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Study of Thermal Frontal Polymerization Utilizing Reactive and Non-Reactive Additives

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The University of Southern Mississippi

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by

Veronika Grace Viner

A Dissertation
Submitted to the Graduate School
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

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ABSTRACT

STUDY OF THERMAL FRONTAL POLYMERIZATION UTILIZING REACTIVE AND NON-REACTIVE ADDITIVES

by Veronika Grace Viner

December 2009

Thermal frontal polymerization is a process that involves a propagating front travelling through a monomer/initiator solution and converting monomer into polymer. The effects of different reactive and non-reactive additives on front temperature, front velocity, and pot life were studied in a thermal frontal polymerization system of multifunctional acrylates. One issue with thermal frontal polymerization of acrylate monomers is the amount of smoke and fumes produced due to high front temperatures. The effect of thermally-expandable microspheres was studied utilizing a variety of monomers. Solid additives including fillers, inert phase changer materials, and high thermal conductive fillers were investigated. The addition of liquid additives such as trithiol and plasticizer were also evaluated for their impact on front temperature, front velocity, and pot life. Most of the tested additives lowered front temperature and front velocity and were added until they caused the propagating front to quench. Only thiol affected pot life. Lowering front temperature reduced the amount of smoke produced, thus allowing these systems to be used in commercial settings. Of all of the tested additives, thiol worked best for lowering front temperature and reducing the amount of smoke produced. The behavior of fronts propagating in bifurcated media in which the front had different velocities was studied and compared to behavior predicted by Snell's law. The spatial inhomogeneities of frontal polymerization were studied using Snell's law, and it was demonstrated for the first time that thermal frontal polymerization systems follow Snell's law of refraction.

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CHAPTER I

INTRODUCTION AND OBJECTIVES OF STUDY

Introduction

Frontal Polymerization

Frontal polymerization is a process in which a monomer is converted into a polymer via a localized reaction zone or propagating front. One of the types of frontal polymerization is thermal frontal polymerization, which requires an external heat source such as a soldering iron to decompose a thermal initiator into free radicals and initiate polymerization.[1] Arrhenius kinetics and thermal diffusion control this self-sustaining process for thermal frontal polymerization.

Thermal frontal polymerization can be performed with different systems including free-radical polymerization.[1] Free-radical polymerization systems involve decomposing a free-radical initiator such as Luperox® 231 (1,1-bis(tert-butylperoxy)-3.3.5-trimethylcyclohexane) (for structure, see Table 3.1) to form radicals. These radicals then can add to a monomer such as TMPTA-n (trimethylolpropane triacrylate) (for structure, see Table 3.1) to initiate a growing polymer chain.[1] During propagation, the growing polymer chain radical adds to unreacted monomer in a series of successive addition steps. Termination occurs when two free radicals react.

Thermal frontal polymerization is illustrated in Figure 1.1:

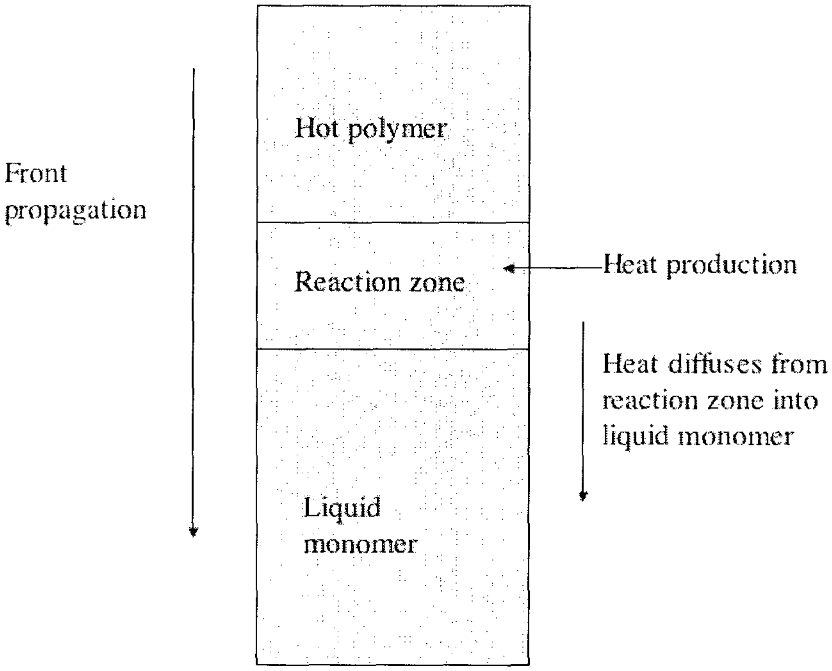


Figure 1. Diagram of Thermal Frontal Polymerization[2]

Heat is applied to the solution containing a monomer and thermal initiator in order to decompose the thermal initiator and form free radicals.[3] A fast polymerization rate occurs at the site of contact with the heat source, and heat from the exothermic reaction diffuses into the adjacent region, thereby raising the temperature of the region, decomposing more thermal initiator, and increasing the polymerization rate in the localized area. A narrow localized reaction zone is then formed and propagates through the monomer solution in the form of a thermal front.

Although thermal frontal polymerization has been around since the 1970s, the effects of reactive and non-reactive additives have not been studied in certain acrylate systems. Previous research has studied pressure, initiator concentration, and the effect of different initiators and their impact on front velocity and temperature.[4-6] The impact of thiol on front velocity in a photo-initiated thermal frontal polymerization system has also been examined.[7] A survey of one or two different representative reactive and non-reactive additives and their impact on front temperature, front velocity, and pot life has not been done before. Each representative additive may impact front temperature, velocity, and pot life in different ways. For instance, to lower front temperature, solid non-reactive additives act as heat sinks and absorb heat from the propagating front whereas inert liquid additives dilute the initiator/monomer solution and absorb heat.

Thermal frontal polymerization has many possible applications including material synthesis of useful products such as epoxy-based composites,[8,9] urethane-acrylate copolymers,[10] thermochromic composites,[11] and functionally gradient materials (materials whose composition varies spatially in a controlled manner).[12,2] Synthesis of polymers using frontal polymerization rather than other types of polymerizations has various advantages in different kinds of systems including: the ability to vary the morphology, lower energy consumption than in batch polymerization, and rapid conversion of a monomer to a polymer.[13] For example, the narrow reaction zone and subsequent rapid rise in temperature in frontal polymerization may prevent phase separation, which is a problem in the batch copolymerization of urethane-acrylate copolymers.[10]

Besides material synthesis, thermal frontal polymerization has also been used to determine whether such systems obey Snell's law of refraction.[14] Snell's law of refraction, which establishes the relationship between the angles of incidence and refraction for a wave propagating through the boundary between two media with different refractive indices, can correlate front velocity to angles of incidence and refraction in the form of $v_r/v_i = \sin \theta_r/\sin \theta_i$. Although Snell's law has been demonstrated in several reaction-diffusion systems including chemical waves in the Belousov-Zhabotinsky system (a series of oscillating chemical reactions that are a classic example of non-equilibrium thermodynamics) and in Liesegang rings (formation of rings that occurs in a chemical system that undergoes a precipitation reaction such as a drop of silver nitrate placed on a thin gel layer containing potassium dichromate), it has not been studied using thermal frontal polymerization.[15] [16] [17-20] By investigating whether Snell's law applied to thermal polymerization systems, initially a simple system composed of Luperox® 231 [1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane] as initiator, TMPTA-n (trimethylolpropane triacrylate) as monomer, and Polygloss 90 as filler was studied in order to confirm that thermal frontal polymerization systems obey Snell's law. Then, findings from this simple system can be applied to more complex systems that suffer spatial inhomogeneities.

By studying different reactive and non-reactive additives and their effect on front velocity and temperature, different systems can be developed that have desirable properties such as being smoke-free and having a long pot life (how long it takes the system to gel or bulk polymerize). Current thermal frontal polymerization systems reach temperatures as high as 250 °C and produce smoke and intense odor if the reactions are performed open to the air, thus eliminating use of them for industrial applications. A system with low front temperature, long pot life (months long compared to minutes long), and fast velocity would be ideal for some industrial applications. For example, current epoxy systems are messy and take 24 hours to cure so that thermal frontal polymerization with its high front velocity is a feasible alternative.

It was hypothesized that one way to lower front temperature is to add filler. However, if too much filler is added, quenching of the front can occur. Another hypothesized way was to add thiol, a reactive additive, which could also lower front temperatures by acting as a diluent and lower front velocity by undergoing a reaction with the acrylate monomer. The thiol can undergo copolymerization with the monomer, a reaction that occurs at a slower rate of reaction than homopolymerization of the monomer itself and produces less heat, so that a lower front velocity might occur.[7] However, addition of the thiol will not only lower front temperature but will also lower front velocity.

It was further hypothesized that the addition of other additives such a plasticizer, which increases the flexibility of a polymer, could act as a diluent and, like a thiol, also lower the front temperature of frontal polymerization system so that less smoke is produced. In addition, by not reacting with any of the other components of the system, the pot life of the system should not be affected. Furthermore, it was predicted that inert phase change materials could also lower front temperatures by melting at temperatures lowering than the front temperature. Thus, inert phase change materials might lower the front temperature without significantly affecting the front velocity.

Besides the production of smoke, cracking from the expansion and contraction of polymer in the propagating front is an issue with thermal frontal polymerization systems.[1] Brittle or easily broken polymers are another problem. Addition of plasticizer or thiol should reduce cracking.

Objectives of Study

The major goal of the dissertation was to determine the effects of different types of additives on the front temperature, front velocity, pot life, and qualitative nature of the products for thermal frontal polymerization of multifunctional acrylates. The additives were chosen in order to identify ones that would lower front temperature without decreasing the pot life. By lowering front temperature, the amount of smoke and fumes produced would be reduced, thus allowing the polymerizable systems to be used in commercial settings. An additional goal was to examine the effect of spatial inhomogeneities on the front propagation.

The first objective was to examine the effects of expansion on frontal polymerization. This was accomplished by adding thermally-expandable microspheres to a frontally polymerizable system. A frontally-polymerized system that expands has potential for use where holes need to be filled with materials and where it is desirable to have a long pot life but also a cure-on-demand capability. Examples include water- and fire-stops, the sealants around pipes and conduits in buildings. The effects of microsphere properties and loading on front properties such as front temperature and front velocity were examined. The influence of microsphere properties and loading on polymer properties such as degree of cracking was also addressed.

The second goal was to determine the effect of reactive and non-reactive additives on front temperature, velocity, and pot life. The qualitative effect of these additives on the degree of cracking (amount and number of cracks compared to other systems), amount of smoke produced, and brittleness of the system (how easy it was to break the polymerized strip apart to extract the thermocouple wire) was also performed. In certain cases, some factors including initiator choice, initiator concentration, monomer choice, filler choice, and/or filler loading were examined in order to confirm that the additive itself rather than the other components in the system was causing the change in front temperature, front velocity, and/or pot life. In one chapter, different monomers were evaluated with thiol or plasticizer in order to determine whether addition of different monomers could lower the front temperature, produce a smoke-free system, and still have complete polymerization of the strip.

Because of the many different types of reactive and non-reactive additives that could be tested, only a one or two representatives of each type were evaluated for its effect on front temperature, front velocity, and pot life. Thus, different types of solid inert additives such as filler and high thermal conductivity filler and liquid additives such as thiols and plasticizers were evaluated. Only in the case of inert phase change materials when nine different materials were evaluated was a more extensive study of one type of additive and its effect on pot life, front temperature, and front velocity done.

After studying the various effects that additives have on thermal frontal polymerization systems, one simple system was studied using Snell's law. Snell's law was studied because it can be used to understand how inhomogeneities can affect frontal polymerization. Snell's law, in particular, was studied because it correlates refractive indexes to velocity, and velocity can be easily controlled by varying initiator concentration in acrylate monomer systems for thermal frontal polymerization systems. Varying initiator concentrations should result in refraction in angle of the propagating front when it passes through boundary between systems with two different initiator concentrations. Thus, inhomogeneities and how they affect frontal polymerization can be studied. A system composed of Luperox® 231, TMPTA-n, and Polygloss 90 with various initiator concentration was studied to determine whether thermal frontal polymerization systems obey Snell's law. By first studying a simple system, the findings of this system can then be applied to a more complex system with inhomogeneities.

Selection of The System To be Studied

Free-radical polymerization fronts[1] were selected because velocities of such fronts can be easily controlled by changing the concentration of the initiator.[21,22] Two initiators, BPO and Luperox® 231, were used. BPO was used because it is cheap and commonly used in industry. Also, BPO can undergo a redox reaction with accelerators such as dimethyl aniline. Luperox® 231 was sometimes used because it produces less gas per initiating radical than any other peroxide initiator and is room-temperature stable.[23] Thus, bubbling, an interference of thermal frontal polymerization, was minimized.

Acrylates, in particular multifunctional acrylates, were selected because acrylates are highly reactive and because multifunctional acrylates have a front velocity a magnitude order greater than monofunctional acrylates.[7,21,22] Thus, more filler could be added without causing a front to quench.

Filler was added in order to give systems the consistency of putty, thus eliminating the effects of buoyancy-driven convection in the medium.[24] Kaolin clay or Polygloss 90 was typically used as filler because of its cohesiveness and more of it than other fillers such as silica could be added without causing a front to quench.

The putty was spread uniformly on a 2-cm thick wooden surface and constrained between wooden strips to provide thermal insulation beneath the putty and at the sides.

By performing the experiments under quasi-adiabatic conditions, the effects of heat losses on the front shape were reduced.

Rationales for the selections of other additives such as inert phase change material, thiols, and plasticizers are explained in later chapters.

CHAPTER II

LITERATURE REVIEW OF FRONTAL POLYMERIZATION

Introduction

Frontal polymerization occurs when a monomer is converted into a polymer in a localized reaction zone.[1] Thermal fronts, one class of frontal polymerization, are initiated using a heat source like a soldering iron. The localized reaction zone in thermal fronts propagates because of the coupling of thermal conduction and Arrhenius reaction kinetics.[25, 26]

Thermal frontal polymerization occurs with different systems including free-radical polymerization.[1] Free-radical polymerization systems involve decomposing a free-radical initiator such as Luperox® 231 (1,1-bis(tert-butylperoxy)-3.3.5-trimethylcyclohexane) to form radicals, which then can add to a monomer such as TMPTA-n (trimethylolpropane triacrylate) to initiate a growing polymer chain.[1] During propagation, the growing polymer chain radical adds to unreacted monomer in a series of successive addition steps. Termination occurs when a free radical polymer chain reacts with another free radical chain.[1]

Thermal frontal polymerization of a free-radical polymerization system is illustrated in Figure 2.1:

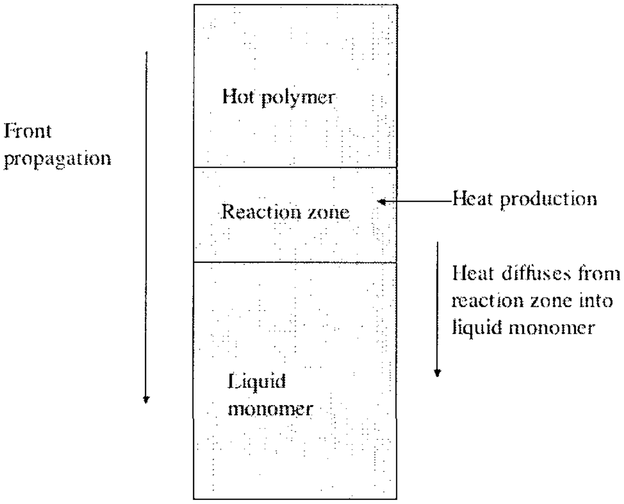


Figure 2.1. Diagram of Thermal Frontal Polymerization[2]

For a free-radical polymerization system, heat is applied to the liquid monomer solution containing a monomer and thermal initiator in order to decompose the thermal initiator and form free radicals.[3] A fast polymerization rate occurs at the site of contact with the heat source, and heat from the exothermic reaction diffuses into the adjacent region, thereby raising the temperature of and increasing the polymerization rate in the localized area. A narrow localized reaction zone is then formed and propagates through the monomer solution in the form of a thermal front.

Thermal Frontal Polymerization: Early Russian Experiments

Chechilo and co-workers were the first to study thermal frontal polymerization in 1972 by investigating the polymerization of methyl methacrylate under high pressure (> 3000 atm).[5] Using benzoyl peroxide as the initiator, the rate of front propagation was studied using thermocouples to record the temperature differences in the system. They studied the system under high pressure and discovered a direct correlation between pressure and front velocity. Increasing the pressure increased the front velocity because of the resulting increase in heat conductivity. The front velocity was also increased by increasing pressure, which effectively increased the polymerization rate constant.

Further studies on the effect of the pressure and initial temperature of the reaction mixture by Chechilo and Enikolopyan revealed that as pressure increases, the maximum temperature gradient at the propagating front, the front rate, and the maximum spontaneous-heating temperature increase.[4] Chechilo and Enikolopyan used a liquid-phase free radical polymerization of methyl methacrylate and found that increasing the pressure prevents boiling in the polymerizing medium and convective breakdown of the propagating front by increasing the viscosity of the monomer. Increasing the initial temperature of the front increased the rate of the front linearly when the initial temperature was between 50-60 °C, but above this range, spontaneous heating of the mixture, inconsistent propagating front rate, and bulk polymerization occurred.

Besides initial temperature and pressure effects on frontal polymerization, Enikolopyan *et al.* also examined the molecular weight distribution in thermal frontal and isothermal but not frontal polymerization and used Arrhenius kinetics to explain that the initiator concentration is irrelevant to calculation of the distribution function of the reaction product according to the molecular weight and its first three moments if the initiator concentration is used in large enough quantities.[27] If, on the other hand, the initial concentration is low, then the consumption of the initiator must be taken into account for calculating the molecular weight distribution, and initiator concentration can limit the maximum conversion so that the maximum temperature gradient of the propagating front is altered very little by increasing the initial temperature. Using mathematical calculations, Enikolopyan *et al.* theorized that the molecular weight distribution should be broader in isothermal polymerization than thermal frontal polymerization.[27, 28]

To study the effect of concentration and the type of free-radical initiator on thermal frontal polymerization, Chechilo and Enikolopyan used di-tert-butyl peroxide, benzoyl peroxide, and cyclohexylperoxide carbonate.[6] They found that the thermophysical properties of the monomers were not substantially altered when the concentration of the initiators was varied within a limited range; this result indicates that, when the initiator contraction is varied, the propagation rate is related to the change in polymerization kinetics and not to any change in thermal diffusivity. Increasing the initiator concentration in a narrow range increases the effectiveness of the initiation of the front so that increase of the maximum temperature gradient of the propagating front and reaction rate in the thermal front occur; however, when the concentration of the different initiators was the same, the maximum temperature gradient values were almost the same, indicating that a change of the initiator has very little effect on the maximum conversion rate of monomer to polymer. Since the concentration and nature of the initiator have limited or minimal effect on the maximum temperature gradient and the rate of conversion, the rate of polymerization in the initial reaction stage in the propagating front mainly determines the propagation rate. However, work in the Pojman lab contradicts these findings and has found that the type of initiator does have a significant impact on the front velocity.[21]

Davtyan *et al.* examined the role of the gel effect (autoacceleration of the polymerization rate) on free radical polymerization of methyl methacrylate and n-butyl methacrylate.[29, 30] For bulk polymerization, the gel effect occurs when, as viscosity increases, the rate of termination decreases and causes autoacceleration of the reaction.[1,29] Autoacceleration of the reaction is mainly dependent on the nature of the monomer and initiator concentration as well as polymerization temperature and system used. Davtyan and his co-workers discovered that the gel effect and high pressure increased the front velocity.

Thermal Frontal Polymerization: Mechanisms

Thermal frontal polymerization has been most studied with free-radical polymerization systems and especially with acrylates. For radical polymerization, the system involves a free-radical initiator, monomer, and sometimes filler. To initiate polymerization, a heat source such as a soldering iron is applied to the free radical system in order to decompose the initiator. In the first step, the free-radical initiator is decomposed to form two free radicals:

$$I \rightarrow 2\,R\bullet \qquad [1]^{1}$$

To start a chain propagation reaction, a free radical then reacts with a monomer:

$$R\bullet + M \rightarrow P_1\bullet \qquad [2]$$

$$P_n\bullet + M \rightarrow P_{n+1}\bullet \qquad [3]$$

The polymer chain continues to grow until a polymer chain radical reacts with another chain radical or initiator radical:

$$P_n\bullet + P_m\bullet \rightarrow P_{n+m} \qquad [4]$$

The autocatalysis of free-radical polymerization is driven by the decomposition of the initiator in equation 1, which has a high energy of activation; however, the major heat release occurs in the propagation step.[31, 6] To establish a connection between the energy of activation for the decomposition of the free-radical initiator and the effective activation energy E_{eff} of the entire polymerization process, a steady-state assumption is made:

$$E_{eff} = E_p + (E_d - E_t)/2 \quad [5]^{31}$$

where E_p is the activation energy of the propagation step; E_d is the activation energy of the initiator decomposition step; and E_t is the activation energy of the termination step. The activation energy of the initiator decomposition step, E_d, depends on the initiator; so because E_d is much larger than the other activation energies, its value generally dominates the effective activation energy.[1, 31] Thus, the initiator plays an important part in determining whether a front will exist and what the front velocity and temperature profile will be. Since free-radical polymerization is not a stoichiometric reaction, a minimal amount of initiator can lead to almost complete polymerization of the monomer.

However, the amount of initiator does influence the front velocity and the molecular weight of the polymer.[22, 21]

Types of Monomers

Different classes of monomer occur. One type is thermosets or cross-linking monomers, which produce rigid cross-linked polymers and provide a sharp interface between the polymer and monomer. Another type is monomers that produce polymers insoluble in the polymer itself, and the third type is thermoplastictics or highly reactive monomers that produce thermoplastic polymers.[1] Examples of thermosets include trimethylolpropane triacrylate (TMPTA-n), divinylbenzene, and tri(ethylene glycol)dimethacrylate (TGDMA). The second class includes acrylic and methacrylic acids. For this second type, an interface between the polymer and monomer occurs during polymerization with the polymers adhering to one another or to the sides of the reaction vessel. However, fingering may occur from Rayleigh-Taylor and double-diffusive instabilities.[1] Fingering is the result of the polymer being denser than its corresponding monomer and melting at the temperature of the propagating front so that drops of polymer descend into the unreacted monomer, thereby removing heat from the propagating front, sometimes quenching the reaction, and igniting spontaneous polymerization.[32] A Rayleigh-Taylor instability occurs when an unstable horizontal layer of more dense fluid is over a less dense fluid.[33]

The third class of monomers forms polymers that are molten at the temperature of the propagating front. Like the second class or type of monomers, the third class can exhibit the Rayleigh-Taylor instability. Examples of this third group include butyl acrylate and methacrylate esters and other acrylates. The addition of an ultra-fine silica gel such as Cabosil or soluble polymer prevents the collapse of the front. However, addition of a filler prevents formation of a homogeneous polymer unless the polymer is miscible in the monomer and is added before polymerization is initiated.[1]

Applications of Frontal Polymerization

Frontal polymerization has a variety of possible applications including material synthesis, preparation of interpenetrating polymer networks, curing large composites, filled materials, and microfluidic uses. Thermochromic composites,[11] interpenetrating polymer networks,[34] thick[35] and film-dispersed[36] liquid crystals materials, and functionally gradient materials (materials whose composition varies spatially in a controlled manner)[12, 2] have been synthesized using frontal polymerization. Synthesis of polymers using frontal polymerization rather than other types of polymerizations has various advantages in different kinds of systems including: the ability to vary the morphology, lower energy consumption than in batch polymerization, and rapid conversion of a monomer to a polymer.[13] For example, the narrow reaction zone and subsequent rapid rise in temperature in frontal polymerization may prevent phase separation, which is a problem in the batch copolymerization of urethane-acrylate copolymers.[10]

In 2006, Hu *et al.* synthesized urethane-acrylate copolymers via free-radical frontal polymerization.[10] Urethane-acrylate copolymers have potential use as precursors for products with hardness, flexibility, and abrasion resistance. Such properties are suitable for aeronautic and automobile industries for composite materials and coatings.

Utilizing an urethane-acrylate macromonomer and 2-hydroxylethyl acrylate, the reactants and ammonium persulfate initiator were dissolved in dimethyl sulfoxide (DMSO), and the front was initiated by applying a soldering iron to the walls of the tube. The persulfate initiator was used to avoid bubbling from peroxide or nitrile initiators. DMSO was used as the solvent to make all reactants and initiator miscible with each other. Thermal gravimetric analysis (TGA) revealed that pure samples of urethane-acrylate polymers were produced and that these copolymers had higher thermal stability (more stable at higher temperatures) than polyurethane samples prepared via frontal polymerization. Synthesizing urethane-acrylate copolymers via frontal polymerization rather than batch copolymerization has several advantages. Because of the narrow reaction zone and swift rise in temperature in frontal polymerization, phase separation due to incompatible compositional drifts, one of the major drawbacks of batch copolymerization, could be reduced so that phase separation is limited and narrow chain composition distributions are produced; Hu *et al.* did not demonstrate this advantage conclusively. Moreover, synthesizing in DMSO creates the problem of purification.

Szalay *et al.* polymerized an alternating styrene-maleic anhydride copolymer using free-radical frontal polymerization.[37] The free-radical initiator was 2,2-azobisisobutyro- nitrile (AIBN). Frontal polymerization provided a simple way to copolymerize styrene and maleic anhydride at high temperatures. In 2004, Chen *et al.* synthesized polyurethane-nanosilica hybrid nanocomposites.[38] The polyurethane hybrids produced via frontal polymerization had the same properties as though synthesized by batch polymerization with stirring, but the frontal polymerization method required less time than the batch polymerization technique.

Free-radical frontal polymerization with a microencapsulated initiator was developed to increase the pot life of the system.[39] The patent-pending invention extends the pot life of a polymerizable curing system, which can be used in adhesive formulations, polymer repair, and reinforcement of construction elements. The front velocity was lower than with dissolved initiator.

In another patent, Pojman *et al.* synthesized functionally gradient polymeric materials with short conversion times and several centimeters in thickness.[12] Frontal polymerization with its shorter conversion times is a greater advantage to the diffusion method, which can require as much as 280 hours to create a gradient over 10 microns. Gradient polymeric materials such as Gradient Refractive Index materials have many applications in optics but are generally prepared by isothermal frontal polymerization. An optical limiter, a device that attenuates intense optical beams but allows high transmittance at low-level light, can protect human eyes from intense laser pulses. Such a device may be made from a gradient material with nonlinear optical dye dissolved in a polymer matrix. Metallophthalocyanine complexes with heavy central atoms are compatible with poly(methyl methacrylate) and are miscible in this monomer; this system offers the advantage of low cost. Although different systems could be designed, use of tricaprylmethylammonium persulfate permitted the formation of bubble-free optical materials.

Frontal polymerization also may be used for the consolidation of the stone of historical landmarks.[40] Polymers, if chosen correctly, tend to have a protective property because of their water-repellent properties and may be better choices than inorganic materials. Sorption and polymerization of the monomer are traditionally done by soaking the stone in the monomer and then heating it for a prolonged period in an oven. Frontal polymerization may be a superior alternative because of a self-sustaining front that propagates throughout the reactor. Higher conversion rates, solvent-free systems, and no need for heat sources offers advantages in no purification procedure needed, low costs, and low environmental impact.

Microporous polymers have interconnected pores with a rigid, extensively cross-linked polymer matrix and have been used as chromatographic materials, catalytic surface and supports, solid-supported reagents, supports for combinatorial synthesis, and in separation and adsorbent media; microporous polymers can also be synthesized more efficiently using frontal polymerization than suspension polymerization.[41] Suspension polymerization occurs when the monomer (discontinuous phase) is suspended in water (continuous phase); a monomer-soluble initiator and suspension stabilizer, which prevents the monomer droplets are coalescing, are added to the monomer and vigorously mixed.[42] A series of glycidyl methacrylate-ethylene dimethacrylate copolymers were created via thermal frontal polymerization and suspension polymerization.[41] With AIBN as the initiator, frontal polymerization generated more microporous polymers with narrow pore size distribution and higher internal pore volume and surface area than microporous material produced from suspension polymerization. Although frontal polymerization was a more efficient and faster reaction than suspension polymerization, the surface morphologies were inferior for its products compared to microporous material formed from suspension polymerization.

Air pollution from volatile organic compounds resulting from the use of low-boiling toxic components in polymeric materials is important in today's environmentallyconscious world.[43] Fiori *et al.* cured unsaturated polyester resins using frontal polymerization and used hydroxyethyl acrylate in place of styrene, an air pollutant commonly used as a curing agent because of its low cost, and prepared unsaturated polyester resins. Frontal polymerization was a faster method than the conventional technique for hydroxyethyl acrylate and did not require continuous energy supply to continue polymerization. Little to no difference in physical properties of the polymers no matter whether frontal polymerization or the conventional technique was used.

Nason *et al.* used a mixture of photoinitiator and thermal initiator for systems composed of a methacrylate or acrylate and trithiol [trimethylolpropane tris-(3-mercaptopropionate)].[7] Using a variety of monomers, they found that the double bond per molecular weight influenced front velocity and how long it took to initiate polymerization. Addition of a trithiol allowed a reaction between the (meth)acrylate and thiol so that the total heat released from the system was reduced and oxygen inhibition was removed. Because of this copolymerization reaction, slower front velocities occurred.

Interferences to Thermal Frontal Polymerization

A significant interference to thermally propagating fronts is bubbles. Bubbles form due to decomposition of peroxide and nitrile initiators. Volatile byproducts such as acetone and carbon dioxide are formed as gases and distort the propagating front, increasing the front velocity by up to 30%.[1] Bubbles may also form due dissolved gas and water in the monomer. Defoaming agents such as BYK-060 N (solution of foam-destroying polymers and polysiloxanes with diisobutylketone as solvent) help to reduce bubbling by lowering the free energy of nucleation and thus creating many small bubbles instead of large ones. High pressure also eliminates bubbles as evidenced by the lack of bubbles in experiments done by Chechilo *et al.*[1, 5]

Low conversion is another inherent problem with frontal polymerization that may result in low conversions of monomer to polymer. A rapid increase in the temperature causes rapid initiator decomposition or "burnout."[1] A dual initiator system or use of a more temperature-stable initiator can circumvent this problem.[44] Pojman *et al.* tested a dual system of benzoyl peroxide and t-butyl peroxide and found an advantage: the least stable initiator determined the front velocity by providing a fast front rate whereas the stable monomer raised the conversion.[21] A stable initiator converts monomer to polymer almost as well as a dual system of initiators but better than a less temperature-stable initiator by itself.

Thermodynamics can also limit conversion so that the front is limited by the ceiling temperature, thereby preventing further polymerization from occurring.[1] Since frontal polymerization reactions are exothermic, as the system temperature increases equilibrium conversion decreases.[45] The entropy and enthalpy of the polymerization system determine the maximum conversion for an adiabatic system:

$$\alpha = 1 - \exp[(\Delta H^0 - T^*\Delta S^0)/R^*T]/[M]_{\text{initial}} \qquad [11]^1$$

where α is the maximum conversion, ΔH^0 is the change in enthalpy, T is the temperature, ΔS^0 is the change in entropy, R is the ideal gas constant, and $[M]_{\text{initial}}$ is the initial monomer concentration. Another equation that establishes the relationship between the temperature and the conversion is:

$$T = T_i + \alpha^*[(\Delta H^0/C_p \qquad [12]^1$$

where T is the temperature, T_i is the initial temperature, α is the maximum conversion, ΔH^0 is the change in enthalpy, and C_p is the specific heat of the monomer. When equations 11 and 12 are solved, the maximum conversion can be calculated. For example, adiabatic polymerization of methyl methacrylate at an initial temperature of 25 °C, the calculated maximum conversion was 0.93.[1] This value indicates that, due to the high front temperature, complete conversion can never occur.

Heat loss due to convection (buoyancy-driven convection in systems with liquid monomers) can also cause distortions in frontal polymerization by causing the front to become curved in shape and can even quench the reaction; convection works by transporting energy from the hot reaction zone to the cool, unreacted monomer. Large thermal gradients between the exothermic reaction zone and cool, unreacted monomers and concentration gradients make polymerization fronts susceptible to convection.[23] Convection plays an important role in frontal polymerization because almost all frontal polymerization systems involve liquid monomers or reactions in solutions.[31] Depending upon the geometry of the system, initiating a front horizontally may help prevent convection in the air outside the polymer system. The application of wooden barriers surrounding the polymer mixture and performing the polymerization on a wooden substance can help reduce heat loss. The addition of inert filler like Polygloss 90 or silica gel will increase the viscosity of a system so that convection is minimized.

Use of filler like fumed silica can also prevent convective fingering, which can distort the shape of the front and remove heat from the hot zone of the propagating front. The filler works by increasing the viscosity of the monomer so that density differences between the monomer and polymer are reduced.[46]

CHAPTER III

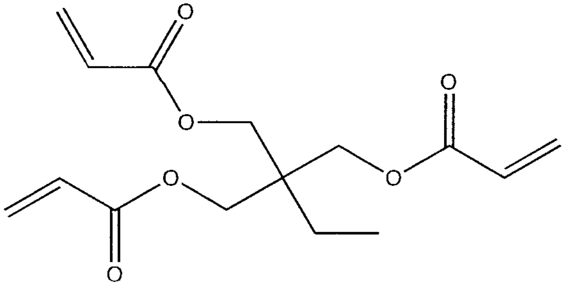
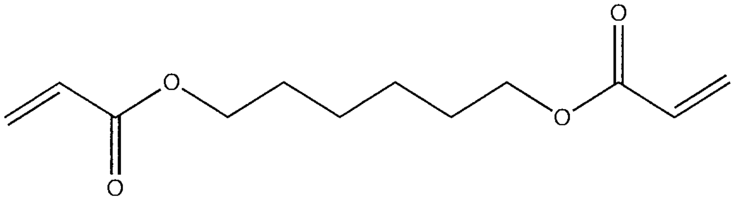
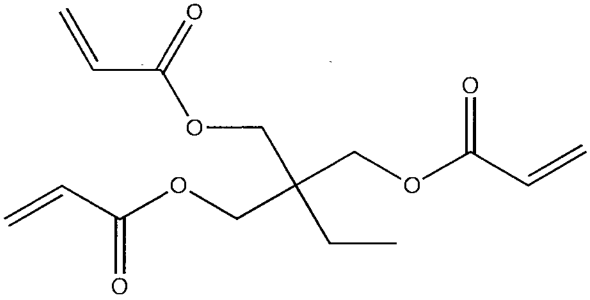
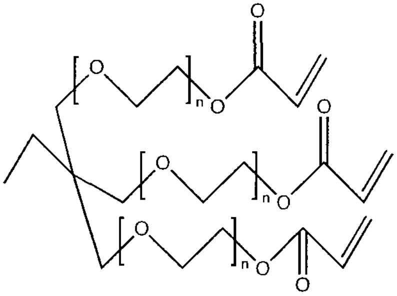
METHODOLOGY

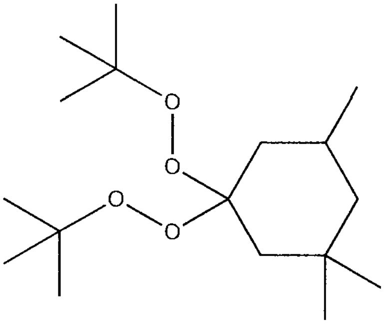
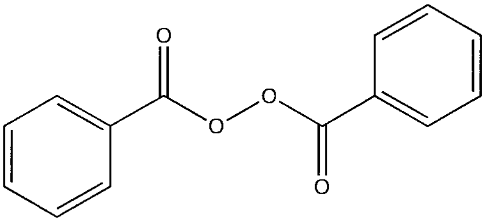
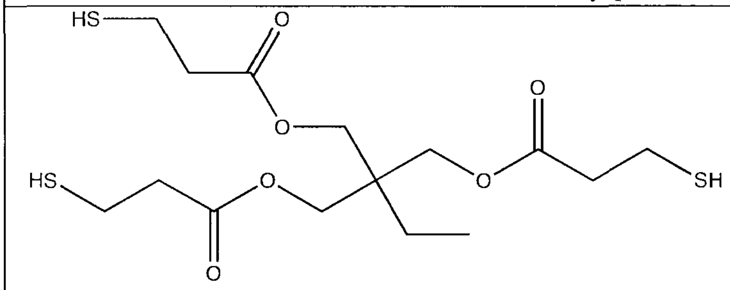
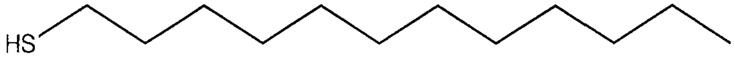
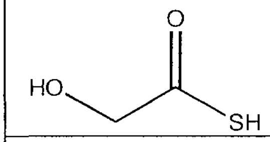
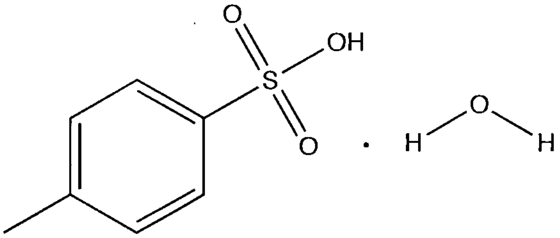
All chemicals were used as received. Trimethylolpropane triacrylate (TMPTA-n) and HDODA were obtained from CYTEC, Surface Specialties. TMPTMA and TMPEOTA I, II, and III were obtained from Sigma-Aldrich. Luperox® 231 was obtained from Atofina and BPO, *tert*-butyl peroxybenzoate, and *para*-toluenesulfonic acid monohydrate from Sigma-Aldrich. Dibutyl phthalate was obtained from Sigma-Aldrich. Trithiol [trimethylolpropane tris-(3-mercaptopropTTionate)], thiolglycolic acid, and 1-dodecanethiol were obtained from Sigma-Aldrich. Polygloss 90 and Cabosil were obtained from Huber materials and US Composites, respectively. Bromophenol blue and DMSO were obtained from Aldrich. Expancel DU 80 was obtained from AkzoNobel. Phase change materials including stearic acid, succinic anhydride, benzophenone, *para*-toluic acid, L-tartaric acid, *trans*-cinnamic acid, phenylacetic acid, *n*-lauric acid, D,L-mandelic acid, and myristic acid were obtained from Sigma-Aldrich. Aluminum powder was obtained from Sigma-Aldrich, and graphite was obtained in the form of graphite lubricant from Wal-Mart. BYK 060 N was obtained from BYK Chemie.

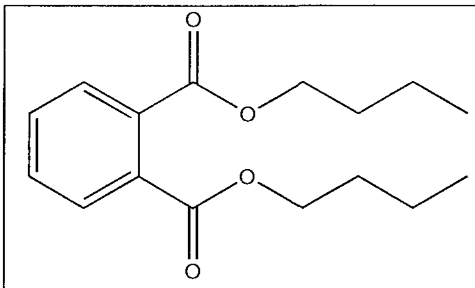
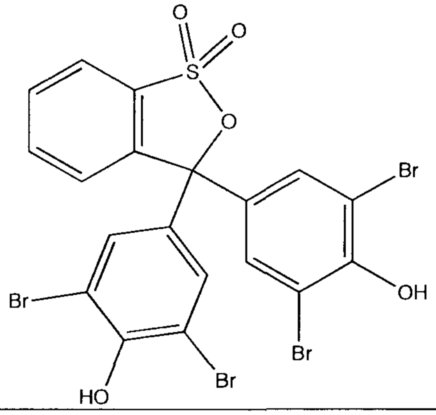
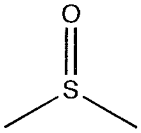
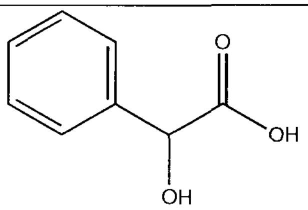
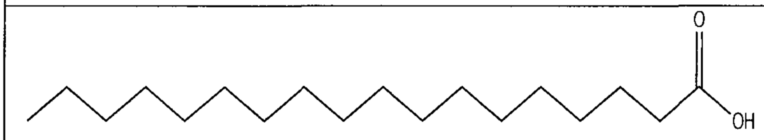
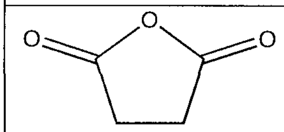
Structures of all chemicals used are listed below in Table 3.1.

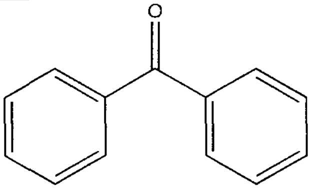
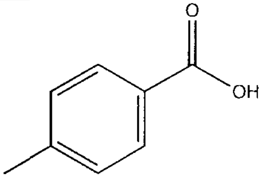
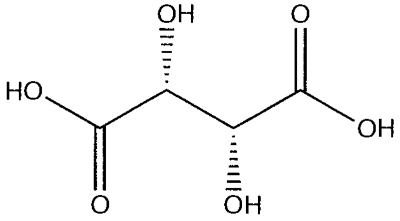
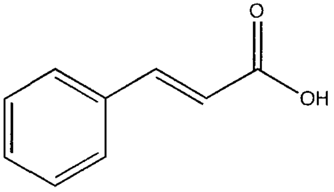
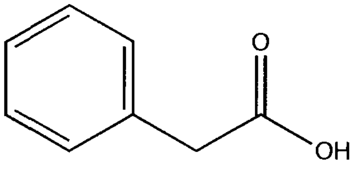
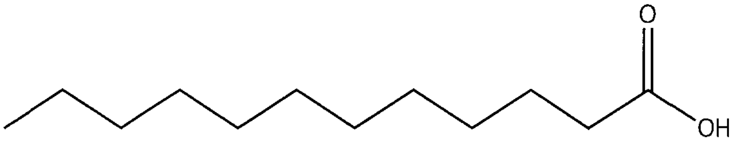
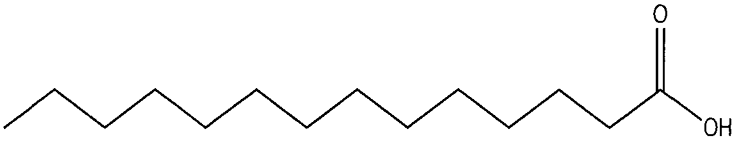
Table 3.1

Structures of Chemicals Used

Structure/Name	Abbreviation
 Trimethylolpropane triacrylate	TMPTA-n
 1,6-hexanediol diacrylate	HDODA
 Trimethylolpropane triacrylate	TMPTMA
 Trimethylolpropane ethoxylate triacrylate	TMPEOTA

 1,1-Bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane	Luperox® 231
 benzoyl peroxide	BPO
 [Trimethylolpropane tris(3-mercaptopropionate)]	Trithiol
 1-dodecanethiol	1-dodecanethiol
Thiolglycolic acid 	Thiolglycolic acid
 Para-toluenesulfonic acid monohydrate	*para*-toluenesulfonic acid monohydrate

 Dibutyl phthalate	DBP
3',3'',5',5''-Tetrabromophenolsulfonephthalein 	Bromophenol blue
 Dimethyl sulfoxide	DMSO
 D,L-mandelic acid	D,L-mandelic acid
 Stearic acid	Stearic acid
 Succinic anhydride	Succinic anhydride

 Benzophenone	Benzophenone
 Para-toluic acid	*Para*-toluic acid
 L-tartaric acid	L-tartaric acid
 Trans-cinnamic acid	*Trans*-cinnamic acid
 Phenylacetic acid	Phenylacetic acid
 n-Lauric acid	*n*-lauric acid
 Myristic acid	Myristic acid

Preparation of x phr BPO or Luperox® 231 in Monomer

1-10.4 g of initiator was added to 100 g of TMPTA-n or other monomers and dissolved overnight in the solution with stirring to make 1-10.4 phr (parts per hundred resin) BPO in monomer or stirred by hand using a wooden tongue depressor to make 1-10.4 phr Luperox® 231 in monomer.

General Procedure

Once initiator was dissolved in monomer, all liquid components were combined together in a sample vial. In a plastic bowl, all solid components including filler were mixed together before being combined with the liquid components. The contents were thoroughly mixed using a wooden tongue depressor before being molded into a strip. For systems with Luperox® 231 as initiator, a dye, 0.040 M bromophenol blue in DMSO, was added to enhance visualization of the propagating front. The strip was then placed on a 2-cm thick piece of wood and surrounded by wooden barriers. A soldering iron was applied to one end of the strip until a front was ignited. A movie of the strip was recorded using an iSight camera connected to a G4 Mac computer. Multiple runs (3-7) of each system were done to confirm reproducibility of the results.

Expancel Systems

Systems with different monomers, initiators, initiator concentrations, fillers, and filler loadings were prepared using the procedure described above and had a total mass of 10.0-25.0 g. In cases where two monomers were used, the initiator was dissolved in the monomer before the two monomers were then mixed together.

Rectangle Set-up

The systems were molded into rectangles 10 cm wide x 15 cm long x 0.5 cm depth with the 15 cm edge of each system touching the other system. Systems with the high initiator concentration had more bromophenol blue indicator added in order to clearly differentiate between two different systems.

Parallel Strips Set-up using Expancel DU 80

Systems were molded into strips (2.0-2.5 cm wide x 12-17 cm long x 3-5 mm), placed parallel to each other with the longest edge of the strips touching, and initiated by having the soldering iron applied at the point where the two strips were molded together.

Unusual Molded Putty Set-ups

The systems were then molded around a 10-mL glass pipette or into a 20-mL scintillation vial with an outer diameter of 28 mm and height of 57 mm or molded into a ball. Fronts were then initiated by application of a soldering iron to the top of the sample vial, an edge of the system wrapped around the pipette, or radially inside the center of the ball.

Ball and Strip Set-ups

The TMPEOTA system was molded into a ball and initiated radially via application of a soldering iron to the surface or interior center of the ball or molded into a 1-2 cm wide x 5-8 cm long x 3-5 mm depth strip, placed on a 2-cm thick piece of wood, surrounded by wooden barriers, and initiated via application of a soldering iron to one end of the strip.

Regular Strip Set-up

Systems were molded into 2.5 cm wide x 5.5-6.5 cm long x 3-5 mm depth strips or 1.0 cm wide x 8 cm x 3-5 mm depth strips, placed on a 2-cm thick piece of wood, surrounded by wooden barriers, and ignited at one end via application of a soldering iron. Front temperatures were measured by placing a type "K" thermocouple wire in the middle of the strip and using a 450 AKT Omega thermocouple thermometer reader. The highest recorded front temperature was taken to be the front temperature of the propagating front.

Fillers Experimental Procedure

Following the general procedure, systems were prepared using different initiators, fillers, and inert phase change materials. TMPTA-n was used as monomer. For the reactive phase change material system, the reactive phase changer material and filler were mixed together before the solid acid, *para*-toluenesulfonic acid monohydrate, was added and mixed with the other solid components. Systems had a total mass of 10.0 or 25.0 g.

Ignition of Propagation in Polymerizable Systems

Strips with dimensions of 2 cm x 4 cm x 4 mm were placed on a 2-cm thick piece of wood and surrounded by wooden barriers. A front was ignited at one end of the strip with a soldering iron. The front temperature was measured using an 456 AKT OMEGA reader and type “K” thermocouple wire with the highest recorded front temperature taken to be the front temperature of the propagating front. Movies of the strips were recorded using an iSight camera connected to a PowerBook G4 Mac computer running iMovie. The movie was then converted into a Quicktime movie before the movie was further converted into a sequence of images at the rate of 1 frame per second. The images were analyzed using Adobe Photoshop. The velocity in each strip was calculated from a plot of position versus time.

Procedure for Liquid Additives and Mixed Monomer Systems

Following the general procedure described above, BPO was used as initiator, and Polygloss 90 was used as monomer. For systems with mixed monomer systems (TMPEOTA/TMPTA-n and dodecyl acrylate/TMPTA-n), the initiator was dissolved in the monomer before the two different monomers were mixed together. Then, any additional liquid additives such as thiol were combined with the two monomers and thoroughly mixed before the filler was added to the liquid components to make a putty. The systems had a total mass of 10.0 g. Systems placed on a wooden substrate followed the same initiation method described for the Filler Experimental Procedure.

Preparation of Systems Containing x ppm LiCl in TMPEOTA II

Various amounts of LiCl (0.001-0.004 g) was added to 20 g of TMPEOTA II and stirred overnight to make 50-200 ppm LiCl in TMPEOTA II. For 25 ppm LiCl, 10 g of TMPEOTA II was added to 10 g of 50 ppm LiCl in TMPEOTA II and stirred overnight to make 25 ppm LiCl in TMPEOTA II. Then, 4.40 g of the resulting x ppm LiCl in TMPEOTA II was mixed with 0.65 g trithiol and 0.85 g 1 phr BPO in TMPTA-n before 4.10 g of Polygloss 90 was added.

Ignition of Propagation in Polymerizable Systems on Stainless Steel Surfaces

Strips with dimensions of 2 cm x 4 cm x 4 mm were placed on a 1-mm thick piece of stainless steel. A front was ignited at one end of the strip with a soldering iron.

Procedure for HDODA and TMPTMA Systems

HDODA Systems

In contrast to the general procedure, the initiator was not dissolved in monomer before mixing any of the components. Instead, solid BPO was mixed with the filler before HDODA was added. In cases where plasticizer was added, DBP and monomer were mixed in a sample vial before being added to the solid components. Systems were molded into balls or 2.5-cm wide and 2-cm long strips and placed on a 2-cm thick piece of wood. Strips were surrounded by wooden barriers. For systems tested with Cabosil, strips were sometimes placed on 1-mm piece of stainless steel. A soldering iron was then applied to the top of the ball or edge of the strip until a front could be seen propagating

Initiation without filler. 0.20 g BPO and 16.01 g HDODA were mixed together. Some of the system (~6 g) was then placed on a glass and had a soldering iron applied to the center of the system. The remaining portion of the system was allowed to sit overnight to allow BPO to dissolve prior to being placed on a glass slide and having an iron applied to the center of the system.

TMPTMA Systems

Following the general procedure described above, systems were prepared with different initiators, initiator concentrations, fillers, and filler loadings and had a total mass of 10.0-50.0 g.

Either strips of 2.0-2.5 cm x 4.0 cm x 1 cm depth, 10.g balls of putty, or wedges with dimensions of 2.0 x 4.0 cm x <1 mm-~1cm depth were prepared. For systems with thiol, strips of 2 cm x 3.5 cm x 3 mm depth and 10.0 g balls of putty were prepared. Strips were placed on a 2-cm thick piece of wood and surrounded by wooden barriers or placed on a 1-mm thick piece of stainless steel or 5-cm thick piece of cement. A soldering iron was applied to the thickest depth of the wedge or one end of the strip. A type "K" thermocouple wire was placed in the center of the strip or ball.

For one 5 phr BPO in TMPTMA system, a wedge 1.6 cm wide x 2.6 cm long and various thickness of 16 mm to less than 1 mm was prepared, placed on a 2 cm thick piece of wood, surrounded by wooden barriers, and ignited at the end with the thickest depth via application of a soldering iron. The set-up is shown below in Figure 3.1.

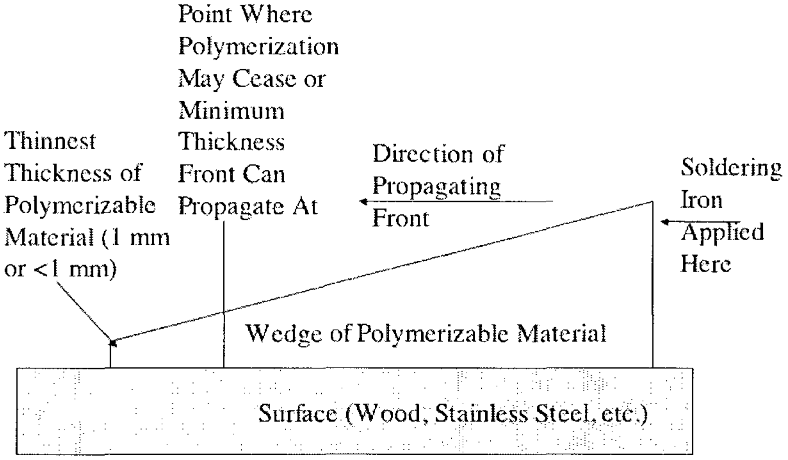


Figure 3.1. Schematic of Wedge Set-Up

Snell's Law Experimental Procedure

Two types of experiments were performed: in the first one, two strips of putty 2.0 cm wide x 17 cm long x 0.5 cm were prepared, each with a different concentration of initiator. The strips were placed parallel and in contact such that 6 cm of each strip was not in contact with the other strip. They were placed on a 2-cm thick wooden surface and surrounded by wooden barriers. A front in the strip containing the higher concentration of initiator was ignited with a soldering iron. The fronts achieved their steady-state velocity in about 3 cm. The velocity in each strip was calculated from a plot of the position versus time for each individual region that did not overlap with the other strip. Front velocities ranged from 0.5 cm min^{-1} for 1.9 phr Luperox® 231 in TMPTA-n to 9 cm min^{-1} for 10.4 phr Luperox® 231 in TMPTA-n, and the front temperatures were about 200°C. The experiments were recorded using an iSight camera and iMovie software.

In the second type of experiment, two larger domains with different initiator concentration were created. A circular propagating front was initiated with a soldering iron in one of the domains. An image of this set-up is shown in Figure 3.2.

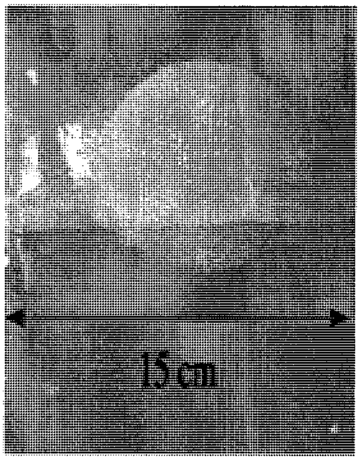


Figure 3.2. Set-up for Circular 2-D Experiments

Rectangles 10 cm wide x 15 cm long x 0.5 cm depth were prepared. Systems with the high initiator concentration had more bromophenol blue indicator added in order to clearly differentiate between two different systems.

CHAPTER IV

EFFECTS OF EXPANDING MICROSPHERES ON FRONTAL POLYMERIZATION SYSTEMS

Thermally-expandable microspheres were added to determine what effect they would have on the front temperature, front velocity, and pot life of a system. The addition of thermally-expandable microspheres have not been studied before with thermal frontal polymerization systems. The thermally-expandable microspheres contain a gas surrounded by a thermoplastic shell and expand when a certain temperature is reached. At this certain temperature, the thermoplastic shell softens, and the pressure inside the shell increases due to the gas, thus resulting in the expansion of the thermally-expandable microspheres. It was predicted that at the high front temperatures of the acrylate monomers, these microspheres would expand and could act as heat sinks like fillers, thus lowering the front temperature. A frontally-polymerized system that expands has potential for use where holes need to be filled with materials that can have a long pot life as well as for other industrial applications. A one-pot system that is easy to handle and cured on demand could be achieved by frontal polymerization with thermally-expandable microspheres.

Controlled expansion is critical because uncontrolled expansion could result in brittle systems that have many cracks or easily fall apart when handled and/or could produce polymerized material that is distorted and twisted from pressure gradient of the amount of gas released. However, enough expansion that can be measured is just as important otherwise the microspheres are simply acting as heat sinkers or like filler such as Polygloss 90. To be able to determine the effect of expansion as a function of thermally-expandable microspheres, a system with a range of Expancel DU 80 loading and with controlled expansion is necessary. To avoid heat loss due to fluid flow, a putty-like consistency must be achieved by addition of a filler to the monomer/initiator system with thermally-expandable microspheres. However, too much filler or the addition of too much thermally-expandable microspheres could quench the front due to absorption of the heat from the propagating front so that a balance must be achieved. Complete propagation of the system is necessary so that front velocities and temperatures must be sufficiently fast enough and high enough, respectively, to ensure complete propagation of the system without quenching.

Fillers such as Polygloss 90 (kaolin clay) and Cabosil (fumed silica) can be used in mixtures or by themselves. Polygloss 90 is the better choice of filler for forming a putty-like consistency and being cohesive, but Cabosil offers the advantages of modifying the rheological properties of a system so that less filler can be added. Less filler added with a less reactive system could allow a system to propagate to completion when it would otherwise quench for a similar system composed of just Polygloss 90. However, use of just Polygloss 90 with a more reactive monomer system could help to control expansion by absorbing heat from the propagating front. Only Luperox® 231 (1,1-bis(tert-butylperoxy)-3.3.5-trimethylcyclohexane) was used for initiator because it produces less gas per initiating radical than other peroxides.[23]

Monomer choice is important because some monomers have higher or lower reactivities than others. Although TMPTA-n (trimethylolpropane triacrylate) is the monomer typically used in the other chapters and used as the reference monomer, other less reactive monomers such as TMPTMA (trimethylolpropane trimethacrylate) may result in more controlled or no expansion. Other monomers such as HDODA (1,6-hexanediol-diacrylate), a diacrylate, is more reactive than TMPTMA and, if mixed with TMPTA-n, could allow for more expansion than TMPTA-n by itself. Ethoxylates also are viable alternatives because of their longer chain lengths could increase the flexibility of a system and help to reduce cracking and/or brittleness but are more reactive than TMPTMA so that they could provide a happy medium for controlled expansion.

No matter what monomer or initiator is used, all of the monomers and thermal initiators undergo the same sequence of reactions for the free-radical system: initiation, propagation, and termination. The general reaction scheme of a thermal initiator and monomer is shown below in Figure 4.1.

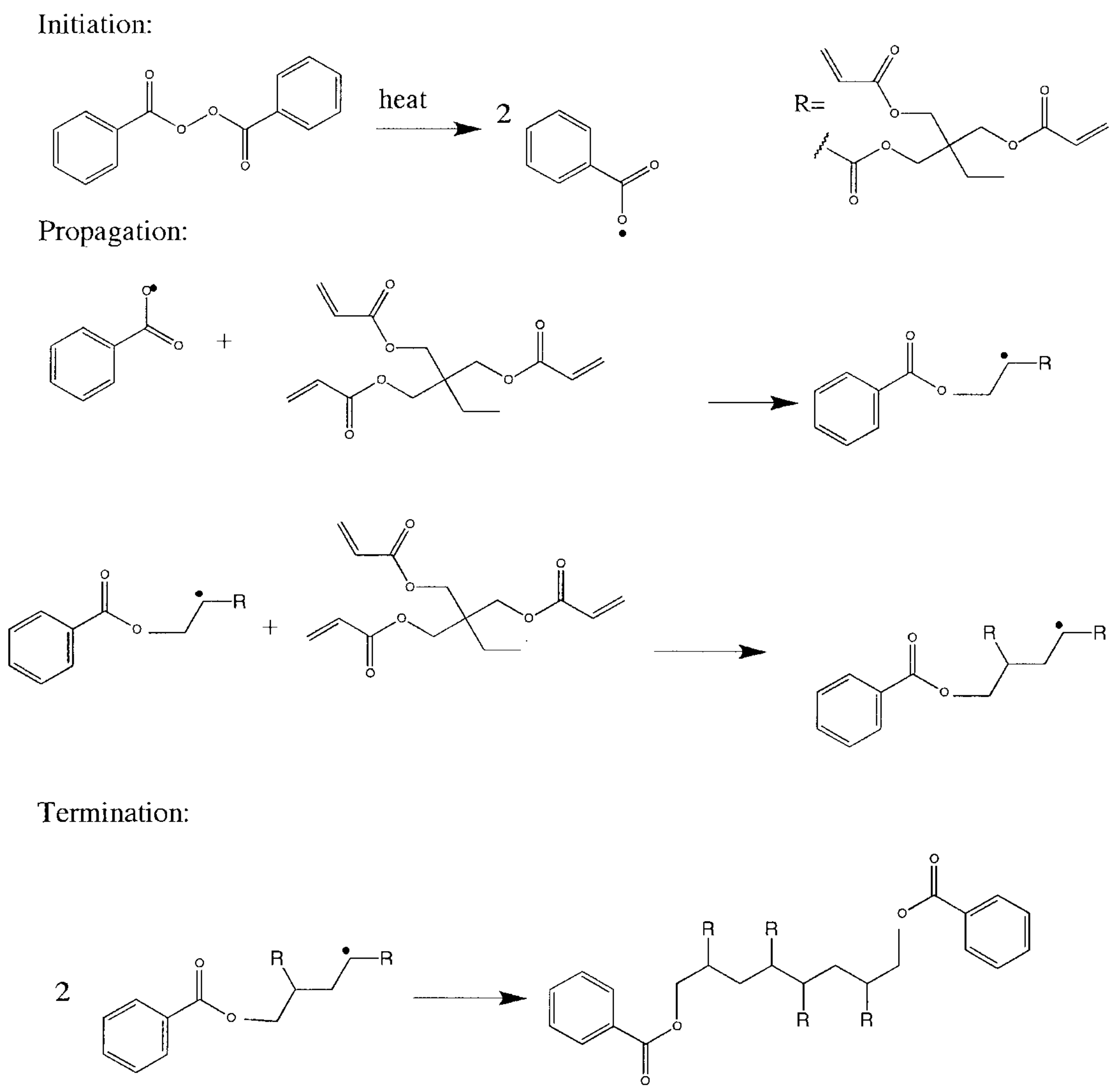


Figure 4.1. General Reaction Scheme of Free-Radical Polymerization[1]

As discussed earlier in Chapter II, heat from an external heat source such as a soldering iron causes decomposition of the thermal initiator in to free radicals. In the propagation reaction, one of those radicals then reacts with the acrylate monomer to form a propagating radical. The propagating radical continues to react more monomer to form a propagating chain radical. Termination finally occurs when two radicals react with each other.

Addition of additives such as a plasticizer or trithiol could also help to improve the properties of a monomer/initiator system. For situations where extensive cracking is a problem, the addition of a plasticizer such as dibutylpthalate could help to increase the fluidity of a system so that less cracking occurs. The addition of a trithiol could help to reduce brittleness of a system and could help to control expansion in a system that has uncontrolled expansion. Because copolymerization of a trithiol and acrylate or methacrylate produces less total heat release than homopolymerization of an acrylate, less heat is available for the thermally-expandable microspheres to expand so that less expansion should occur.[7]

Expancel DU 80 was used because it expands at a temperature of 120-128 °C and hits its maximum expansion at 176-186 °C. Although front temperatures can be as high as 250 °C when using acrylates as monomers, addition of other additives such as filler or thiol can help to lower front temperatures to varying degrees so that a broad range of front temperatures could be obtained. (Later chapters discuss to what degree the front temperatures are lowered.) Through this broad range of front temperatures, the expansion of thermally-expandable microspheres theoretically could be controlled.

Effects of Expancel DU 80 on Free-Radical Systems

Effects of Expancel DU 80 on TMPTA-n Systems

Initial experiments using 2 phr and 6 phr Luperox® 231 in TMPTA-n determined the maximum loading of Expancel DU 80 that could be added and still have frontal polymerization. Holding steady at 53% mass 2 or 6 phr Luperox® 231 in TMPTA-n, systems with 23.5% mass Polygloss 90 and 23.5% mass Expancel DU 80 were prepared, but no frontal polymerization could be initiated because too much Expancel DU 80 was quenching frontal polymerization due to its insulation effect and possibly absorption of heat from the propagating front. Further reduction of the expandable microsphere loading to 5% mass and increasing filler loading to 42% mass failed to resulted in propagation unless a system with 47% mass Polygloss 90 and 53% mass 6 phr Luperox® 231 in TMPTA-n was molded into a strip parallel to it and initiated with a soldering iron. Then, as the front propagated through the system with no Expancel DU 80, frontal polymerization from the Expancel DU 80 occurred not from the site of contact with the soldering iron but from further down the strip along the side of the strip touching the system without Expancel DU 80. An image of the propagating fronts is shown below in Figure 4.2.

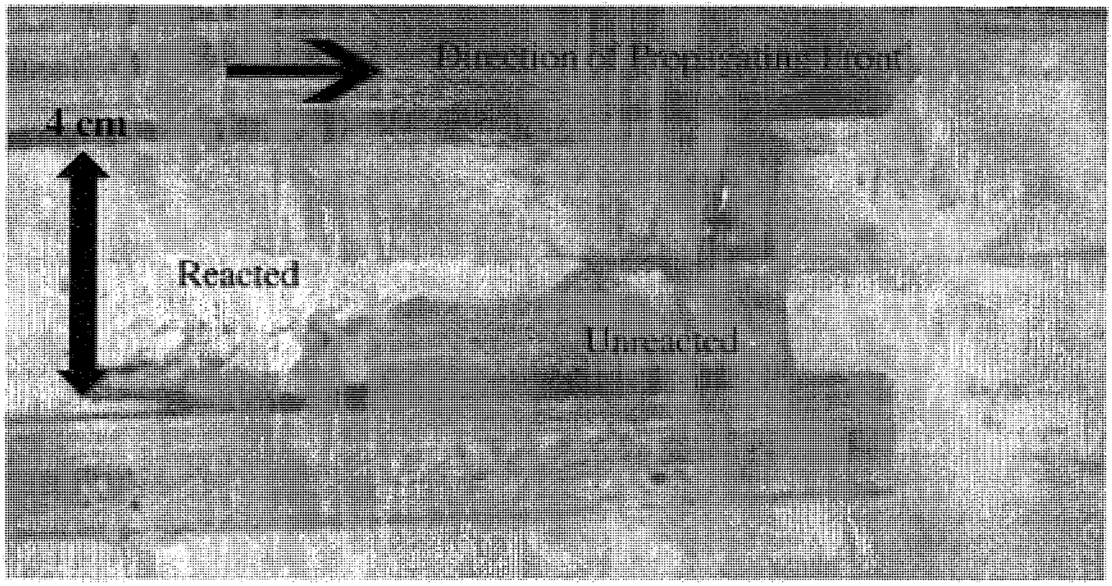


Figure 4.2. Image of Reacting Polygloss 90 and 6 phr Luperox® 231 in TMPTA-n Fronts With and Without 5% mass Expancel DU 80

Complete polymerization of the system without expandable microspheres occurred, but the system with 5% mass Expancel DU 80 was only partially polymerized. All of the side of the strip touching the system without Expancel was polymerized, but the portions of the 5% mass Expancel DU 80 system farthest away from the region with no Expancel failed to polymerize, thus indicating that the input of heat from the propagating front of the system without Expancel DU 80 helped the system with 5% mass Expancel DU 80 to propagate. Stark differences between the two systems can be clearly seen in Figure 4.2. The system without Expancel DU 80 (labeled 47% Polygloss 90 in image) has a smooth polymerized surface whereas the surface of the system with Expancel DU 80 (labeled 42% Polygloss 90 in the image) is rough. The system without Expancel had a straight (not curved) front propagating whereas the system with Expancel is propagating with a curved front, indicating that heat loss is occurring. This heat loss could be due to the insulating expandable microsphere preventing heat from reaction zone to flow the surrounding area and raise the temperature. The image in Figure 4.2 also clearly shows how the addition of expandable microspheres is causing the strip to expand so that the wooden barrier is pushed away from the strip, possibly leading to more heat loss. This expansion does not occur in systems without microspheres; the edge of the strip touching the wooden barrier is a smooth line – unlike the system with 5% mass Expancel DU 80.

When the expandable microsphere loading was further reduced to 1% mass and Polygloss 90 was increased to 50% mass, a smoother surface than with 5% mass Expancel DU 80 (not as smooth as the surface without expandable microspheres) and complete polymerization of the strip occurred. Other positive characteristics include a smooth front and more controlled expansion (system expanded more uniformly and less erratically than the 5% mass Expancel DU 80 system in Figure 4.2). An image of the reacting front is shown in Figure 4.3.

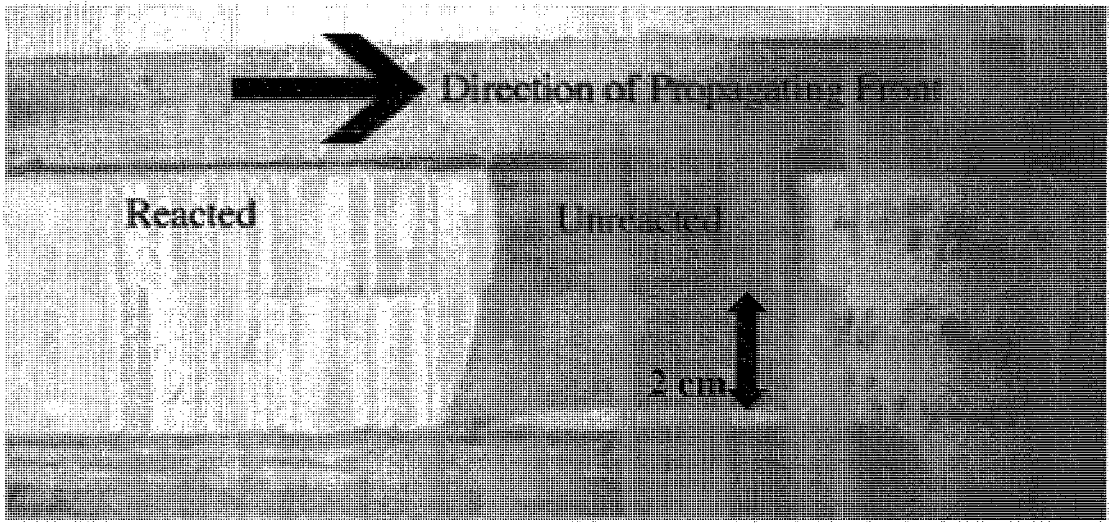


Figure 4.3. Image of Propagating Fronts for 0% mass Expancel DU 80 and 1% mass Expancel DU 80 Systems with 53% mass 6 phr Luperox® 231 in TMPTA-n and Various Amounts of Polygloss 90

However, the 1% mass Expancel DU 80 system still has more cracks than the system without Expancel DU 80. Another problem with using 1% mass Expancel DU 80 is that these positive characteristics occurred only if the system was molded parallel to a strip with no Expancel DU 80.

When this system composed of 1% mass Expancel DU 80, 46% mass Polygloss 90, and 53% mass 6 phr Luperox® 231 in TMPTA-n was initiated by itself, incomplete propagation and erratic expansion near the end of the strip occurred. An image of this zigzagging pattern is shown in Figure 4.4 with the unreacted portion of the polymerizable system shown in dark gray and reacted polymer in white.

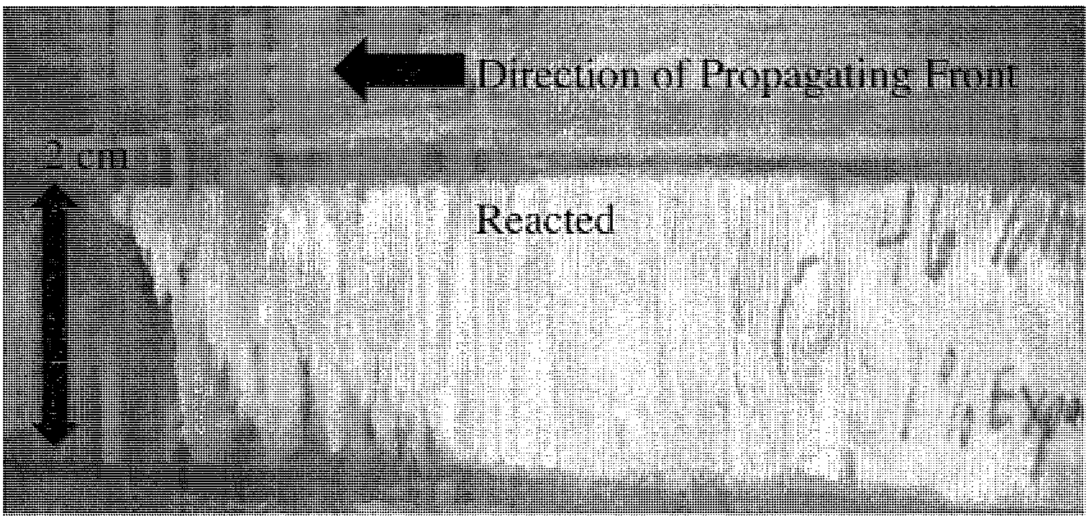


Figure 4.4. Image of Erratic Expansion of System with 1% mass Expancel DU 80, 46% mass Polygloss 90, and 53% mass 6 phr Luperox® 231 in TMPTA-n

More cracks than the same system in Figure 4.3 and a zigzag pattern can be observed in Figure 4.4. Thus, although a system with 1% mass Expancel DU 80 can propagate by itself, heat from the reacting front of the system without Expancel DU 80 helped to ensure complete polymerization of the strip (except for tiny portion expanded away from the reacting zone after polymerization of system without Expancel is complete) and more controlled expansion so that this zigzag pattern was very slight at end of strip. Because the strip expanded from a width of 2.5 cm to 3.3-3.9 cm and a length of 12 cm to 16 cm (polymerized), it does indicate that addition of expandable microspheres can readily cause a system composed of TMPTA-n, Luperox® 231, and Polygloss 90 to expand if only a small amount of Expancel DU 80 was added.

Effects of Expancel DU 80 on TMPTMA Systems

Because of the brittleness of the polymers (readily crumbled into lots of tiny pieces and chunks when measured with a ruler), lack of controllable expansion, and unusable Expancel DU 80 ranges in TMPTA-n systems, another monomer, TMPTMA, was selected. Two systems, one composed of 53% mass 6 phr Luperox® 231 in TMPTMA and 47% mass Polygloss 90 and the other composed of 53% mass 6 phr Luperox® 231 in TMPTMA, 1% mass Expancel DU 80, and 46% mass Polygloss 90, were placed in the same set-up displayed in Figure 4.3, but because of the more stable methacrylate radical, front polymerization failed to occur in either system due to lower reactivity.

From experiments and tested systems discussed in a later chapter, a system composed of 80.7% mass 14.3 phr Luperox® 231 in TMPTMA, 9% mass Polygloss 90, 10% mass Cabosil, and 0.1 % mass Expancel DU 80 was developed. Complete polymerization occurred for the system if no Expancel DU 80 was added, and complete polymerization occurred if the system had 0.1% mass Expancel DU 80 when the system was wrapped around a 10-mL glass pipette (2-cm length and 3-mm depth for system) or molded into a 2-cm thick and 28 mm-wide circular disc that could fit into a 20-mL sample vial. Cracking occurred each time. For the system molded around a 10-mL glass pipette, a large crack formed 180 degrees from the site of initiation with smaller, finer cracks along the edges of the polymerized material. For the sample molded into the opening of a sample vial, finer and fewer cracks occurred. Expansion of 3-4 mm occurred along the width and length; a small amount of depth expansion (1-2 mm) could have occurred but was hard to determine. One problem with this system was that the system was dried out and tended to crumble apart when molded around or into anything. Another problem was the small amount of expansion, which could not be attributed to expandable microspheres or normal expansion and contraction of a frontal polymerization system. A third problem was that much smoke could be seen pouring into the bottom of the sample vial as the front propagated through the disc.

Increasing the % mass Expancel DU 80 to 1% mass, reducing % mass Cabosil to 9% mass, and increasing Polygloss 90 loading to 10% mass resulted in more cracking (larger and more numerous) and expansion than the system with 0.1% mass Expancel DU 80. This time, the 2-cm thick and 28-mm wide disc expanded 0.5-1 cm above the top of the sample vial, and the sample failed to adhere to the 10-mL pipette. Instead, the sample expanded and fell apart as it propagated. Although the system was slightly less dried out, the expansion was uncontrollable because the polymer fell apart. The polymer fell apart as it propagated due to uneven expansion and a dried out system that failed to adhere to itself. Compared to the system with 0.1% mass Expancel DU, more smoke was also produced, further indication that TMPTMA was not a good choice of monomer. However, when polymerized in a ball, the polymer was not brittle (did not shatter into pieces when dropped 4 feet off the ground) because TMPTMA has a longer chain length than TMPTA-n.

Effect of Expancel DU 80 on TMPEOTA Systems

TMPEOTA was then selected because it was not a methacrylate so that it would not have such a stable radical but should create a polymer that would be more flexible than TMPTA-n because of the ether linkages. Different ethoxylates were tested including TMPEOTA I (7/3 EO/OH, average M_n ~604 g/mol, 500 ppm monomethyl ether hydroquinone inhibitor) and TMPEOTA II (1/1 EO/OH, average M_n ~428 g/mol, no inhibitor). The initial tested system was based upon one discussed in a later chapter

(Chapter VII) and based upon different tested TMPTMA systems. For the system composed of 5% mass Cabosil, 17% mass Polygloss 90, 1% mass Expancel DU 80, and 77% mass 10 phr Luperox® 231 in TMPEOTA I, the consistency of the system was putty-like, and the putty adhered to itself, much more so than any system with TMPTMA. Other positive characteristics of this system were that it had few cracks (cracking occurred only with the system was wrapped around the 10-mL pipette) and that less smoke than the TMPTMA systems was produced. Despite these desired qualities, initiation of the front was difficult and sometimes required multiple contacts with the soldering iron. Another problem was that no observed expansion occurred.

Increasing the initiator concentration to 14.9 phr Luperox® 231 in TMPEOTA I for this same system resulted in a better, putty-like consistency and a system that was easier to initiate. The same positive characteristics as before were produced with only slightly more cracking than before. Another problem was that a little bit of circular disc in the opening of the sample vial failed to polymerize. A third issue was the lack of visible expansion.

To ensure complete propagation of the system and more expansion, a system composed of 2% mass Cabosil, 11% mass Polygloss 90, 10% mass Expancel DU 80, and 77% mass 24.2 phr Luperox® 231 in TMPEOTA I was tested. However, this system had a liquid-like/broth-like consistency and failed to polymerize because of buoyancy-driven convection and possibly the addition of too much Expancel DU 80. Increasing the filler loading to 16% mass and reducing Expancel DU 80 loading to 5% mass resulted in frontal polymerization for 5-20 seconds after removal of the soldering iron, thus indicating that too much Expancel DU 80 had been added in the previous system. However, buoyancy-driven convection quenched frontal polymerization.

Another system derived from tested TMPTMA systems involving methacrylate systems was used as a launching point for potential TMPEOTA I/Expancel DU 80 system. The system composed of 4% mass Cabosil, 19% mass Polygloss 90, 5% mass Expancel DU 80, 72% mass 33.3 phr Luperox® 231 in TMPEOTA I was a little dried out but still putty-like. Because of the inhibitor in the monomer and higher average M_n than TMPEOTA II, no sustained frontal polymerization occurred. To confirm that it was the initiator, Expancel DU 80 was removed, and a system composed of 72% mass 33.3 phr Luperox® 231 in TMPEOTA I, 4% mass Cabosil, and 24% mass Polygloss 90 was tested. Only 1-1.5 cm of the strip slowly polymerized after sustained contact with a soldering iron, thus indicating that Expancel DU 80 could be quenching the system and that the choice of monomer itself (because of its inhibitor and higher average M_n than TMPEOTA II) could also be inhibiting polymerization. If molded into a ball, complete polymerization occurred, thus potentially indicating that Expancel DU 80 was the main problem.

Because TMPEOTA I contains an inhibitor to prevent spontaneous polymerization, a new ethoxylate, TMPEOTA II, was tested. For the system composed of 4% mass Cabosil, 19% mass Polygloss 90, 5% mass Expancel DU 80, 72% mass 33.3 phr Luperox® 231 in TMPEOTA II, a putty-like consistency similar to toothpaste was achieved and complete polymerization occurred. Unfortunately because of the high initiator concentration, much more smoke than the other tested TMPEOTA I systems was produced and singed/browned spots occurred throughout the molded ball. Because of the amount of heat produced from the reaction zone and amount of expansion, the ball unwound and fell apart as the front propagated and expanded in all directions. Large cracks or fissures in the unwound ball also occurred. For the strip, as the front propagated, the strip was pushed up and away from the wooden surface it was placed on. Lengthwise, the strip expanded from 6.5 cm to 9.0 cm. The width expanded from 2.5 cm to ~3.5 cm; depth expansion also occurred. Like the ball, deep crack formation and browning of the putty occurred. Much more smoke than the other tested TMPEOTA systems or a system composed of 59% mass 1 phr BPO in TMPTA-n and 41% mass Polygloss 90 was produced.

Because the high initiator concentration was the major reason for the browned polymer, different initiator concentrations were tested with and without 5% mass Expancel DU 80. For systems that had no Expancel DU 80, Polygloss 90 was used as a replacement. The silica loading remained the same (4% mass), and the total initiator/monomer and total % mass of the solid components remained the same. For a system with 72% mass 9.1 phr Luperox® 231 in TMPEOTA II and 5% mass Expancel DU 80 (with 19% mass Polygloss 90 and 4% mass Cabosil), no true frontal polymerization occurred -- despite the putty-like consistency and expansion in all directions (particularly width). However, expansion was the most controlled (no zigzagging or pushed up and away from the wooden surface) than any other Expancel DU 80 system tested to that point, and only slight expansion in length and depth cold be observed. The surface of the polymerized material was rough – similar to the Expancel DU 80 system in Figure 4.4. Expansion towards the end of the 5.5-cm long strip was more erratic and spread out. An image of the polymerized strip is shown in Figure 4.5.

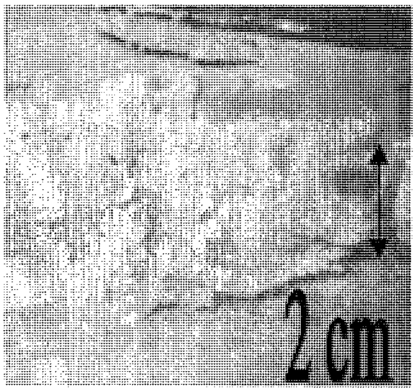


Figure 4.5. Polymerized Material with 5% mass Expancel DU 80, 72% mass 9.1 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and 19% mass Polygloss 90

To reduce the time the soldering iron had to be applied, the initiator concentration was increased to 14.3 phr Luperox® 231 in TMPEOTA II. Although the putty-like consistency (similar to toothpaste) of the system was maintained, increased initiator concentration resulted in shorter time of initiation and more uncontrolled expansion so that the strip was pushed up and away from the wooden surface that it was originally placed on and twisted itself due to pressure gradient of the propagating front, amount of smoke produced, and amount of heat being released. An image of the polymerized material is shown in Figure 4.6.

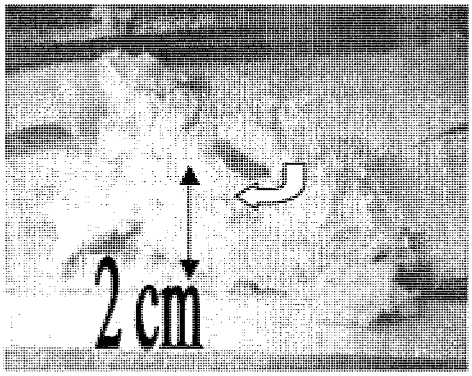


Figure 4.6. Twisted, Polymerized Material with 5% mass Expancel DU 80, 72% mass 14.3 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and 19% mass Polygloss

The system with the lower initiator concentration did not appear to form cracks except where expansion of the strip occurred under the wooden barriers. For the system with 14.3 phr Luperox® 231 in TMPEOTA II, it was difficult to observe cracking attributed to expansion and contraction of the front and not attributed to pressure gradient of the propagating front. Both systems produced similar amounts of smoke – similar to the amount of smoke produced by a system composed of 41% mass Polygloss 90 and 49% mass 1 phr BPO in TMPTA-n. Both systems also tended to crumble apart at the edges of the strips that had the most expansion.

With a system that had a initiator concentration between 9.1 and 14.3 phr Luperox® 231 in TMPEOTA II, >95% of the 2.5-cm wide strip polymerized for the system with 5% mass Expancel DU 80 and 72% mass 10.8 phr Luperox® 231 in TMPEOTA II. The length of the strip increased from 7 cm to 8.5 cm, and the width expanded about 0.5-1.0 cm. Thickness expansion also occurred. At the beginning of propagation, a small portion of the strip was pushed up and away from the wooden surface so that the amount of pressure gradient was between the amounts suffered from systems containing 9.1 and 14.3 phr Luperox® 231 in TMPEOTA II. Expansion of the strip was much more controlled or less erratic than the system with 14.3 phr Luperox® 231. When no Expancel DU 80 was added to the system with an initiator concentration of 10.8 phr Luperox® 231, complete polymerization of the strip occurred with a smaller time for initiation. A smoother surface, no expansion, and no visible cracks were the positive aspects of this system. One of the drawbacks of this system was that slight bubbling marred the smooth surface of the polymerized strip. Addition of degasser such as BYK 060 N could help to eliminate this bubbling. Images of the polymerized strips for the systems with and without 5% mass Expancel DU 80 are shown in Figure 4.7.

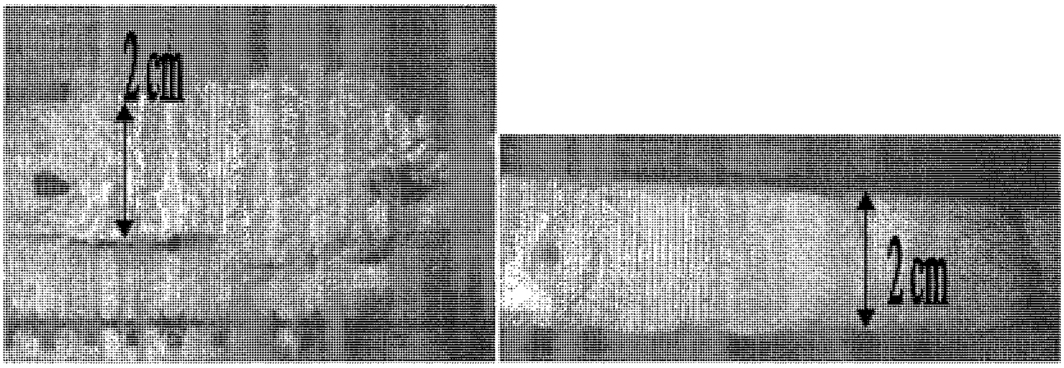


Figure 4.7. Images of Polymerized Material for Systems with 5% mass Expancel DU 80, 72% mass 10.8 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and 19% mass Polygloss (left) and 5% mass Expancel DU 80, 72% mass 10.8 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and 19% mass Polygloss (right)

These images illustrate that this initiator concentration was a good choice for testing different mass percentages of Expancel DU 80 because of the amount of expansion from the system with 5% mass Expancel DU 80, lack of expansion from the system with 0% mass Expancel DU 80, small amount of pressure gradient, and complete (or almost complete) polymerization of the strip. The tuna salad (putty-like) consistency and amount of cracking (very little to no fine cracks for system with no Expancel) were also positive aspects. Thus, strips that were 1 cm wide x 8 cm long x 3-5 mm depth were tested for systems with 0-5% mass Expancel DU 80, 19-24% mass Polygloss 90, 72% mass 10.8 phr Luperox® 231 in TMPEOTA II, and 4% mass Cabosil. Because of the narrower width and longer length of the strips, complete polymerization did not always occur. Pressure gradient also caused systems with 2%, 3%, and 4% mass Expancel DU 80 to curl so that the strip was not always completely linear but curved or twisted so that measurement of the length could be difficult. The amount of expansion is tabulated in Table 4.1.

Table 4.1

Expansion of 72% mass 10.8 phr Luperox® 231 in TMPEOTA II Systems with 4% mass Cabosil and Various Amounts of Polygloss 90 and Expancel DU 80

% mass Expancel DU 80	Length Expansion	Width Expansion	Final Depth
0	0 cm	0 cm	3 mm
1	1 cm	0-1 cm for portions	3-4 mm
2	2.5 cm	0.3-0.5 cm	4-5 mm
3	3.0 cm	0.3-0.8 cm	4-6 mm
4	3.0 cm	0.8-1.3 cm	6 mm
5	1.0 cm	0.8 cm	1 cm

Complete polymerization did not occur for systems with 4% mass and 5% mass Expancel DU 80. Less of the 5% mass Expancel DU 80 strip was polymerized than of the 4% mass Expancel DU 80 strip. Because of the differences in expansion, all of the strips were placed in a 100-mL graduated cylinder filled with 50 mL deionized water to determine how much water they displaced. Systems with Expancel DU 80 floated so that they had to be submerged beneath the water with the tip of a metal spatula. The amount of water displaced by each strip for 0-3% mass Expancel DU 80 is tabulated in Table 4.2.

Table 4.2

Displacement of H_2O for Systems with 72% mass 10.8 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and Various Amounts of Polygloss 90 and Expancel DU 80

% mass Expancel DU 80	Amount of H_2O Displaced by Strip 1	Amount of H_2O Displaced by Strip 2
0	5 mL	N/A
1	6 mL	5 mL
2	6 mL	5 mL
3	7 mL	6 mL

Systems with 4% and 5% mass Expancel DU 80 could not be tested because they were too wide and would not fit into the graduated cylinder. Because the numbers are so close to each, no discernable trend can be determined for the systems with 0-3% mass Expancel DU 80 except that water displacement increased by 20% or the addition of 3% mass Expancel DU 80 displaced. Thus, the system with 3% mass Expancel DU 80 displaced Because of the pressure gradient, which resulted in curling of the strip so that it was no longer completely linear or straight in length, width, and depth, determination of expansion was difficult. An example of this type of curling is shown in Figure 4.8.

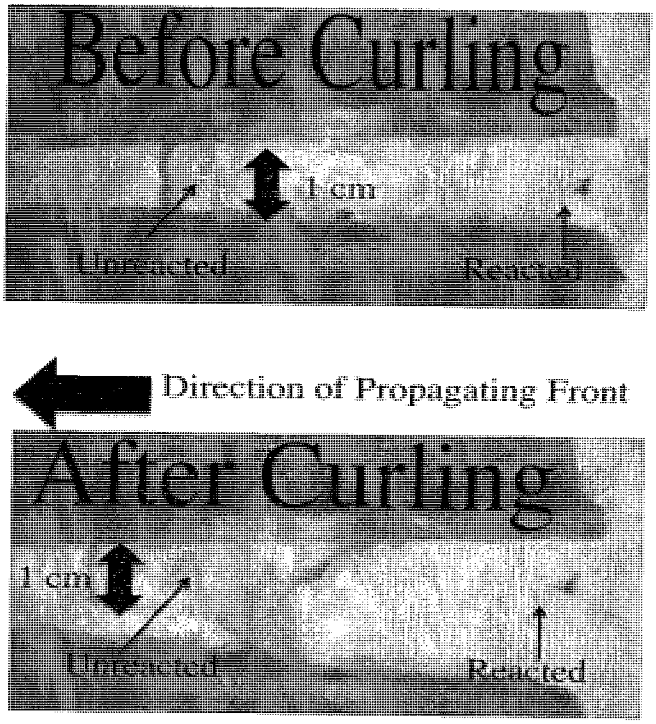


Figure 4.8. Example of Curling in System Composed of 2% mass Expancel DU 80, 72% mass 10.8 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and 19% mass Polygloss

However, all of the tested systems had good putty-like consistencies and typically had some large or medium cracks due to pressure gradient, expansion of the expandable microspheres, and being pushed up and away from the wooden surface.

Lower initiator concentrations of 5.9 phr Luperox® 231 in TMPEOTA II and 7.5 phr Luperox® 231 in TMPEOTA II resulted in systems with putty-like consistencies, but the system with 5.9 phr Luperox® 231 in TMPEOTA II had the most viscous consistency. Despite the thicker widths (2.5 cm) and shorter strips (6-6.5 cm long), incomplete polymerization or frontal propagation still occurred. However, the amount of curling was nonexistent. Instead, only the beginning of the strip where polymerization was initiated was pushed up and away from the wooden surface for systems with either

5.9 phr Luperox® 231 in TMPEOTA II or 7.5 phr Luperox® 231 in TMPEOTA II. Wider widths produced rough surfaces similar to one produced in Figure 4.2 for the system with Expancel DU 80. The surfaces were rougher than the system with 5% mass Expancel DU 80, 72% mass 9.1 phr Luperox® 231 in TMPEOTA II, 4% mass Cabosil, and 19% mass Polygloss 9 (Figure 4.5). The system with the lowest initiator concentration (5.9 phr Luperox® 231) had the roughest surface.

Although some smoke was produced, the system with the lowest initiator concentration produced the least amount of smoke for the TMPEOTA systems with various amount of Expancel DU 80, 4% mass Cabosil, various amounts of Polygloss 90, and 72-77% mass TMPEOTA/Luperox® 231 systems. Expansion occurred in all directions with irregularly-shaped front propagation for the system composed of 72% mass 5.9 phr Luperox® 231 in TMPEOTA II, 5% mass Expancel DU 80, 4% mass Cabosil, and 19% mass Polygloss 90. Various tiny tendrils with diameters of 1-5 mm would propagate due to expansion of the thermally-expandable microspheres and distort the normally linear propagating front. The system with 7.5 phr Luperox® 231 in TMPEOTA II required less time for initiation (less time for application of soldering iron) and had a slightly more linear-shaped propagating front. The initiator concentration with the least brittleness was the one with 10.8 phr Luperox® 231 in TMPEOTA II because it had the least amount of curling and portions of the strip did not break apart into tiny pieces when measured (harder to break when measuring depth of strip) – unlike the other tested systems composed of various amount of Expancel DU 80, 4% mass Cabosil, various amounts of Polygloss 90, and 72-77% mass TMPEOTA/Luperox® 231 systems.

Addition of trithiol reduced the brittleness of the system so that the strip was harder to break in half when measuring the depth of the strip and tended to have less cracking. For a system composed of 19% mass Polygloss 90, 4% mass Cabosil, 5% mass Expancel DU 80, 20% mass trithiol, and 52% mass 10.6 phr Luperox® 231 in TMPEOTA II, complete polymerization of the 1.2 cm wide x 8.0 cm long strip occurred. The strip widened to 1.5 cm and lengthened to 8.5 cm. Very little smoke (least amount out of all TMPEOTA systems without trithiol) and a smooth surface very similar to a system with no Expancel DU 80 shown in Figure 4.7 were produced. Another positive characteristic was the putty-like consistency. A very slow front propagated with no visible cracks. Lack of or very little expansion was problematic because controlled expansion was one of the objectives for the use of thermally-expandable microspheres. When molded into a ball, more smoke and cracking than in strip form occurred.

Increasing the Expancel DU 80 loading to 10% mass and reducing the kaolin clay (Polygloss 90) loading to 14% mass resulted in complete polymerization of the strip and more expansion than the system with 5% mass Expancel DU 80. The length of the strip increased from 8 cm to 9 cm, and the width of the strip increased from 1.1 cm to 1.3-1.5 cm. Because of the thiol added, little to no smoke was produced (approximately the same amount for a system composed of 19% mass Polygloss 90, 4% mass Cabosil, 5% mass Expancel DU 80, 20% mass trithiol, and 52% mass 10.6 phr Luperox® 231 in TMPEOTA II). As discussed in a later chapter, the addition of thiol can lower the total amount of heat released and can lower front temperature and velocity, resulting in less smoke being produced.[7] The system had a front velocity of ~0.83 cm/min, slower than any tested TMPEOTA II/trithiol system discussed in a later chapter. The system had a front temperature of 109 °C, lower than any other tested system with Expancel DU 80 (102 °C for system without Expancel DU 80). Despite the lack of cracking, good putty-like consistency, smooth polymer surface, lack of brittleness (one of the hardest Expancel DU 80 system to break in half by hand and still have only 2 large pieces rather than lots of tiny ones), and lack of or little smoke produced, very little to no expansion occurred – rendering this system useless.

Increasing the Expancel DU 80 loading to 15% mass and 20% mass by reducing the Polygloss 90 loading still resulted in very little to no expansion. With 15% mass Expancel DU 80, less expansion than the 10% mass Expancel DU 80 system occurred: 0.2 cm width x 0.5 length expansion. This expansion is well within experimental uncertainty and can be attributed to regular expansion of a frontal polymerization system rather than to expansion of the thermally-expandable microspheres which expand at temperatures of 120-128 °C for Expancel DU 80. The lack of smoke indicates that the front temperatures of the system were below 150-170 °C so that the front temperature could have been too low for the microspheres to expand. Also, with 20% mass Expancel DU 80, incomplete polymerization occurred, indicating that too much thermally-expandable microspheres had been added and was quenching frontal polymerization. For the system with 15% mass Expancel DU 80, the front velocity was 0.78 cm/min, well within experimental uncertainty for the system with 10% mass Expancel DU 80. Despite the incomplete polymerization for 20% mass Expancel DU 80, the 10-20% mass Expancel DU 80 systems with 9-19% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, and 52% mass 10.6 phr Luperox® 231 in TMPEOTA II were not brittle, had no cracks, had putty-like consistencies and smooth polymerized surfaces for the strips, and produced very little to no smoke, all desired characteristics. Only the slow front velocity and lack of expansion rendered these systems useless.

For the system composed of 19% mass Polygloss 90, 4% mass Cabosil, and 5% mass Expancel DU 80, reducing the % mass trithiol to 16% mass and increasing the % mass of 10.9 phr Luperox® 231 in TMPEOTA II to 61 % mass resulted in more smoke being produced but no expansion. Although complete polymerization of the strip occurred, multiple contacts with the soldering iron were required otherwise incomplete polymerization occurred. Sustained front propagation briefly occurred for 25-50% of the strip so that multiple contacts of the soldering were required to ensure complete propagation of the strip. The consistency of the system was mud-like rather than putty-like so that molding the system into strip form was difficult.

Because of the poor consistency and incomplete polymerization, the initiator concentration was increased to 11.1 phr Luperox® 231 in TMPEOTA II and the % mass trithiol was increased to 20%. A putty-like consistency and complete polymerization of the 8-cm long strip were achieved. The system had a front velocity of 1.1 cm/min, and no smoke or cracking was produced. Also, the polymer surface was smooth. The addition of trithiol seemed to increase the strength of the polymer so that it was not as brittle as any other Expancel DU 80 system that had less than 20% mass trithiol and any other monomer than TMPEOTA II. The pot life of the system was 2 days – shorter than the best smoke-free TMPEOTA II/trithiol system discussed in a later chapter. For expansion, the strip expanded from 8.1 cm to 8.7 cm for the length. No width or depth expansion could be detected. Thus far, this system exhibited all of the desired characteristics – except for the amount of expansion, which could not be attributed to only thermally-expandable microsphere expansion.

Because this system and initiator concentration seemed promising, the % mass Expancel DU 80 was increased to 15% mass Expancel DU 80 and the % mass Polygloss 90 was reduced to 9% mass in order to increase the amount of expansion. Lack of smoke and cracking were two of the positive attributes maintained. However, the consistency of the system was creamier than the system described above and harder to mold into strips. Also, polymerization of 50% or less of the strip occurred because too much thermally-expandable microspheres had been added, and no expansion was observed, thus negating any potential use for the system composed of various amounts of Polygloss 90, 4% mass Cabosil, 20% mass trithiol, 52% mass 10 phr Luperox® 231 in TMPEOTA II, and various amounts of mass Expancel DU 80.

Effect of Expancel DU 80 on HDODA Systems Mixed with Different Monomers

Because of difficulty in controlling expansion in TMPEOTA systems, a diacrylate, HDODA, was mixed with TMPTA-n in various molar ratios in order to have more uniform or controlled expansion. The initial system was based on the one most successful trithiol-free one for TMPEOTA. The HDODA/TMPTA-n system was composed of 19% mass Polygloss 90, 5% mass Expancel DU 80, 4% mass Cabosil, 37% mass TMPTA-n, 28% mass HDODA, and 7% mass Luperox® 231 with a 1:10 mole:mole HDODA:TMPTA-n ratio. Although the consistency of the system was putty-like, much more smoke than any TMPEOTA system or TMPTA-n/BPO system was produced. Pressure gradient and released gas/smoke caused the strip to push itself up and away from the wooden surface and to curl into a twisted configuration. An image of this curling is shown in Figure 4.9.

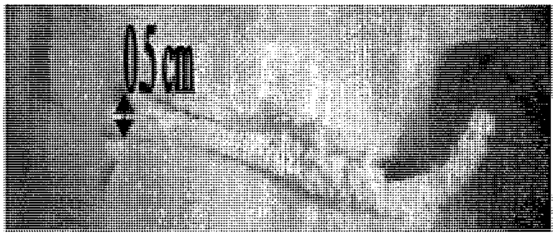


Figure 4.9. Twisted, Polymerized Material for 1:10 mole:mole HDODA:TMPTA-n System Composed of 19% mass Polygloss 90, 5% mass Expancel DU 80, 4% mass Cabosil, 37% mass TMPTA-n, 28% mass HDODA, and 7% mass Luperox® 231

Many deep cracks formed due to thermal stress from uncontrolled expansion and pressure gradient, resulting in a very brittle polymer that fell apart into tiny pieces when broken in half to measure the thickness of the strip. This pressure gradient could have been due to the (1) amount of expandable microspheres added, (2) mole:mole HDODA:TMPTA-n ratio, and/or (3) high initiator concentration (18.9 phr Luperox® 231 in TMPTA-n and 25.0 phr Luperox® 231 in HDODA).

Reduction of the initiator concentration (10.4 phr Luperox® 231 in TMPTA-n and 13.5 phr Luperox® 231 in HDODA) and reducing the HDODA:TMPTA-n mole:mole ratio to 1:1 resulted in more curling than before and pieces of polymerized, expanded material breaking apart as the front propagated through the 8-cm long strip. Images of the curled strip are shown in Figure 4.10.

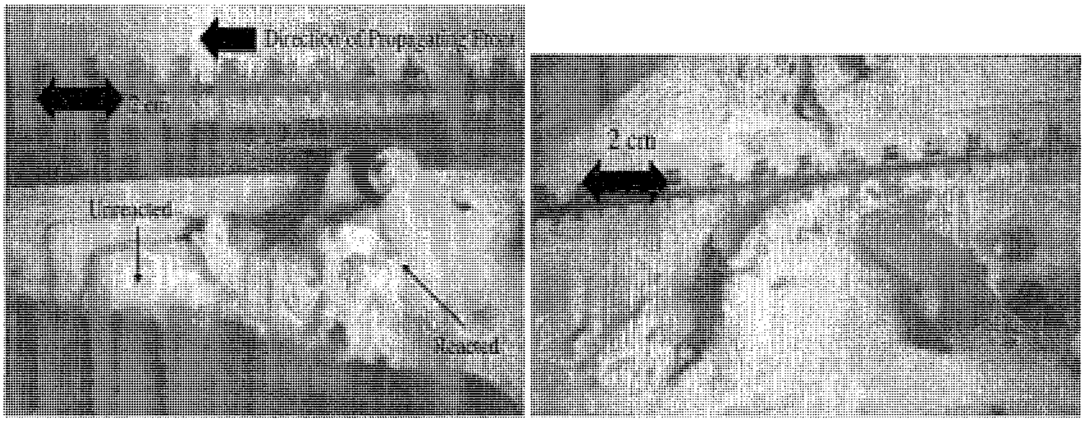


Figure 4.10. Twisted, Polymerized Material for 1:1 mole:mole HDODA:TMPTA-n System Composed of 19% mass Polygloss 90, 5% mass Expancel DU 80, 4% mass Cabosil, 29.6% mass HDODA, 38.4% mass TMPTA-n, and 4% mass Luperox® 231

The image on the right for Figure 4.10 demonstrates that there is a larger curl in the polymerized material than for the image in Figure 4.9. Reducing the HDODA:TMPTA-n mole:mole ratio from 1:10 to 1:1 simply increased the amount of pressure gradient so that strip was pushed further up and away from the wooden surface. More uncontrolled expansion than the system with 1:10 mole:mole HDODA:TMPTA-n also occurred as shown in the image to the left for Figure 4.10. Small tendrils of expanded, polymerized material propagated away from the strip due to the thermally-expandable microspheres expanding in all directions. A small piece of polymerized material that broke away as the front reached the zenith of its curl can be seen near the top of the right-hand image in Figure 4.10. Less smoke was produced -- probably because of the reduction of the initiator concentration, which would have resulted in a lower front temperature and velocity. On the other hand, reducing the % mass of TMPTA-n, which would have increased the amount of cross-linking, increased the amount of pressure gradient produced and allowed for more uncontrolled expansion. Without the cross-linking of the triacrylate, more cracking and uncontrolled expansion occurred so that pieces of polymerized material could fall away from the propagating front. A more brittle polymer than before occurred because the polymer was so fragile or brittle. The strip could not be measured with a ruler without falling apart into numerous small bits and pieces. However, expansion occurred in all directions.

Further lowering the initiator concentration to 5.05 phr Luperox® 231 in TMPTA-n and 6.49 phr Luperox® 231 in HDODA for a system with 1:1 mole:mole HDODA:TMPTA-n ratio caused less pressure gradient so that less curling or distortion of the front occurred. The reduction in curling or distortion can be seen in Figure 4.11.

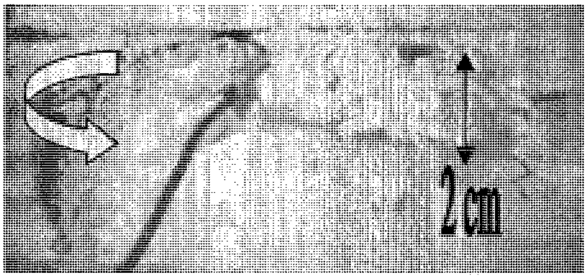


Figure 4.11. Polymerized Material for 1:1 mole:mole HDODA:TMPTA-n System Composed of 19% mass Polygloss 90, 5% mass Expancel DU 80, 4% mass Cabosil, 30.4% mass HDODA, 39.6% mass TMPTA-n, and 2% mass Luperox® 231

Less smoke and brittleness also occurred. However, the polymer was still very brittle and crumbled into to tiny pieces when extracting the thermocouple wire. The system had a front temperature of 203 °C, close to a BPO/TMPTA-n system with 41% mass Polygloss 90 and within experimental uncertainty for a system composed of 20% mass trithiol, 52% mass 4 phr Luperox® 231 in TMPTA-n, 5% mass Expancel DU 80, 19% mass Polygloss 90, and 4% mass Cabosil (front temperature 186.5 °C).

Effect of Expancel DU 80 on Trithiol/TMPTA-n Systems

Because systems with mixtures of HDODA and TMPTA-n resulted in the worst distortions or curling for Expancel DU 80 systems but TMPEOTA II/trithiol systems produced very little to no expansion, TMPTA-n systems were tested and were based on the most successful TMPEOTA II systems. TMPTA-n has a lower double bond per acrylate molecular weight TMPEOTA II so that more expansion should and did occur. For a system composed of 4% mass Cabosil, 5% mass Expancel DU 80, 19% mass Polygloss 90, 20% mass trithiol, and 52% mass 10.6 phr Luperox® 231 in TMPTA-n, complete polymerization of the strip occurred. However, the polymer was more brittle than corresponding TMPEOTA II system and more viscous in its consistency. Another issue was the curling or distortion of the strip occurred due to pressure gradient from the propagating front. An image of the distorted polymer is shown in Figure 4.12.

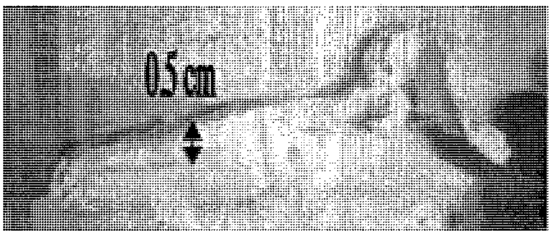


Figure 4.12. Polymerized Material for System Composed of 5% mass Expancel DU 80, 19% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, and 52% mass 10.6 phr Luperox® 231 in TMPTA-n

However, this distortion is much less than almost any of the tested systems with HDODA/TMTPA-n. Also, this system was less brittle than any HDODA/TMPTA-n system so that measurements of the expansion could be done. The length, width, and depth expanded from 8 cm to 10 cm or more, 1.0 to 1.3-1.7 cm, and 3-5 mm to 5-7 mm depth, respectively. Much less cracking also occurred than for HDODA/TMPTA-n systems so that systems were less brittle. Addition of a trithiol and no addition of a diacrylate also helped to reduce the brittleness of the polymer and reduced the amount of cracking. The polymer surface was also much smoother since small tendrils of expanded material were not curled every which way on the surface of the strip. The pot life of this system was 3-4 days due to addition of the trithiol; spontaneous polymerization began 20-60 minutes after the system was prepared.

Because curling still occurred at the beginning of strip, the initiator concentration was further reduced from 10.6 to 4 phr Luperox® 231 in TMPTA-n. Although the strip was not pushed up and away from the wooden surface as much, curling of the strip did occur, and more distortions occurred at the end of the strip. An image of the polymerized material is shown in Figure 4.13.

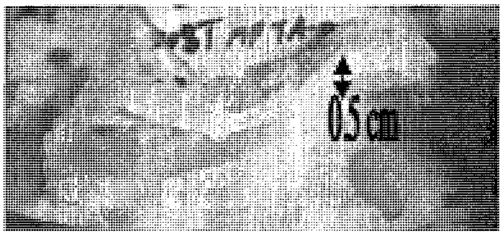


Figure 4.13. Polymerized Material for System Composed of 5% mass Expancel DU 80, 19% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, and 52% mass 4 phr Luperox® 231 in TMPTA-n

Thus, although reduction of the initiator concentration reduced the extent of the curl, it failed to reduce the distortion of the front so that it was easier to measure the extent of expansion. For length, width, and depth, the system expanded from 7.9 cm to at least 11 cm (possibly 12-14 cm with curvature of the strip), from 1 cm to 1.0-1.8 cm, and from 3-

5 mm to 5-7 mm depth. Because of the amount of distortion, it is difficult to determine whether reduction in the initiator concentration affected expansion of the strip.

However, this system produced less smoke than any of the systems tested for Snell's Law but more smoke than the corresponding TMPEOTA II systems. Also, this system was more brittle and had a shorter pot life than the corresponding TMPEOTA II systems and more brittle than even TMPTMA systems with 20% mass trithiol and no Expancel. The more flexible TMPEOTA with its ether linkages could be the reason for this difference. In addition, the front temperature (186.5 °C) of this system was lower but within experimental certainty for a similar system composed of 4% mass Cabosil, 24% mass Polygloss 90, 20% mass trithiol, and 52% mass 10.6 phr Luperox® 231 in TMPTMA (198.6 °C) but higher than the corresponding system with 10.6 phr Luperox® 231 in TMPEOTA II (109 °C). However, the trithiol/TMPTA-n/Expancel DU 80 system had a putty-like consistency similar to corresponding TMPEOTA II/trithiol systems except slightly more viscous.

Systems composed of 5% mass Expancel DU 80, 19% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, and 52% mass 4 or 10.6 phr Luperox® 231 in TMPTA-n had similar pot lives (20-29 minutes for system with 4 phr Luperox® 231 and 20-60 minutes for system with 10.6 phr Luperox® 231) and similar amounts of cracking. Further reduction of the initiator concentration to 3.13 phr Luperox® 231 in TMPTA-n and reduction of % mass trithiol to 10% mass actually resulted in more uncontrolled expansion and distortion of the front and more smoke being produced. However, less curling than the system with 10.6 phr Luperox® 231 in TMPTA-n occurred. Also, reduction of % mass trithiol increased the pot life from 20-60 minutes to 90-150 minutes.

However, the front temperature was increased from 186.5 °C to 200 °C and above. Thus, addition of trithiol alleviated some of the pressure gradient that caused curling and distortion of the strip, possibly by reducing the total heat loss of the system and reducing the brittleness of the polymer so that pieces of polymerized material could not fall away from the propagating front.

Conclusions

Systems with TMPTA-n typically failed because too much Expancel DU 80 was added and was inhibiting frontal polymerization by insulating the strip from the reaction zone so that less heat leached from the reaction zone and into the surrounding area. Brittleness, lack of a usable Expancel DU 80 range, and uncontrolled expansion were other major problems with use of TMPTA-n. TMPTMA was not a good choice of monomer with expandable microspheres because the tested systems smoked too much, were too dried out so that it typically failed to adhere to itself when wrapped around something, formed large cracks, and had no usable range for the expandable microspheres.

Systems with ethoxylates such as TMPEOTA I and TMPEOTA II had the least amount of distortions but still suffered from distortion or curling of the strip unless trithiol was added. Although the addition of trithiol alleviated curling or distortions of the front or uncontrolled expansion, it failed to allow very little if any expansion at all. The best system was composed of 19% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, 52% mass 11.1 phr Luperox® 231 in TMPEOTA II, and 5% mass Expancel DU 80 had many desirable characteristics including being smoke-free, putty-like, and not brittle and not having cracks and even having some expansion. However, this expansion could have been due to normal expansion and contraction of a propagating front and not just due to expansion of thermally-expandable microspheres. The other problem with this system was that there was no range that could be used for it.

Systems with various HDODA:TMPTA-n mole:mole ratios typically produced the worst distorted, polymerized strips because of high initiator concentrations and of the amount of pressure gradient produced from thermally expanding microspheres and gas/smoke produced. Even low initiation concentration (4-6 phr Luperox® 231 in monomer) tended to produce distorted fronts because of the amount of pressure gradient produced from the propagating front. Systems were also much more brittle than any of the triacrylates or methacrylates. Thus, polymerized strips were much more likely to crumble into tiny pieces when measured with a ruler.

Although TMPTA-n systems derived from the most successful TMPEOTA II system were much less brittle than HDODA/TMPTA-n systems, had fewer cracks, and less smoke, they still failed because of distortions and curling. Low initiation concentrations could not alleviate the curling or distortions because of the amount of pressure gradient being produced due to expansion of the thermally-expandable microspheres or monomer used. Despite being a cross between TMPEOTA II/trithiol systems and HDODA/TMPTA-n systems, expansion could not be successfully controlled. Use of different fillers such as Polygloss 90 or a mixture of Cabosil and Polygloss 90 also failed to allow controllable expansion with various monomer systems. Thus, no matter what monomer, initiator concentration, filler, additives, or mixtures of monomers were used, controlled expansion of Expancel DU 80 could not be done. Either no or too much expansion occurred. Also, potentially useful systems that showed a little controlled expansion had no useful range that could be measured or determined because of distortions and curling of the strip.

Besides the effect of expansion, the addition of thermally-expandable microspheres had no effect on pot life but impacted front temperature and velocity by acting as an insulator. Because of this insulating effect, lower front temperatures and velocities than systems with no Expancel DU 80 occurred. Thus, thermally-expandable microspheres had a behavior similar to filler by acting as a heat sink or having an insulating effect on front temperature and velocity. Like a solid non-reactive additive, the thermally-expandable microspheres had no impact on pot life because they were not a reactive additive or did not react with any of the components of the polymerizable system.

CHAPTER V

EFFECTS OF SOLID ADDITIVES

Previous studies in the Pojman lab and by other researchers have studied the impact of silica or inorganic fillers on viscosity or front velocity.[23, 47] However, the impact of filler on front temperature and velocity has not been studied before with thermal frontal polymerization of a triacrylate. The addition of phase change materials and high thermal conductivity fillers and their effect on pot life, front temperature, and front velocity has also never been investigated.

Because thermal frontal polymerization of multifunctional acrylates produces front temperatures as high as 250 °C, smoking and the release of volatile compounds prevent the use indoors or in potential industrial applications.[14] One way to reduce the smoking would be to add filler, which can lower the front temperature and front velocity. However, too much filler could also quench a propagating front. Polygloss 90 was initially selected because of its cohesiveness and ability to produce a putty when mixed with a thermal initiator and monomer. Addition of other fillers such as Cabosil, which takes up more space than an equivalent weight of Polygloss 90, could help to modify the rheological properties of a polymerizable system so that less filler is required and, thus, is less likely to quench the front. Addition of fillers also could help to minimize buoyancy-driven convection and thus minimize heat loss.[24] Addition of various fillers and the filler loading were also tested to examine their impact on front velocity and temperature and qualitative study of properties such as consistency of polymerizable system, cracking, brittleness, and amount of smoke produced.

Use of an inert phase change materials should allow lower front temperatures than fillers to occur without lowering the front velocity as much and causing quenching of the front. Inert phase change materials melt at temperatures lower than kaolin clay (Polygloss 90) or Cabosil so that the front temperature should be lowered without having much impact on front velocity. Thus, the amount of smoking and fumes may be reduced without quenching of the front. Different inert phase change materials have different heat capacities, melting points, and heats of fusions; all of these differences can lead to a range of front temperatures and front velocities. Inert phase change materials were selected with a range of melting points. Some phase change materials were selected because they shared similar values for two of the three factors (melting point, heat of fusion, and heat capacity) and very different values for the third factor. Melting points lower than that of the original filler, kaolin clay (melting point 740-1585 °C)[48] should result in lower front temperatures (if they have lower melting points than the front temperature) because the inert phase changer material will melt; however, this melting should not affect the front velocity as much as the addition of fillers since it is not absorbing heat from the propagating front but releasing heat.

The addition of an acid such as *p*-toluenesulfonic acid can speed the reaction of reactive phase change material with itself that may self-react and was selected because it is a catalyst for the polyesterification reaction of mandelic acid with itself.[49] The reaction is illustrated below in Figure 5.1.

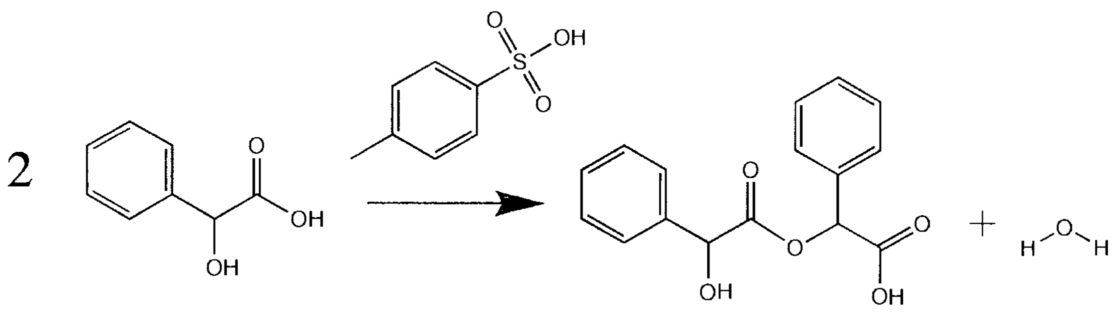


Figure 5.1. Reaction Scheme of Polyesterification of Mandelic Acid

With the aid of the acid as a catalyst, the alcohol group of one mandelic acid adds to the carbonyl carbon of the acid group of a second mandelic acid, resulting in the formation of an ester group and in the hydroxyl group of the acid being kicked off in the form of water. The acid or catalyst works by adding a hydrogen to the carbonyl oxygen of the second mandelic acid. Addition of phase change material should lower the front temperature, but with the addition of an acid to reactive phase change material system, front velocities should not be reduced but may be increased instead, possibly contrary to systems with just inert phase change material. However, the pot life of the systems may be affected adversely and may shorten them like the addition of other additives such as trithiol.

Addition of high thermal conductivity fillers might be expected to affect front velocity since front velocity is proportional to the square root of thermal diffusivity, and increasing thermal diffusivity of the system by adding a higher thermal conductivity filler should increase the front velocity would having much impact on the front temperature. Thus, high thermal conductivity fillers could be used in systems with low front temperatures and velocities in order to increase the front velocity without really increasing the front temperature. By increasing the front velocity of low front temperature systems, rapid repair or complete polymerization could occur without increasing the amount of smoke or fumes produced so that the system could have industrial applications. Yet even if dispersed evenly throughout the putty, high thermal conductivity fillers should not affect either front velocity or temperature since the tiny particles of the high thermal conductivity filler could be too far apart for them to affect the front temperature or velocity of the polymerizable system. Instead, the difference in consistencies of the polymerizable systems should have a larger impact on the front velocity and temperature than the substitution of kaolin clay with high thermal conductivity filler because broth-like systems will have more heat loss due to fluid flow than a polymerizable system with a putty-like consistency. This heat loss can cause the smooth propagating front to become curved (nonlinear) and even to quench so that incomplete polymerization can occur.

High thermal conductivity fillers were chosen because one material was carbon-based (with a thermal conductivity, heat capacity, and thermal diffusivity of ~1 W cm^{-1} K^{-1} at 300 K, 0.7 J g^{-1} K^{-1}, and 0.65 cm^2 sec^{-1}, respectively, for pyrolitic graphite)[50] and the other was a metal with a high thermal conductivity and thermal diffusivity (with a thermal conductivity, heat capacity, and thermal diffusivity of 2.37 W cm^{-1} K^{-1} at 300 K, 0.9 J g^{-1} K^{-1}, and 0.98 cm^2 sec^{-1}, respectively).[51] Kaolin clay itself has a heat capacity of 1.2 J g^{-1} K^{-1} (higher than either of the two high thermal conductivity fillers) and a thermal diffusivity and conductivity of 0.0060 cm^2 sec^{-1} and 0.020 W cm^{-1} K^{-1} at 300 K, which are much lower than either of the two high thermal conductivity fillers tested.[52] The lower heat capacities of the thermal conductivity fillers mean that they will absorb less heat than the same mass of Polygloss 90 and should instead act as a conductor rather than an insulator because of the higher thermal conductivity. The higher thermal conductivity and diffusivity of aluminum powder means that it should increase the front velocity more than graphite because velocity is proportional to the square root of thermal diffusivity, but the higher heat capacity means that it will also absorb more heat than graphite. So, higher heat capacities means that lower front temperatures and velocities should occur in these systems if heat capacity is the dominant factor.

Use of three different types of systems (various % mass high thermal conductivity filler while holding percentage mass kaolin clay constant; various % mass high thermal conductivity filler while holding % mass initiator/monomer steady; and various % mass Polygloss 90 while holding % mass high thermal conductivity filler steady) allow for determination of whether the variation of initiator/monomer was causing a decrease in front velocity and temperature, whether the high thermal conductivity filler was causing the decrease in front temperature and velocity, or whether it was the kaolin clay itself that had a bigger impact on the decrease of front velocity and temperature than the high thermal conductivity fillers themselves. Since the high thermal conductivity fillers could have little on impact on front temperature and velocity for the reasons discussed above, use of high thermal conductivity fillers will be like substituting Polygloss 90 for another filler and determining its impact on front velocity and temperature as well as degree of cracking, brittleness, consistency of polymerizable system, and amount of smoke produced. Previous experiments with sand and HDODA have already demonstrated that Polygloss 90 is the best filler to use to achieve a putty-like consistency, but other fillers such as graphite or aluminum powder, which take up the same amount of space or volume as Polygloss 90 (in contrast to Cabosil), could be just useful as Polygloss 90 to achieve a desired viscosity. Thus, addition of high thermal conductivity fillers can also help to determine whether Polygloss 90 itself or any other filler could be used for thermal frontal polymerization systems that produce less smoke, have less cracking and brittleness (breaks into the biggest and least number of pieces when smashed with a foot-long piece of wood to extract the thermocouple wire), and have the most putty-like consistency for potential industrial applications.

Filler Loading and Its Effect on Front Velocity and Temperature

The minimal amount of filler needed to form a free-standing putty was the baseline for determining the lower limit of filler to add. The filler loading was increased until the filler loading prevented a front from propagating. In the case of Polygloss 90, the minimal amount of filler needed to form a putty was 27% mass. As the filler loading was increased from 27% to 41% mass, the front temperature dropped as shown in Figure 5.2.

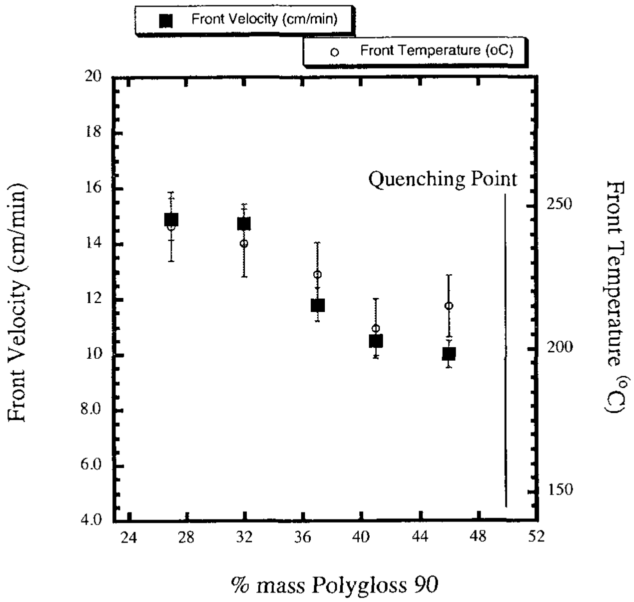


Figure 5.2. Front Temperature and Front Velocity vs. % mass Polygloss 90

However, at 46% mass, the front temperature was higher than at 41% mass Polygloss 90. The 8°C or 4% difference between the two systems was due to the uncertainty in recording front temperatures and that fact that temperature fluctuations occur throughout the strip during thermal frontal polymerization (rather than one constant temperature at all thicknesses and at different positions of the strip) so that the highest temperature of multiple runs was recorded but may not be necessarily the highest front temperature. Excluding runs with faulty thermocouples, temperature variations were typically within 14% or less of the highest front temperature. Greater reproducibility with fewer front temperature variations (10% or less) occurred with systems with higher filler loading (41% and 46% Polygloss 90), possibly due to having a putty-like consistency. Systems with 27% mass Polygloss 90 had a more gel-like or broth-like consistency so that heat loss due to fluid flow could have occurred and could have caused more fluctuations in front temperature measurements. At 50% mass, the filler loading was too high to allow a front. The front velocity steadily decreased as the filler loading of Polygloss 90 was increased. Because of the high front temperatures, adding more filler slows the rate of propagation by reducing the front temperature but failed to show any reduction in fumes or smoking.

With increased filler loading, the amount of cracking decreased and the polymer became less brittle (it was harder to break the strip to extract the thermocouple wire). Filler loading did not affect the pot life, which was months long. However, the consistency of the polymerizable system became more putty-like as % mass Polygloss 90 was increased from 27% to 41% mass.

Effect of Other Fillers on Front Velocity and Temperature

To determine the effects that another filler may have on front temperature and front velocity, Cabosil, fumed silica, was mixed with Polygloss 90. Replacing some Polygloss with Cabosil modified the rheological properties of the polymerizable system by allowing less filler to be added than an equivalent weight of Polygloss 90. Thus, substitution of Polygloss 90 with Cabosil increased the front temperature and front velocity as more Cabosil and less Polygloss 90 was added. As demonstrated in Table 10.1, decreasing the Polygloss 90 loading from 46% mass to 36.5% and increasing the Cabosil loading from 0% to 1.9% mass increased the front temperature from 215 °C to 225 °C and increased the front velocity from 10 cm/min to 12 cm/min.

Table 5.1

Front Temperature and Front Velocity as a Function of Polygloss 90 and Cabosil Loading

% Mass Polygloss 90	% Mass Cabosil	Front Temperature (^{o}C)	Front Velocity (cm/min
46	0	215	10
36.5	1.9	225	12
16.3	9.3	250	18

Variation of Mixtures of Polygloss 90 and Phase Change Materials

As demonstrated above, increasing filler loading led to a decrease in front temperature and velocity. Adding more filler slows the rate of propagation by reducing the front temperature. Mixtures of Polygloss 90 and Cabosil where Cabosil loading was increased and Polygloss 90 was decreased led to an increase in front velocity and temperature due to modification of the rheological properties which allowed less filler to be added so that front velocity and temperature increased. Because Cabosil takes up more space or volume than the same mass of Polygloss 90, a smaller amount of Cabosil had to be added in order to still have a putty; thus, the % mass of initiator/monomer solution with the same mass of initiator/monomer solution added for different systems was different for systems containing Polygloss 90 or Cabosil and that were putty-like. If the same amounts of Polygloss 90 and Cabosil were added to the same amount of initiator/monomer solution, then the system with Cabosil would be more dried out or less putty-like than the system with Polygloss 90. Thus, because the same mass of initiator/monomer solution but different total masses of filler were added (only enough to have a putty-like system was added), the % mass of initiator/monomer was different for systems containing only Polygloss 90 or a mixture of Polygloss 90 and Cabosil and was higher in systems containing Cabosil and Polygloss 90 than systems containing only Polygloss 90. Because of the higher % mass of initiator/monomer solution, higher front temperatures and velocities occurred.

On the other hand, substitution of an inert phase change filler such as succinic anhydride for Polygloss decreased the front velocity and temperature as shown in Figure 5.3.

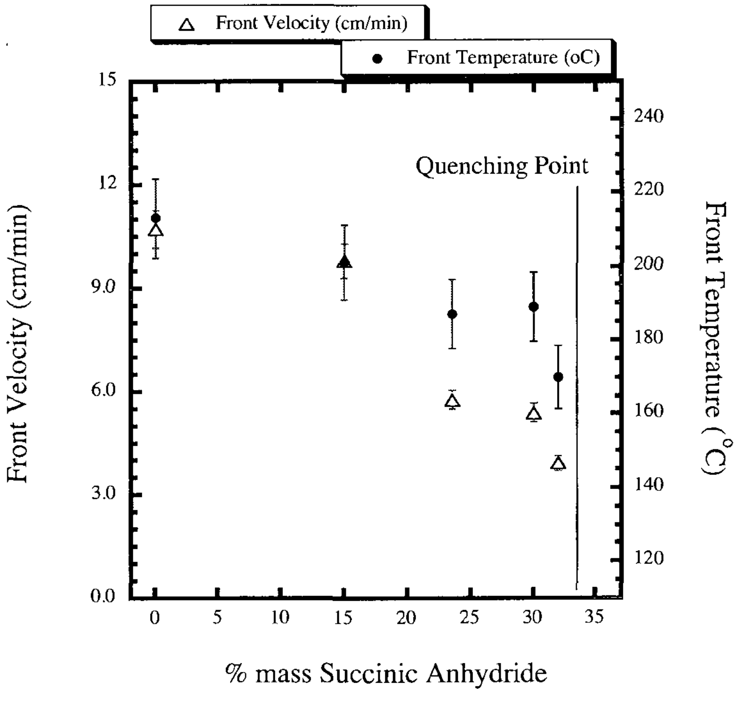


Figure 5.3. Front Temperature and Front Velocity vs. % mass Succinic Anhydride with 53% mass 10.4 phr Luperox® 231 in TMPTA-n and Various Amounts of Polygloss 90

More % mass phase change material was added until frontal polymerization could no longer be initiated. The viscosity of the system changed as more % mass succinic anhydride was added. The system retained its putty-like consistency but became more "dried out" or lost its cohesiveness as more inert phase change material was added. With other polymerizable systems such as lauric acid or benzophenone, as more phase change material was added, the system lost its putty-like consistency and became more gel-like or broth-like. However, despite the differences in consistencies for the systems, all other inert phase change materials followed this same trend of having the front velocity and temperature decrease as more phase change material was added despite having different heat of fusions, heat capacities, and melting points, any of which alone could have caused a decrease in front velocity and temperature. Addition of phase change material had no impact on the pot life of the systems (months-long like the original system with no PCM), little impact on the amount of smoke produced unless the front temperatures were below 170 °C, and some impact on the strength of the polymer by making polymers more brittle (more numerous, smaller pieces when hit with a foot-long piece of wood) as more inert phase change was added (not entirely due to a slight increase in cracking for some systems).

Due to different size particles, solubilities of PCM in monomer/initiator solution, and other properties such as hygroscopicity (ability to absorb water from the air), different ranges (0-32% mass vs. 0-17% mass for various PCM) of phase change material could be added and still have frontal polymerization. For example, 0-35% mass succinic anhydride could be added; however, only 0-15% mass D,L-mandelic acid could be added. If more than 15% mass D,L-mandelic acid was added to a polymerizable system containing 53% mass 10.4 phr Luperox® 231 in TMPTA-n and a combined 47% mass of filler and D,L-mandelic acid, then no polymerization occurred except at the site of contact with the soldering iron. Yet, as shown in Figure 5.4, the polymerizable system containing D,L-mandelic acid followed the trend as the system containing succinic anhydride despite the different % mass of phase change material added.

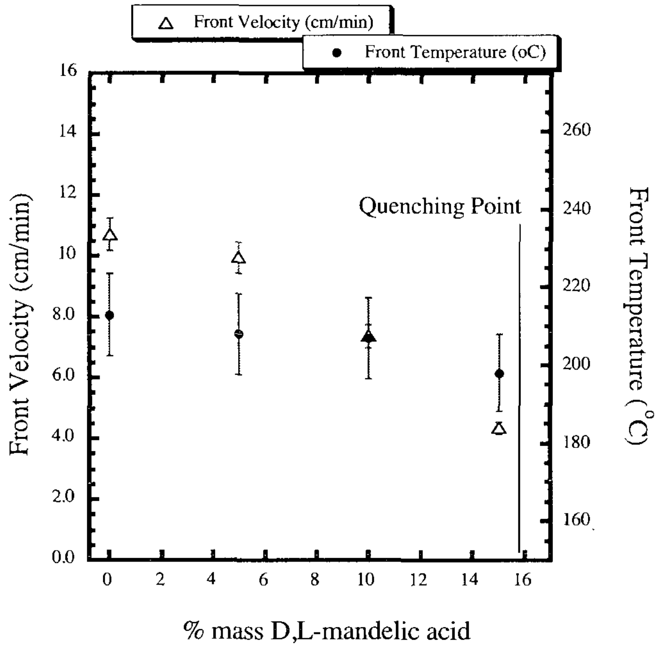


Figure 5.4. Plot of Front Velocity and Temperature as a Function of % mass D,L-Mandelic Acid

Although phase change materials had different heat capacities, heats of fusion, and melting points, no one factor showed a singularly dominant impact on front velocity or front temperature as shown in Figures 5.5-5.7.

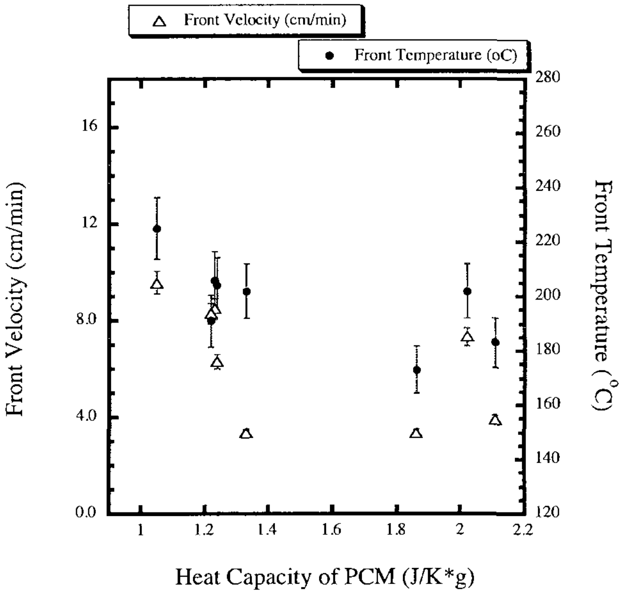


Figure 5.5. Front Velocity and Temperature vs. Heat Capacity of PCM (Phase Change Materials) with 15% mass PCM

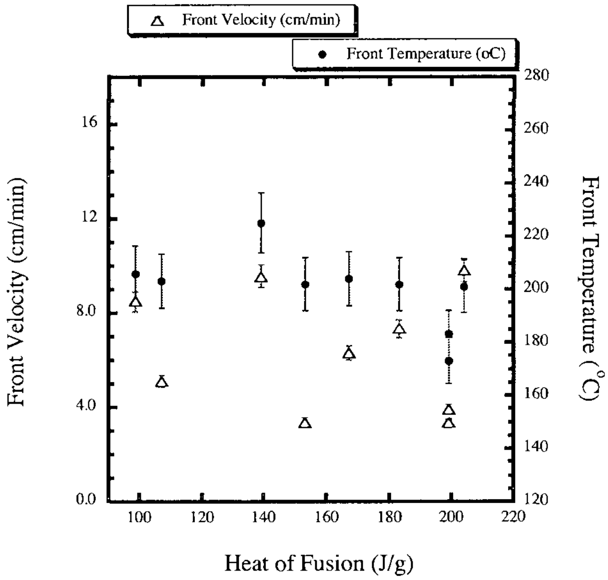


Figure 5.6. Front Velocity and Temperature vs. Heat of Fusion of PCM with 15% mass PCM

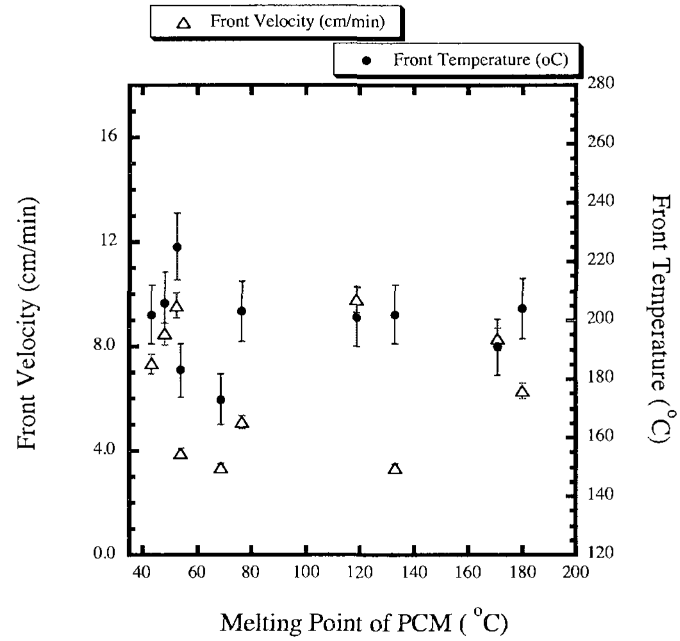


Figure 5.7. Front Velocity and Temperature as a Function of Melting Point of PCM

Instead a complex combination of heat capacity, heat of fusion, and melting point of phase change materials caused the trends demonstrated in Figure 5.3 and 5.4. Plotting front velocity and temperature vs. heat of fusion/heat capacity of PCM shows a simpler trend for the plot in Figure 5.8 than those for Figures 5.5-5.7 because fewer data points (fewer literature values could be found) could be plotted; Figures 5.5-5.7 initially showed a similar trend when fewer data points were plotted.

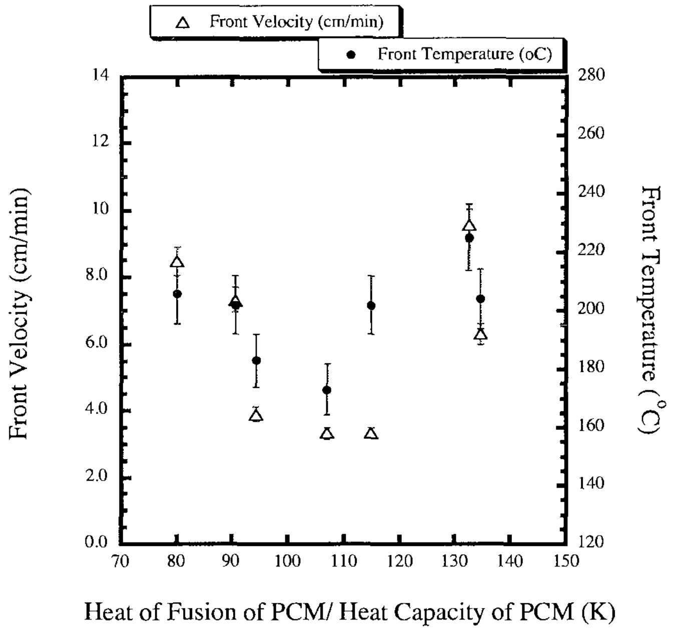


Figure 5.8. Front Velocity and Temperature vs. Heat of Fusion of PCM/Heat Capacity of PCM with 15% mass PCM

These trends were observed not only for systems containing 15% mass PCM but also for systems containing 23.5% mass PCM. Plots of front velocity and temperature as a function of heat capacity, heat of fusion, and melting point of PCM for systems with 23.5% mass inert PCM are shown in Figures 5.9-5.11. Both sets of data for 15% mass PCM and 23.5% mass PCM show the same trends that occur for various heats of fusion, melting point, and heat capacities of inert PCM, thus validating that this trend does not occur for only one % mass of PCM. The only difference between these two sets of data is that the plots with 15% mass PCM (Figures 5.5-5.7) have more data points so that some of the figures seem more complicated than those with 23.5% mass PCM (Figures 5.9-5.11).

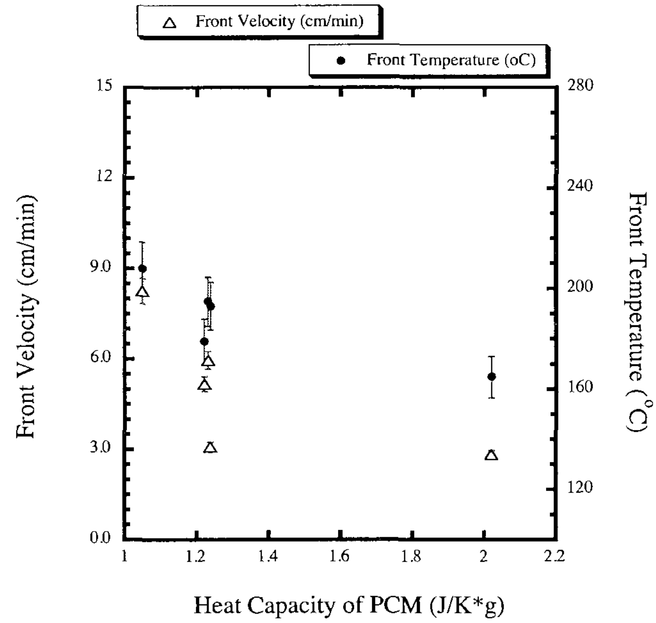


Figure 5.9. Front Velocity and Temperature as a Function of Heat Capacity of PCM with 23.5% mass PCM

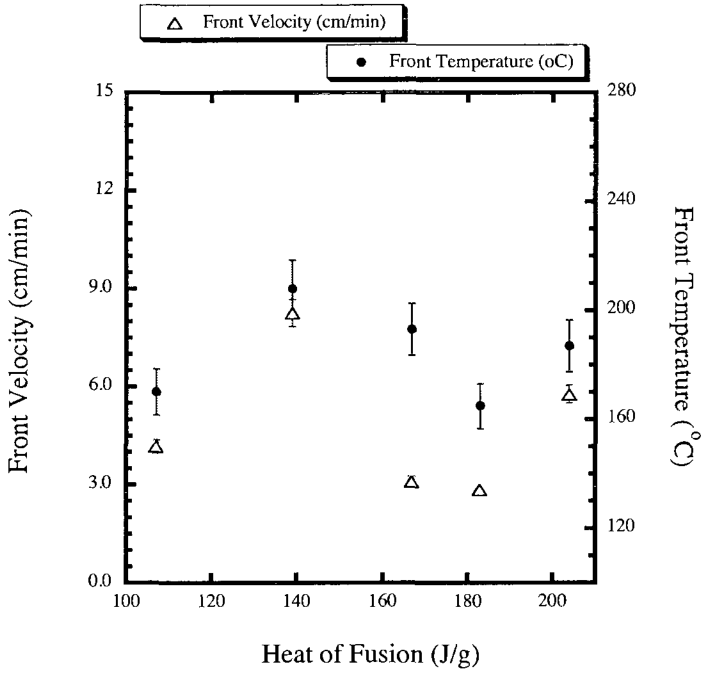


Figure 5.10. Front Velocity and Temperature as a Function of Heat of Fusion of PCM with 23.5% mass PCM

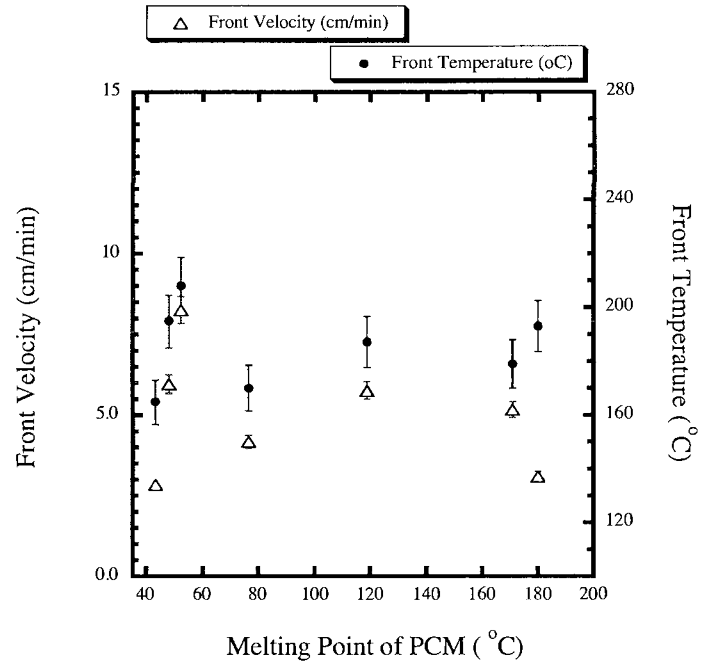


Figure 5.11. Front Velocity and Temperature as a Function of Melting Point of PCM with 23.5% mass PCM

Addition of p-Toluenesulfonic Acid Monohydrate to PCM

When the loading of phase change material of D,L-mandelic acid was maintained at 15% mass and the % mass of *p*-toluenesulfonic acid was increased, the front temperature decreased slightly after, and the front velocity increased as shown in Figure 5.12.

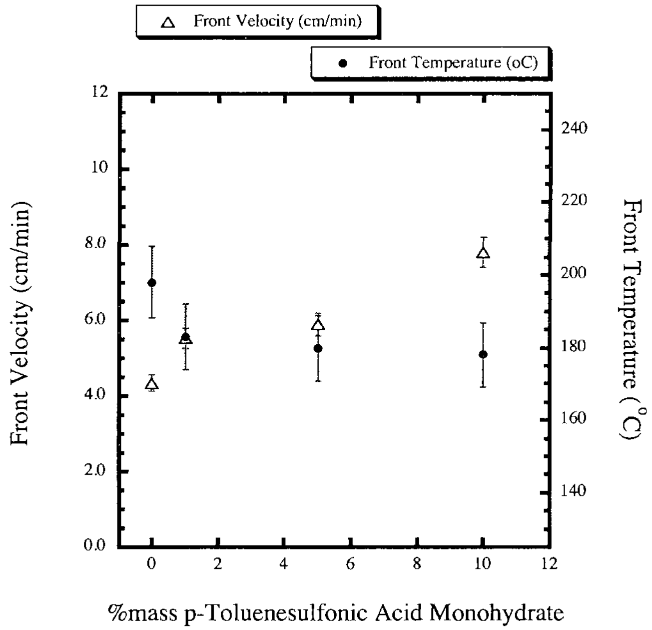


Figure 5.12. Front Velocity and Temperature as a Function of % mass *p*-Toluenesulfonic Acid with D,L-Mandelic Acid

The *p*-toluenesulfonic acid is a catalyst for the polyesterification of mandelic acid so that homopolymerization of the acrylate was not the only process occurring when the front propagated through the strip. The addition of catalyst increased front velocity because it was helping to catalyze the polyesterification of mandelic reaction and because the presence of certain Lewis or Bronsted acids have been shown to enhance the thermolysis rates for the decomposition of a peroxide initiator.[53, 54] However, the slight drop in front temperature could be due to the reaction of D,L-mandelic acid and vaporization of water are slightly endothermic so that the total heat loss of the polymerizable system was reduced. Also, the product of the self reaction of D,L-mandelic acid might not be soluble in the polymerizable system or was melting when the front propagated through the strip so that fingering could be occurring. At room temperature, addition of 10% mass catalyst lowered the pot life from months to 24 hours; smaller amounts of catalyst only caused a tiny, if any, portion of the polymerizable system to harden within 24 hours, possibly because the acid could be slightly soluble in the monomer/initiator solution.

The addition of *p*-toluenesulfonic acid monohydrate also acted as a catalyst to the decomposition of the initiator when no phase change material was present; the presence of certain Lewis or Bronsted acids can and have been shown to enhance the thermolysis rates for the decomposition of a peroxide initiator.[53, 54] As shown in the plot in Figure 5.13, when a polymerizable system containing 53% mass 10.4 phr Luperox® 231 in TMPTA-n and a combined 47% mass of Polygloss 90 and *p*-toluenesulfonic acid was used, increasing % mass catalyst and reducing the filler loading resulted in a similar trend seen in Figure 5.12.

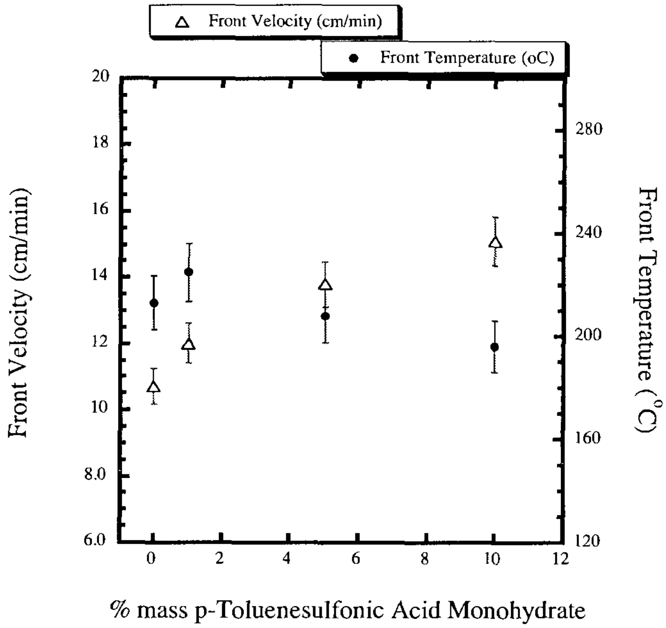


Figure 5.13. Front Velocity and Temperature vs. % mass *p*-Toluenesulfonic Acid Monohydrate with No Phase Change Material

The smaller maximum front velocity for the plot in Figure 5.13 compared to the plot in Figure 5.12 indicates that both frontal polymerization and the reaction of D,L-mandelic acid reacting with itself utilized *p*-toluenesulfonic acid as a the catalyst. A comparison of the front temperatures for the plots in Figures 5.4, 5.12, and 5.13 indicates that the reaction of D,L-mandelic acid helped to lower the front temperature when a catalyst was present in the system. Neither the sole addition of catalyst nor D,L-mandelic acid affected the front temperature as much as when the two were both present in the polymerizable system, possibly because the polyesterification reaction was endothermic and produced water so that front temperature was lowered more. Different consistencies of the polymerizable systems alone cannot account for the bigger drop in front temperature that occurred when a combination of catalyst and D,L-mandelic acid was present rather than when only one of the two chemicals was present. Besides an impact on front velocity, the addition of *p*-toluenesulfonic acid monohydrate also reduced the pot life of the systems from months to 60-90 minutes when 10% mass *p*-toluenesulfonic acid was added for systems containing no D,L-mandelic acid; addition of small amounts of catalyst caused only a tiny portion of the polymerizable system to harden or spontaneously polymerize within 60-90 minutes. Systems with 5% mass *p*-toluenesulfonic acid and no D,L-mandelic acid completely hardened or spontaneously polymerized after 3-5 days whereas systems with 1% mass *p*-toluenesulfonic acid and no D,L-mandelic acid had almost completely gelled or spontaneously polymerized after 2-3 weeks. Yet some portions of systems with 1% mass *p*-toluenesulfonic acid and no D,L-mandelic acid still had not hardened or bulk polymerized after 3 weeks.

High Thermal Conductivity Fillers

Variations of Systems with 15% mass High Thermal conductivity filler

Systems with 15% mass high thermal conductivity filler had the percentage mass Polygloss 90 and percentage mass 1 phr BPO in TMPTA-n varied. When this things were varied for high thermal conductivity fillers (graphite and aluminum powder), the front temperature decreased as % mass Polygloss 90 was increased. This result is shown in Figure 5.14.

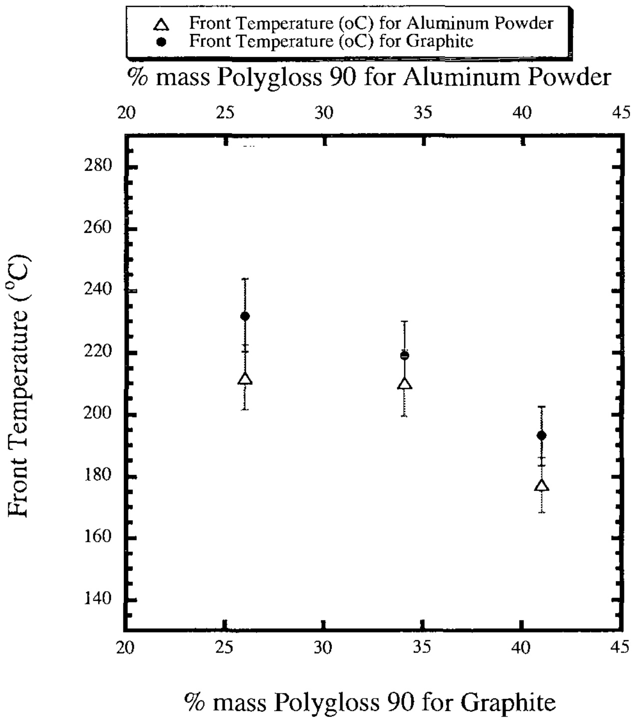


Figure 5.14. Front Temperature as a Function of % mass Polygloss 90 for 15% mass Aluminum Powder and for 15% mass Graphite

As more filler was added and replaced the initiator/monomer solution, the front temperature decreased because less initiator/monomer was present in the polymerizable system. Also, a drop in front temperature occurred because the ratio of high thermal conductivity filler:Polygoss 90 decreased as the % mass of Polygloss 90 was increased. Thus, as the total % mass of filler increased, front velocity and temperature decreased. Too much filler quenched the propagating front.

Despite the two high thermal conductivity fillers having the same trends of a reduction in front temperature as % mass Polygloss 90 increased, the front temperature of the system containing graphite was higher than the front temperature of the system containing aluminum powder because graphite has a lower heat capacity than aluminum powder so that it absorbs less heat. Despite having the lower thermal conductivity and diffusivity, systems with graphite actually have higher front temperatures than systems with aluminum powder even though systems with high thermal conductivity and diffusivity should result in higher front temperatures and velocities. The higher thermal conductivity and diffusivity of aluminum powder means that it should increase the front velocity more than graphite because velocity is proportional to the square root of thermal diffusivity, but the higher heat capacity means that it will also absorb more heat than graphite. If the high thermal conductivity powder had its particles connected to each other rather than dispersed in a more insulating material (kaolin clay), then the high thermal conductivity and diffusivity would have had an impact on front velocity, and aluminum powder would have had a higher front velocity since front velocity is directly proportional to the square root of thermal diffusivity, which is directly proportional to thermal conductivity. Thus, a higher thermal conductivity with a lower heat capacity should result in a faster front velocity, which could then lead to a higher front temperature because less heat loss from the propagating front occurs – if the high thermal conductivity material particles were connected to each other, a state called the percolation threshold, rather than being dispersed in powder form.[55] Instead, heat capacity was the controlling factor on front temperature and velocity with systems with lower heat capacities having higher front temperatures and velocities. This trend is illustrated in the plot in Figure 5.15.

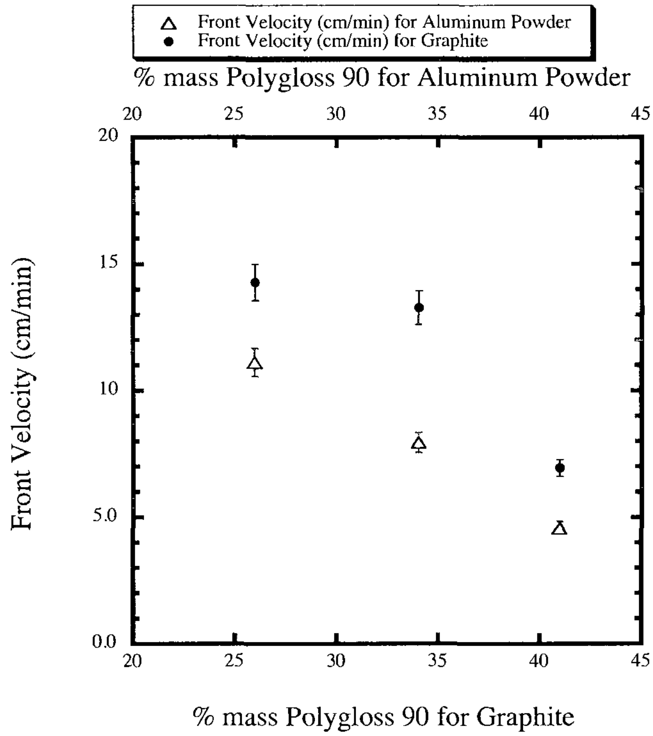


Figure 5.15. Front Velocity as a Function of % mass Polygloss 90 for 15% mass Aluminum Powder and for 15% mass Graphite

The polymerizable system containing graphite had a higher front velocity than the polymerizable system containing aluminum powder for the reasons discussed above. Because the amount of high thermal conductivity filler added was below the percolation threshold, its higher thermal diffusivity had no impact; instead the different heat capacity of the high thermal conductivity filler had an impact on the front temperature and velocity.

Both the polymerizable system containing graphite and the system containing aluminum powder had the same downward trend as % mass Polygloss 90 increased. This result was due to the fact the total % mass filler increased as % mass Polygloss 90 was increased and the % mass 1 phr BPO in TMPTA-n was decreased. Also, as seen previously, as more filler was added to a polymerizable system, eventually enough filler was added to the point where quenching of the propagating front occurred.

Effect of High Conductivity Filler Loading with 41% Mass Polygloss 90

Like polymerizable systems with 15% mass high conductivity filler and, changing the relative amounts of the high conductivity filler loading and 41% mass Polygloss 90 followed the same trends demonstrated in Figures 10.13 and 10.14. When the % mass Polygloss 90 was held constant at 41% mass and the % mass 1 phr BPO in TMPTA-n and % mass high thermal conductivity filler were varied, the front temperature decreased as % mass high thermal conductivity filler was increased and % mass 1 phr BPO in TMPTA-n was decreased as illustrated by the plot in Figure 5.16.

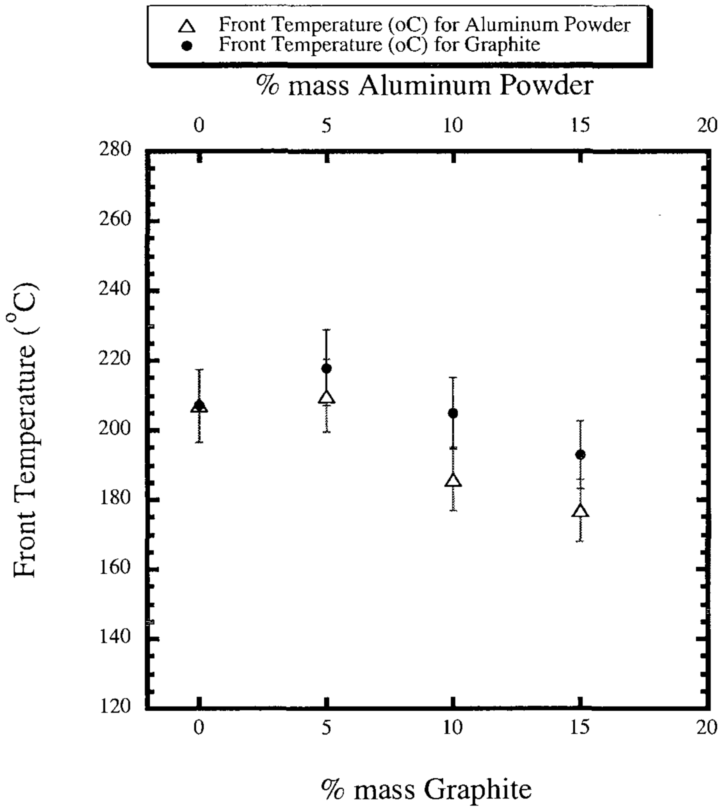


Figure 5.16. Front Temperature vs. % mass Aluminum Powder and % mass Graphite for 41% Polygloss 90 and Various Amounts of 1 phr BPO in TMPTA-n

The first data points of the plot in Figure 5.16 were well within experimental uncertainty of each other so that the trend that initially occurred was irrelevant. However, looking at the overall trend as % mass high thermal conductivity filler increased from 5% mass to 15% mass, the front temperature decreased. This downward trend occurred because the total % mass of filler was increased with % mass initiator/monomer solution decreased.

Like the plots in Figure 5.14, the plot in Figure 5.16 demonstrates that the polymerizable system containing graphite had a higher front temperature than the polymerizable system containing aluminum powder for the reasons previously discussed. When comparing the plots in Figures 5.14 and 5.16, little difference occurred in the two plots. No matter whether Polygloss 90 or high thermal conductivity filler was added to replace % mass 1 phr BPO in TMPTA-n, both sets of data had similar temperature differences for the aluminum powder-containing systems illustrating that the replacement of monomer/initiator with either Polygloss 90 or aluminum powder had the same effect. However, in the case of the graphite-containing systems, there is a 39 °C and 25 °C difference for, respectively, the 26-41% mass Polygloss 90 and 5-15% mass graphite systems. The 36 % difference in the two ranges of front temperatures indicated that substituting Polygloss 90 for the initiator/monomer solution had a bigger impact than substituting graphite for the initiator/monomer solution.

For systems that had 41% mass Polygloss 90 and various high thermal conductivity filler loading, the front velocity followed the same trend illustrated in Figures 5.14-5.16. As the percentage mass high conductivity filler was increased and the % mass initiator/monomer was decreased, the front velocity decreased. This result is shown in Figure 5.17.

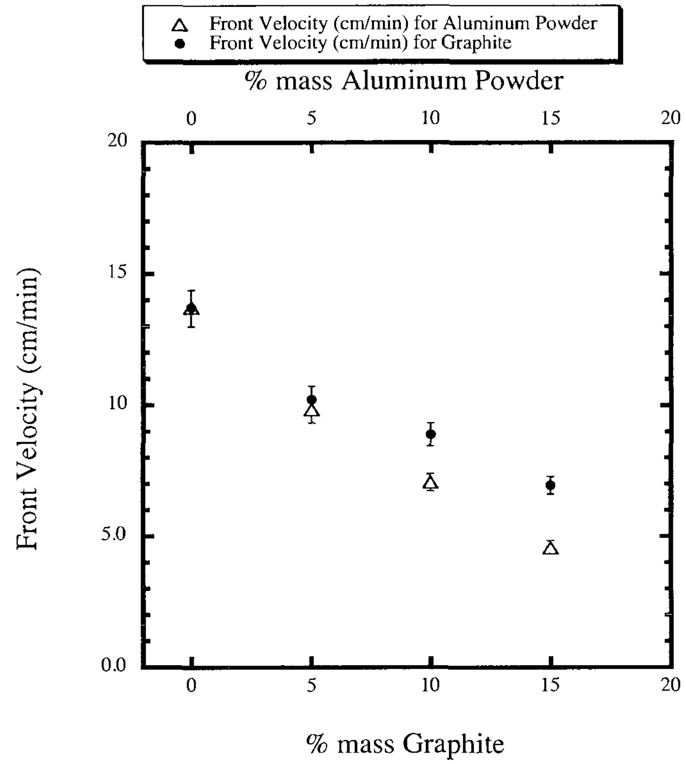


Figure 5.17. Front Velocity vs. % mass Aluminum Powder and % mass Graphite for 41% Polygloss 90

The velocity decreased as the initiator/monomer was replaced by graphite. Like the plot in Figure 5.15, the plot in Figure 5.17 demonstrated that no matter which filler (high thermal conductivity filler or Polygloss 90) was added to replace the initiator/monomer solution, the front velocity decreased. Also, the polymerizable system containing graphite had a higher front velocity than the system containing aluminum powder for the reasons discussed above.

However, unlike the plots in Figures 5.14 and 5.16, which had little difference in trends they demonstrated, the plots in Figures 5.15 and 5.17 reflect the effect of replacing the initiator/monomer solution with Polygloss 90 or high thermal conductivity filler. For example, when looking at the 15% mass difference in the aluminum powder-containing systems in the plots in Figures 5.15 and 5.17, there was a large difference in the dependence of front velocity as a function of % mass filler or the slope of the line as velocity was plotted as a function of % mass filler. For the systems containing 26-41% mass Polygloss 90, there was a 6.5 cm/min front velocity difference in the 26% and 41% mass Polygloss systems. However, for the systems containing 5-15% mass aluminum powder, there was a 5.2 cm/min front velocity difference in the 5% and 15% mass aluminum powder systems. Thus, the front velocities range differed by 20% whereas the front temperatures range differed by 5.7%. The difference in the front velocity dependence on the filler indicated that it does matter whether Polygloss 90 or a high thermal conductivity filler was used to replace the initiator/monomer solution – definitely because of the differences in the heat capacity of aluminum powder (0.9 J g^{-1} K^{-1}) and that of kaolin clay (1.2 J g^{-1} K^{-1}).

An even more dramatic example is the front velocity dependence for the graphite-containing systems. For the data plotted in Figure 5.15, the 26-41% mass Polygloss 90 systems (graphite-containing systems) had a front velocity difference of 7.4 cm/min; for the data plotted in Figure 5.17, the 5-15% mass graphite systems had a front velocity difference of 3.3 cm/min. Thus, a 56% difference in the front velocity rates occurred when either Polygloss 90 or graphite was used to replace initiator/monomer solution. So, Polygloss 90 had a bigger impact on the rate of front velocity than graphite when it is used to substitute for 1 phr BPO in TMPTA-n possibly because of the differences in the heat capacity of graphite (0.7 J g^{-1} K^{-1}) and that of kaolin clay (1.2 J g^{-1} K^{-1}).

Polygloss 90 also had a bigger impact because of its effect on the consistencies of the polymerizable system. The systems containing 41% Polygloss 90 and 5-15%

graphite had similar putty-like consistencies with only the 15% graphite system having a putty-like consistency that was a little dry. In contrast, the systems containing 15% graphite and 26-41% Polygloss 90 had consistencies ranging from a little dry and putty-like for 15% graphite and 41% Polygloss 90 system to a consistency that was somewhat putty-like but a little gel-like (mud-like consistency) for the 15% graphite and 26% Polygloss 90 system. The systems that were a little dry indicate that a front was more likely to quench because the filler acted like a heat sink and was absorbing the heat from the propagating front. Thus, less heat was absorbed with the mud-like consistency than with the putty-like consistency that was a little dry so that a higher front velocity or front temperature could result. A putty-like consistency ensures that heat loss due to fluid flow is minimized. In a system with gel-like or mud-like consistency, some heat loss could be due to slight fluid flow or buoyancy-drive convection.

In contrast, the aluminum powder-containing systems had much more similar consistencies. The system containing 15% aluminum powder and 41% Polygloss 90 was a little dry, but the systems containing either 15% aluminum powder and 26% Polygloss 90 or 41% Polygloss 90 and 5% aluminum powder had either somewhat putty-like consistencies or putty-like consistencies. So, the difference in the front velocity decreased would have been smaller because the aluminum powder-containing systems had similar consistencies so that for different amounts of % mass aluminum powder, similar amounts of heat were being absorbed

Variation in Filler Loading and High Thermal Conductivity Filler Loading

To eliminate the effects of replacing monomer/initiator with filler, systems with 51% mass 1 phr BPO in TMPTA-n and various filler loading and high thermal conductivity filler loading were tested. When the % mass of 1 phr BPO in TMPTA-n was held steady at 59% and the % mass high thermal conductivity filler was increased, the front temperature stayed relatively constant as demonstrated in the plot in Figure 5.18.

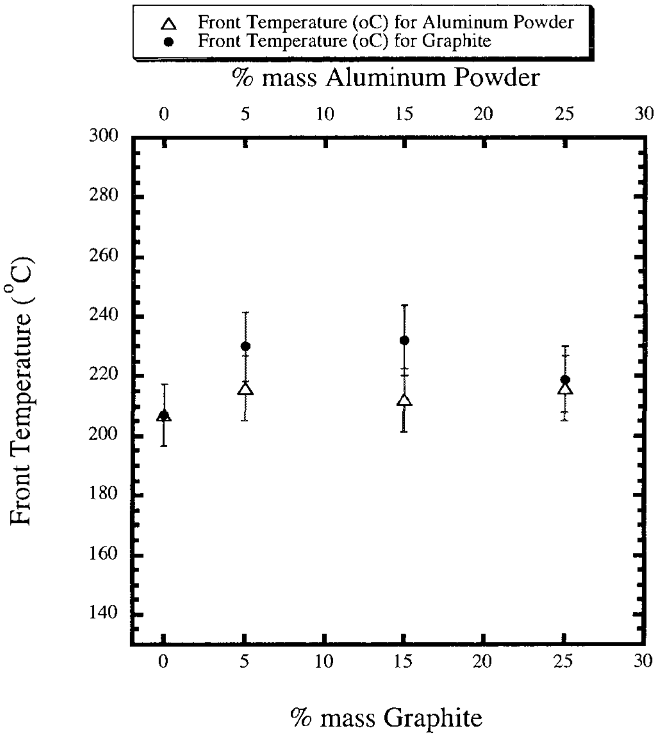


Figure 5.18. Plot of Front Temperature vs. % mass Aluminum Powder and % mass Graphite for 59% mass 1 phr BPO in TMPTA-n

Again, the front temperatures of systems containing graphite were higher than the front temperatures of the systems containing aluminum powder. Yet, all front temperatures for the systems containing 5-15% aluminum powder were within experimental uncertainty of the system containing 0% high thermal conductivity filler, 59% 1 phr BPO in TMPTA-n, and 41% Polygloss 90. In contrast, most of the front temperatures for the graphite-containing polymerizable systems were either within experimental uncertainty or slightly above experimental uncertainty of the original 0% mass high thermal conductivity filler system.

Thus, although aluminum powder did not appear to affect the front temperature of the polymerizable system, graphite did appear to have at least a small impact on the front temperature of the polymerizable system. Because the % mass of the initiator/monomer was held steady, the impact cannot be attributed to removal of any of the initiator/monomer solution. Instead, the impact was due to the consistency of the polymerizable system and to the lower heat capacity of the graphite compared to aluminum powder and kaolin clay. The polymerizable system containing 25% mass graphite and 16% mass Polygloss 90 had a somewhat putty-like/gel-like consistency whereas the 5% mass graphite and 36% mass Polygloss 90 had a putty-like consistency. The system containing 15% mass graphite and 26% mass Polygloss 90 had a somewhat putty-like but a little gel-like consistency.

Despite having a gel-like consistency for the 25% mass aluminum and 16% mass Polygloss 90, the front temperature of this system was within experimental uncertainty of the front temperature for the initial system that contains 0% mass high thermal conductivity filler and has a putty-like consistency. So, consistencies of the systems cannot fully explain why systems containing graphite either have front temperatures slightly above experimental uncertainty of the front temperature or within experimental uncertainty of the initial system. Instead, because being far apart from each other and not being to really thermally conduct or diffusive heat away from the propagating front, thermal conductivity or diffusivity of the high thermal conductivity filler particles have no effect. Thus, only heat capacity has any impact on the front temperature, below the percolation threshold.

In contrast to the plot in Figure 5.18, as % mass graphite was increased and % mass 1 phr BPO in TMPTA-n was held steady at 59% mass, no real trend emerged. Instead, the front velocity stayed within experimental uncertainty of the initial value of the frontal polymerization system that contained no high thermal conductivity filler. This result is shown in Figure 5.19.

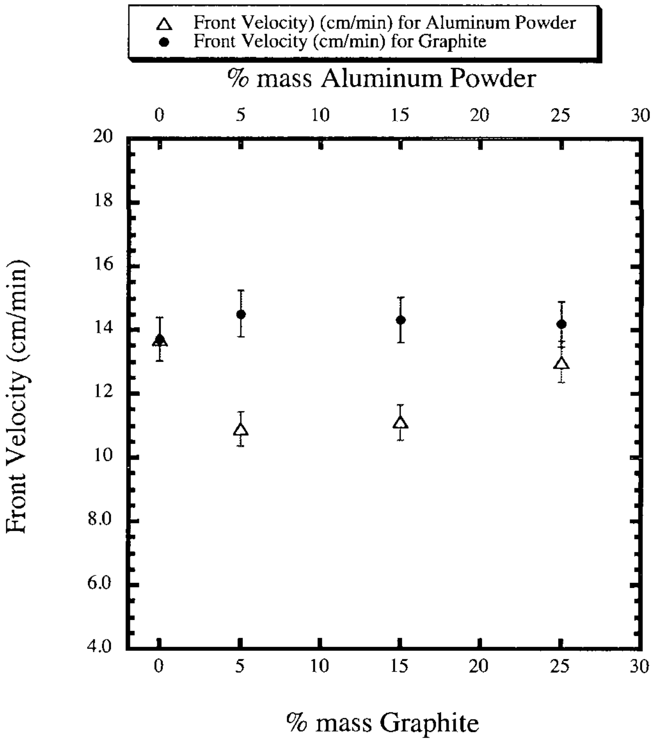


Figure 5.19. Front Velocity vs. % mass Aluminum Powder and % mass Graphite for 59% mass 1 phr BPO in TMPTA-n

On the other hand, when % mass aluminum powder was increased from 0% to 5% mass, an initial decrease in front velocity occurred. Then, front velocity increased as % mass aluminum powder increased. Aluminum powder appeared to have a two-fold effect. On the one hand, as % mass aluminum powder was increased, the consistency of the polymerizable system became more gel-like so that less heat was likely to be absorbed and a higher front velocity should result. On the other hand, aluminum powder seemed to have an inhibitory effect on front velocity because the front velocities for the systems containing 5% and 15% mass aluminum powder were actually lower than the front velocity of the initial system containing no high thermal conductivity filler, and only 25% aluminum powder appeared to have a front velocity close to that of the initial system. In the end, the rheological properties of the polymerizable system appeared to overcome any inhibitory effect that aluminum powder may have on the front velocity. The initial decrease in front velocity was not due to heat capacity because aluminum powder had a higher heat capacity than graphite, and for graphite-containing systems, front velocities were not affected by replacing kaolin's higher heat capacity with the lower one of graphite via substitution of kaolin clay for graphite. Because aluminum powder with its higher thermal conductivity and diffusivity should have increased the front velocity if thermal diffusivity or conductivity had any effect on front velocity, something else in the aluminum powder was causing this initial drop in front velocity when 5% mass aluminum powder was added. The reason for the inhibitory effect is not apparent at this time.

Conclusions

Although the addition of filler, Polygloss 90, lowered the front temperature and velocity when a putty-like consistency was achieved, increased Polygloss 90 loading did not shorten the pot life of the polymerizable system. However, not all fillers had the same effect on temperature. Substituting Cabosil for Polygloss 90 increased the front temperature and velocity by reducing the total amount of filler that needed to be added to form a moldable putty, thus a higher concentration of monomer/initiator was present. Yet too much filler could dry out the system and quench the propagating front. Substitution of filler with inert phase changer materials caused a decrease in front velocity and temperature due changing the consistency of the system and melting of the phase change material, which could have quenched the propagating front a little. A combination of different heat capacities, heats of fusion, and melting points of PCM could also be lowering the front temperature and velocity with no singularly dominant factor -- no matter whether systems had 15% or 23.5% mass PCM. However, both sets of systems showed the same trend, demonstrating that this trend occurred for more than one set of PCM systems. No discernable effect in pot life occurred in the months-long pot life despite the reduction in smoke for some polymerizable systems.

The addition of a catalyst such as *p*-toluenesulfonic acid had little impact on front temperature but increased front velocity because it catalyzed the decomposition of the peroxide. However, the addition of *p*-toluenesulfonic acid also reduced the pot life of the system from months to 24 hours for systems containing D,L-mandelic acid and 60-90 minutes for systems containing only *p*-toluenesulfonic acid, 10.4 phr Luperox®231 in TMPTA-n, and Polygloss 90 when 10% mass catalyst was added. Thus, addition of a catalyst such as *p*-toluenesulfonic acid demonstrated that pot life can be manipulated and controlled to some exact by various the amount of catalyst added, but one large disadvantage of this catalyst is that strong, unpleasant fumes occurred when 5% mass or more of it was used.

For high conductivity filler, substituting the monomer/initiator with filler (Polygloss 90) had a bigger and more visible impact on the front temperature and front velocity than when Polygloss 90 was replaced with high thermal conductivity filler, thereby proving that below the percolation threshold, the thermal diffusivity of the medium was not affected by the presence high thermal diffusivity particles. Thus, little, if any, impact on the front temperature and velocity occurred due to the addition of high thermal conductivity fillers. Clearer trends were also more visible when Polygloss 90 rather than high thermal conductivity filler replaced monomer/initiator. The % mass of 1 phr BPO in TMPTA-n had the biggest impact on front velocity and front temperature, but consistencies of the polymerizable system and choice of filler could also impact the front temperature and front velocity. When % mass 1 phr BPO in TMPTA-n is varied, systems containing graphite had a bigger impact on front velocity and front temperature than systems containing aluminum powder. Also, despite the decrease in front velocity and front temperature as % mass filler increased, higher front temperatures and front velocities occurred in systems containing graphite than in systems containing aluminum. This difference was due to graphite having a lower heat capacity than aluminum powder

Yet thermal conductivity was only a tiny, if any, part affecting the front velocity and front temperature. Modification of the consistency of the polymerizable system had a higher impact as demonstrated by the fact that systems containing a various range of

Polygloss 90 (which had a wide variety of consistencies) had a wider range of front velocities and front temperatures than when % mass high thermal conductivity filler (which had typically only putty-like consistencies) was varied. The non-existent impact of thermal conductivity or thermal diffusivity was further demonstrated when % mass 1 phr BPO in TMPTA-n was held steady and only the % mass of the fillers was varied. Then, only a small difference in front temperature for and no real difference in front velocity occurred for systems containing graphite with this difference in front temperature attributed to the lower heat capacity of graphite.

No difference in front temperature and a strange trend in front velocity occurred for systems containing aluminum powder. Modification of consistency and some kind of inhibitory effect of aluminum powder can explain the strange trend that occurred for the aluminum powder-containing systems.

Overall, % mass of 1 phr BPO in TMPTA-n and consistencies of the polymerizable system had much bigger impacts on front velocity and front temperature than density or any other characteristic that may be causing an inhibitory effect on front velocity. Despite the addition of high thermal conductivity fillers particles, they had no impact on the thermal diffusivity of the medium because they were below the percolation threshold. For this reason, the high thermal conductivity filler particles failed to have any impact on front velocity and temperature as evidenced by no increase in front velocity. Thus, replacement of Polygloss 90 with a high conductivity filler has little practical use for potential industrial applications.

Thus, the solid non-reactive additives had no impact on pot life since none of them reacted with the initiator and/or monomer. Only the addition of a catalyst influenced the pot life. The addition of different fillers, inert phase change materials, and high thermal conductivity fillers had the same impact on front temperature and velocity: with increasing % mass solid additive, a decrease in front temperature and velocity occurred until the quenching point was reached. Because D,L-mandelic acid could react with itself in a polyesterification reaction, an increase in % mass D,L-mandelic acid resulted in a decrease in front velocity but no change in front temperature, but because the reactive phase change material did not react with the acrylate monomer or thermal initiator, it had no impact on pot life. The addition of *para*-toluenesulfonic acid monohydrate had the opposite effect. With increasing % mass catalyst, an increase in front velocity occurred.

The bottom line of this chapter is that Polygloss 90 is the best choice for filler because it produces the least amount of fumes, cracking, and brittleness and forms the best putty-like consistency so that heat loss due to buoyancy-driven convection is minimized.

CHAPTER VI

EFFECTS OF LIQUID ADDITIVES AND MIXED MONOMERS

Although the addition of thiol has been studied in acrylate monomer systems, it has been studied in photoinitiated rather than thermally initiated systems.[7, 47] Also, the effect of thiol on front temperature for a thermally initiated system with triacrylate monomer has not been studied. The effect of different thiols including a monothiol and multifunctional thiol has not been studied in a triacrylate monomer system that is thermally initiated. The impact of a plasticizer on front temperature, front velocity, and pot life has never been studied with thermally initiated systems. Mixed monomer systems and their impact on front temperature, front velocity, and pot life for a thermally initiated system have also never been investigated.

The front temperature of frontal polymerization systems with multifunctional acrylates can be as high as 250 °C.[14] Such high temperatures result in smoking and the release of volatile compounds that prevent the use of frontal polymerization systems indoors. Addition of a trithiol can lower the front temperature and front velocity because a trithiol can undergo copolymerization with an acrylate so that less smoke is produced and enables the system to be used for industrial applications. This copolymerization has a lower enthalpy (15 kcal/mole of ene) than for acrylate homopolymerization, which is ~19 kcal/mole of acrylate.[7] However, pot lives of the system could be lowered from months to minutes -- like systems composed of BPO/TMPTA-n (benzoyl peroxide and trimethylolpropane triacrylate,) and trithiol [trimethylolpropane tris-(3-mercaptopropionate)] so that although less smoke would be produced, the systems would be useless for industrial applications for one-pot systems. Trithiol was selected because it has been used by other researchers for photo-induced thermal frontal polymerization.[7, 47] Another thiol, 1-dodecanethiol, was selected because it had a higher molecular weight per thiol than trithiol.

Copolymerization of a thiol and acrylate is similar to the reaction scheme in Figure 4.1 except that a thiol can react with the monomer and/or the initiator. Like homopolymerization of an acrylate, the reactions of initiator, propagation, and termination occur. A reaction scheme for the copolymerization reaction of TMPTA-n and trithiol with BPO as initiator is shown below in Figure 6.1.

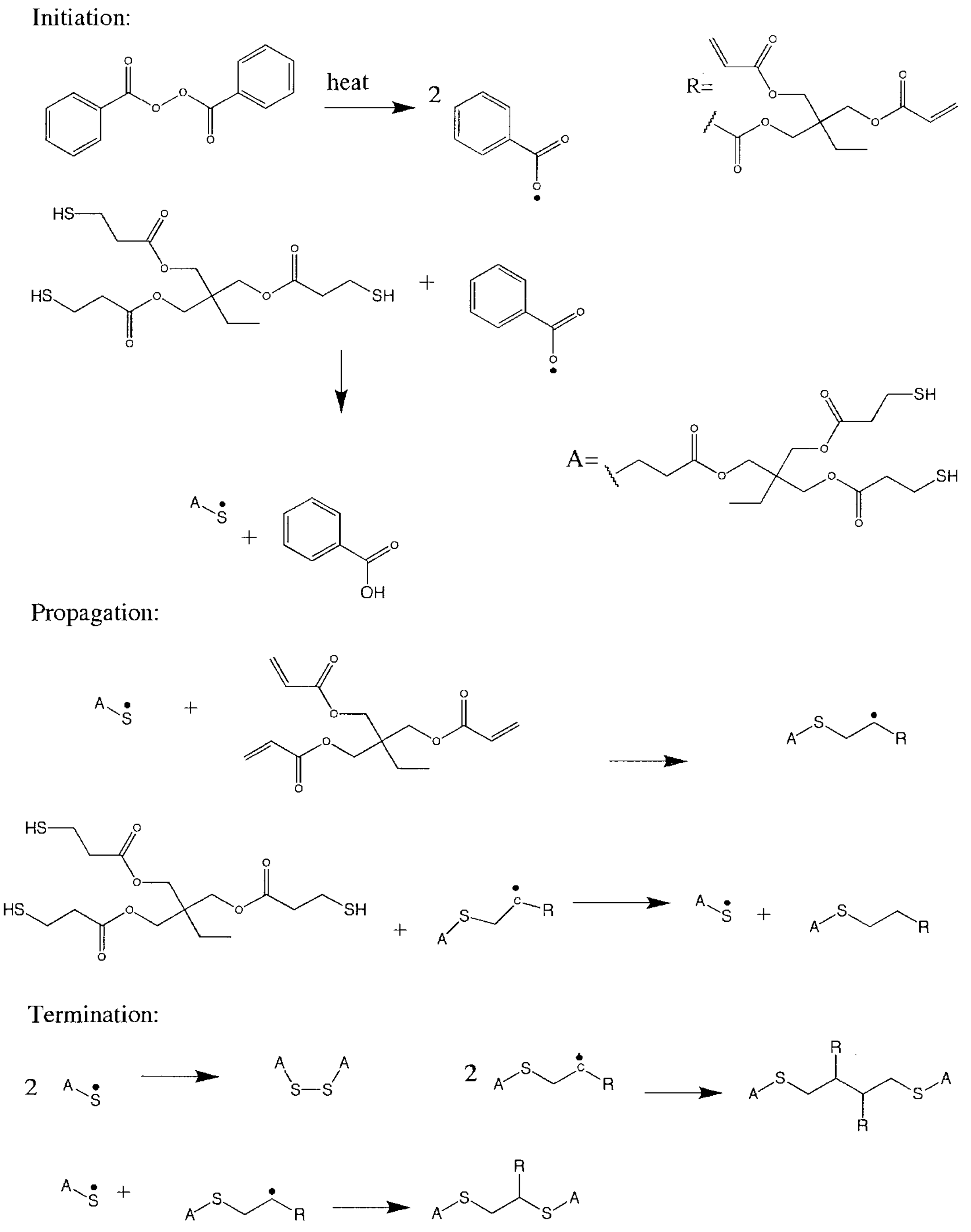


Figure 6.1. General Reaction Scheme of Acrylate and Thiol Copolymerization[56]

Like the homopolymerization of an acrylate illustrated in Figure 4.1, the general steps of initiation, propagation, and termination occur for the copolymerization of a thiol and acrylate. Like the reaction scheme illustrated in Figure 4.1, an external heat source such as a soldering iron decomposes the thermal initiator into free radicals. However, because of the addition of a reactive additive, thiol, the copolymerization process can involve the addition of a thiol to the free radical of the decomposed thermal initiator (in the case of Figure 6.1, BPO) so that a thiyl radical is formed. In the propagation reactions, this thiyl radical can then add to the acrylate monomer to form a carbon radical. Then, in a chain transfer reaction, the radical is transferred from the carbon radical to the thiol, resulting in the formation of a thiyl radical. Termination occurs when two radicals react together. Three possible termination reactions are illustrated in Figure 6.1.

Use of different initiators such as Luperox® 231 [1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane) or benzoyl peroxide (BPO) could impact the effect that a trithiol has on the polymerizable system due to solubility of the initiator in monomer or trithiol. Solubility can affect pot life with more soluble systems having a shorter pot life than those that have slightly immiscible initiator. Choice of monomer and the miscibility of the monomer/initiator systems may also influence the pot life of polymerizable systems. Use of different monomers or mixture of monomers (TMPTA-n with another monomer with a higher molecular weight per double bond) lowered the front temperature and velocity more than a system composed of just TMPTA-n for monomer.[7] Although a longer time of initiation would be required, lower front temperatures could reduce the amount of smoke and fumes produced without lowering the front velocity too much for potential industrial applications.

Addition of a metal salt such as LiCl (lithium chloride) can reduce pot life but can acts as an accelerator so that the slowed front velocity of systems containing trithiol can be increased to a faster rate that ensures complete propagation of the polymerizable system.[26, 53, 57] Faster front velocities than those for systems with trithiol would be more suitable for potential industrial applications.

Addition of a plasticizer should reduce cracking and could reduce the front velocity and temperature, thus reducing the amount of smoke produced without impacting the pot life of a system and could produce systems with faster front velocities than those with trithiol. Previous research with frontal polymerization utilized diethyl phthalate (298-299 °C for boiling point and 156 °C for flash point).[23, 58] but dibutyl phthalate was used in this dissertation because of its higher boiling point (350 °C) and slightly higher flash point (171 °C), thus ensuring that no boiling of the plasticizer occurred.

A mixed monomer system composed of dodecyl acrylate and TMPTA-n was done in order to determine whether replacement of TMPTA-n with dodecyl acrylate could lower front temperature. Because a mixed monomer system composed of TMPEOTA and TMPTA-n resulted in a lower front temperature than pure TMPTA-n systems, it was predicted that a mixture of TMPTA-n and dodecyl acrylate (a less reactive monomer than TMPTA-n) should result in lower front temperatures. Dodecyl acrylate is less reactive than TMPTA-n because it has a higher molecular weight per ene (240 g/mol per double bond) than TMPTA-n (99 g/mol per ene), and previous research has demonstrated that acrylates with more molecular weight per ene are less reactive than those with smaller molecular weights per acrylate double bond.[7]

Addition of Trithiol to TMPTA-n System

Effect of Trithiol on TMPTA-n/BPO System

When the % mass Polygloss 90 was held steady at 41% and the % mass of 1 phr BPO in TMPTA-n and trithiol were varied but had a combined percentage mass of 59%, the front temperature and front velocity decreased upon the addition of trithiol. As shown in Figure 6.2, the addition of small amounts (6.5% mass) of trithiol lowered the front temperature and front velocity.

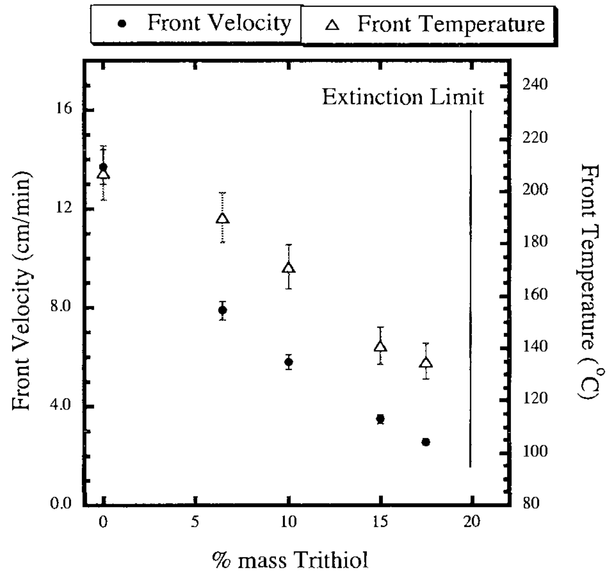


Figure 6.2. Front Velocity and Front Temperature as a Function of percentage mass Trithiol for 1 phr BPO in TMPTA-n with 41% mass Polygloss 90

Increasing the % mass trithiol steadily reduced the front temperature and velocity until the addition of too much trithiol inhibited front propagation and only bulk polymerization occurred. One reason is that the thiol can undergo copolymerization with the acrylate monomer; this process has an enthalpy of ~15 kcal/mole, which is lower than ~19 kcal/mole for the homopolymerization of the acrylate. [7] Hence, less heat is released from the copolymerization reaction so that a slower front velocity and lower front temperature occurred as % trithiol was increased. Because a trithiol reduces oxygen inhibition, the pot life was shortened.[7, 42, 47] Addition of 15% mass or more of trithiol resulted in very little smoke being produced in a system that normally produces a great deal of smoke and reduced the pot life of such systems from months to minutes (~10-20 minutes). Cracking due to expansion and contraction of the polymerizable system and brittleness were also reduced.

An image of the propagating front for the system with 15% mass trithiol is shown in Figure 6.3.

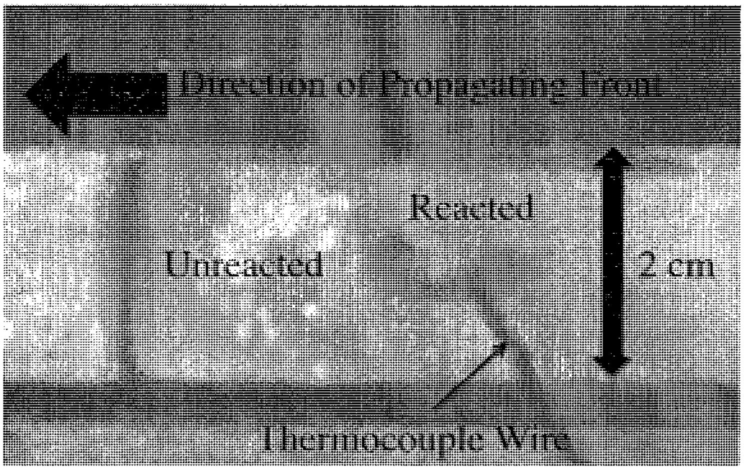


Figure 6.3. Propagating Front for System Composed of 41% mass Polygloss 90, 15% mass Trithiol, and 54% mass 1 phr BPO in TMPTA-n

In contrast to the system composed of Polygloss 90 and 1 phr BPO in TMPTA-n, no cracking can be observed in the polymerized material for the system containing trithiol. This lack of cracking is due to the addition of trithiol.

Addition of Trithiol to TMPTA-n/Luperox® 231 Systems

Using Luperox® 231 (1,1-bis(tert-butylperoxy)-3.3.5-trimethylcyclohexane) as initiator and TMPTA-n (trimethylolpropane triacrylate) as monomer, % mass 1 phr Luperox® 231 in TMPTA-n and % mass trithiol (trimethylolpropane tris(3-mercaptopropionate)) were varied while holding the filler (Polygloss 90) loading at 47% mass. When 1 phr Luperox® 231 in TMPTA-n was tested with different percentages of trithiol, as amount of trithiol increased, then the front velocity and front temperature decreased as shown in Figure 6.5. Increasing % trithiol lowered front temperature and front velocity for several reasons discussed above. An image of the system composed of 1 phr Luperox® 231 in TMPTA-n and 10% mass trithiol in Figure 6.4 demonstrates slightly more cracking than the system composed of 41% mass Polygloss 90, 14% mass trithiol, and 54% mass 1 phr BPO in TMPTA-n shown in Figure 6.3.

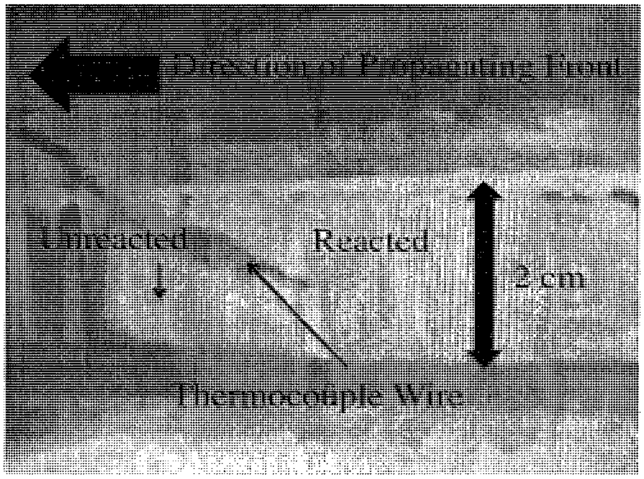


Figure 6.4. Reacting Front for System Composed of 10% mass Trithiol, 43% mass 1 phr Luperox® 231 in TMPTA-n, and 47% mass Polygloss 90

This cracking is difficult to see because it is so small or fine. However, the slight difference in cracking demonstrated that the initiator choice had an impact on the properties of the polymer.

When the initiator concentration was increased from 1 phr to 10.4 phr Luperox® 231, a decrease in front velocity and temperature with increasing % mass trithiol occurred as shown in Figures 6.5. Plots in Figures 6.5 demonstrate similar trends for front temperature and front velocity.

When front velocity was plotted as a function of % mass trithiol for 1 phr and 10 phr Luperox® 231 in TMPTA-n, a clear difference in the shape of the plotted data points can be seen in Figure 6.5.

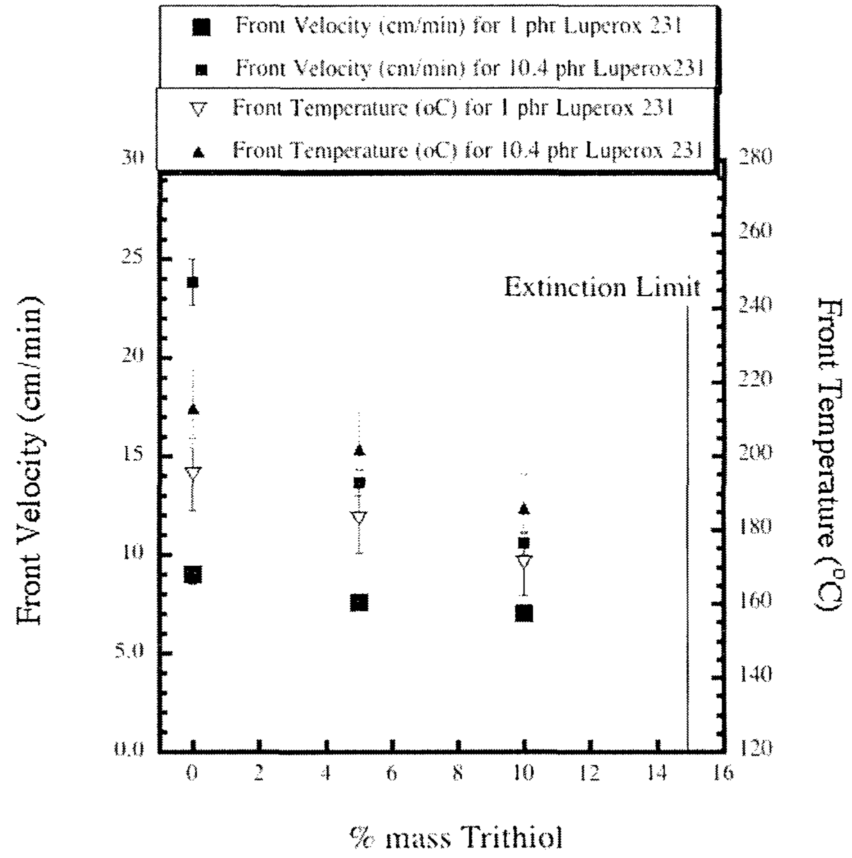


Figure 6.5. Front Velocity and Temperature vs. % mass Trithiol for 1 phr Luperox® 231 in TMPTA-n and % mass Trithiol for 10.4 phr Luperox® 231 in TMPTA-n with 47% mass Polygloss 90

With a smaller initiator concentration, the shape of the plotted data points was almost a straight line parallel with the x-axis; with 10.4 phr Luperox® 231 in TMTPA-n, a sharper slope occurred. The plot for front velocity vs. % trithiol for 10.4 phr Luperox® 231 had a stronger dependence on the thiol concentration than the front velocity with 1 phr Luperox® 231 plot. The graph in Figure 6.5 also showed that a higher initiator concentration resulted in a higher front velocity at different % mass trithiol.

When front temperature vs. % mass trithiol for 10.4 phr Luperox® 231 in TMPTA-n and % mass trithiol for 1 phr Luperox® 231 in TMPTA-n was plotted as shown in Figure 6.5, front temperature decreased with increasing % mass trithiol no matter what the initiator concentration was. However, unlike the trend with front velocity, a higher initiator concentration resulted in higher values for front temperature no matter what the % mass trithiol was.

Effect of Initiator Type and Concentration on Trithiol/TMPTA-n Systems

To compare the effects of different initiators at the same concentration and different % mass trithiol, front velocity vs. trithiol:monomer mass ratios for 1 phr Luperox® 231 in TMPTA-n and trithiol:monomer mass ratio for 1 BPO (benzoyl peroxide) in TMPTA-n were plotted. Trithiol:monomer mass ratios rather than % mass trithiol was plotted because different amounts of filler were used. For the system containing 1 phr BPO in TMPTA-n, 41% mass Polygloss 90 was used whereas 1 phr Luperox® 231 in TMPTA-n had 47% mass Polygloss 90. Hence, even though the percentage mass trithiol would be the same for both systems, the % mass initiator in monomer would be different so trithiol:monomer mass ratios were compared instead. As shown in Figure 6.6, choice of initiator does influence how trithiol will affect the front velocity.

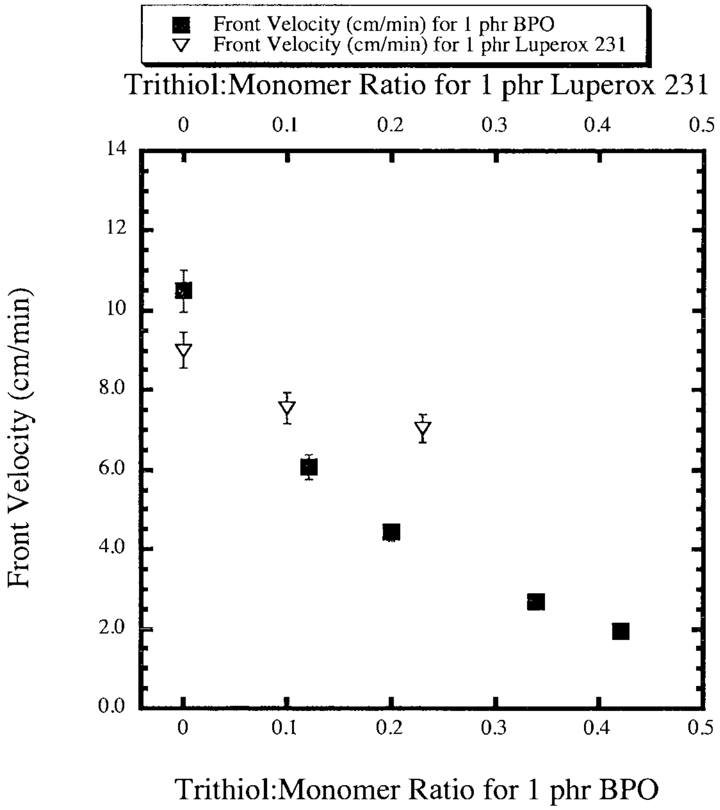


Figure 6.6. Front Velocity vs. Trithiol:Monomer Mass Ratio for 1 phr Luperox® 231 in TMPTA-n with 47% mass Polygloss 90 and for 1 phr BPO in TMPTA-n with 41% mass Polygloss 90

With small amounts of thiol (1% mass), front velocity increased due to removal of oxygen inhibition or the thiol reacting directly with the initiator.[59] Also, trithiol is more reactive with an electron-rich monomer than electron-poor monomers so that if a small amount of trithiol reacted with initiator, it should react with the more electron-rich initiator.[60] Luperox® 231 is a more stable free-radical initiator and more electron rich than benzoyl peroxide so that at lower initiation trithiol:monomer mass ratios, it should have a slower front velocity than BPO. Hence, a slower velocity would occur. This trend can be seen in Figure 6.6.

Another trend that can be seen in Figure 6.6 is that as the trithiol:monomer mass ratio was increased, front velocity decreased. Since the trithiol-acrylate copolymerization can occur and is ~15 kcal/mol versus ~19 kcal/mol for homopolymerization for the acrylate by itself, the trend was not surprising because the copolymerization reaction rate was slower than the homopolymerization reaction.[7] Nason *et al.* demonstrated this finding using acrylates and methacrylates with trithiol and Luperox® as thermal initiator and Darocur 4265 and 1173 as photoinitiators.[7] Another possibility is that the trithiol could be preventing the gel effect which causes an acceleration in front velocity.

A larger amount of trithiol can be added to 1 phr BPO in TMPTA-n than 1 phr Luperox® 231 in TMPTA-n because trithiol was miscible with the Luperox® 231/monomer solution and readily formed a gel- or Jell-O-like substance in the sample whereas two layers can form when trithiol was mixed with a solution containing BPO and monomer. This lack of miscibility means that it took longer for the trithiol to interact with the initiator and monomer so that a slightly longer pot life occurred with the systems with BPO as initiator than with systems with Luperox® 231 as initiator. This slight difference in pot life allowed higher concentrations of trithiol to be tested without fear of bulk polymerization occurring before thermal frontal polymerization could place.

When front temperature vs. trithiol:monomer mass ratio was plotted for 1 phr BPO in TMPTA-n and 1 phr Luperox® 231 in TMPTA-n as shown in Figure 6.7, similar trends to Figure 6.6 were observed.

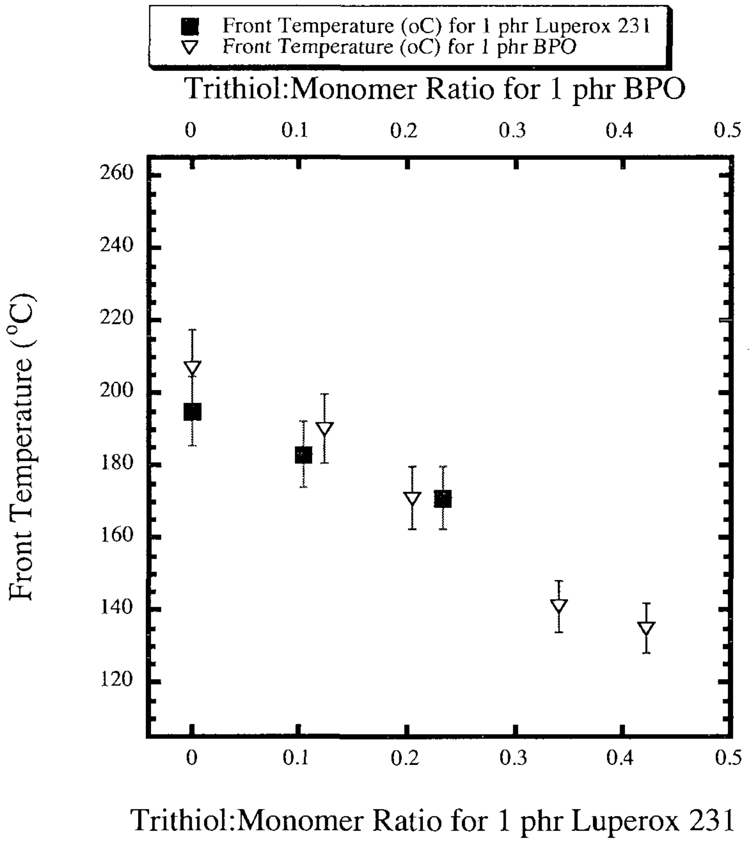


Figure 6.7. Front Temperature vs. Trithiol:Monomer Mass Ratio for 1 phr Luperox® 231 in TMPTA-n with 47% mass Polygloss 90and 1 phr BPO in TMTPA-n with 41% mass Polygloss 90

Like the thiol-acrylate copolymerization reaction discussed by Naseon *et al.*, the front temperature was lower for the system containing Luperox® 231 because more heat was lost to the surroundings than for the BPO-containing system because of the slower front velocities.[7]

More data points were obtained for the system containing BPO than for the system containing Luperox® 231 because trithiol was less miscible in BPO-containing systems than in Luperox® 231-containing systems. Because of the shorter pot lives of Luperox® 231-containing systems, fewer systems with pot lives long enough to record a propagating front could be obtained. Trithiol can immediately react with the monomer and initiator in the Luperox® 231-containing system and shorten the pot life of the system but took longer to become miscible with the BPO-containing system so that a slightly longer pot life occurred for the BPO-containing system since less trithiol could be present than for a similar system with Luperox® 231. The lower solubility of the BPO-containing system could mean that a lower trithiol concentration was present than for a corresponding Luperox® 231-containing system. As demonstrated in many of the figures and published literature, increased thiol concentration reduced front temperature and velocity if a large enough amount of thiol (more than 1% mass) was added.[7, 59] Another possibility is that BPO is an acyl peroxide and thus might react more slowly than Luperox® 231 with the thiol because the COO group of BPO could stabilize the free radical more than any radical formed from the decomposition of Luperox® 231.

Dependence of Velocity and Front Temperature on Amount of Trithiol in TMPEOTA II/TMPTA-n Systems

TMPEOTA II has a higher molecular weight per double bond than TMPTA-n so that a polymerizable system had a lower front temperature and velocity when TMPEOTA II was substituted in place of TMPTA-n.[7] The addition of trithiol helped to lower the front velocity and temperature even further. As the percentage mass trithiol was increased and % mass 1 phr BPO in TMPTA-n was decreased, the front velocity and temperature decreased as shown in Table 6.1.

Table 6.1

Front Temperature and Velocity as a Function of % mass Trithiol and % mass 1 phr BPO in TMPTA-n for TMPEOTA II

% mass Trithiol	% mass 1 phr BPO in TMPTA-n	Front Temperature (^{o}C)	Front Velocity (cm/min)
0	15	193	3.7
5	10	16	3.1
6	9	152	2.5
6.5	8.5	117	2.4

Substitution of TMPTA-n with TMPEOTA II allowed smaller amounts of trithiol to be added with greater reduction of front temperature and velocity; however, after 6.5% mass trithiol, further addition of trithiol prevented propagation. In results discussed above, 15% mass trithiol had to be added to lower the front temperature to 150 °C. Also, TMPEOTA II could be more flexible than TMPTA-n due to the ether linkages in the ethoxylate that increased the spacing between the acrylate monomers in the propagating polymer chain. The greater flexibility and/or increased spacing could be reducing cracking occurring from the expanding and contracting of the propagating front The greater flexibility could reduce the gel effect so that rate of polymerization was reduced compared to TMPTA-n. The addition of trithiol decreased the pot life from weeks to minutes. Substitution of TMPTA-n with TMPEOTA II resulted in an increase in pot life, which increased from minutes to 3-5 days. Also, the system was smoke-free.

Replacement of TMPEOTA II with TMPEOTA III resulted in different front temperatures, front velocities, and pot lives. TMPEOTA III, which has a typical M_n of

912 g/mol and no inhibitor, in a contrast to TMPEOTA II, which has a typical M_n of 428 and no inhibitor. Also, TMPEOTA III was more viscous than TMPEOTA II so that systems were more putty-like. As a result, less TMPEOTA III than TMPEOTA II had to be added in order to have complete polymerization. Thus, TMPEOTA III systems were composed of 25% mass 1 phr BPO in TMPEOTA III, 41% mass Polygloss 90, and 34% mass 1 phr BPO in TMPTA-n rather than 44% mass 1 phr BPO in TMPEOTA and 15% mass 1 phr BPO in TMPTA-n like TMPEOTA II systems. However, despite the difference in amount of ethoxylate and TMPTA-n added, only a maximum amount of 6.5% mass trithiol could be added for both ethoxylate-containing systems. For TMPEOTA III systems, as % mass trithiol was increased and % mass 1 phr BPO in TMPTA-n was decreased, the front velocity and temperature decreased as shown in Table 6.2.

Table 6.2

Front Temperature and Velocity as a Function of Percentage Mass Trithiol and Percentage mass BPO/TMPTA-n Solution for TMPEOTA III

% mass Trithiol	% mass 1 phr BPO in TMPTA-n	Front Temperature (°C)	Front Velocity (cm/min)
0	15	174	3.1
5	10	144	1.6
6.5	8.5	140	1.6
7	8	133	1.3

Like systems in Table 6.1, replacement of 1 phr BPO in TMPTA-n with trithiol resulted in lower front velocities and temperatures. With 7% mass trithiol, incomplete front propagation of the strip occurred for half of the trial runs. Substitution of TMPEOTA II with TMPEOTA III resulted in much lower front velocities and pot lives decreasing from 5-7 days to 24 hours. For the TMPEOTA III system with no trithiol, the pot life was 4 days, which is in sharp contrast to the months-long pot life of the corresponding TMPEOTA II system. Similar amounts of cracking (very little to none) and smoke (very little to none) occurred for both TMPEOTA II and TMPEOTA III systems except for the 0% trithiol systems. The lack of cracking for the TMPEOTA III system is demonstrated in Figure 6.8.

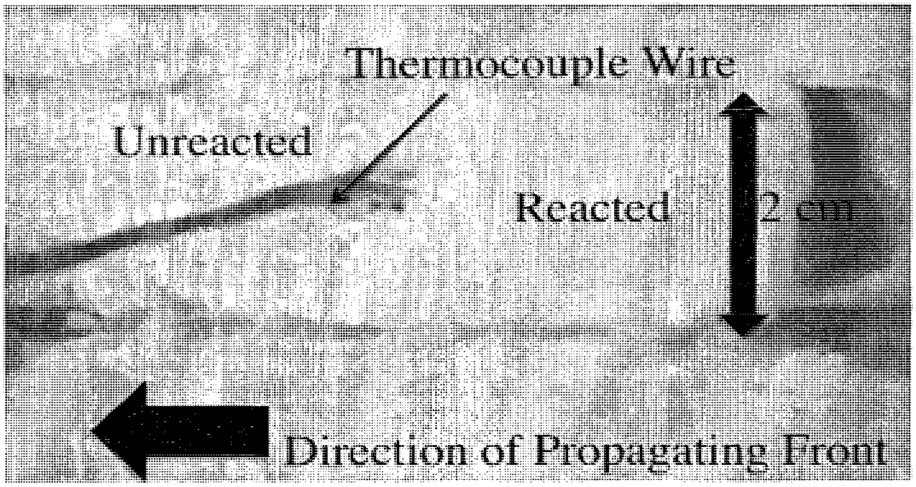


Figure 6.8. Image of Lack of Cracking in System Composed of 25% mass 1 phr BPO in TMPEOTA III, 27.5% mass 1 phr BPO in TMPTA-n, 6.5% mass Trithiol, and 41% mass Polygloss 90

Despite having a higher percentage of 1 phr BPO in TMPTA-n, no cracking occurred in this TMPEOTA III system. This lack of cracking can also be seen in TMPEOTA II systems in Figure 6.9. For the 0% trithiol system, the lower front temperature of the TMPEOTA III system resulted in less smoke being produced than for the corresponding TMPEOTA II system. Once trithiol was added, this advantage of TMPEOTA III disappeared, and both systems (TMPEOTA II and TMPEOTA III) produced very little smoke for 5% mass trithiol and no smoke at all for systems containing 6% mass or more trithiol.

Placement of TMPEOTA II/TMPTA-n Systems on Stainless Steel Surface

Two systems, one containing 41% mass Polygloss 90, 44% mass 1 phr BPO in TMPEOTA II, and 15% mass 1 phr BPO in TMPTA-n and the other containing 41% mass Polygloss 90, 44% mass 1 phr BPO in TMPEOTA II, 6.5% mass trithiol, and 8.5% mass 1 phr BPO in TMPTA-n, were placed on 1-mm thick stainless steel surface and ignited at one end to see how front velocity and temperature were affected and to determine whether the system would adhere to the metal surface. In Table 6.3, the front velocities and temperatures of systems on a wooden surface and aluminum metal surface are shown.

Table 6.3

Comparison of Front Velocity and Temperature for Systems on Wooden and Metal Surfaces

% mass Trithiol	% mass 1 phr BPO in TMPTA-n	Front Temp. (°C)	Front Velocity (cm/min)	Surface
0	15	193	3.7	Wood
0	15	175	3.9	Metal
6.5	8.5	117	2.2	Wood
6.5	8.5	80	2.4	Metal

For systems without trithiol, ignition of frontal polymerization on different surfaces resulted in little difference in front temperature and velocity with data points within the 10% experimental uncertainty of each other. However, for systems containing thiol, the front temperature was almost 40 °C lower, well beyond experimental uncertainty, for the strip propagated on the metal surface, but the front velocity was within experimental uncertainty. The lower front temperatures for systems propagated on a metal surface was due to the metal conducting heat away from the strip; wood was an insulator and did not conduct heat away from the propagating fronts.

Systems containing 15% mass 1 phr BPO in TMPTA-n, 44% mass 1 phr BPO in TMPTEOTA II, and mass 41% Polygloss 90 could propagate to thinner thicknesses (1.5 mm) than systems containing 6.5% mass trithiol, 8.5% mass 1 phr BPO in TMPTA-n, 44% mass 1 phr BPO in TMPEOTA II, and 41% mass Polygloss 90 (2 mm), but more unreacted monomer/initiator remained on the 1-mm stainless steel metal surface for the system containing no trithiol. Also, slightly more cracking and smoking occurred in the system with no trithiol; no smoking occurred for the system with trithiol. Images of the differing degrees of cracking are shown in Figure 6.9.

Figure 6.9. Image of Polymerized Material Containing 6.5% mass Trithiol, 8.5% mass 1 phr BPO in TMPTA-n, 44% mass 1 phr BPO in TMPEOTA II, and 41% mass Polygloss 90 (left) and Polymerized Material Containing 15% mass 1 phr BPO in TMPTA-n, 44% mass 1 phr BPO in TMPTEOTA II, and mass 41% Polygloss 90 (right)

The images in Figures 6.9 demonstrate that the system with trithiol had the least amount of cracking for systems.

All of the above tested systems could not propagate in strips with a thickness of less than 3 mm. However, the system containing 1 phr BPO in TMPEOTA II and 6.5% mass trithiol had the lowest front temperature of 80 °C because of the copolymerization of thiol and acrylate monomer. The system containing no trithiol had a front temperature of 175 °C. The front velocity for the system with no trithiol was 3.9 cm/min, and the system with 6.5% mass trithiol had a front velocity of 2.2 cm/min because of the copolymerization of thiol and monomer. Of the two systems, the only smoke-free system was the system containing trithiol. The other system smoked at least a little.

Because the system containing trithiol had a pot life that was not months-long, a 3-6 mm depth strip was prepared, thermally initiated, and allowed to sit for 24 hours in order to determine if it would adhere to the stainless steel surface after being polymerized. After 24 hours, the strip containing 6.5% mass trithiol, 8.5% mass 1 phr BPO in TMPTA-n, 44% mass 1 phr BPO in TMPTEOTA II, and 41% mass Polygloss 90 had adhered completely to the metal surface and could not be removed. This occurred because the sulfur from the trithiol could have bonded to the stainless steel in the metal surface.

Addition of LiCl to TMPEOTA II/TMPTA-n Systems with 6.5% mass Trithiol

The system with the lowest front temperature and slowest front velocity was tested with LiCl in order to determine whether the addition of this metal catalyst could increase the front velocity with also causing an increase the amount of smoke produced. Using a system consisting of 44% mass 1 phr BPO in TMPEOTA II, 8.5% mass 1 phr BPO in TMPTA-n, 6.5% mass trithiol, and 41% Polygloss 90, different amounts of LiCl were added to 1 phr BPO in TMPEOTA II to see how front velocity, front temperature, and pot life were affected, in particular to see whether a faster front velocity could be achieved without increasing the amount of smoke produced or eliminating or reducing the other positive attributes of adding a trithiol. To ensure that LiCl was thoroughly mixed and dissolved in 1 phr BPO in TMPEOTA II, LiCl was added to the monomer/initiator solution and magnetically stirred overnight.

The system without LiCl had a pot life of 5-7 days. When 25-200 ppm LiCl was added to the system, the pot life was significantly reduced to hours. The addition of LiCl also affected the front temperature and front velocity. As more LiCl was added, the front velocity increased and was a maximum for the system containing 100 ppm LiCl, as shown in Figure 6.10.

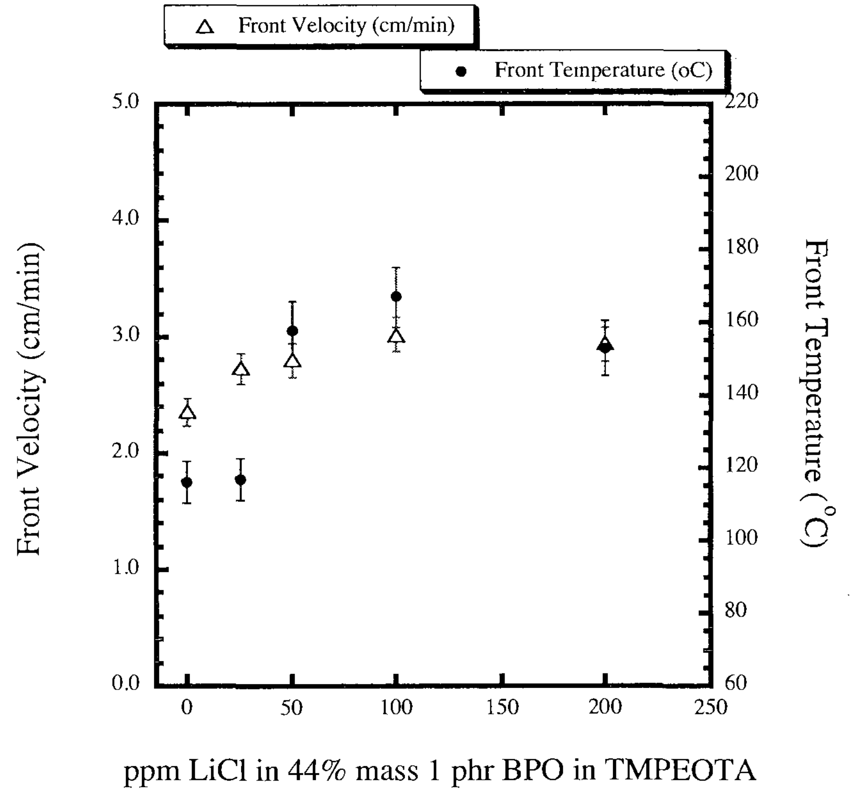


Figure 6.10. Plot of Front Velocity and Front Temperature vs. ppm LiCl in 44% mass 1 phr BPO in TMPEOTA II with 8.5% mass 1 phr BPO in TMPTA-n and 6.5% mass Trithiol

Thereafter, the front velocity reached a plateau and remained steady even at a LiCl concentration of 200 ppm LiCl. The plot in Figure 11.10 demonstrated that any addition of LiCl to the original system containing 1 phr BPO in TMPEOTA II, 1 phr BPO in TMPTA-n, Polygloss 90, and trithiol caused an increase of the front velocity. Therefore, LiCl acted like as accelerator in combination with the trithiol and peroxide initiator and increased the front velocity so that complete propagation of a system took a short amount of time, an important characteristic for potential industrial application.[57] Similar behavior was demonstrated in a patent by Giovando *et. al.* for the polymerization of unsaturated polyesters using peroxide initiators, thiols, and metal salts such as lithium chloride.[57] Although the patent discusses the use of many metal salts including $AlCl_3$, $MgCl_2$, $ZnCl_2$, and $SnCl_4$ as accelerators or catalysts, the patent does not explain how these metal salts can cause an acceleration in the curing process except to claim that the metal salt is able to form a complex with the thiol and an added oxygenated compound such as diethylene glycol.

The front temperature followed a similar trend as the front velocity. As shown in Figure 6.10, the front temperature steadily increased as the concentration of LiCl was increased from 0 ppm to 100 ppm LiCl. Systems containing 50-200 ppm LiCl had front temperatures that are 37 °C higher than the system containing no LiCl. Thus, the addition of 50 ppm and higher concentrations of LiCl increased not only front velocity but front temperature as well. Only the system containing 25 ppm LiCl failed to increase the front temperature.

Thus, as demonstrated by its effect on pot life, front temperature, and front velocity, lithium chloride acted as an accelerator and decreased the effect of the trithiol, which normally causes a decrease in front velocity and front temperature. However, despite the increased front temperature, all systems containing LiCl were still "smoke-free" so that higher front temperatures did not detract from the potential use of this system for potential industrial applications. Also, a putty-like consistency of the polymerizable system, either no or almost no cracking in the polymer, and a strong polymer were also positive characteristics that were maintained despite the increase in front velocity and front temperature. This lack of cracking is illustrated in Figure 6.11.

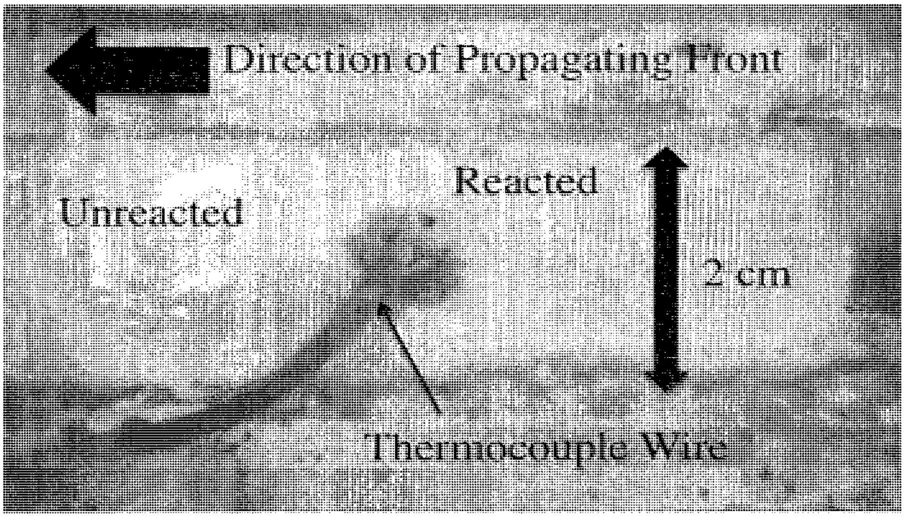


Figure 11.11. Reacting Front for System Composed of 41% mass Polygloss 90, 6.5% mass Trithiol, 8.5% mass 1 phr BPO in TMPTA-n, and 44% mass 1 phr BPO in TMPEOTA II with 100 ppm LiCl

Solubility and TMPEOTA II

When no filler was added, trithiol in 1 phr BPO in TMPTA-n systems formed two immiscible layers. When 1 phr BPO in TMPTA-n was mixed with 1 phr BPO in TMPEOTA II, then one slightly gel-like layer formed. Then, when trithiol was added, two layers initially formed. Once the contents were mixed, then one cloudy, gel-like layer formed.

To examine the miscibility of the components for the system containing 1 phr BPO in TMPTA-n, 1 phr BPO in TMPEOTA II, and trithiol, various solutions were prepared. When a sample vial containing 0.85 g of 1 phr BPO in TMPTA-n, 4.40 g 1 phr BPO in TMPEOTA II, and 0.65 g of trithiol were initially mixed together and allowed to sit for 5 minutes, the sample vial appeared to have two layers: a slightly gel-like looking top layer and a very thin bottom layer. After an additional 3 g of trithiol was added to the sample and the contents mixed and allowed to sit for 10 minutes, a thin clear top layer and large slightly gel-like or Jell-O-like bottom layer formed.

Another sample vial containing 4.40 g 1 phr BPO in TMPEOTA II was mixed with 0.65 g trithiol, and a gel formed before the contents were mixed. Then, 0.87 g 1 phr BPO in TMPTA-n was added and mixed with the contents. Initially, two layers appeared to form: a large middle slightly gel-like looking layer and a very thin bottom layer. After an additional 0.85 g of 1 phr BPO in TMPTA-n was added and mixed with the contents of the sample vial, one slightly gel-like or Jell-O-like layer eventually appeared to form. Then, to confirm that 1 phr BPO in TMPTA-n was soluble with 1 phr BPO in TMPEOTA II with a tiny amount of trithiol, an additional 1.50 g of 1 phr BPO in TMPTA-n was added to the sample, and the contents were then swirled and allowed to sit for over 10 minutes. One slightly gel-like or Jell-O-like layer formed.

Individual solutions of 3.5 g 1 phr BPO in TMPEOTA II with 3.0 g trithiol and of 3.6 g 1 phr BPO in TMPEOTA II with 3.6 g 1 phr BPO in TMPTA-n were also prepared. The sample vial containing 1 phr BPO in TMPTA-n and 1 phr BPO in TMPEOTA II formed one slightly cloudy or oily layer, indicating they were miscible with each other, whereas the sample vial containing 1 phr BPO in TMPEOTA and trithiol formed two layers, indicating only slight solubility. The top layer was clear and large, and the bottom layer was thin but clear. So, 1 phr BPO in TMPEOTA II was miscible with 1 phr BPO in TMPTA-n and was somewhat soluble with trithiol. However, trithiol was less soluble in 1 phr BPO in TMPTA-n than in 1 phr BPO in TMPEOTA II because the bottom trithiol layer was larger.

These solubility experiments could help to explain why systems containing 1 phr BPO in TMPEOTA II, 1 phr BPO in TMPTA-n, and trithiol had longer pot lives (2-5 days) than corresponding systems containing only 1 phr BPO in TMPTA-n and trithiol, which had pot lives that are typically only 30 minutes or less. By having the ethoxylate and triacrylate slightly soluble in each other, less trithiol can be added to the triacrylate. Because less thiol can be added, less oxygen inhibition can be removed, and longer pot lives can be achieved.

Addition of 1-Dodecanethiol to Systems with Different Monomers

Addition of 1-Dodecanethiol to TMPTA-n/BPO Systems

When a monothiol rather than a trithiol was added to a system containing Polygloss 90 and 1 phr BPO in TMPTA-n, front velocity and temperature decreased as the percentage mass 1-dodecanethiol was increased as shown in the plot in Figure 6.12.

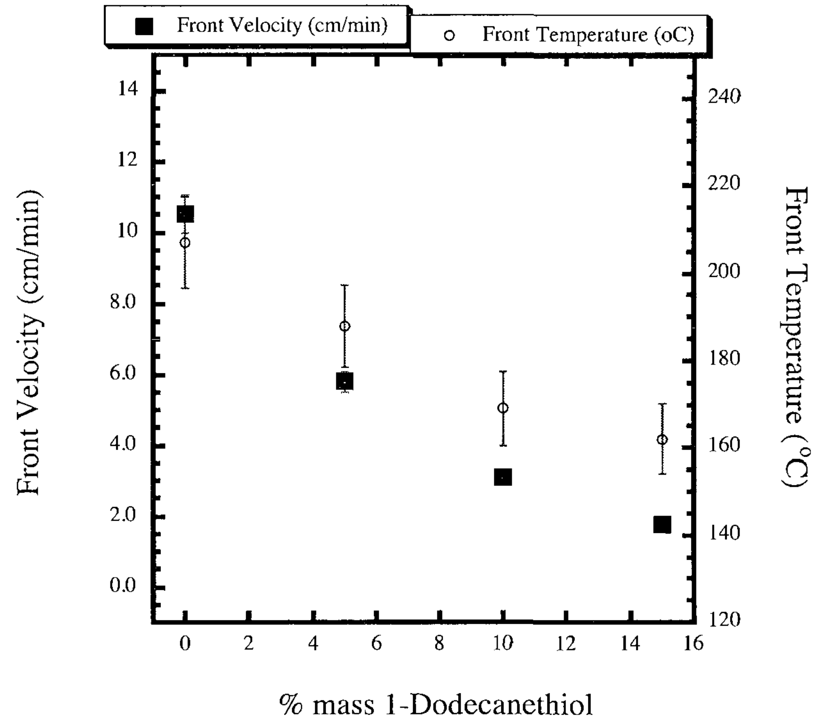


Figure 6.12. Plot of Front Velocity and Temperature as a Function of % mass 1-Dodecanethiol

Thus, both a monothiol and trithiol had similar effects on the front velocity and temperature. However, the monothiol had a higher molecular weight per thiol value (202 g/mol) than the trithiol (133 g/mol) and had a larger impact on front velocity and smaller impact on front temperature. Because 1-dodecanethiol had a larger molecular weight per thiol value than trithiol, the front temperature was reduced. The front velocity was slowed because of the lower front temperature or possibly because it took longer for the thiol to add to the acrylate and undergo copolymerization for 1-dodecanethiol than for trithiol. Another possibility is the effect of decreased cross-linking on front velocity for the system containing 1-dodecanethiol since it is a monothiol rather than a trithiol.

Besides front velocity and temperature, trithiol had a higher % mass that could be added and still have complete propagation.

For 1-dododecanethiol, a smaller impact on front temperature occurred possibly because the copolymerization of the monothiol and triacrylate was hindered by the larger molecular weight per thiol so that homopolymerization of the acrylate occurred more readily. Although the copolymerization of the thiol and acrylate would result in a lower front temperature because of the lower enthalpy of thiol-acrylate polymerization (~14.8 kcal/mole of ene) than homopolymerization of the acrylate (~19.2 kcal/mole of ene), the larger molecular weight per thiol for 1-dodecanethiol than trithiol means that fewer thiols are present in the 1-dodecanethiol than in the trithiol for an equivalent amount added to a triacrylate system.[7] Because fewer thiols were present for 1-dodecanethiol-containing systems than an equivalent amount of trithiol and due to the large molecular weight per thiol than trithiol, homopolymerization of acrylate is more likely to occur for 1-dodecanethiol-containing systems than trithiol-containing systems. Thus, polymerization of systems containing 1-dodecanethiol had a higher front temperature than polymerization of systems containing trithiol.

Despite having an impact on front velocity and temperature, the choice of thiol had little impact on polymer brittleness, the amount of smoke produced, and the degree of cracking. Because of the similar front temperatures, systems containing either 1-dodecanethiol or trithiol produced relatively similar amounts of smoke, degrees of cracking, and strength of polymer. Systems with 15% mass trithiol were slightly stronger (broke into fewer, bigger pieces when smashed with a foot-long piece of wood), produced slightly less smoke, and had slightly less cracking than corresponding systems with 15% mass 1-dodecanethiol. Less cracking and less brittle polymers occurred for trithiol-containing systems than for 1-dodecanethiol-containing systems because trithiol has a higher functionality than 1-dodecanethiol so that more cross-linking can occur in the trithiol-containing systems. Increased cross-linking means that less stress-induced cracking can occur. More cross-linking also means that systems are more viscous so that the rate of termination is slowed for systems containing trithiol, and a faster rate of propagation occurs.

Although addition of a thiol shortened the pot life of systems containing initiator, monomer, and filler, addition of 1-dodecanethiol or trithiol impacted how much the pot life of the system was shortened. For example, addition of trithiol to systems containing BPO, TMPTA-n, and Polygloss 90 reduced the pot life of the polymerizable system from months to minutes. Yet substitution of trithiol with 1-dodecanethiol lengthened pot lives from minutes to hours. For example, a system containing 41% mass Polygloss 90, 10% mass trithiol, and 49% mass 1 phr BPO in TMPTA-n has a pot life of 10-20 minutes whereas a similar system containing 41% mass Polygloss 90, 10% mass 1-dodecanethiol, and 49% mass 1 phr BPO in TMPTA-n had a pot life of over 90 minutes. The larger molecular weight per thiol of 1-dodecanethiol not only impacted front velocity but also lengthened the pot life of a system because it did not remove oxygen inhibition as much as trithiol, possibly did not react as much with the initiator as the trithiol, and had fewer thiols per gram than trithiol, further highlighting how critical thiol choice is for an equivalent amount of thiol added.

Effect of 1-Dodecanethiol on Front Velocity, etc. of TMPEOTA II/TMPTA-n Systems

For systems that contain 1 phr BPO in TMPTA-n, 1 phr BPO in TMPEOTA II, and Polygloss 90, substitution of trithiol with 1-dodecanethiol resulted in lower front temperatures and a smaller % mass of thiol that could be added. Table 6.4 summarizes the results of a system containing 44% mass 1 phr BPO in TMPEOTA II, 41% mass Polygloss 90, and amounts of % mass 1-dodecanethiol and % mass 1 phr BPO in TMPTA-n.

Table 6.4

Front Temperature and Velocity as a Function of % mass 1-Dodecanethiol and % mass 1 phr BPO in TMPTA-n for TMPEOTA II

% mass Trithiol	% mass 1 phr BPO in TMPTA-n	Front Temperature (°C)	Front Velocity (cm/min)
0	15	193	3.7
5	10	148	1.7
6	9	147	1.7

Unlike polymerizable systems with only TMPTA-n as monomer, addition of two monomers, TMPEOTA II and TMTPA-n, resulted in both lower front temperatures and velocities for systems with 1-dodecenethiol in place of trithiol. As discussed above, the higher molecular weight per thiol for 1-dodecanethiol resulted in a smaller amount of thiol that can be added and still have complete propagation. Also, a slower front velocity occurred for the same reason discussed above. However, lower front temperatures occurred for systems with 1-dodecanethiol than for systems containing trithiol. TMPEOTA II has a higher molecular weight per double bond than TMPTA-n. The higher molecular weight per double bond for TMPEOTA II required a longer time for initiation of frontal polymerization so that homopolymerization of the acrylate was harder to initiate than for systems containing only TMPTA-n. The longer time for activation or initiation for the mixed monomer systems negated the smaller effect on front temperature that 1-dodecanethiol had in place of trithiol for systems containing only TMPTA-n. Thus, for both the monothiol and trithiol, copolymerization of the monomers and thiol resulted in the same effects except substitution of trithiol with 1-dodecanethiol now resulted in both a lower front temperature and velocity rather than only a slower front velocity.

A mixed monomer system resulted in being able to add less thiol and also lessened the impact on pot life. Systems containing either trithiol or 1-dodecanethiol had similar pot lives that were days-long, similar degrees of cracking (very little fine cracking or none), the same amount of brittleness of polymer (strong polymer that is hard to break in two when extracting the thermocouple wire), and similar amounts of smoke (very little to none). The similar amounts of cracking or lack of cracking in the 1-dodecanethiol system compared to the corresponding trithiol system in Figure 6.9 is illustrated in Figure 6.13.

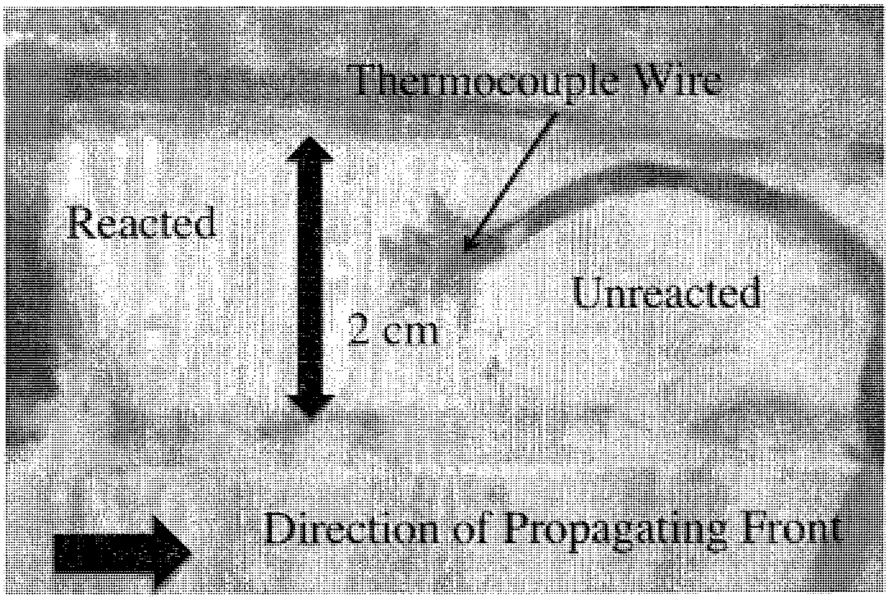


Figure 6.13. Image of Propagating Front for System Composed of 44% mass 1 phr BPO in TMPEOTA II, 6% mass 1-Dodecanethiol, 9% mass 1 phr BPO in TMPTA-n, and 41% mass Polygloss 90

Also, all systems containing either trithiol or 1-dodecanethiol had a putty-like consistency. The higher functionality and ability to cross-link for trithiol in comparison to the monothiol was negated by the higher molecular weight per double bond of the ethoxylate monomer and the longer, more flexible ethoxylate monomer, thereby ensuring that molecular weight per thiol is the only important thiol factor influencing front temperature and velocity.

Addition of Plasticizer

Addition of a plasticizer, dibutyl phthalate (DBP), can help to reduce cracking in a system and may help lower front temperature as a diluting effect so that the initiator/monomer solution concentration was lower than if initiator/monomer solution without plasticizer or another additive was mixed with filler. From the variation of filler loading, the polymerizable system with the lowest front temperature (41% mass Polygloss 90) was chosen so that the filler loading was held constant and the amounts of DBP and amounts of initiator dissolved in monomer were varied. As shown in Figure 6.14, addition of DBP lowered the front temperature very little (compared to similar systems with trithiol) as % mass DBP was increased.

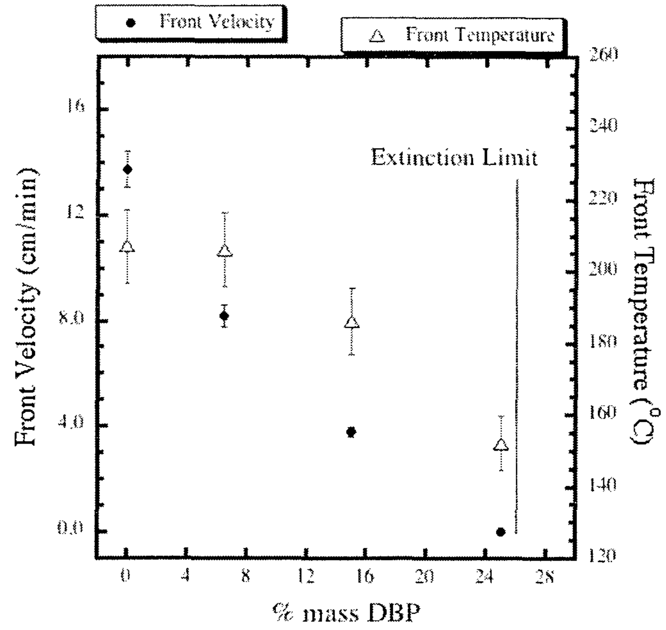


Figure 6.14. Front Velocity and Temperature as a Function of % mass DBP

The DBP affected front velocity by diluting the reactants and by absorbing heat. Unlike the addition of a thiol, no additional reactions occurred, thereby maintaining the same months-long pot life that occurred for systems with only monomer, initiator, and filler. Like trithiol-containing systems, increasing the % mass DBP resulted in less cracking, less brittleness, and slightly less smoke, but the impact on fumes and smoke production was less for systems containing DBP. The amount of cracking present in the DBP-containing systems is illustrated in Figure 6.15.

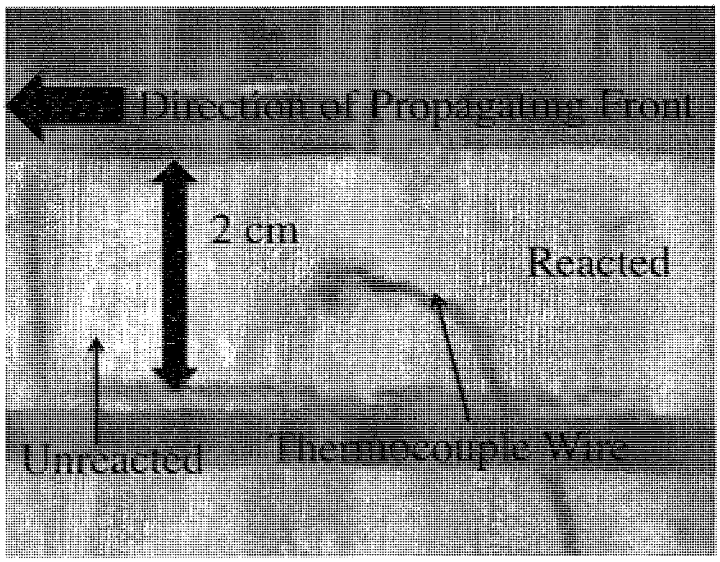


Figure 6.15. Image of a Propagating Front for System Composed of 15% mass DBP, 44% mass 1 phr BPO in TMPTA-n, and 41% mass Polygloss 90

The system with DBP had more cracking along the edges of the polymerized material than the corresponding trithiol system pictured in Figure 6.3. Also, unlike trithiol, increasing the % mass DBP reduced the putty-like consistency of the.

Adding monomer solutions that had higher concentrations of initiator to a system with 41% mass Polygloss 90 and 15% trithiol or 15% mass DBP increased front velocity but had no effect on front temperature when the initiator concentration was increased from 1 phr to 5 phr. As shown in Figure 6.16, front velocity increased at similar rates for systems with 15% mass trithiol or 15% mass DBP.

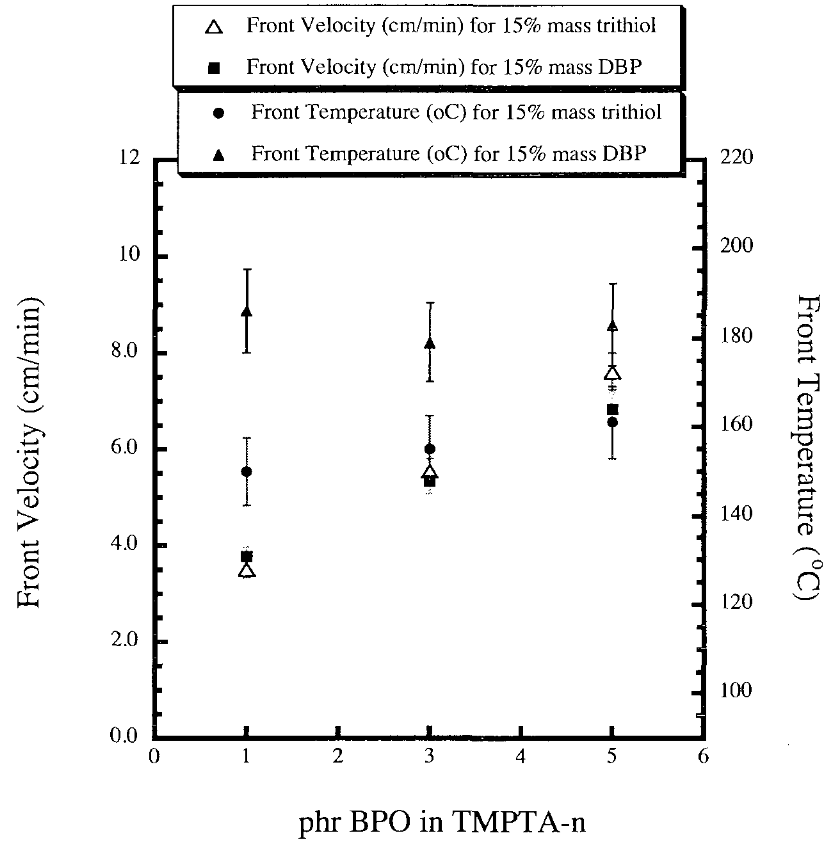


Figure 6.16. Plot of Front Velocity and Temperature vs. x phr BPO in TMPTA with 41% mass Polygloss 90 and 15% mass Trithiol or 15% mass DBP

Increasing BPO concentration increased front velocity because the rate of polymerization is dependent upon the initiator concentration.[42] When the front velocity increased, the amount of smoke produced from the propagating front also increased. For systems with 15% mass trithiol, all three systems had either no cracking or almost no cracking and similar pot lives, i.e., bulk polymerization occurred within 10 minutes of systems being prepared.

Because DBP acted as a diluent and did not undergo additional reactions with the acrylate, increasing the initiator concentration caused the front velocity to increase with no impact on front temperature. This result was similar to systems with trithiol.

According to Figure 6.16, no change in front temperature occurred when the initiator concentration was increased from 1 to 5 phr BPO in TMPTA-n for systems with 15% mass DBP. Like systems with 15% mass trithiol, increasing the initiator concentration for systems with 15% mass DBP failed to influence anything else including degree of cracking, pot life of the system, and brittleness of the polymer. Unlike systems with 15% mass trithiol, increasing the initiator concentration did not impact the amount of smoke produced because of the higher front temperatures for systems with plasticizer than with trithiol.

Development of TMPEOTA I Systems with Trithiol or TMPTA-n

TMPEOTA I (7/3 EO/OH) with 500 ppm monomethyl ether hydroquinone inhibitor and an average of M_n of 604 g/mol was the first tested in a mixed monomer system with 1 phr BPO in TMPTA-n to determine if it would be a better additive than DBP for reducing front temperature without lowering front velocity too much. No matter whether TMPEOTA I or 1 phr BPO in TMPEOTA I was used, systems composed of 41% mass Polygloss 90, 44% mass 1 phr BPO in TMPTA-n, and 15% mass TMPEOTA I or 1 phr BPO in TMPEOTA I had lower front temperatures (188 °C and 180 °C for TMPEOTA I and 1 phr BPO in TMPEOTA I, respectively) than systems composed of just 59% mass 1 phr BPO in TMPTA-n and 41% mass Polygloss 90 (207 °C). Systems with TMPEOTA I (or 1 phr BPO in TMPEOTA I) had front temperatures similar to those with 15% mass DBP (186 °C) and higher than corresponding systems with trithiol (150 °C). The higher double bond per molecular weight of TMPEOTA I compared to

TMPTA-n meant that a lower front temperature occurred with a longer time for initiation of the front.[7]

Unlike DBP, replacement of TMPTA-n with TMPEOTA I did not lower front temperature because of a dilution effect but lowered it because of the lower heat released per gram of monomer. The front velocity decreased when TMPEOTA I (5.2 cm/min) or 1 phr BPO in TMPEOTA I (5.2 cm/min) replaced some of the 1 phr BPO in TMPTA-n for a system originally composed of 49% mass Polygloss 90 and 51% mass 1 phr BPO in TMPTA-n (10.5 cm/min). These velocities were much higher than corresponding systems with DBP (3.8 cm/min) or trithiol (2.7 cm/min) and so would be more helpful as an additive than plasticizer for rapid repair because of the faster front velocities but similar front temperatures as systems with DBP. Less smoke than systems with just 1 phr BPO in TMPTA-n and Polygloss 90 was produced with less cracking and a more putty-like consistency.

However, systems composed of 59% mass 1 phr BPO in TMPEOTA I and 41% mass Polygloss 90 failed to polymerize completely because of the higher molecular weight per double bond, which caused quenching of the front. A similar system with just TMPTA-n in place of TMPEOTA I had complete polymerization because of the lower molecular weight per double bond (50% mass Polygloss 90 was the quenching point for systems with 1 phr BPO in TMPTA-n) so that a lower filler loading than 41% mass or higher initiator concentration or mixture of two monomers was necessary for complete propagation of a BPO/TMPEOTA I system with 41% mass Polygloss 90.

Increasing the percentage mass of 1 phr BPO in TMPEOTA I to 44% mass and addition of 15% mass 1 phr BPO in TMPTA-n with 41% mass Polygloss 90 resulted in front temperatures of 166 °C and a front velocity of 1.4 cm/min. Despite the hard polymer (hard to break in two to extract the thermocouple wire), which was similar in terms of brittleness to systems composed of trithiol and TMPEOTA II, the system itself had a consistency of peanut butter rather than toothpaste and so was harder to mold and required longer times for initiation than systems composed of TMPEOTA II and TMPTA-n. Although very little smoke was produced (similar in quantity to systems with 15% mass trithiol, 44% mass 1 phr BPO in TMPTA-n, and 41% mass Polygloss 90), incomplete propagation of the strip sometimes occurred, and the front velocity was slower than systems composed of 1 phr BPO in TMPTA-n, 1 phr BPO in TMPEOTA II, trithiol, and Polygloss 90 (2.4-3.1 cm/min) so that it would not be useful for rapid repair applications.

Substituting trithiol in place of 1 phr BPO in TMPTA-n for systems composed of 44% mass 1 phr BPO in TMPEOTA I, 15% mass additive, and 41% mass Polygloss 90 resulted in systems with no smoke produced, but bulk polymerization occurred within 6-10 minutes of systems being prepared. Also, no frontal polymerization could be initiated despite sustained contact with a soldering iron for over 3 minutes. Thus, because of the lack of frontal polymerization, TMPEOTA I was not a useful monomer to use for systems composed of mixed monomers or monomer and trithiol despite the low front temperatures and lack of smoke produced.

Replacement of TMPTA-n with Dodecyl Acrylate

Using the initial system composed of 59% mass 1 phr BPO in TMPTA-n and 41% mass Polygloss 90, % mass 1 phr BPO in TMPTA-n was replaced with 1 phr BPO in dodecyl acrylate to determine whether a lower front temperature and velocity than those of a mixed monomer system composed of ethoxylate and TMPTA-n would be produced. As shown in Figure 6.17, as % mass 1 phr BPO in dodecyl acrylate increased, the front velocity and temperature decreased.

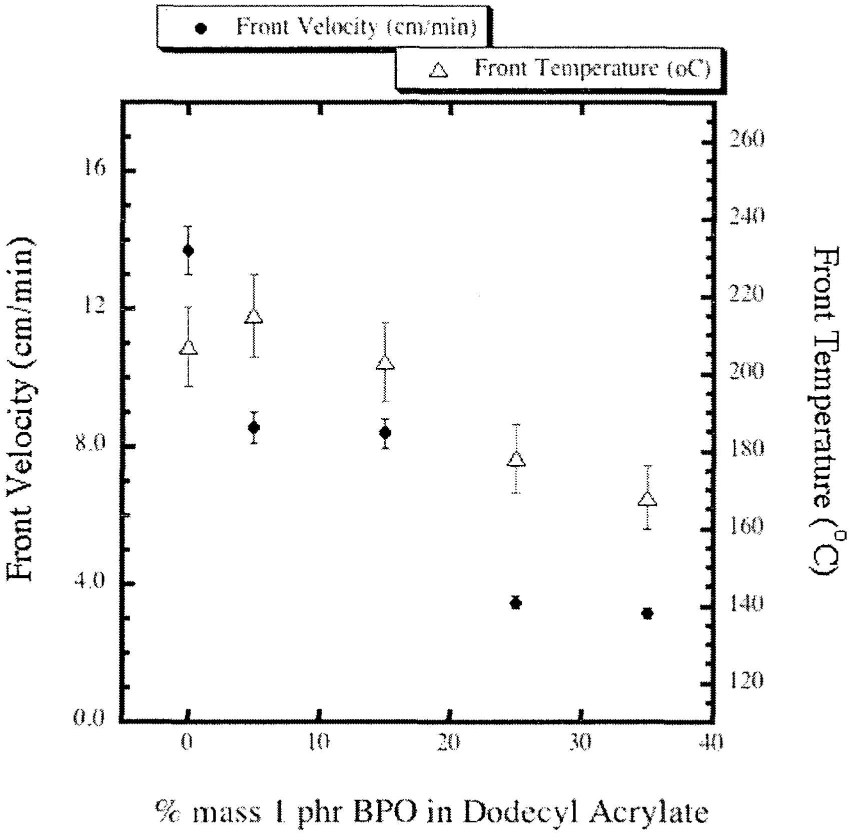


Figure 6.17. Front Velocity and Temperature vs. % mass 1 phr BPO in Dodecyl Acrylate with Various Amounts of 1 phr BPO in TMPTA-n and 41% mass Polygloss 90

Initially, when 5% and 15% mass 1 phr BPO in dodecyl acrylate were added, the front temperature stayed within the experimental uncertainty of the system with no dodecyl acrylate. However, when 25% mass 1 phr BPO in dodecyl acrylate was added, the front temperature dropped below experimental uncertainty of the initial system without dodecyl acrylate. With 35% mass 1 phr BPO in dodecyl acrylate, some strips had incomplete propagation despite the same putty-like consistency that was found in all other frontal polymerization systems. Thus, no systems beyond 35% mass 1 phr BPO in dodecyl acrylate were tested.

In contrast to the front temperature, front velocity decreased when 5% mass 1 phr BPO in dodecyl acrylate was added and continued to decrease as more 1 phr BPO in dodecyl replaced 1 phr BPO in TMPTA-n. Because dodecyl acrylate had a higher molecular weight per double bond than TMPTA-n, the frontal polymerization system lost less heat to the surrounding region, which resulted in less heat being available to raise the temperature of the surrounding region of the hot zone. Less heat was produced per gram of material with dodecyl acrylate because of the larger molecular weight per double bond so that the reaction rate decreased as the fraction of monoacrylate was increased, resulting in a lower front velocity.

The amount of cracking in the polymer also increased as % mass 1 phr BPO in dodecyl acrylate was increased. The increase in cracking compared to the system composed of 41% mass 1 phr BPO in TMPTA-n and 59% mass Polygloss 90 is demonstrated in Figure 6.18.

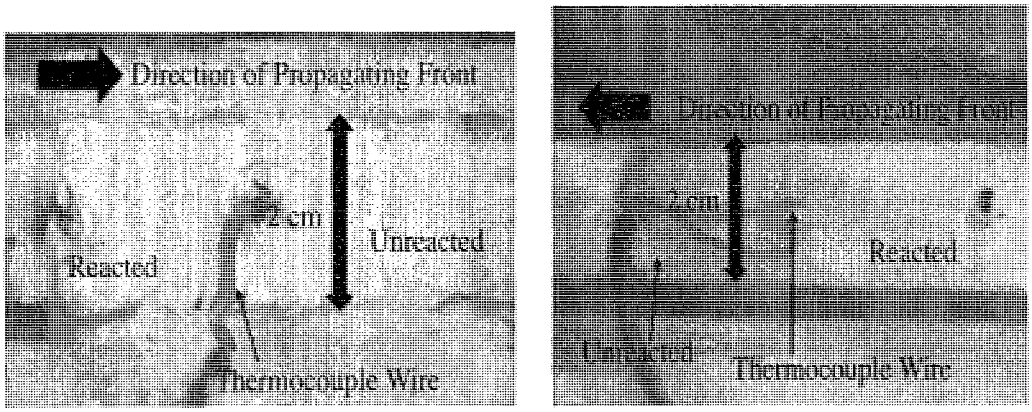


Figure 6.18. Images of Propagating Fronts for System Composed of 24% mass 1 phr BPO in TMPTA-n, 35% mass 1 phr BPO in Dodecyl Acrylate, and 41% mass Polygloss 90 (left) and for System Composed of 41% mass Polygloss 90 and 59% mass 1 phr BPO in TMPTA-n (right)

Much more cracking occurred in the system with dodecyl acrylate than in the system with only TMPTA-n as monomer, whose propagating front is difficult to observe in the image. More cracking occurred because less crosslinking occurred in the dodecyl acrylate system. A triacrylate such as TMPTA-n can crosslink; a monoacrylate such as dodecyl acrylate cannot. Since TMPTA-n can crosslink, less cracking occurred because expansion and contraction of the polymerizable system was hindered by the crosslinked monomers and so was reduced. One advantage of using 1 phr BPO in dodecyl acrylate in place of 1 phr BPO in TMPTA-n was that less smoking occurred as more 1 phr BPO in dodecyl acrylate was added. However, because of the amount of cracking produced, the system was more brittle (broke into more numerous smaller pieces when hit with a foot-long piece of wood to extract the thermocouple wire) and thus was not as good as a mixed monomer system composed of TMPEOTA II and TMPTA-n for potential industrial applications.

Conclusions

The addition of trithiol to TMPTA-n/BPO systems dramatically reduced the front temperature and front velocity. The front temperature was reduced from 207 °C to 135 °C when the percentage trithiol was increased from 0% to 17.5%. By lowering the front temperature and front velocity, the amount of smoke produced was greatly reduced. However, addition of trithiol reduced the pot life of the system from weeks to less than 10 minutes. For strips with dimensions of 2 cm x 4 cm x 3-5 mm, increasing BPO concentration increased both the front temperature and front velocity, thereby allowing complete propagation of the strip to occur more quickly and helping to eliminate the potential that spontaneous polymerization might occur before frontal polymerization of the strip was complete

Addition of trithiol to TMPTA-n/Luperox® 231 systems had the same impact on front velocity and temperature as the addition of trithiol to TMPTA-n/BPO systems. The choice of initiator is important because of differences in pot lives. Shorter pot lives means that less thiol can be added, thus resulting in higher front temperatures and the production of more smoke. Thus, BPO is a better choice of initiator than Luperox® 231 for trithiol systems because slightly longer pot lives occurred and more trithiol could be added.

The addition of trithiol decreased the front velocity and temperature and reduced pot life from months to minutes when TMPTA-n was the only monomer used, but because the majority of TMPTA-n was replaced with TMPEOTA, the pot life of the trithiol-containing system was extended from 10 minutes to 3-5 days. Reduced brittleness, very little cracking of the polymer, and adhesion to stainless steel and wood surfaces are also advantages of the polymerizable system consisting of 1 phr BPO in TMPTA-n, 1 phr BPO in TMPEOTA II, trithiol, and Polygloss 90. The addition of trithiol allowed adhesion to stainless steel surfaces because of interactions between the sulfur of the thiol and the metal of the surface. Substitution of TMPEOTA II with TMPEOTA III resulted in only slight advantages -- unless a shortened pot life is desired. Systems with TMPTA-n, trithiol, and either TMPEOTA II or TMPEOTA III resulted in longer pot lives than for polymerizable systems that have trithiol and only TMPTA-n as the monomer. So, for smoke-free systems, TMPEOTA II is a better choice of monomer than TMPEOTA III. Placement of TMPEOTA II/TMPTA-n systems on different surfaces had no difference in front velocity and temperature. Only for the system containing 6.5% mass trithiol is the front temperature drastically lowered beyond experimental error (~40 °C difference). Thus, addition of trithiol in mixed monomer systems has many positive characteristics that make it ideal for use in an industrial setting including good adhesion to a stainless steel surface, no cracking, controllable pot life, and no smoking and very few fumes.

Addition of tiny amounts of LiCl to the TMPEOTA II monomer for the system consisting of 44% mass 1 phr BPO in TMPEOTA II, 8.5% mass 1 phr BPO in TMPTA-n, 6.5% mass trithiol, and 41% mass Polygloss 90 resulted in a shortened pot life, a faster front velocity, and higher front temperature; however, systems were still smoke-free and strong and had little to no increase in cracking. Lithium chloride acted as an accelerator and had a bigger impact than the effect of the trithiol, which normally caused a decrease in front velocity and front temperature and increase in pot life, so that a better balance between good pot life and fast front velocity was obtained. Thus, the addition of LiCl enhanced rather than detracted from the possible industrial use of this polymerizable system and was more advantageous than replacing TMPEOTA II with TMPEOTA III.

Substitution of trithiol with 1-dodecanethiol produced different results for systems containing either mixed monomers or only TMPTA-n. Like trithiol, replacement of 1 phr BPO in TMPTA-n with 1-dodecanethiol resulted in lower front temperatures velocities, but the degree of impact on front velocity was greater for 1-dodoecenthiol. In contrast to trithiol, 1-dodecanethiol had a smaller impact on front temperature for systems containing only TMPTA-n. Choice of thiol was important for systems containing only TMPTA-n, but the higher molecular weight per thiol for 1-dodecane resulted in a lower front velocity for any type of system. Because of the higher molecular weight per double bond of TMPEOTA II, the advantages of using a trithiol in place of a monothiol and the potential for increased cross-linking was negated so that the molecular weight per thiol was more important for mixed monomer systems. Thus, use of 1-dodecanethiol had a bigger impact on the front temperature and velocity than trithiol for mixed monomer systems.

Addition of plasticizer helped to reduce the amount of cracking that sometimes occurred along the edges of the strip but failed to have the same dramatic effect on front temperature as trithiol. Like trithiol, it acted as a diluent. However, DBP did not undergo additional reactions with the monomer and initiator so that the pot life of the system was not affected. In addition, DBP cannot remove oxygen inhibition like trithiols so that it cannot impact pot life. Like trithiol-containing systems, increasing the initiator concentration for DBP-containing systems resulted in higher front velocities, but DBP-containing systems had no change in front temperature whereas increasing initiator concentration for trithiol-containing systems resulted in a slight increase in front temperature.

Addition of TMPEOTA I to mixed monomer systems of TMPTA-n/TMPEOTA I had no advantage compared to similar systems composed of TMPEOTA II/TMPTA-n or even TMPEOTA III/TMPTA-n except that less TMPEOTA I needed to be added in order to lower the front temperature to produce systems with less smoke than systems composed of 59% mass 1 phr BPO in TMPTA-n and 41% mass Polygloss 90. The inhibitor in TMPEOTA I rendered the monomer useless compared to similar ethoxylates (TMPEOAT II and TMPEOAT III) so that less ethoxylate could be added without quenching the propagating front.

Substitution of TMPTA-n with dodecyl acrylate resulted in less smoke being produced, but a reduction in front velocity and, eventually, cessation of complete propagation of the strip occurred. An increase in cracking due to less crosslinking also was a disadvantage of using dodecyl acrylate in place of TMPTA-n because the polymer became much more brittle due to cracking and less crosslinking. Thus, TMPTA-n is a better choice of monomer than dodecyl acrylate despite the few advantages that use of dodecyl acrylate presents.

Thus, the addition of a thiol (trithiol or 1-dodecanethiol) resulted in lower front temperatures and velocities and reduced pot lives because the thiol can react with monomer in a copolymerization reaction. The addition of a plasticizer had less of an impact on front temperature and velocity than the addition of a thiol because it did not react with the initiator or monomer. Because the plasticizer did not react with the initiator or monomer, it also had no impact on pot life. Addition of less reactive monomers than TMPTA-n in a mixed monomer system resulted in lower front temperatures and velocities than systems with pure TMPTA-n but had no impact on pot life. However, the addition of a mixed monomer system had less impact on front temperature and velocity than the addition of trithiol (reactive liquid additive), which can react with the acrylate monomer and initiator.

The bottom line is that systems containing a mixture of monomers and trithiol produced systems with the lowest front temperatures and longest pot lives, least amount of cracking, adhesion to wooden and metal surfaces, good putty-like consistency, and least amount of brittleness.

CHAPTER VII

FRONTAL SYSTEMS WITH HDODA AND TMPTMA

Although HDODA (1,6-hexanediol diacrylate) and TMPTMA (trimethylolpropane trimethacrylate) have previously been used with silica for spherical frontal polymerization or for the study of photoinitiated systems with thermal initiator,[7, 23] they have not been studied for thermal frontal polymerization with Polygloss 90 as filler. Because of their lower reactivity than TMPTA-n (trimethylolpropane triacrylate), HDODA and TMPTMA should have lower front temperatures and velocities than TMPTA-n. The challenge with studying these less reactive monomers is to develop a low front temperature polymerizable system that can undergo complete polymerization of the strip. Addition of a thiol can ensure that complete polymerization eventually occurs.

Besides TMPTA-n (trimethylolpropane triacrylate), other monomers including HDODA (1,6-hexanediol diacrylate) were tested. With its lower molecular weight per double bond (99 g/mol per ene), TMPTA-n is more reactive than HDODA (113 g/mol per ene) and thus is less likely to quench if filler is added.[7] However, less reactive monomers may propagate more slowly so that lower front temperatures occur. With lower front temperatures, less smoke may be produced. For this reason, HDODA was selected.

Although Polygloss 90, a kaolin clay, was used for many of the TMTPA-n systems, different fillers including sand and Cabosil (fumed silica) or mixtures of fillers were evaluated with HDODA systems to determine whether they could lower front temperature. Thus, the effective of non-reactive additives on a polymerizable system were studied.

A plasticizer, dibutyl phthalate (DBP), was added to HDODA/BPO (benzoyl peroxide) systems in order to determine whether it could help to reduce the cracking observed in systems studied in previous TMPTA-n systems and in earlier tested HDODA systems with different types of fillers. Addition of a plasticizer could help to increase the flexibility of the acrylate systems so that the cracking due to expansion and contracting of the propagating front should be reduced. Also, the plasticizer acts as a diluent and reduces the amount of smoke produced so that the developed system could be used outside of a hood. Thus, the effect of a non-reactive liquid additive and its effect on front temperature were studied.

To develop a system for potential industrial applications, a thermally polymerizable system must be smoke-free. Systems with HDODA typically produced more smoke because they were more reactive than TMPTMA. TMPTMA systems are even less reactive than HDODA because of the more stable methacrylate radical and so should produce less smoke. However, development of a TMPTMA system that completely polymerizes and propagates throughout the strip is more difficult than TMPTA-n-containing systems because TMPTMA is less reactive than TMPTA-n so that quenching could occur more easily in similar systems.

To counter this problem, variation of different fillers such as Polygloss 90 or Cabosil were done. Although Polygloss 90 was the filler of choice in previous chapters because systems typically had putty-like consistencies and so minimized heat loss due to fluid flow, the addition of Cabosil would allow less filler to be added since it takes up more volume than an equivalent mass of Polygloss 90. Thus, quenching would be less likely.

Addition of an additive such as trithiol [trimethylolpropane tris-(3-mercaptopropionate)] could also help to lower the front temperature by reducing the total heat loss of the system since copolymerization of a methacrylate and thiol is lower than for homopolymerization of a methacrylate.[7] Lower front temperatures could reduce the amount of smoke being produced and could increase the amount of cross-linking in the polymerized product so that fewer cracks produced from expansion and contraction of the propagating front could be formed. Addition of a plasticizer could also help to reduce cracking by increasing the plasticity of the system.

HDODA and Fillers

To determine the appropriate filler loading for Polygloss 90, systems with 1% mass BPO and different amounts of HDODA and Polygloss 90 were tested. Systems with 60% mass Polygloss 90 were too dried out and required sustained contact with a soldering iron for over 3.5 minutes for propagation to occur. A front temperature of 255 °C was recorded. Lowering filler loading and increasing the % mass monomer resulted in a system with a more putty-like consistency and a front temperature of 285 °C. Although the initiator concentration was reduced from 2.6 to 2.0 phr BPO by increasing the % mass monomer, the front temperature increased because of the increase in % mass monomer and decrease in filler loading. Although the system with 50% mass Polygloss 90 had a higher front temperature, this system was less brittle because the system had a putty-like consistency and was not dried out like the system with 60% mass Polygloss 90.

Another advantage of reducing filler loading is that initiation of frontal polymerization occurred more quickly.

When HDODA systems were molded into 2-cm wide and 5-cm long strips, the degree of cracking could be observed. For systems with 5 phr BPO in HDODA, a system with 58% mass Polygloss 90 and 42% mass 5 phr BPO in HDODA had a dried out consistency and produced much smoke and failed to stick together as a front propagated. Instead, the system crumbled apart when a soldering iron was applied to end of the strip so that the degree of cracking could not be determined. Lowering the Polygloss 90 loading to 47.5% mass-produced a putty-like consistency and complete propagation of the strip, but much cracking including large cracks occurred. Further reducing the Polygloss 90 loading to 37% mass-produced a system with a gooey consistency that was not as putty-like as the system with 47.5% mass Polygloss 90. However, only many fine cracks rather than large cracks were formed. All of the systems produced much smoke. Due to the short length of the strips and the difficulty of observing a front propagate, no front velocities were determined. Addition of 5% mass plasticizer, DBP, to a system with 47.75% mass Polygloss 90 and 47.25% mass 5 phr BPO in HDODA had a putty-like consistency and reduced some cracking, but cracking still occurred.

Replacement of Polygloss 90 with fine quartz sand produced systems that were either dried out or failed to absorb all of the monomer and form a putty-like consistency. Use of fine quartz sand as filler resulted in no systems that had the consistency of putty. Systems with 79% mass sand and 21% mass 5 phr BPO in HDODA produced a system that was dry and brittle. Lowering the % mass of sand to 68.5% mass and produced a system that was less dried, but only 75-80% of the monomer was absorbed by the sand

and molded into a strip. The rest of the monomer remained in the bowl. Further reducing the filler loading for sand to 58% mass increased the amount of strip that polymerized but not all of the monomer was absorbed. Also, the consistency of the system was more like mud, and the system tended to crumble rather than adhere together like Polygloss 90 systems. A system with 73.8% mass sand, absorbed 90-95% of the monomer, but none of the systems with sand exhibited complete propagation. All systems were hard to mold, smoked, and produced brittle polymers that easily crumbled into numerous tiny pieces when extracting the thermocouple wire. The addition of a plasticizer to a system with 74% mass sand and 21% mass 5 phr BPO in HDODA also failed to have complete propagation of the strip and allowed 90-95% of the liquid components to be absorbed by the sand.

Addition of enough Cabosil to form broth-like consistency was tested with 2.5 phr BPO in HDODA. On a wooden surface, the system had a front temperature of 211 °C; on a 1-mm stainless steel metal surface, the system had a front temperature of 197 °C. Under both conditions, the strips had a depth of 1-3 mm or less. The polymers were more brittle than for systems with Polygloss 90 (broke into more numerous, tiny pieces when extracting the thermocouple wire) and failed to adhere to the stainless steel surface despite complete propagation. Much smoke was produced.

Without the addition of filler, no front would propagate in a system composed of 1.25 phr BPO in HDODA despite sustained contact with a soldering iron. The formation of a putty is critical in order to prevent buoyancy-driven convection from absorbing heat from the soldering iron and thus not allowing frontal polymerization to be initiated and maintained.

HDODA and DBP

Based upon the system with the best putty-like consistency, an initial system composed of 50% mass Polygloss 90 and 50% mass 2.0 phr BPO in HDODA was used to determine the effect of plasticizer (DBP or dibutyl phthalate) on a diacrylate system. The % mass of BPO and Polygloss 90 were maintained at 1% and 50%, respectively, while the percentage mass HDODA and percentage mass DBP were varied. This resulted in higher initiator concentrations since % mass BPO remained constant and % mass monomer was reduced when % mass DBP was increased. The data in Table 7.1 highlight how increasing DBP:monomer mass ratio resulted in lower front temperatures despite the increase in initiator concentration.

Table 7.1

Front Temperature as a Function of DBP:HDODA Mass Ratio

% mass DBP	% mass HDODA	DBP:HDODA Mass Ratio	Front Temperature
0%	49%	0	285 °C
5%	44%	0.11	261 °C
20%	29%	0.69	199 °C

Increasing the percentage mass of the plasticizer reduced the putty-like consistency and produced a polymerizable system with a more dried-out consistency because the plasticizer was less viscous than the monomer. Despite the reduction in putty-like consistency and increase in initiator concentration from 2.0 to 3.4 phr BPO in HDODA, a lower front temperature occurred because of dilution of the monomer loading or % mass HDODA. Increasing the plasticizer from 0% to 5% mass failed to result in much difference in cracking, but increasing the % mass to 20% resulted in less cracking and a less brittle polymer due to increased fluidity of the system.

TMPTMA and Viable Frontal Polymerization Systems

TMPTA-n vs. TMPTMA Systems

To determine the proper amount of filler loading for systems containing TMPTMA in place of TMPTA-n, the standard filler loading using for systems containing Luperox® 231 and TMPTA-n was used as the reference point. For a system with 6 phr Luperox 231, 47% mass Polygloss 90 is typically used for systems using TMPTA-n as monomer. As demonstrated in previous chapters, complete propagation of a 2.5-cm wide and 4 cm-long strip for a system containing 47% mass Polygloss 90 and 53% mass 6 phr Luperox® 231 in TMPTA-n occurred. However, for systems containing 5.3 phr Luperox® 231 in TMPTMA, no propagation of a 2.5-cm wide strip occurred when 36% mass Polygloss 90 was used. Reducing filler loading to 20% mass Polygloss 90 and increasing the monomer/initiator to 80% mass 5.3 phr Luperox® 231 in TMPTMA resulted in only 3 mm of polymerization due to heat from the soldering iron. Use of less than 20% mass Polygloss 90 was not possible because a putty-like consistency could not be obtained so that heat loss due to buoyancy-driven convection or fluid flow could occur. Systems that were viable for frontal polymerization for TMPTA-n were not feasible with TMPTMA because methacrylate propagates at a slower rate than acrylates due to the more stable and hindered methacrylate radical. The higher molecular weight per double bond of TMPTMA (113 g/mol) compared to TMPTA-n (99 g/mol) also results in a slower front velocity

Addition of Cabosil and Replacement of TMPTMA with Other Monomers

The addition of Cabosil, fumed silica, would modify the rheological properties of the system so that more monomer and less filler could be added and a putty-like consistency could still be achieved. Addition of 5% mass silica and 31% mass Polygloss 90 (kaolin clay) with 5.2 phr Luperox® 231 in TMPTMA resulted in no polymerization except at site of contact with the soldering iron. Increasing the Cabosil loading and reducing the kaolin clay loading to 10% mass and 21% mass to a system with 7.8 phr Luperox® 231 in TMPTMA resulted in no polymerization except at the site of contact with the soldering iron. This system was so dried out that a putty-like consistency was not achieved. Increasing the initiator concentration and reducing the kaolin clay loading to 14.3 phr Luperox® 231 in TMPTMA and 10% mass, respectively, resulted in complete propagation of the ball – although more heat had to be applied to the system than with TMPTA-n systems. Fronts could be ignited no matter whether this system had depths of 5 mm or less when molded around the test tubes or was molded into thick balls. However, more cracking occurred than for TMPTA-n systems, but these systems had much less cracking than TMPTA-n systems with DMA.

For the system composed of 10% mass Cabosil, 10% mass Polygloss 90, and 80% mass 14.3 phr Luperox® in monomer, replacement of TMPTMA with either HDODA or TMPEOTA resulted in different behavior. Less cross-linking in the diacrylate resulted in the ball unwinding like a peeled onion as a front propagated through the ball. Pieces of polymerized metal broke off as they were pushed upward. For the TMPEOTA system, the system was less viscous and more dried out (lacks all fluid properties) than the system with HDODA, which had the consistency of tuna salad or toothpaste; however, the resulting front in the ball did not unwind like an onion being peeled although some cracking did occur. More cracking than the corresponding TMPTMA system but less cracking than a similar DMA/BPO system occurred. Like the TMPTMA, a large crack appeared in the ball along with much smoke. Reducing the Cabosil loading to 5% mass and increasing the kaolin clay loading to 20% mass with a lower initiator concentration (7.14 phr Luperox® 231 in TMPEOTA) resulted in a better putty-like consistency, and complete polymerization occurred. Very little cracking occurred, but it took longer to initiate polymerization.

Addition of Plasticizer to BPO/TMPTMA Systems

A system composed of 59% mass 1 phr BPO in TMPTMA and 41% mass Polygloss 90 did not propagate in the samples with thicknesses of 1 cm or less, but when the system was modified and contained 76% mass 1 phr BPO in TMPTMA, 4% mass DBP (plasticizer), 16% mass Polygloss 90, and 4% mass Cabosil, then a front did propagate with a strip with a thickness of 1 cm. However, incomplete polymerization did occur, and the soldering iron needed to be applied for 2.5 minutes in order to initiate polymerization. One other problem with this system was that large cracks occurred as the front propagated slowly through the strip on a 2-cm thick wooden surface.

When the initiator concentration was increased to 5 phr BPO in TMPTMA, complete propagation of a strip with dimensions of 2 cm x 5 cm x 1.1 cm occurred if placed on a 2-cm thick piece of wood and surrounded by wooden barriers, but large cracks or fissures in the polymerized strip formed as the front propagated through the putty. Although some smoke was produced, less smoke than a system containing 59% mass 1 phr BPO in TMPTA-n and 41% mass Polygloss 90 was. If the same system containing 76% mass 5 phr BPO in TMPTMA, 4% mass DBP (plasticizer), 16% mass Polygloss 90, and 4% mass Cabosil was placed on a stainless steel surface, complete propagation did occur if the thickness of the strip was 9 mm, and the polymer lightly adhered to the 1-mm thick stainless steel surface. However, if the metal surface was tilted at a 45^{o} or 90^{o} angle and tapped lightly against a bench top, the polymerized strip fell away from the metal surface, leaving some unreacted putty on the surface and indicating that the polymer did not adhere strongly to the metal surface unlike different tested trithiol systems. If this same system was placed on a cement surface and a drop of DMPT was spotted on top of the putty, bulk polymerization of the top half of the 3-5 mm thick strip did occur within 4 days, but the bottom half of the strip on the cement slab was still putty-like and remained unreacted even after 5-7 days. Thus, for good adhesion to a metal surface, a thiol needed to be added.

For a system composed of 76% mass 5 phr BPO in TMPTMA, 4% mass DBP, 16% mass Polygloss 90, and 4% mass Cabosil, the system propagated from a thickness of 13 mm to 1.5 mm when placed on a 2-cm thick wooden surface and from a thickness of 10 mm to 5 mm when placed on a 1-mm thick stainless steel surface. The metal surface conducted heat away from the system so that the portion of the strip closest to the metal surface could not polymerize. The wooden surface did not conduct heat away from the propagating front so that complete propagation at thinner thicknesses could occur.

Addition of Trithiol

In a TMPTMA system composed of 24% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, and 53% mass 9.4 phr Luperox® 231 in TMPTMA, the addition of trithiol inhibited front polymerization when the system was molded into a 2.5-cm wide strip, but if the strip was molded into a ball, complete propagation occurred with much less smoke than if no trithiol had been added. However, this system had more smoke than a similar system with Expancel DU 80 and TMPEOTA in place of Cabosil and TMPTMA, respectively. Less cracking occurred than for other TMPTMA systems without trithiol.

For a system composed of 44% mass 1 phr BPO in TMPTMA, 15% mass trithiol, and 41% mass Polygloss 90, no cracking, little to no smoke, and a stronger polymer occurred when Cabosil was completely removed, kaolin clay loading was increased, and the % mass of trithiol was reduced. When 10 g of this system was molded into a ball, a front temperature of 120 °C was recorded, but only 90-95% of the ball was polymerized. For a 3.5-cm long trip, only 0.5 cm of strip was polymerized despite sustained contact with a soldering iron. Unlike a similar TMPTA-n system that had a pot life of ~10 minutes, the pot life of this TMPTMA system was over 20 minutes.

In another system with 20% mass trithiol, 41% mass Polygloss 90, and 39% mass 1 phr BPO in TMPTMA, the pot life was reduced to 10-20 minutes, and no propagation of the strip occurred despite sustained contact with a soldering iron for over 3 minutes.

However, when molded into balls, complete propagation of the 10 g balls occurred. One problem with the balls is that no front could be seen propagating so that the ball had sustained contact with the soldering iron for 6-7 minutes. One reason for this finding could be that heat from the soldering iron itself was locally heating the system so that bulk polymerization, not frontal polymerization, occurred. Front temperatures were between 66-84 °C, and no smoking or cracking occurred.

Because no front could be seen propagating in the system with 20% mass trithiol, the amount of trithiol was reduced to 17% mass and the % mass of 1 phr BPO in TMPTMA was increased to 42% mass. The resulting ball had front temperatures of 63-86 °C, similar to a system with 20% mass trithiol. No smoke or cracking occurred, and the polymer was hard. A negative attribute was that the soldering iron was left on for 6-6.5 minutes because no front could be seen propagating. Reduction of % mass trithiol increased the system's inhibition to oxygen so that the pot life was extended to 25-35 minutes.

Since the system with 15% mass trithiol had the most frontal propagation, the initiator concentration was increased to 3 phr BPO in TMPTMA to see how front temperature would be affected. The front temperature was increased to a maximum of 154 °C (124 °C was the second highest), and the amount of sustained contact with a soldering iron was reduced to ~4.3-5 minutes. Increased initiator concentration also reduced the pot life to 10-20 minutes; however, positive characteristics include no cracks, no smoke, and a hard polymer.

Further increasing the initiator concentration to 5 phr BPO in TMPTMA produced front temperatures of 123-139 °C, but the pot life remained the same (10-20 minutes).

The other positive characteristics include formation a hard polymer with no smoking or cracking during propagation. The soldering iron was on for 4-4.67 minutes because no front could be seen propagating. When molded into a wedge, it was determined that a front would propagate from a thickness of 16 mm to a minimum thickness of 3 mm. After a depth of 3 mm was reached, frontal polymerization ceased despite having the soldering iron on (soldering iron was still on because no front could be seen propagating). At a depth of 8-9 mm (in the center of the wedge with the thermocouple wire pushed all the way to the bottom of the wedge), the front temperature was 104 °C.

Conclusions

Although Polygloss 90, Cabosil, and quartz sand were all tested as fillers, only Polygloss 90 demonstrated the ability to form the proper consistency necessary for complete propagation of a polymerizable system in strip or ball form. However, cracking and achieving a putty-like consistency were issues for Polygloss 90 systems because many systems were too dried out and hindered frontal polymerization due to absorption of heat from the reaction zone. Without filler, heat loss due to buoyancy-driven convection or fluid flow prevented frontal polymerization from being initiated.

Addition of plasticizer reduced the degree of cracking if a large amount of DBP was added due to increased flexibility of the system. Front temperatures were also lowered due to dilution of the monomer concentration but were not lower to temperatures where smoking and fumes were reduced. Smoking and brittleness were problems for all of the tested systems although brittleness was reduced with large amounts of plasticizer added, and because of the difficulty observing frontal polymerization, front velocities could not be determined.

Various TMPTMA systems with different initiators, fillers, and additives were tested. TMPTMA systems typically have slower front velocities than TMPTA-n systems because the methacrylate radical is more stable and hindered than the triacrylate radical and typically required longer initiation times or application of the soldering iron.[7] However, despite this fact, larger cracks appeared in TMPTMA than in similar TMPTA-n systems, but less smoke was produced because of the lower temperatures. The best developed TMPTMA system was composed of 76% mass 5 phr BPO in TMPTMA (3 phr BPO in TMPTMA also works), 4% mass DBP, 4% mass Cabosil, and 16% mass Polygloss 90. The other systems had major problems of cracking, quenching, or failure to even initiate.

Thus, the addition of less reactive monomers such as TMPTMTA resulted in lower front temperatures and velocities than similar systems with TMPTA-n, but the addition of HDODA resulted in higher front temperatures than similar TMPTA-n systems. However, they had no impact on pot life. Because of the difficulty in achieving a propagating front, development of a system that could undergo complete polymerization of a strip and still be smoke-free was difficult and more challenging than using a more reactive monomer like TMPTA-n. Unlike TMPTA-n systems, many HDODA and TMPTMA systems suffered from extensive cracking, which is problematic for their use in industrial applications.

The bottom line for this chapter is that HDODA is not a good choice of monomer because many systems are too dried out or lack the proper consistency for frontal polymerization. Many TMPTMA systems failed because of the lower reactivity of TMPTMA compared to HDODA and TMPTA-n.

CHAPTER VIII

SNELL'S LAW OF REFREACTION OBSERVED IN THERMAL FRONTAL POLYMERIZATION

Snell's law has never been studied using thermal frontal polymerization. From the previously discussed chapters, a simple system was selected and studied using Snell's law because it correlates refractive indexes to velocity, and velocity can be easily controlled by varying initiator concentration in acrylate monomer systems for thermal frontal polymerization systems. Then, these findings can be applied to more complex systems or to study inhomogeneities and how they affect different aspects of thermal frontal. polymerization including front velocity.

Snell's law establishes the relationship between the angles of incidence and refraction for a wave passing through the boundary between two media with different refractive indices:

$$n_i/n_r = \sin \theta_r/\sin \theta_I \qquad (1)$$

For equation 1, n_i and n_r are the refractive indices for the refractive and incident angles, respectively, and θ_r and θ_I are the angles of refraction and incident, respectively.

Instead of using refractive indices in this relationship, the front velocity can be used instead because n_r/n_i is proportional to v_i/v_r so that equation 1 can be rearranged to another form:

$$v_r/v_i = \sin \theta_r/\sin \theta_I \qquad (2)$$

For this equation, v_r is the refracted velocity and v_i is the incident velocity.

Experimentally, the applicability of Snell's law to chemical waves in the Belousov-Zhabotinsky system was demonstrated by Zhabotinsky and Epstein[15] as well as other groups.[16-18] Sainhas and Dilão simulated refraction and reflection in reaction-diffusion systems.[18] Fialkowski *et al.* demonstrated refraction and reflection with Liesegang rings.[19] Steinbock *et al.* studied BZ waves propagating along adjacent strips in which the fronts had different velocities.[20] Generally, however, the angle between refracted and incident fronts in reaction-diffusion systems does not have to obey Snell's law. Indeed, Mornev has recently shown that refraction of chemical waves might follow a tangent rule when mass diffusion is sufficiently fast.[61] There have been several reports that thermal fronts, generated by rapid heating, follow Snell's law.[62, 63] Frontal polymerization was selected as the model system for studying thermal fronts.

Selection of System

Free-radical polymerization fronts[1] were selected because velocities of such fronts can be easily controlled by changing the concentration of the initiator.[21, 22] The experiments used a mixture of the monomer trimethylolpropane triacrylate (TMPTA-n), the initiator Luperox®231[1,1-Bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane], and a kaolin clay filler, Polygloss 90. The filler constituted 47% of the total weight in each trial, giving the mixture the consistency of putty and eliminating the effects of buoyancy-driven convection in the medium.[24] Convection in the air caused by the heat from the reaction was not controlled. The clay did not quench the fronts because acrylates are highly reactive, and multifunctional acrylates like TMPTA-n support fronts with velocities at least an order of magnitude greater than monofunctional acrylates.[7, 21, 22] Bubbling was minimized by using Luperox® 231, which releases less gas per initiating radical than other peroxide initiators.[23]

The putty was spread uniformly on a 2-cm thick wooden surface and constrained between wooden strips to provide thermal insulation beneath the putty and at the sides. By performing the experiments under quasi-adiabatic conditions, the effects of heat losses on the front shape were reduced. By performing the experiments horizontally, convective heat transfer from the front did not influence the polymerization of the rest of the putty. In order to enhance detection of the front, small amount of the *p*H-sensitive dye bromophenol blue was dissolved in dimethyl sulfoxide (DMSO) and mixed with the putty.[64] The free radicals in the reaction bleached the dye, making the demarcation between reacted and unreacted regions evident.

Results

Experiments with strips

Figure 8.1 presents images of incident and refracted fronts traveling to the left in strips that support different traveling-wave velocities.

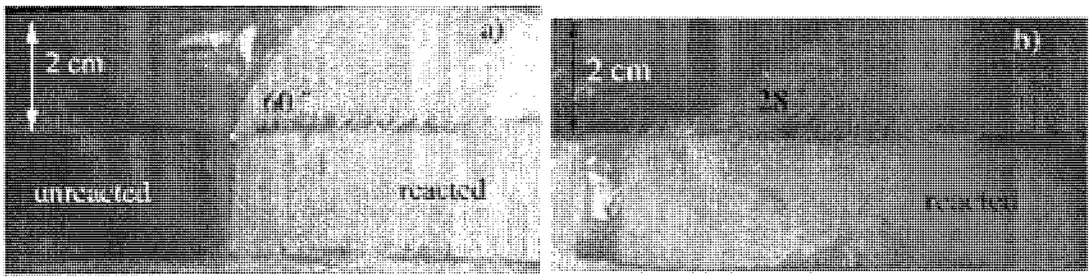


Figure 9.1. Refraction of Polymerization Fronts between Parallel Strips (a) Fronts with 2% (top) and 3% (bottom) Mass Initiator (b) Fronts with 1% (top) and 3% (bottom) Mass Initiator and Incident Angles

In Figure 8.1(a), the velocities of the fronts in the individual strips were closer to each other than those in the two strips in Figure 8.1(b). Thus, the refracted angle was larger in Figure 8.1(a) than in Figure 8.1(b). In the strip experiments the faster front had an incident angle of approximately 90°. Any discrepancies with a 90° angle can be attributed to several factors including slight variations in the composition, minor nonuniformity in the thickness of the sample, heat losses, and thermal stress.

The sine of the incident angle in the experiments was assumed to be equal to 1. Figure 8.2 shows a plot of the sine of the refracted angle versus the ratio of the velocity of the refracted front to the velocity of the incident front for experiments shown in Figure 8.1, as well as for similar experiments.

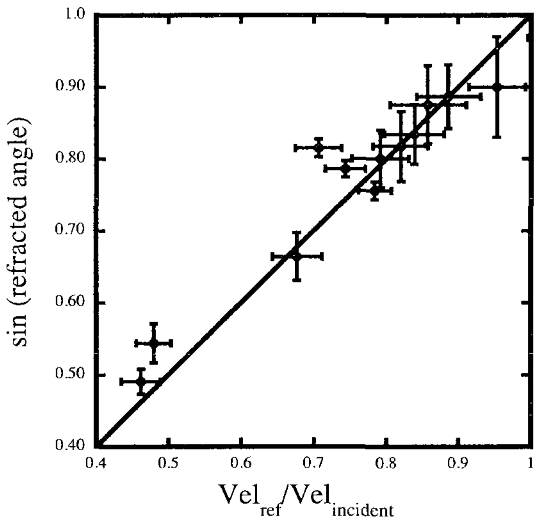


Figure 8.2. Plot of the Sine of the Refracted Angle vs. the Ratio of the Refracted and Incident Velocities for the Type of Experiments Shown in Figure 8.1

The agreement between experiment and theory is very good. Agreement for velocity ratios smaller than about 0.50 could not be tested. To do so would require much longer samples to allow the fronts to reach steady-state propagation.

Circular Experiments

Inspired by the experiments of Hwang and Halpin-Healy[16] and Fialkowski *et al.*[19], the circular 2-D experiments were done, and fronts were ignited near the boundary between regions of different velocities. These experiments tested indirectly the validity of Snell's law: the front shape to analytical predictions derived from the assumption that Snell's law holds on the boundary between the two media. Figures 8.3 and 8.5 show the experimental configurations.

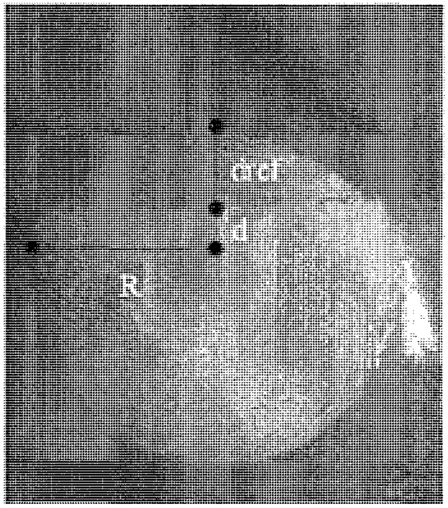


Figure 8.3. Refracted Front Propagating from a "Fast" Region (bottom) Containing 3% mass Initiator into a "Slow" Region (top) with 1% mass Initiator with Horizontal Width 15 cm

The radius of the front in the "fast" region or R was equal to 3.5 cm.

The analysis of Hwang and Halpin-Healy[16] was applied for the front shape after refraction in the regime that corresponds to Figure 8.3. Equations 4 and 5 provided the coordinates for the refracted wave front relative to the point of initiation when the front propagates from a high-velocity region to a low-velocity region as in Figure 8.3. The time-dependent radius of the incident reaction front was given by R. The front was initiated at the perpendicular distance $d = 1$ cm from the boundary between the regions (Figure 8.3).

$$x = \frac{\left[d(\left(n^2 - 1\right)\tan\alpha + R\sin\alpha\right]}{n^2} \qquad (4)$$

$$y = \frac{\left[\left(R - d\sec\alpha\right)\sqrt{n^2 - \sin^2\alpha}\right]}{n^2}, \qquad (5)$$

$$0 < \alpha < \cos^{-1}(d/R)$$

The maximum distance between the refracted front and the boundary between the regions was denoted by *dref*. The refractive index *n* was calculated by

$$n = \frac{R - d}{dref} \qquad (6).$$

The maximum vertical distance between the refracted front and the boundary between the regions was denoted by *dref*. The fronts calculated from Equations 4 and 5 are compared to experimental fronts in Figure 8.4.

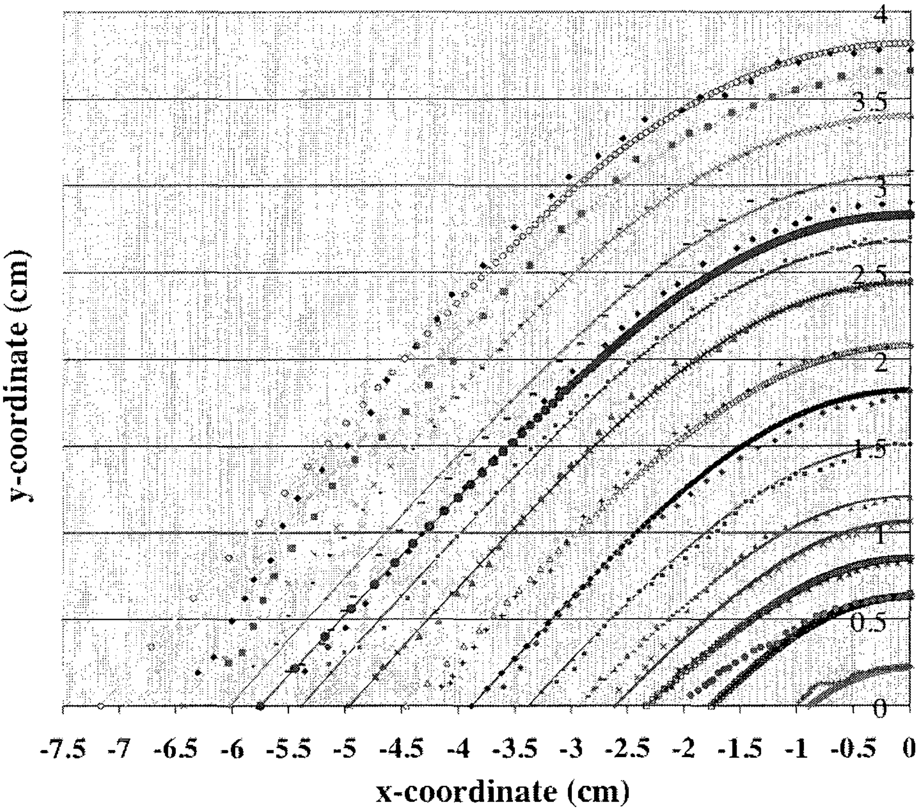


Figure 8.4. Positions of the Front at Various Times between $t = 10$ s and $t = 48$ s for the Refracted Wave Front Shown in Figure 5.3 (discrete points) and Analogous Front Positions Calculated from Equations 4 and 5 (solid lines)

The theory agreed very well with the experimental results.

The experiment and predicted coordinates were also calculated for when the polymerization front propagated from the region with slower velocity to the region with the faster velocity (Figure 8.5).

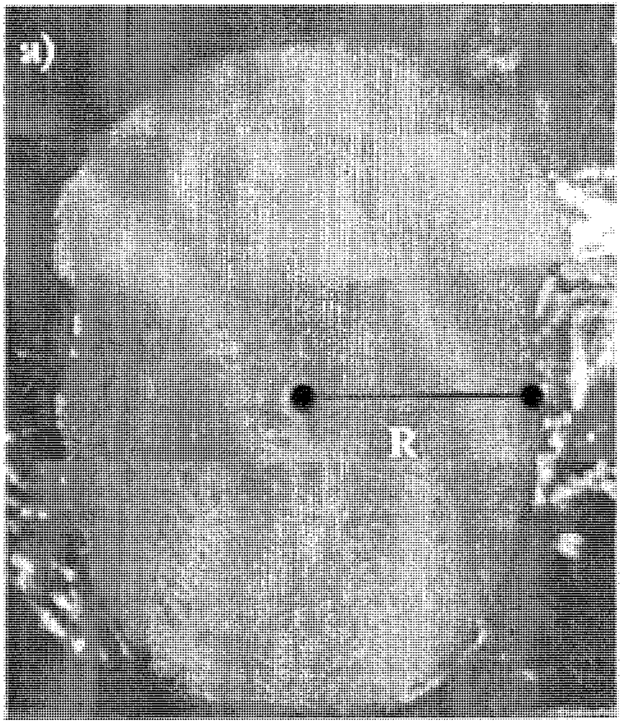


Figure 8.5. Refracted Front Propagating from a “Slow” region (bottom) Containing a 3% mass Initiator into a “Fast” Region (top) with 1% mass Initiator with Horizontal Width of 15 cm

The radius in the “fast” region or R was 3.5 cm. The front calculated from Equations 4 and 5 were compared to experimental data in Figure 8.6.

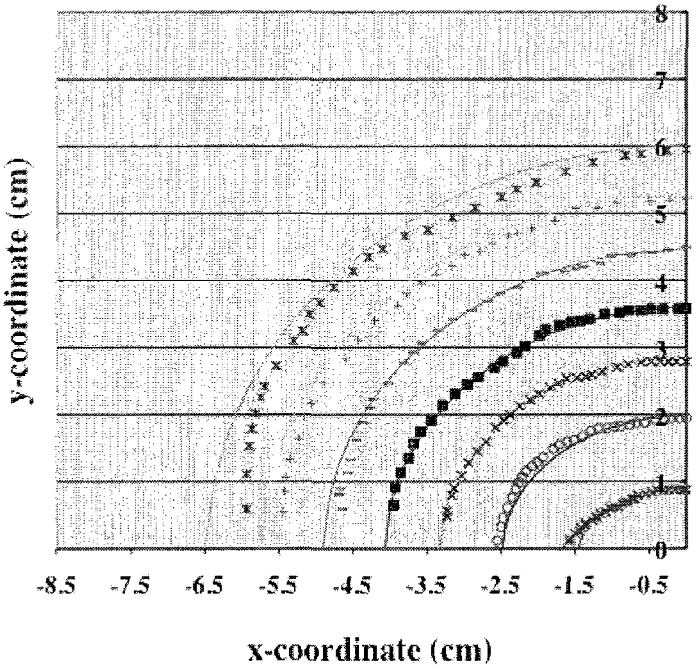


Figure 8.6. Positions of the Front at Various Times between $t = 32$ s and $t = 65$ s for the Refracted Wave Front in Figure 5.5 (discrete points) and Analogous Front Positions Calculated from Equations 4 and 5 (solid lines)

Good agreement between the experimental and predicted coordinates occurred. The analysis of Hwang and Halpin-Healy still applied for short times after the incident front crosses the boundary from the region with a slower velocity (bottom) region in Figure 8.5 to the region with faster velocity (top) region in Figure 8.5. When $t = d / (v^*(1-n^2)^{0.5})$, the front in the region with faster velocity was orthogonal to the boundary between the regions and it began to propagate along that boundary. The faster front was then refracted toward the region with slower velocity. Thus the refracted front became an incident front and vice versa as can be seen from the "mushroom" shape of the fronts in Figure 8.5.

The final experimental setup consisted of three parallel strips of putty: two identical outer strips with 6% mass initiator and a significantly narrower inner strip with

5% mass initiator (Figure 8.7).

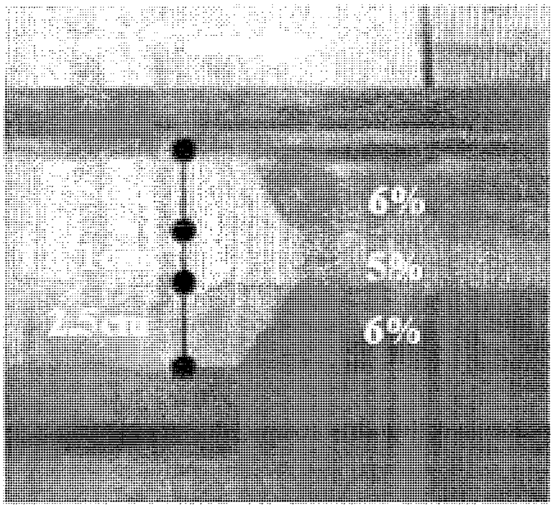


Figure 8.7. Refracted Front Propagating through Three Parallel Strips with 6% mass-5% mass-6% mass Initiator Concentration

The front propagation speed in the regions with 5% mass initiator was about 10% faster than in the regions with 6% mass initiator. The front velocity was a maximum with 5% mass initiator and decreases with higher initiator concentration. The three- strip configuration mimicked the setup of Steinbock *et al.* for BZ waves.[20]

The fronts in the three-strip system remained essentially straight within each strip and continuous between the strips (Figure 8.7). This indicates that Snell's law holds on both inter-strip boundaries present in the system. The main difference between this three-strip experiment and a similar experiment by Steinbock *et al.*[20] was that the front remained straight in the middle strip in the three-strip setup. This difference was due to the fact that, although the middle strip was narrow in the three-strip setup experiments, it was an order of magnitude wider than that in Steinbock *et al.* Notice that the front was slightly curved on the boundary between two strips (Figure 8.7). When the middle strip was sufficiently narrow, the curved parts of the front combined resulting in the curved profile observed by Steinbock *et al.*

Discussion

For all studied concentration differences of the initiator mixtures, most data points from the two-strip experiments fell on the line predicted by Snell's law as shown in Figure 8.2. Further, error bars demonstrated that experimental data points that did not fall precisely on the theoretical curve were, however, within experimental error of their predicted values. Some bubbling under the surface of the higher concentration of peroxide initiator occurred and could have slowed the front and distorted the angle, thereby leading to a discrepancy with Snell's law. Additional causes for variations from predicted angles of refraction are expansion and contraction of the system during polymerization and stress-induced cracking. However, the graph of the sine of the refracted angle versus the ratio of the refracted and incident velocities demonstrated the good agreement between the theoretical and experimental data. From this plot, it can be concluded that the strip experiment obeyed Snell's law of refraction.

The circular fronts demonstrated the same result as for the parallel strips. The graph in Figure 8.3 showed the good agreement between the experimental refracted fronts initiated in a region with a faster velocity of propagation and those predicted by Equations 4 and 5 of Hwang and Halpin-Healy.[16] Initially, the theoretical and experimental fronts differed, but the discrepancy disappeared about 15 s from initiation. Thereafter, the predicted and experimental curves agreed closely. The experimental front profiles shown in Figure 8.5 matched with those predicted by the same analytical formula as well in Figure 8.6.

Even though the fronts were essentially flat in the strip studies and obeyed Snell's law, the incident and refracted fronts passed through a narrow transition zone near the boundary between the two media in which the reaction front appears curved (Figure 8.1). The evolution of sharp reaction fronts propagating in systems with slow diffusion can be described by a generalized eikonal equation with an additional curvature term that vanishes as the (heat) diffusion coefficient tends to zero. This term had an effect of curving the front in a transition zone between the incident and the refracted fronts. In other words, for frontal reactions discussed thus far, the heat exchange between the "fast" and the "slow" strips was significantly slower than the speed of a sharp front (which was established through a balance between the rates of reaction and diffusion). Then the propagation of the "fast" front was not affected by the presence of the "slow" strip away from the boundary between the regions and vice versa. The slow heat exchange between the regions led only to slight curving of the front near the boundary between the two media, while the refraction was still governed by Snell's law.

If, on the other hand, the diffusion was stronger, then the front in the "fast" region would be significantly affected by the heat exchange with the "slow" region and vice versa; the angle between the reaction fronts in two regions would be dictated by the continuity of the heat flux through the boundary between the regions, and the fronts would deviate from the linear shape farther from their junction at the boundary. The two fronts would no longer appear flat.

To see whether curved fronts could be observed in the experimental system, a three-strip experiment was performed with the narrowest middle strip that could be molded. Even in this case, the front remained essentially linear in each region (Figure 8.7). Hence, the angles between segments were determined by Snell's law.

Conclusions

A system with reaction-diffusion fronts based on an exothermic reaction was studied using two different types of experiments. In the first experiment, either two or three strips with different concentrations of the peroxide initiator concentration were placed side-by-side in contact with each other. Decreasing the initiator concentration difference between the domains decreased the angle of refraction as the ratio of incident and refracted velocities decreased. Independent of variation of the initiator concentration between the domains, the sine of the incident angle was approximately equal to 1. Thus, it was verified that the reaction front propagation in these systems follows Snell's law of refraction.

In the second type of experiment, the validity of Snell's law for radially propagating fronts was established by comparing experimental fronts to those predicted by an analytical formula of Hwang and Halpin-Healy.[16] Good agreement occurred between these predicted and experimental results. Thus, it was demonstrated for the first time that Snell's law of refraction holds for reaction-diffusion fronts based on an exothermic reaction.

From this study of a simple system, understanding of how inhomogeneities affect thermal frontal polymerization was established and can then be applied to more complex systems and for use in potential applications such as filling a hole.

CHAPTER IX

CONCLUSIONS AND FUTURE WORK

This dissertation demonstrated for the first time what impact thermally-expandable microspheres have on front temperature, front velocity, and pot life of thermal frontal polymerization systems. Study of thermally-expandable microspheres in thermal frontal polymerization demonstrated that thermally-expandable microspheres have an impact on front temperature and velocity but no impact on pot life. Because of their insulating effect, these microspheres lowered front temperature and velocity.

Although numerous systems with different fillers, monomers, and initiators were tested using thermally-expandable microspheres, a system with controlled expansion and that could be used with a variety of Expancel DU 80 loading could not be developed -- possibly due to the use of chain growth polymers for thermal frontal polymerization. Systems with mixtures of reactive monomers such as TMPTA-n and HDODA suffered from uncontrolled expansion in all three directions and distortions of the strip during propagation. These distortions were due to pressure from gas released. With less reactive monomer systems such as TMPTMA, no expansion or no frontal polymerization occurred at all because the thermally-expandable microspheres were acting as insulators or too little heat from the propagating front could be used to cause expansion in the thermally-expandable microspheres. Increased initiator concentration, lower filler loadings, and mixtures of fillers (Cabosil and Polygloss 90) failed to increase the ability of the TMPTMA-containing systems to have controlled expansion.

Use of TMPEOTA II, a monomer that was less reactive than TMPTA-n but more reactive than TMPTMA, allowed for some controlled expansion – particularly when a mixture of fillers, Polygloss 90 and Cabosil, was used. The best system that demonstrated controlled expansion and had some range for Expancel DU 80 loading was composed of 0-5% mass Expancel DU 80, 19-24% mass Polygloss 90, 72% mass 10.8 phr Luperox® 231 in TMPEOTA II, and 4% mass Cabosil. Although some strips with widths of 1 cm demonstrated controlled expansion with increasing expansion with increased thermally-expandable microsphere loading, strips with widths of 2-2.5 cm suffered from slight curling or distortions in the polymerized strips. These distortions prevented determining how much expansion actually occurred.

However, the best system to demonstrate controlled expansion contained an additive, trithiol, to prevent distortions by reducing the amount of gas or total amount of heat released. The best system composed of 19% mass Polygloss 90, 4% mass Cabosil, 20% mass trithiol, 52% mass 11.1 phr Luperox® 231 in TMPEOTA II, and 5% mass Expancel DU 80 had many desirable characteristics including being smoke-free, putty-like, and not brittle and not having cracks and even having some expansion. However, this expansion could have been due to normal expansion and contraction of a propagating front and not just due to expansion of thermally-expandable microspheres. The other problem with this system was that there was no range that could be used for it. By not having a range of systems that could be tested, expansion as a function of Expancel DU 80 loading could not be done.

One reason for the lack of controlled expansion could be that all of the tested systems gelled faster than expansion of the microspheres could occur. Use of step growth polymers or frontal polymerization systems that gel slower than the systems tested in this dissertation could allow for controlled expansion without distortions of the front. Future work could include testing step growth systems or frontal polymerization systems that gel slower than the ones tested in this dissertation. Thus, more controlled expansion could occur by allowing the thermally-expandable microspheres to expand after gelation has occurred or in systems that gel more slowly than the ones tested.

Thermally expandable microspheres had a similar impact on front temperature and velocity as the addition of fillers. They lowered front temperature and velocity until they quenched a propagating front. Different tested fillers quenched a propagating front at different filler loadings. A study of different fillers including Polygloss 90 and Cabosil and their impact on front temperature, front velocity, and pot life has never been studied in a thermal frontal polymerization system of a triacrylate monomer. The impact of other solid additives including phase change materials and high thermal conductivity fillers and their impact on front temperature, front velocity, and pot life has also never been studied for a triacrylate monomer.

To determine the best filler to use for lowering front temperature, different fillers including quartz sand, Polygloss 90, and Cabosil were tested. Polygloss 90 was the best filler to use because it produced the most putty-like consistency and systems that were cohesive. Also, it typically produced systems that had lower temperatures than mixtures of Polygloss 90 and Cabosil. In cases of less reactive monomers such as TMPTMA, use of a mixture of Polygloss 90 and Cabosil was ideal because use of Cabosil allowed for less filler to be added and still have a putty-like consistency. By using less filler, quenching of the front was less likely to occur. Use of quartz sand failed miserably because of the poor consistency, lack of cohesion, and failure to absorb all of the monomer/initiator solution for some systems.

Use of solid non-reactive additives such as inert phase change materials typically lowered the front temperature more than the addition of Polygloss 90 but were less effective than DBP because they produced much more brittle polymers than the original Polygloss 90 system and had much more cracking than the original Polygloss 90 systems. Although they had lower front temperatures more than the original Polygloss 90 systems, many of the inert phase change material systems still produced smoke and sometimes harsh fumes. Only a few systems such as lauric acid produced pleasant fumes. Although use of inert phase change materials were initially used to lower front temperatures without lowering front velocities, both front temperatures and velocities decreased with increasing phase changer material loading, thus negating their use.

Use of a phase change material (D,L-mandelic acid) that could react with itself and addition of a catalyst, *para*-toluenesulfonic acid, helped to lower front temperatures a little with an increase in front velocity as a function of % mass *p*-toluenesulfonic acid. Also, the use of catalyst reduced the pot life from months to hours or weeks, depending upon catalyst concentration and % mass D,L-mandelic acid. However, with high % mass catalyst, foul odors were also produced.

Two initiators, BPO and Luperox® 231, were used in various concentrations for different reactive and non-reactive additives. BPO was typically used in systems considered for current industrial applications whereas Luperox® was the initiator of choice when room-temperature stability and the least amount of gas per initiating radical was desired. In some cases for some additives, both initiators were used to determine whether the additive had an effect on the initiator and for some of the most promising systems. For example, trithiol was tested for both initiators in order to determine which initiator worked bested with the trithiol. BPO was the better initiator to use because systems containing it had longer pot lives than corresponding Luperox® 231 systems.

Different liquid reactive and non-reactive additives including trithiol and dibutyl phthalate were tested, and their impact on front temperature, front velocity, and pot life were investigated. Use of trithiol in systems reduced front temperature and velocities so that no smoke was produced if an appropriate amount of trithiol was added. However, if too much trithiol was added, then the pot lives of the systems would be shortened from months to minutes for TMPTA-n systems. Use of a mixed monomer system, particularly one composed of TMPTA-n and TMPEOTA II, produced a smoke-free system with only a small amount of trithiol (5-6.5% mass) added. Also, for the system composed of 44% mass 1 phr BPO in TMPEOTA II, 8.5% mass 1 phr BPO in TMPTA-n, 6.5% mass trithiol, and 41% mass Polygloss 90, the system had a pot life of 3-5 days, produced no smoke, had no cracks, was hard to break in half when extracting the thermocouple wire (one of the least brittle system tested for this dissertation), and adhered to stainless steel surfaces. All of these attributes make it useful for potential industrial applications. Because of its days-long rather than months-long pot life, this system has a fail-safe system (some way of ensuring complete polymerization of the system will occur), a characteristic that is sometimes desired in industry.

However, this system had a slow front velocity so that it could not be used readily for rapid repair. Addition of LiCl as a catalyst helped to increase the front velocity without increasing the front temperature so high that smoke was produced. Also, the pot life was reduced from days to hours. Thus, with addition of LiCl, a system composed of 44% mass 1 phr BPO in TMPEOTA II, 8.5% mass 1 phr BPO in TMPTA-n, 6.5% mass trithiol, and 41% mass Polygloss 90 was one of the most potentially useful systems developed. Like the addition of *para*-toluenesuflonic acid monohydrate, LiCl shortened the pot lives of thermally activated systems and caused an increase on front velocity with little increase in front temperature.

Addition of other thiols such as 1-dodecanethiol were not as useful as trithiol because monothiol-containing systems could have less thiol added than trithiol. Also, for systems with mixed monomers, which had lower front temperatures than TMPTA-n systems, lower front temperatures and front velocities with 6% mass trithiol occurred for the trithiol systems, but because up to 6.5% mass trithiol can be added (in contrast to 1-dodecanethiol), a lower front temperature can occur. For comparable trithiol-containing systems, the much slower front velocities and temperatures of the 1-dodecaenthiol-containing systems mean that 1-dodecanethiol is less useful than trithiol for industrial applications.

In cases where a months-long pot life was desired and a fail-safe mechanism was not necessary, use of a plasticizer, DBP, might work because it helped to reduce the front temperature and thus produce a smoke-free system. However, DBP acted as a diluent and did not reduce the front temperature as much as the trithiol. Since the trithiol undergoes a reaction with the acrylate and this reaction occurs at a slower rate than homopolymerization of an acrylate, this finding is not surprising. Thus, although DBP had potential use, it does not have the same degree of potential usefulness as trithiol for being used in industrial applications. Because DBP-containing systems produced more smoke than a corresponding trithiol system, this finding also lessens its usability compared to trithiol.

Besides it impact on front temperature, the addition of DBP also lowered front velocity but did not impact pot life. Unlike trithiol, DBP did not react with the initiator or monomers so that it had no impact on pot life. DBP also had less of an effect on front velocity than the addition of trithiol.

The majority of this dissertation dealt with reactive and non-reactive additives and how they affected front velocity, temperature, and pot life. Most TMPTMA systems suffered from incomplete polymerization due to the more stable tertiary radical or less reactive monomer. They had lowered front temperatures than TMPTA-n systems. Most HDODA systems suffered from too much cracking and were very brittle so that they broke into many tiny pieces when handled. Also, HDODA had front temperatures much higher than TMPTA-n systems because of the differences in the experimental setup (length of the strip). The shorter length of the HDODA strips resulted in placement of the soldering iron closer to the thermocouple wires so that higher front temperatures could have occurred. Because of the high front temperatures, they produced much more smoke than the corresponding TMPTA-n systems. The TMPTA-n systems had complete polymerization (unlike many TMPTMA or HDODA systems). So, TMPTA-n typically was the choice of monomer for the addition of reactive and non-reactive additives.

Future work with reactive and non-reactive additives could go many different directions including testing different plasticizers, different thiols, and different fillers or other types of additives that could have an effect on front temperature, front velocity, and pot life. Although the addition of thiols appeared to be the most promising type of additive to continue testing, other fillers besides Polygloss 90 could be just as cohesive as the kaolin clay filler but allow less filler to be added like Cabosil so that quenching of the propagating front is less likely to occur. Other plasticizers besides DBP could be better for increasing the flexibility of the polymer while lowering the front temperature through a dilution effect. Different acrylate monomers (TMPTA-n, etc.) with different initiators such as AIBN (2,2'-azobisisobutyronitrile) or *tert*-butylperoxybenzoate (two initiators typically used in the Pojman lab) are another area of study that could be investigated. These systems could be tested with the additives that were found to be the most useful in affecting front temperature and velocity for this dissertation.

The third objective was achieved, and Snell's law was clearly demonstrated in TMPTA-n systems with various Luperox® 231 concentrations. With increasing differences in initiator concentration, the difference between angle of refraction and incidence increased. A plot of the sine of the refracted angle versus the ratio of the velocity of the refracted front to the velocity of the incident front for experiments demonstrated agreement between the theory and experimental results as well as thermal frontal polymerization systems following Snell's law of refraction. For the circular 2-D experiments, good agreement between the experimental and predicted results also occurred and demonstrated Snell's law of refraction. From these findings, future work using more complicated systems that have inhomogeneitities and used to fill holes in wood can be done based upon the work using the simple system.

The bottom line of this dissertation is that out of all of the tested additives, the addition of trithiol showed the most promising results for lowering front temperature and producing the most smoke-free systems. Of all of the thiol-tested systems, the one with mixed monomer (TMPEOTA II and TMPTA-n) worked best because it had the longest pot life (5-7 days), had the lowest front temperature and least amount of cracking, and was smoke-free, all qualities that make this system the most feasible for industrial applications. Future work should focus on similar systems with different thiols or different mixed monomer systems to determine whether other thiols or mixed monomer systems could lower the front temperature more than the TMPEOTA II/TMPTA-n system without a corresponding reduction in pot life.

REFERENCES

1. Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M., Free-Radical Frontal Polymerization: Self-Propagating Thermal Reaction Waves. *J. Chem. Soc. Faraday Trans.* **1996,** *92*, 2825-2837.

2. Chekanov, Y. A.; Pojman, J. A., Preparation of Functionally Gradient Materials Via Frontal Polymerization. *J. Appl. Polym. Sci.* **2000,** *78*, 2398-2404.

3. Lewis, L. L.; DeBisschop, C. S.; Pojman, J. A.; Volpert, V. A., Isothermal Frontal Polymerization: Confirmation of the Mechanism and Determination of Factors Affecting Front Velocity, Front Shape, and Propagation Distance with Comparison to Mathematical Modeling. *J. Polym. Sci. Part A Polym. Chem.* **2005,** *43*, 5774-5786.

4. Chechilo, N. M.; Enikolopyan, N. S., Effect of Pressure and Initial Temperature of the Reaction Mixture during Propagation of a Polymerization Reaction. *Dokl. Phys. Chem.* **1976,** *230*, 840-843.

5. Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S., On the Phenomenon of Polymerization Reaction Spreading. *Dokl. Akad. Nauk SSSR* **1972,** *204* (N5), 1180-1181.

6. Chechilo, N. M.; Enikolopyan, N. S., Effect of the Concentration and Nature of Initiators on the Propagation Process in Polymerization. *Dokl. Phys. Chem.* **1975,** *221* (5), 392-394.

7. Nason, C.; Roper, T.; Hoyle, C.; Pojman, J. A., UV-Induced Frontal Polymerization of Multifunctional (Meth)Acrylates. *Macromolecules* **2005,** *38*, 5506-5512.

8. Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A., Frontal Curing of Epoxy Resin: Comparison of Mechanical and Thermal Properties to Batch Cured Materials. *J. Appl. Polym. Sci.* **1997,** *66*, 1209-1216.

9. Washington, R. P.; Steinbock, O., Frontal Polymerization Synthesis of Temperature-Sensitive Hydrogels. *J. Am. Chem. Soc.* **2001,** *123*, 7933-7934.

10. Hu, T.; Chen, S.; Tian, Y.; Pojman, J. A.; Chen, L., Frontal Free-Radical Copolymerization of Urethane-Acrylates. *J. Poly. Sci. Part A. Polym. Chem.* **2006,** *44*, 3018-3024.

11. Nagy, I. P.; Sike, L.; Pojman, J. A., Thermochromic Composite Prepared Via a Propagating Polymerization Front. *J. Am. Chem. Soc.* **1995,** *117*, 3611-3612.

12. Pojman, J. A.; McCardle, T. W., Functionally Gradient Polymeric Materials. U.S. Patent 6,057,406, April 18, 2000.

13. Washington, R. P.; Steinbock, O., Frontal Free-Radical Polymerization: Applications to Materials Synthesis. *Polymer News* **2003,** *28*, 303-310.

14. Pojman, J. A.; Viner, V.; Binici, B.; Lavergne, S.; Winsper, M.; Golovaty, D.; Gross, L., Snell's Law of Refraction Observed in Thermal Frontal Polymerization. *Chaos* **2007,** *17*, 033125.

15. Zhabotinsky, A. M.; Eager, M. D.; Epstein, I. R., Refraction and Reflection of Chemical Waves. *Phys. Rev. Lett.* **1993,** *71*, 1526-1529.

16. Hwang, S.-C.; Halpin-Healy, T., Chemical Wave Refraction Phenomena. *Phys. Rev. E* **1996,** *54*, 3009-3012.

17. Lazar, A.; Forsterling, H. D.; Volford, A.; Noszticzius, Z., Refraction of Chemical Waves Propagating in Modified Membranes. *J. Chem. Soc. Faraday Trans.* **1996,** *92*, 2903 - 2909.

18. Sainhas, J.; Dilão, R., Wave Optics in Reaction-Diffusion Systems. *Phys. Rev. Lett.* **1998,** *80*, 5216–5219.

19. Fialkowski, M.; Bitner, A.; Grzybowski, B. A., Wave Optics of Liesegang Rings. *Phys. Rev. Lett.* **2005,** *94*, 018303.

20. Steinbock, O.; Zykov, V. S.; Müller, S. C., Wave Propgation in an Excitable Medium along a Line of a Velocity Jump. *Phys. Rev. E* **1993,** *48*, 3295-3298.

21. Pojman, J. A.; Willis, J.; Fortenberry, D.; Ilyashenko, V.; Khan, A., Factors Affecting Propagating Fronts of Addition Polymerization: Velocity, Front Curvature, Temperature Profile, Conversion and Molecular Weight Distribution. *J. Polym. Sci. Part A: Polym Chem.* **1995,** *33*, 643-652.

22. Goldfeder, P. M.; Volpert, V. A.; Ilyashenko, V. M.; Khan, A. M.; Pojman, J. A.; Solovyov, S. E., Mathematical Modeling of Free-Radical Polymerization Fronts. *J. Phys. Chem. B* **1997,** *101*, 3474-3482.

23. Binici, B.; Fortenberry, D. I.; Leard, K. C.; Molden, M.; Olten, N.; Popwell, S.; Pojman, J. A., Spherically Propagating Thermal Polymerization Fronts. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 1387-1395.

24. Bowden, G.; Garbey, M.; Ilyashenko, V. M.; Pojman, J. A.; Solovyov, S.; Taik, A.; Volpert, V., The Effect of Convection on a Propagating Front with a Solid Product: Comparison of Theory and Experiments. *J. Phys. Chem. B* **1997,** *101*, 678-686.

25. Mariani, A.; Bidali, S.; Fiori, S.; Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A., UV-Ignited Frontal Polymerization of an Epoxy Resin. *J. Polym. Sci. Part A. Polym. Chem.* **2004,** *42*, 2066-2072.

26. Frulloni, E.; Salinas, M. M.; Torre, L.; Mariani, A.; Kenny, J. M., Numerical Modeling and Experimental Study of the Frontal Polymerization of the Diglycidyl Ether of Bisphenol a/Diethylenetriamine Epoxy System. *J. Appl. Polym. Sci.* **2005,** *96*, 1756-1766.

27. Enikolopyan, N. S.; Kozhushner, M. A.; Khanukaev, B. B., Molecular Weight Distribution during Isothermal and Frontal Polymerization. *Dokl. Phys. Chem.* **1974,** *217* (3), 676-678.

28. Khanukaev, B. B.; Kozhushner, M. A.; Enikolopyan, N. S., Theory of Polymerization-Front Propagation. *Combust. Explos. Shock Waves* **1974,** *10* (5), 562-568.

29. Davtyan, S. P.; Gukasova, E. A.; Makarova, S. B.; Enikolopyan, N. S., Gel Effect During Adiabatic Polymerization of n-Butyl Methacrylate. *Dokl. Phys. Chem.* **1976,** *231* (6), 1279-1281.

30. Davtyan, S. P.; Surkov, N. F.; Rozenberg, B. A.; Enikolopyan, N. S., Influence of the Gel Effect on the Kinetics of Radical Polymerization under the Conditions of the Polymerization Front Propagation. *Dokl. Phys. Chem.* **1977,** *232* (2), 64-67.

31. Pojman, J. A.; Curtis, G.; Ilyashenko, V. M., Frontal Polymerization in Solution. *J. Am. Chem. Soc.* **1996,** *118*, 3783-3784.

32. Mariani, A.; Fiori, S.; Malucelli, G., Recent Chemical Advances in Frontal Polymerization. In *Nonlinear Dynamics in Polymeric Systems, ACS Symposium Series No. 869*, Pojman, J. A.; Tran-Cong-Miyata, Q., Eds. American Chemical Society: Washington, DC, 2003; pp 121-134.

33. Taylor, G., The Instability of Liquid Surfaces when Accelerated in a Direction Perpendicular to their Planes. I. *Proc. Roy. Soc. (London)* **1950,** *Ser. A. 202*, 192-196.

34. Pojman, J. A.; Elcan, W.; Khan, A. M.; Mathias, L., Binary Polymerization Fronts: A New Method to Produce Simultaneous Interpenetrating Polymer Networks (SINs). *J. Polym. Sci. Part A: Polym. Chem.* **1997,** *35*, 227-230.

35. Pojman, J.; Gill, N.; Willis, J.; Whitehead, J. B., Polymer Dispersed Liquid Crystal (PDLC) Materials Produced via Frontal Epoxy Curing. *Polym. Mater. Sci. Eng. Prep.* **1996,** *75*, 20-21.

36. Castellano, M.; Fiori, S.; Mariani, A.; Marsano, E. In *PDLC Films Obtained by Frontal Polymerization*, III Convegno Nazionale sulla Scienza e Tecnologia dei Materiali, Trento (Italy), Trento (Italy), 2001; p B34.

37. Szalay, J.; Nagy, I.; Báyai, I.; DeáK, G.; Bazsa, G.; Zsuga, M., High Temperature Copolymerization of Styrene and Maleic Anhydride in Propagating Polymerization Front. *Macromol. Rapid Comm.* **1999,** *20*, 315-318.

38. Chen, S.; Sui, J.; Chen, L.; Pojman, J. A., Polyurethane-Nanosilica Hybrid Nanocomposites Synthesized by Frontal Polymerization. *J. Polym. Sci. Part A Polym. Chem.* **2005,** *43*, 1670-1680.

39. Pojman, J. A.; McFarland, B.; Popwell, S., Free-Radical Frontal Polymerization with Microencapsulated Monomers and Initiators. U.S. Patent Pending

40. Vicini, S.; Mariani, A.; Princi, E.; Bidali, S.; Pincin, S.; Fiori, S.; Pedemonte, E.; Brunetti, A., Frontal Polymerization of Acrylic Monomers for the Consolidation of Stone. *Polymers for Advanced Technologies* **2005,** *16*, 293-298.

41. Pujari, N. S.; Vishwakarma, A. R.; Pathak, T. S.; Kotha, A. M.; Ponrathnam, S., Functionalized Polymer Networks: Synthesis of Microporous Polymers by Frontal Polymerization. *Bull. of Mater. Sci.* **2004,** *27*, 529-536.

42. Odian, G., *Principles of Polymerization, 4th Ed.* 3rd ed. ed.; Wiley: New York, 2004.

43. Fiori, S. M., G.; Marianai, A.; Ricco, L.; Casazza, E., Synthesis and Characterization of a Polyester/Styrene Resin obtained by Frontal Polymerization. *e-Polymers* **2002,** *57*, 1-10.

44. Crivello, J. V.; Bulut, U., Dual Photo- and Thermally Initiated Cationic Polymerization of Epoxy Monomers. *J. Polym. Sci. Part A: Polym. Chem.* **2006,** *44*, 6750-6764.

45. Sawada, H., *Thermodynamics of Polymerization.* Marcel Dekker: New York, 1976.

46. Pojman, J. A.; Craven, R.; Khan, A.; West, W., Convective Instabilities In Traveling Fronts of Addition Polymerization. *J. Phys. Chem.* **1992,** *96*, 7466-7472.

47. Cameo Chemicals. Kaolin. NOAA: 2009. http://cameochemicals.noaa.gov/chemical/25036 (accessed April 17, 2009).

48. Whitesell, J. K.; Pojman, J. A., Kinetics of Formation of Homochiral and Heterochiral Polyesters: Polymers derived from Mandelic Acid. *Chem. Mater.* **1990,** *2*, 248-254.

49. Goodfellow. Metals, Alloys, Compounds, Ceramics, Polymers, Composites. http://www-ferp.ucsd.edu/LIB/PROPS/PANOS/c.html (accessed April 17, 2009).

50. e-Fundeamentals. Aluminum. www.efunda.com (accessed April 17, 2009).

51. Katz, H.S.; Milewski, J.V., *Handbook of Fillers for Plastics.* Van Nostrand Reinhold: New York, 1987; p 467.

52. Moad, G.; Solomon, D. H., *The Chemistry of Radical Polymerization.* Pergamon: Oxford, 1995.

53. Luo, R.; Ying, C.; Sen, A., Effect of Lewis and Bronsted Acids on the Homopolymerization of Acrylates and Their Copolymerizaiton with 1-Alkenes. *J. Polym. Sci. Part A: Polym. Chem.* **2008,** *46* (16), 5499-5505.

54. Grimmett, G., *Percolation.* 2nd ed.; Springer: 1999; Vol. 321, p 444.

55. Nason, C.; Pojman, J. A.; Hoyle, C., The Effect of a Trithiol and Inorganic Fillers on the Photo- Induced Thermal Frontal Polymerization of a Triacrylate. *J. Polym. Sci. Part A Polym. Chem.* **2008,** *46*, 8091-8096.

56. Devadoss, D. E.; Pojman, J. A.; Volpert, V. A., Mathematical Modeling of Thiol-Ene Frontal Polymerization. *Chem. Eng. Sci.* **2006,** *61*, 1257-1271.

57. Giovando, G. Thiolic Compound Polymerization Cocatalysts. U.S. Patent 5,310,826, May 10, 1994.

58. Masere, J.; Pojman, J. A., Period-Doubling Behavior in Propagating Polymerization Fronts of Multifunctional Acrylates. *Polym. Mater. Sci. Eng. Prep. Div. Polym. Mater. Sci. Eng.* **1998,** *79* (2), 80-81.

59. Pojman, J. A.; Varisli, B.; Perryman, A.; Edwards, C.; Hoyle, C., Frontal Polymerization with Thiol-Ene Systems. *Macromolecules* **2004,** *37*, 691-693.

60. Hoyle, C. E.; Lee, T. Y.; Roper, T., Thiol–Enes: Chemistry of the Past with a Promise for the Future. *J. Poly. Sci. Part A. Polym. Chem.* **2004,** *52*, 5301-5338.

61. Mornev, O. A., Refraction of Autowaves: Tangent Rule. *JETP Letters* **2004,** *80*, 721–724.

62. Bertolotti, M.; Liakhou, G. L.; Voti, R. L.; Paoloni, S.; Sibilia, C., Thermal Wave Reflection and Refraction: Theoretical and Experimental Evidence. *J. App. Phys.* **1999,** *85*, 3540-3545.

63. Mandelis, A.; Nicolaides, L.; Chen, Y., Structure and the Reflectionless / Refractionless Nature of Parabolic Diffusion-Wave Fields. *Phys Rev Lett.* **2001,** *87*, 020801.

64. Masere, J.; Pojman, J. A., Free Radical-Scavenging Dyes as Indicators of Frontal Polymerization Dynamics. *J. Chem. Soc. Faraday Trans.* **1998,** *94* (7), 919-922.