tan δ data. Results presented here are from the initial ramp in temperature.

Atomic Force Microscopy - Atomic force microscopy (AFM, Easy Scan 2 Nanosurf) was used to image heterogeneous networks post ambient photopolymerization. All images were

collected in tapping mode using conical tapping mode AFM probes with a spring constant of 50 N/m (Aspire CT-170). The images presented in this study are phase contrast maps.

8.3 Results and Discussion

Viscosity of Initial Monomer Formulations – The viscosity of all monomer formulations was measured using a parallel plate rheometer. A series of control samples, which are composed of just monomer and filler, were analyzed in addition to those which included prepolymer to induce phase separation, to elucidate the effect of just incorporating the inorganic filler into the matrix. The increase in viscosity with increasing loading level of filler, both in systems modified by prepolymer, and those only with filler, is displayed in Figure 8.1, below. The viscosity of the resins without any prepolymer (black circles) increases substantially as a function of filler content. A significant increase in the resin viscosity, almost two orders of magnitude, is observed when the filler loading is increased from 40 wt% to 60 wt%. This is indicative of a threshold at approximately 40 wt% filler loading beyond which, critical particle-particle interactions become dominant as interparticle spacing progressively decreases.

The viscosity of resins modified with both filler and prepolymer were also analyzed. For both prepolymers tested, the loading level of filler was varied while the prepolymer loading was maintained at 10 wt%. This value was chosen since the addition of 10-20 wt% these prepolymers has already been shown to promote PIPS in bulk TEGDMA.^{13,27} It should be noted that by fixing the prepolymer content at 10 wt% of the overall composite formulation, the actual prepolymer loading relative only to the TEGDMA monomer will vary between 10-20 wt% based on the filler content. Therefore, with increasing filler content, there is no concern that there will be an insufficient increase in the overall free energy to promote phase separation during polymerization. The increase in filler will actually increase the entropy of mixing in the system,

which should further promote phase separation during these polymerizations. However, the change in enthalpy with filler introduction is unknown, and could either negate or further enhance this effect.



Figure 8.1 – Viscosities of TEGDMA-formulations, modified with varying filler contents, and where applicable prepolymer. Total resin modification is the combined weight fraction of filler and prepolymer (where applicable) introduced into the matrix (n=3).

As seen in Figure 8.1, the initial resin viscosity is significantly higher when PEMA is the modifying prepolymer (green squares) compared to PBMA (red triangles) at an equivalent modification level. This is not unexpected, since our previous studies into the viscosity of prepolymer-modified, unfilled TEGDMA resins displayed the same behavior.^{13*} With PEMA as the modifying prepolymer, when the combined loading level of prepolymer and filler goes above 30 wt% the viscosity increases significantly, and approaches the viscosity observed in a TEGDMA/60 wt% filler formulation. For this reason, no PEMA-modified resins were explored with total modification higher than 40wt%, as the initial viscosity will begin to limit the ability to

^{*} This is described in detail in Chapter 3.3 of this thesis.

process these materials in ambient conditions. When PBMA is the modifying prepolymer, the viscosity also increases exponentially with filler loading level, with the most significant increase occurring as the total modification is increased from 30-40 wt%.

It is likely that a similar phenomena of a significant decrease in the interparticle spacing predicted in the non-prepolymer modified resins also influences the observed high viscosity of the 30 and 40 wt% modified resins of PEMA and PBMA, respectively. This is harder to predict theoretically, since in addition to having dense, high modulus particles integrated into the liquid monomer, there are also long, elastic polymer chains. The prepolymer should be entangled with other prepolymer molecules but it could also interact with the silane-treated filler particle surface to effectively extend the interphase region, so the assumption of perfect dispersion might not be valid.

Different approaches to estimate the interparticle distance in a colloidal solution have been presented based on the volume fraction and dimensions of the particles dispersed in the solution.^{21,26} Since the monomer utilized in this study, TEGDMA, is of low viscosity the initial resins can be treated as colloidal systems. Therefore the equation presented by Chen²¹ can be used to calculate interparticle spacing in a TEGDMA-resin:

$$\tau = R \left(\frac{4\pi}{3\phi}\right)^{1/3}$$

Where: $\tau =$ interparticle spacing (µm) R= filler particle radius (µm) ϕ =volume fraction of filler

Here, the average radius is 0.74µm and the density of filler, which was used to calculate volume fraction, was 2.7g/cm³. The density of the monomer TEGDMA, also used to calculate volume fraction was 1.092 g/cm³. This relationship assumes monodisperse, hard spheres. Therefore,

significant variations in particulate filler size within a single batch would lead to deviations from this theoretical prediction of the resulting interparticle spacing. The results of these calculations are displayed in Figure 8.2.



Figure 8.2 – Calculated interparticle spacing as a function of filler content (wt%) in a TEGDMA resin. Interparticle spacing calculated from theoretical relationship assuming monodispersed, hard spheres in a colloidal solution.

As expected, the interparticle distance decreases exponentially with the loading level of filler, and eventually approaches zero. The volume fraction as a function of weight-based loading level is presented in Table 8.2 to highlight and acknowledge differences between the mass-based and volume-based fractions. The decrease in interparticle spacing ties in very well with the viscosity results, because as the volume fraction reaches a critical value, the viscosity increases exponentially, likely due to very low value of interparticle spacing. When the filler content is as great as 60 wt%, the interparticle spacing is reduced to 1.4 μ m, whereas at 10 wt% it is 12 μ m. Since the prepolymer-modified systems also have long polymer chains dispersed in the reaction medium and not just low molecular weight monomer molecules, a critical threshold where

interparticle, as well as filler and polymer entanglements become significant will occur at greater interparticle spacing.

Table 8.2 – Volume Fraction of Filler from Weight- based loading in TEGDMA resins	
Weight Fraction of Filler	Volume Fraction of Filler
0.10	0.04
0.20	0.09
0.30	0.15
0.40	0.21
0.50	0.29
0.60	0.38

The significant increase in viscosity observed in prepolymer modified resins may decrease the likelihood for compositionally different phases to form through PIPS. To test this, the tan delta profile of the different resins was evaluated. All networks were photopolymerized under ambient conditions (I_0 =5mW/cm²) and then thermally post-cured (180°C, 1 h) to ensure methacrylate conversion >90%. First, the resins modified only with filler and without prepolymer present were analyzed (Figure 8.3).

The tan delta profile in the 20 and 40wt% modified materials generally displays one broad peak, indicative of a single-phase material with slight heterogeneity associated with it. This type of profile is typical, and expected for dimethacrylate-based resins. The glass transition temperature of each material, which is assigned as the temperature at which tan delta passes through a maximum, stays centered around 147-150°C. However, as the loading level of filler increases, the breadth at half height of the peak increases from 70°C at 20 wt% to 103°C at

40wt%, indicating that the network becomes more heterogeneous in nature with the addition of more filler.



Figure 8.3 – Tan delta profiles of fully converted TEGDMA matrices modified with 20, 40, and 60 wt% barium glass filler.

When the loading level of filler in the TEGDMA resin is sufficiently high, as indicated by the 60 wt% filler profile, the tan delta peak broadens considerably, and the maximum shifts to a lower temperature (104°C). Additionally, a shoulder appears at ~47 °C, and the profile has broadened significantly. The observed significant decrease in T_g and increase in breadth of the tan delta profile corresponds with the significant increase in viscosity of the monomer formulation (Figure 8.1) and substantially decreased interparticle distance (Figure 8.2). One consequence of the decreased interparticle spacing is that much more of the continuous monomer resin will be located in regions very close to the resin-particle interface. At these interphase regions near the solid-liquid interface, the local viscosity will increase. In samples with low filler contents and high interparticle spacing these higher regions of viscosity do not influence the extent of network formation and cross-linking, since this interphase region is minimal compared to the total continuous matrix volume. However, in samples with higher filler content, this variation in local viscosity becomes significant. The increased fraction of interphase region in the continuous resin may result in a decrease in network connectivity due to diffusional constraints during polymerization, causing the unexpected decrease in T_g with in highly filled resins. This point will be examined in more detail in future work.

Knowing these relationships between viscosity, interparticle spacing and resulting homopolymer network structure, we probed the resulting heterogeneity of filled resins modified with prepolymer. First, we evaluated the behavior of PEMA-modified resins, which have a significantly higher viscosity. In Figure 8.4, we have compared the tan delta profile, post-cure of a TEGDMA resin loaded with 30 wt% filler, and one modified with 20 wt% filler and 10 wt% PEMA. Again, the TEGDMA/30 wt% filler polymer displays one peak centered about 148°C. In the PEMA-modified resin, the tan delta peak has broadened considerably. This profile can be deconvoluted into two separate Gaussian peaks, with centers at 152°C and 105°C, indicating compositionally different domains. The higher temperature domain falls very close to that of a filled poly(TEGDMA) resin, while the other falls between that of TEGDMA and pure PEMA (Table 8.1) indicating a second phase that is compositionally enriched in that of PEMA.



Figure 8.4 - Tan delta profiles of TEGDMA with 30 wt% total modification of the resin. The control matrix is TEGDMA/30 wt% Filler. In the second series plotted, PEMA is added to the matrix to induce phase separation during polymerization.



Figure 8.5 - Tan delta profiles of TEGDMA with 40 wt% total modification of the resin. The control matrix is TEGDMA/40 wt% Filler. In the second series plotted, PEMA is added to the matrix to induce phase separation during polymerization.

When the loading level of filler is increased by 10 wt% in both the control and the PEMA-modified resin, the differences between the tan delta profiles become less severe (Figure 8.5). Both profiles display one single transition. The temperature at which the maximum of tan delta is observed varies slightly, either at ~146°C or 136°C for the non-PEMA and PEMAmodified resins, respectively. Both curves have very similar shapes indicative of single-phase structure, with a degree of heterogeneity associated with it. The shift of the PEMA-modified resin to a lower T_g is expected, as linear PEMA has a T_g \sim 72.5°C (Table 8.1). If the prepolymer is randomly dispersed, and not segregated into phase domains it will slightly decrease the matrix T_g in an additive manner relative to its volume fraction, which is the behavior observed in Figure 8.5. This indicates that compositionally different phases do not form in these resins. Despite the thermodynamic driving force for diffusion of partially miscible phases, which has been observed in resins with similar PEMA loading levels in other studies,¹³ the kinetic and spatial constraints imposed by the addition of filler prohibit distinct phase separation. At this loading level of filler, the interparticle spacing is calculated to be \sim 3.5 µm. It is likely that based on the rate of reaction and diffusive properties of this resin, phase structure on this scale is not permitted. In PEMAmodified resins with lower filler contents, it is likely that the resulting domain size is larger than this value. This concept will be explored in future studies.

The same analysis was conducted on resins modified by PBMA prepolymer. We have previously demonstrated that a TEGDMA matrix modified by PBMA will have a lower solution viscosity in the monomer state than one modified by PEMA at an equivalent loading of both prepolymer and filler (Figure 8.1). With this behavior, we anticipate that the physical limitations to phase separation will be less in the PBMA-modified resins that also contain filler particles. To test this hypothesis, a loading level of 10 wt% PBMA was introduced into resins with varying

quantities of filler, as in the PEMA-based studies. The impact of PBMA modification in resins with low filler content is displayed in Figure 8.6 below.



Figure 8.6 - Tan delta profiles of TEGDMA with 20 wt% total modification of the resin. The control matrix is TEGDMA/20 wt% Filler. In the second series plotted, PBMA is added to the matrix to induce phase separation during polymerization.

As already highlighted (Figure 8.3), the TEGDMA resin modified with 20 wt% filler displays one asymmetric peak in the tan delta profile, indicating a single glass transition temperature. The resin with PBMA, which has the modification of 10 wt% filler and 10 wt% PBMA, has two local maxima, indicating two glass transition temperatures. Again, this indicates multi-phase structure of varying compositions. The transition encountered at a higher temperature (150°C), falls very close to the ultimate glass transition temperature of the TEGDMA/20 wt% filler resin (148°C), indicating one phase with similar composition to that of the composite control. The lower temperature transition, at 79°C, occurs between that of the bulk TEGDMA matrix and the pure prepolymer, which has a T_g of 22.4 °C. This intermediate T_g indicates a phase composed of TEGDMA, filler and PBMA. However, the exact composition is more difficult to predict without further investigation into whether the filler remains uniformly

dispersed throughout the entire material, or if there is segregation in the compositionally different phases.



Figure 8.7 -Tan delta profiles of TEGDMA with 50 wt% total modification of the resin. The control matrix is TEGDMA/20 wt% Filler. In the second series plotted, PBMA is added to the matrix to induce phase separation during polymerization.

The same analysis was conducted on resins modified with PBMA and with significantly higher filler content. The results are displayed in Figure 8.7, and show similar trends as the lower filler content resins modified with PBMA. Here, the total modification of both resins is 50 wt%. Again, two transitions are observed in the PBMA-modified resin. The higher temperature transition at nearly 150°C, again reasonably approximates the transition observed in TEGDMA/50 wt% filler, indicating a phase rich in poly(TEGDMA) with filler particles uniformly dispersed throughout. The slight reduction in this higher temperature transition compared with the prepolymer-free composite suggests a more significant residual prepolymer content compared to what was observed previously for prepolymer-modified, unfilled TEGDMA resin.¹³ The lower temperature transition falls between that of the bulk TEGDMA/filler

composite and the prepolymer, indicating a phase-enriched in prepolymer. The predicted interparticle spacing in the control resin here is \sim 1.8 µm. Based on these observations, compared to the PEMA-modified systems, the resins modified with PBMA appear capable of forming domains of smaller size scale.

Phase Morphology Analysis through Atomic Force Microscopy – To begin to probe our hypothesis of the decrease in domain sizes as a function of filler loading level, AFM images were collected for the TEGDMA/10wt% PBMA/40wt% Filler material, post-ambient photopolymerization (Figure 8.8). Phase structure, on the order of 1 µm or less is observed. As mentioned, at a loading level of 40-50 wt% filler into a TEGDMA matrix, the interparticle spacing will vary between 1.8 and 2.4 µm. In the image below (which in total encompasses a 3 x 3µm region of the material), it is apparent that phase domains on a smaller scale than this spacing form. However, while this result is promising, it is not conclusive from this image whether the differing phase angles measured result from PBMA-rich and PBMA depleted domains, or if the differing phase domains result from the filler and the continuous matrix. To further examine this behavior, future work will explore utilizing scanning electron microscopy (SEM) to analyze and quantify the dispersion of particulate filler in both control and phase separating resins. While SEM is not the most appropriate technique to detect differences between a poly(TEGDMA)-rich and TEGDMA/PBMA-rich phase (as they both have similar electron densities), it should be able to detect very easily the dispersion and location of filler particles. The results obtained from this can then be compared to AFM images, such as Figure 8.8.



Figure 8.8 – Phase morphology of TEGDMA/10wt% PBMA/40wt% Filler network cured at $I_o=5mW/cm^2$, post-polymerization. Scale bar = 1 μ m.

8.4 Conclusions

This study has demonstrated that PIPS is possible in spatially constricted, compositebased resins with sufficiently large interparticle spacing. In non-phase separating resins composed of TEGDMA-homopolymer and filler, the interparticle spacing decreases exponentially with increasing filler content. This corresponds to an observed exponential increase in the bulk solution viscosity in the monomeric state. Additionally, with the inclusion of filler, the glass transition temperature decreases slightly from that of poly(TEGDMA), from 161°C to ~150°C. This behavior is also accompanied by an increase in the breadth of the tan delta profile of polymerized composite materials, indicating an increase in the level of heterogeneity of the materials. When the loading level of filler into the TEGDMA-resin exceeds 60 wt%, the interparticle spacing decreases such that the T_g decreases to ~100°C and a shoulder is observed in the tan delta profile, indicating segregation of the different components and a nonuniform composite material.

Two different non-reactive linear prepolymers were introduced into the composite materials to induce phase separation during the polymerization. Again, the viscosity increases exponentially with increasing level of filler in prepolymer-modified resins. However, the magnitude of the increase is greater, as the linear prepolymer will become more entangled as the filler content increases, which can significantly increase the solution viscosity.

Both prepolymer modified resins underwent phase-separation during photopolymerization at ambient conditions. However, there exists a threshold in terms of filler content, above which phase separation is suppressed. This is likely due to physical limitations of diffusion within the resin. This threshold occurs when TEGDMA is modified by 10 wt% PEMA/30 wt% filler. When a lower viscosity prepolymer is used to induce phase separation, such as PBMA, phase separation is observed at as high loadings as TEGDMA/10 wt% PBMA/40wt% filler. Above this total modification, the pure TEGDMA resin modified with filler starts to display heterogeneous network formation, so probing phase separation at this level would be difficult as there is no control resin with which to compare.

This study exposes the ability to develop phase separated in spatially constricted resins formed under rapid, ambient photopolymerizations, which has not been explored previously. While the phase-separated structure can be developed, there does exist a threshold at which the filler content becomes sufficiently high such that phase separation is suppressed. The level at which this occurs varies based on the modifying thermoplastic prepolymer, it's molecular weight, and perhaps most importantly, it's impact on initial solution viscosity. Future studies towards this aim will investigate the resulting domain size of phase separated filled resins, and how this varies with increasing filler content.

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CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The overall goal of this dissertation is to understand the relationship between phase separation during polymerization and the resulting network properties, specifically when applied to ambient photopolymerizations. For this, a model system, which involves the bulk polymerization of a cross-linked network composed of methacrylate monomers modified with non-reactive linear prepolymers, was chosen and studied in detail.

This model system was tested for efficacy at developing phase-separated networks during ambient photopolymerizations in Chapter 3. A purely dimethacrylate resin (triethylene glycol dimethacrylate, TEGDMA) was modified by three different, non-reactive linear prepolymers (poly-methyl, ethyl and butyl methacrylate) at loading levels ranging from 0-30 wt%. A conventional photo-initiator (DMPA) was utilized so the materials could be cured through UVirradiation. At ambient conditions, all TEGDMA/prepolymer monomer resins were homogeneous and stable. With increasing modification by prepolymer, the initial resin viscosity increased exponentially. This increase in viscosity also corresponded to an overall decrease in bulk polymerization rate occurring between 10-20wt% modification, depending on the prepolymer in use. A unique feature of this model, phase-separating system is that neartransparency is recovered at the end of ambient photopolymerization. All materials tested displayed an initial decrease in light transmission, or onset of turbidity associated with the beginning of phase separation and the formation of compositionally different domains. It was found that the onset of phase separation always coincided or preceded the onset of network macrogelation. While the degree of turbidity increases at the beginning of the polymerization, between roughly 30-60% methacrylate conversion, a visible recovery of transparency in the material was observed. The exact onset of this recovery period, as well as the minimum degree of light transmission varies with the modifying prepolymer, which is an aspect that is studied in detail in later chapters. The compositions of phases formed during polymerization were estimated through the observed shift in glass transition temperature (T_g). In all cases, a phase that was essentially neat TEGDMA homopolymer, and a phase composed of 40-60 wt% prepolymer formed.

Since phase-separated polymer networks have been shown to reduce bulk polymerization development integrity shrinkage, the mechanical property and of the model TEGDMA/prepolymer system was evaluated in Chapter 4. It was demonstrated, that at significant loading levels of prepolymer (10-20wt%), volumetric shrinkage was reduced beyond what was expected based on the volume fraction of modifying prepolymer, and the same behavior was observed when monitoring polymerization stress. Despite the reduction in polymerization stress, the phase-separated networks still had a final bulk modulus equivalent to that of the TEGDMA homopolymer control. The phase-structure was probed post-ambient cure and it was found that with increasing loading level of prepolymer, the phase morphology evolves from a prepolymer dispersion to a regular co-continuous structure. The onset of macrogelation was observed as a function of conversion, and the formation of co-continuous morphology was only permitted when macrogelation was significantly delayed to higher degrees of conversion. The formation of co-continuous structure also corresponded to the most significant decrease in polymerization stress.

In Chapters 5 and 6, we explored how inherent characteristics of the non-reactive prepolymer influences phase separation during polymerization. The effect of prepolymer chainlength was the property of focus in Chapter 5. To study this, three PMMA-based prepolymers

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with molecular weights varying by an order of magnitude were developed and introduced into the TEGDMA matrix. It was found that modification of the chain-length could be utilized to alter the interplay between the competing kinetic and thermodynamic factors influencing the extent of phase separation. At an equivalent loading level, the overall free energy decreases with decreasing prepolymer chain length, as it increases the overall entropy. Therefore, as the prepolymer molecular weight decreases, a higher loading level of prepolymer is needed to induce phase separation during polymerization. If the prepolymer chain length is sufficiently small, it will behave like an inert filler in the TEGDMA matrix, and will not promote phase separation. With increasing prepolymer chain length, the kinetic limitations to phase separation during polymerization become more significant. This was attributed to increases in resin viscosity and increased entanglements between different components that limited the diffusivity of the reaction medium. It was observed that phase separation could be suppressed in rapid polymerizations containing high molecular weight prepolymers. To address this limitation, a staged-curing approach was developed. In this approach, low irradiation intensity was employed at early stages of the polymerization to provide sufficient time for phase separation via diffusion, while a latestage flood cure was utilized to ensure a high degree of conversion and modulus.

The influence of prepolymer T_g was the focus in Chapter 6. A photo-iniferter was introduced into TEGDMA-based polymerizations to produce thermally stable networks at varying extents of conversion that could be analyzed via dynamic thermal mechanical analysis. The T_g development of the neat homopolymer matrix, TEGDMA, was monitored and found to follow a second order relationship with respect to methacrylate conversion. The development of T_g in both the prepolymer-rich and TEGDMA-rich domains was monitored in phase-separating matrices. It was found that the development of TEGDMA-rich domains was accelerated in phase-separating resins when compared to the neat homopolymer at equivalent degrees of measured bulk conversion. Knowing the T_g -conversion relationship in neat-TEGDMA, the local conversion of TEGDMA-domains was estimated in phase-separating polymerizations, thus providing significant evidence for local property differentials during cure. When the modifying prepolymer had a T_g much lower than that of TEGDMA, thus maximizing the differential in thermal properties between the domains formed, the development of polymerization stress was delayed to a much higher extent of conversion, as the low T_g domains that flow more readily at ambient temperatures can compensate for volumetric changes during polymerization.

Chapters 7-8 study how structural adjustments to the bulk homopolymer matrix can be utilized to influence the resulting phase structure and expand the conditions under which these heterogeneous networks can be processed. In Chapter 7, varying amounts of a structurally similar mono-vinyl monomer was introduced as a comonomer into the bulk matrix. This modification results in a reduction of the solution viscosity and also significantly delays the onset of network gelation. This delay in gelation significantly increases the period for phase separation via diffusion in prepolymer modified systems. With increasing mono-vinyl modification of the bulk resin, a phase more enriched in prepolymer forms, as diffusional constraints are minimized compared to a bulk dimethacrylate resin. Additionally, with the extended period for phase separation, it was found that a broad range of UV-irradiation intensities (300 μ W/cm²-100mW/cm²) could be employed to form distinct phase structure. Furthermore, it was demonstrated that the incident UV-irradiation intensity could be employed as a simple tunable parameter to adjust the phase morphology.

Inorganic barium glass filler was introduced into the TEGDMA matrix to probe the efficacy of polymerization induced phase separation in spatially constricted domains associated

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with moderate to highly filled composite materials. This work, summarized in Chapter 8, focused on identifying the critical threshold at which filler modification suppresses the formation of phase-separated domains. In a pure-TEGDMA resin, the viscosity increased exponentially with increasing filler content due to a decrease of the filler interparticle spacing. To study the effect of filler content on phase separation, a constant prepolymer modification of 10wt% was maintained as the filler content in the TEGDMA resin was steadily increased. In PEMA-modified resins, which have the highest viscosity, phase separation was suppressed when the filler loading level exceeded 30 wt%, which corresponds to an interparticle spacing of approximately 5-6µm. In the matrices modified with PBMA, which contributed a slightly lower viscosity than PEMA-modified samples, no suppression of phase separation was observed up to 50 wt% filler (interparticle spacing: 3-4µm), indicating that with PBMA modification the resulting phase morphology can be constrained to smaller length scales.

9.2 Future Work & Recommendations

Recommendations for future work on this subject include two topics. The first is to define and implement approaches to probe the local differential in properties and morphology of phase structure during PIPS. A distinct advantage to the system studied in this thesis is that ondemand, rapid formation of heterogeneous networks is possible. However, the rate at which these networks form makes real-time analysis of the evolving phase structure instrumentally difficult. We have presented one approach, in Chapter 6, to estimate the local differential in thermal properties. These studies provided some understanding as to the difference in local reaction rate and thermal stability of phases formed during PIPS. However, to support these results, measurements of the local stiffness and modulus should be done using nano-indentation techniques. The use of nano-indentation as a means to estimate local properties has been successfully demonstrated in phase-separated networks formed from the copolymerization of acrylate and methacrylates.¹ With this demonstrated success, nano-indentation should be an appropriate technique for the resins we have studied in this thesis.

With this analysis, critical information about the network structure at the completion of ambient photopolymerization can be determined. First, absolute values concerning the local differential in modulus can be obtained on the phase-separated networks, which is something that cannot be de-convoluted reliably utilizing dynamic mechanical analysis. Furthermore, the resulting domain size can be extracted, and can be used to support the characterization that has already been done with AFM phase imaging. Besides post-ambient cure characterization, this analysis can also be conducted on materials that have not yet reached their full extent of conversion, thus providing experimental evidence to further support the relative differential in properties as a function of conversion, which we have estimated in Chapter 6. Little work been done to probe the relative domain size and volume fraction of phases during PIPS, and the use of nano-indentation, while only extendable to post-gelation materials, could begin to probe that property. Specifically, this analysis could provide information as to the extent free monomer diffusion and changes in relative volume fraction of phases during phase separation (again, only after network macro-gelation).

The second recommendation for future work is to expand the scope of the studies presented in Chapter 8 on PIPS in spatially constricted matrices. The decrease in size of the continuous matrix was estimated through theoretical calculations of the expected interparticle spacing. We did observe a limit, in certain materials systems, at which phase separation is suppressed. This effect has been characterized in terms of increases in solution viscosity, as well as an expected decrease in interparticle spacing. A remaining question that needs to be addressed

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in these studies is whether the estimated interparticle spacing relates to the domain size of phaseseparated morphology formed. To accomplish this, detailed analysis of the resulting phase morphology must be done. In Chapter 8, we began work on this topic using atomic force microscopy. However, this approach has proven inadequate. It is difficult to differentiate whether differing phase domains are detected from the difference between filler particles and continuous matrix, or if they are contributed from the compositionally different domains formed within the continuous matrix. Therefore, scanning electron microscopy should be utilized, as it will show significant contrast between the particulate filler and resin phase. While it may not provide enough contrast in the continuous matrix, it will at least give an estimate as to how the average interparticle spacing decreases with filler loading as theoretically expected and whether the filler remains uniformly dispersed within the separate phases when PIPS is allowed.

As mentioned, we anticipate that the suppression of PIPS in filled composite materials is due to physical and kinetic limitations, with viscosity being the most significant factor. Since similar concentrations of TEGDMA-homopolymer and prepolymer have induced phase separation in bulk, we do not anticipate that the free energy of mixing is decreasing significantly to make the phase separation process energetically unfavorable. There is a delicate balance between physical limitations to phase separation and the overall free energy of the resin that impacts the driving force for phase separation, as detailed throughout the majority of this thesis. Specifically, in Chapter 5 we addressed the influence of prepolymer chain length and how it not only impacts the physical limitations to phase separation, but also how it can either promote or suppress phase separation through changes in the overall free energy of the polymerizing resin. Furthermore, in Chapter 7 we analyzed how the bulk continuous matrix can be altered to decrease physical and kinetic constraints on PIPS. Therefore, using our knowledge of the influence of matrix and prepolymer properties, a system that can still phase separate, even in resins with high filler content, can be engineered and designed. Specifically, a combination of lower molecular weight prepolymers and continuous matrices with a lower degree of cross-linking could be utilized. By reducing the physical limitations to PIPS, and assuming that phase separation is still thermodynamically preferred, this approach could help create distinct phase domain structure on a much smaller scale than we have observed thus far (our studies have been limited to phase domains on the order of ~1µm or greater).

Beyond pushing the domain size to a level we have not observed before, this approach could also increase the interfacial area between compositionally different domains, which may enhance the observed stress reduction. This effect may be more difficult to isolate, as the interaction between filler and resin will also impact the stress reduction mechanism. However, approaches such as the introduction of reactive functionalities on the particulate filler surface could be explored to mitigate issues with the filler/continuous matrix interface.

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