THE DEVELOPMENT OF TRANSPARENT, PROCESSABLE, THERMALLY-
RESPONSIVE COATINGS

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by
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TITLE: THE DEVELOPMENT OF TRANSPARENT, PROCESSABLE,
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ABSTRACT

Development of Transparent, Processable, Thermally-Responsive Coatings

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Polymer matrices are commonly used as guest-host systems for organic chromophores for use in non-linear optical materials. The chromophores must be aligned or poled in an electric field in order to impart anisotropy and non-linear activity to the material. This poling process raises several issues, the two largest being the eventual relaxation of the chromophores back into random orientations due to brownian motion, and high molecular weight polymer matrices limiting chromophore mobility during poling. The prevention of this relaxation process is an area of significant interest, especially in applications that require long term coating stability and activity. In this study, a polymer matrix is synthesized that seeks to solve both of these problems with one system. The ideal system would be one that allows for chromophore mobility during processing, but once chromophores have reached the desired orientation, limits mobility and relaxation during in-service usage. A copolymer of methyl methacrylate and a Diels-Alder adduct cross-linking monomer was synthesized in order to meet these challenges. This polymer was blended with commercially available acrylic polymer and organic chromophore molecules in order to test the viability of the solution. It was found that at the percent composition of cross-linker being utilized in the study, the Diels-Alder linkages were not reforming in any measurable amount due to the low amount of Diels-Alder active monomer units. This led to

the development of a new system based on mixing polyfuran based polymers with polymaleimide based polymers during processing. This method allows for high amounts of cross-linking after processing ceases, which achieves both initial goals of the project, as well as allowing facile synthesis of the desired polymer components.

Another attempt to address these issues in polymer matrix formation led to the use of a novel inimer system. The cross-linking agent was also the polymerization initiator, and these functionalities were separated by a Diels-Alder linkage that would fall apart upon exposure to thermal stimulus. These polymers were synthesized and isolated easily, although in some cases gelation occurred. In order to observe the extent of the cross-linking inimer being incorporated into the matrix, cleavage experiments were performed to induce the breaking of the Diels-Alder adduct. Analyzing the Diels-Alder cleaved polymer led to an interesting result: all polymers showed an increase in apparent molecular weight when analyzed by gel permeation chromatography. The increase in molecular weight occurring upon cleavage of main chain bonds has never before been observed in literature. The explanation proposed was that the polymer adopted a "ropeball" like topology consisting of tightly coiled loops and knots. Upon cleavage of the cross-links, the ropeball was able to unwind into a much more linear topology, occupying a much larger hydrodynamic volume. This increase in hydrodynamic volume would cause the gel permeation chromatography results to show an apparent increase in molecular weight.

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Chapter 1: Introduction

1.1 Polymer Matrices

Polymer matrices can be described as any polymer employed as a host system for some sort of additive. Polymer matrices and guest-host systems are commonly used in applications such as thin film formation^[1], in associative thickener applications^[2] and as optical materials^[3]. Polymer matrices are specifically useful for guest-host materials as they provide physical support for the system, and act as a solvent or dispersant for the guest molecules. The long chain lengths and high molecular weights typically used for host polymers cause additives incorporated into the matrix to have low mobility due to chain entanglements and hinderance by steric interactions. Prudent selection of the polymer matrix allows great control over the physical properties of the guest-host system. Glass transition temperature, structure, molecular weight, intermolecular forces, and any set of unique properties that could be desired in the matrix can easily be incorporated during synthesis. Being able to easily switch the properties allows for these matrices to fill an astounding number of different needs. Besides altering the chemical structure of the background matrix, there are several other areas that can be manipulated in order to achieve desirable properties. The additive can be adjusted separately, or the interactions between the matrix and the additive may be altered. For example, to control matrix-additive interactions, the polymer and/or additive may be altered to allow hydrogen bonding between the two molecules, decreasing additive mobility in the matrix. In some cases the additive may even be attached to a pendant polymerizable group and

incorporated into the polymer chain in that fashion, further increasing rigidity.

While these are both chemical changes, there are many steric effects that can cause changes in the property of the matrix as well. By increasing/decreasing the size of the additive, the ability of the additive to move or re-orient itself within the matrix will be decrease/increased, respectively. Additive mobility is an extremely important aspect of the formation of these matrices. In most cases, and especially in the case of large scale commercial processes for production, it is incredibly important that there is uniform distribution of the additive. Having uniform composition throughout the matrix ensures consistent physical properties, and if this uniformity cannot be achieved, then there are serious problems with the matrix. A lack of consistent physical properties will create weak points in the matrix that will be much more likely to crack, bend or deform in other ways. Achieving this uniform distribution is assisted by high additive mobility within the polymer matrix.

1.2 Molecular Weight and Topology

The molecular weight of a polymer greatly affects the physical properties of the resultant bulk material. Polymers of high molecular weight can have excellent physical properties due to their chain entanglements but may be difficult to process conventionally. In addition, as molecular weight increases the incorporation of additives into the matrix becomes more difficult. On the other hand, low molecular weight polymers are easy to process and incorporate additives into, but lack the desirable physical properties of their high molecular weight counterparts.

There are six different topologies polymer samples can assume, linear, branched, star, graft, gel (or network), and dendrimer. The topology is highly dependent on the latent functionality, or potentially polymerizable active sites, present in the monomers and initiators utilized. Examples of these can be found in Figure 1.1.

Figure 1.1: The six common polymer topologies.

The simplest topology is obviously a linear arrangement; synthesized using only monofunctional monomer units and initiators. A branched polymer can be easily created by incorporating monomer units with a functionality of two into a normally linear polymer. Dendrimers are a special case of the branched polymer in that all monomer units share the same functionality greater than one, causing uniform branching throughout the polymer. Star polymers can be created using a

multifunctional initiator and monofunctional monomer, expanding out in many directions at once. Finally a gel is a highly cross-linked polymer sample which in extreme cases can lead to the synthesis of one giant polymer chain. It is clear to see that the different shape of the polymer chain leads to wildly different interactions when incorporated into a guest-host system such as a polymer matrix, most importantly affecting the mobility of additives.

1.3 Hyperbranched Materials

An interesting type of the branched topology is the hyperbranched topology, which can best be described as the gray area between a dendrimer and a branched topology. A dendrimer is a perfectly branched molecule where all branching points are fully reacted (branched), in contrast, in a hyperbranched system a branching point will contain linear chain “defects” interspersed with the branch points, resulting in a less-densely packed overall structure. An example can be found in Figure 1.2.

Figure 1.2: A general example of a hyperbranched topology.

These materials exhibit unique properties due to the hyperbranched character of the matrix, and are used in imprint resists^[4], light emitting materials^[5], and in non-linear optical materials. There are typically two main methods of polymerizing these materials; the single monomer method (SMM) and the double monomer method (DMM)^[6]. While these methods are not focal to this study, it is important to understand the general ideas presented. Intuitively, the single monomer method utilizes one monomer to form the branching, and is commonly done using condensation polymerization. The monomers typically contain functionality AB_x where A and B react to form the polymer backbone. The n value of B can vary, and simply affects the overall amount of branching present in the final product. In this case, every repeat unit of the polymer is also a potential branching point with n branches coming off of it. In a dual monomer method, a copolymer is polymerized of some standard monomer unit coupled with a high functionality cross-linking agent. Several examples of double monomer pairings to yield hyperbranched materials can be found in Figure 1.3.

Figure 1.3: Several simpler pairings that can be utilized for the synthesis of hyperbranched materials utilizing the double monomer method.

These reactions are also commonly called $A_2 + B_x$ polymerization, where $x > 2$. It is apparent that the copolymerization of these pairings together would yield a hyperbranched material. The method utilized in this study is very similar to the double monomer method, but utilizes conventional free radical and controlled radical polymerization techniques to achieve this topology as opposed to the condensation reactions shown in Figure 1.3.

1.4 Non-Linear Optical Materials

Non-Linear optical materials are a field of materials that have a polarization constant P that react non-linearly (anisotropically) upon exposure to

the electric field of incident light. The relationship between polarization and electric field can be found in equation 1.1.

$$P^{NL} = \chi^{(2)}E^2(t) \quad (1.1)$$

This equation is valid for any material, and $E^2(t)$, the mathematical representation of the magnetic field, is a Taylor series expansion. In linear media, all terms after the first term may be ignored as they are negligibly small, causing linear behavior. In non-linear media, these extra terms are non-negligible, but still do not have a major effect unless the intensity of the light is incredibly high. A common example used to cause this behavior is high intensity lasers. Non-linear optical materials are used in a variety of applications, such as signal processing, multi-photon absorption, multiple photoionization, and in frequency mixing processes. One of the most fascinating aspects of these materials is the ability to affect the frequency of incident light. Materials can be made that can add, combine, and subtract the frequencies of incident light, releasing new photons of different frequencies^[7].

These materials are generally plastics containing anisotropic compounds. The first non-linear compounds discovered were inorganic crystals, but research has recently focussed upon the study of highly conjugated π -systems with many free electrons. This is due to the ability of the π electrons to react more rapidly than typical inorganic based systems^[8]. When parts are made using inorganic based materials, the non-linear active crystals are typically incorporated using a guest-host system, and are simply mixed within a polymer matrix. This can also

be performed with organic non-linear active molecules, but it leads to some serious problems in the overall effectiveness of the material. Unlike inorganic complexes, organic molecules must all be poled in the same direction in order to be effectively non-linear. This poling is usually achieved by exposing the material to an extremely high voltage electric field, achieving voltages between 50 and 70 volts per micron. This process can be incredibly harsh on the material, but research has shown that as voltages are increased in the materials, the overall non-linear activity increases^[9]. Poling these non-linear active organic molecules, which are referred to as chromophores, creates a very ordered, low entropy state. Immediately upon removal of the electric field, the Brownian motion of these chromophores causes them to begin to fall out of alignment, and for an organic based non-linear optical material, falling out of alignment means the material is no longer effectively non-linear. The most important part of any organic based non-linear optical material is maintaining this poling for as long as possible. To this end, researchers have found a variety of ways in which to incorporate these chromophores into polymer matrices. The most basic, and least effective at maintaining poling, is a simple guest-host system. This system simply mixes in chromophore with a high-molecular weight polymer during processing. The downside of this method is that the chromophore is free within the matrix to relax upon removal of poling, another flaw is that during poling, the polymer matrix is typically heated to its glass transition temperature, in order to increase chromophore mobility. This increased mobility in some cases can cause the chromophore to leech out of the system and evaporate or sublime. Many of

the organic chromophores typically used are exceptionally toxic, and leeching them into the environment can significantly increase health risks for the technicians creating the materials. Another method for creating these materials is by incorporating the chromophore moiety directly into the polymer chain backbone. This can be done by copolymerizing the chromophore or a pendant group attached to the chromophore, or through homopolymerization of the chromophore by itself. These methods produce much more reliable non-linear optical materials in terms of effective lifetime, as the chromophores are physically bound into the matrix. If the chromophore is attached to a pendant group, reduced distance between the chromophore and the polymer backbone may provide steric stabilization of the oriented chromophore, resulting in longer-lived non-linear optical activity^[10]. This is likely due to a much higher resistance to relaxation of the chromophore because of the high steric bulk of the polymer backbone inhibiting free rotation and movement of the chromophore functionality^[11]. In main chain non-linear optical polymers, the polymers synthesized are extremely unusual from those seen in typical radical polymerization methods in that polymers are synthesized that have highly conjugated π -systems that maintain stability even through polymerization. Polymers such as polybenzene, polypyrrole, and polythiophene are excellent examples of these polymers that could not possibly be synthesized well using conventional methods. In many cases reactions such as Heck coupling or oxidative polymerization are utilized in order to achieve these unusual polymers.

1.5 Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a well understood method of polymerization, useful for synthesizing block copolymers. In a traditional free radical polymerization, termination is irreversible and ends the life of the polymer chain. In an ATRP system, reversible termination is utilized to increase the lifetime of the chains and control the rate of polymerization. A general scheme can be found in Figure 1.4, and each part will be discussed in detail.

Figure 1.4: General scheme for an ATRP^[6].

Where P_n-X is the reversibly terminated polymer chain, Mt^n/L is the metal-ligand complex, P_n^* is the active polymer chain, and $X-Mt^{n+1}/L$ is the metal-ligand complex bound to the terminating halide. An ATRP reaction requires several things in order to proceed. As depicted above, the initiator must contain a bond between a carbon atom and a halide. This is the bond that acts as the reversible terminating agent. There must also be a metal, typically copper, and a ligand, which depends on desired kinetics, present that will complex the halide atom when it is not connected to the polymer chain. If all these requirements are met, then ATRP can occur. Note the size of the k_{act} and k_{deact} arrows; this is to indicate the relative rates of the reaction. The rate of polymerization, k_p , is also

significantly smaller than the rate of deactivation. This is the crux of an ATRP reaction, as the rate of deactivation of the chains is large compared to the rates of activation and polymerization, many times when the chains become activated, they are almost immediately deactivated again. This prevents any one chain from excessively propagating, allowing for a polydispersity close to 1 in many cases. In an ideal ATRP, only a few chains are propagating at a time, limiting the rate of irreversible termination to essentially zero. This lack of irreversible termination has led many to call ATRP a "living" radical polymerization, but this is incorrect. A living polymerization refers to a cationic or anionic polymerization that lacks the ability to terminate, while an ATRP has the ability to irreversibly terminate, it is just unlikely it will do so.

The mechanism of ATRP is best described using a metaphor. Picture a group of 1000 screw top soda bottles that are being filled with liquid, and must all be completely filled around the same time. The liquid is unpredictably dispensed into the bottles, and the cap can be removed and replaced, but liquid can only be added while the top is removed from the bottle. The individual responsible for filling the bottles can only remove the screw tops from several bottles at the same time, but must replace the caps within a fraction of a second. This will lead to many bottles being opened without any liquid actually being deposited in them. In this case the liquid being deposited is a monomer unit adding to the polymer chain, the screw top is the halide ion that reversibly terminates the polymer chain, and the individual that removes and replaces the screw top is the metal ligand complex.

Another interesting aspect of ATRP is the flexibility of the initiator. As mentioned earlier, any molecule containing a carbon-halide bond may act as an initiator in an ATRP reaction. In many cases it is prudent to choose an initiator similar in structure to the monomer being polymerized, as the initiator structure will affect the kinetics of initiation. If the structures are too different, and the rate of activation for the initiator molecule is significantly lower than that of the monomer-halide molecule, a phenomenon called slow initiation occurs. Slow initiation will increase polydispersity, this happens if chains containing monomer are faster to activate than initiator molecules. If the chains already containing monomer are more likely to propagate than initiator molecules the polydispersity will be radically affected.

1.6 Inimer Systems

Inimer is a name given to a specific set of materials that act as both ***Initiators*** of radical polymerization as well as containing monomer functionality as well. These molecules can be used to create unique topologies during polymerization by allowing the active chains to polymerize back onto themselves, essentially creating a loop. The inimer in this study also features a Diels-Alder linkage separating the monomer and initiator functionalities. The Diels-Alder reaction is a type of click chemistry involving an electron rich diene and an electron poor dienophile. A general scheme can be found in Figure 1.5.

Figure 1.5: General form of a Diels-Alder reaction between a furan (red) and maleimide (blue) to form the Diels-Alder adduct (purple).

The Diels-Alder reaction is also reversible, giving the Diels-Alder an incredible amount of versatility. The reaction can be catalyzed by a variety of sources such as heat, magnetic fields, mechanical energy, and microwaves. At low energy the endo adduct is favored, as it is more thermodynamically stable. At higher energy, however, the adduct falls apart into the constituent pieces, returning to the reactants. The reaction is reversible almost indefinitely. The energy required to shift the equilibrium of the reaction back and forth can be tailored by utilizing different dienes and dienophiles. Some of the more common combinations and the relevant temperatures can be seen in Table 1.1.

Table 1.1: Common Diels-Alder compounds and temperatures of adduct dissociation.

Diene	Dienophile	Temperature (C°)
Furan	Maleimide	90
Dimethylfulvene	Maleimide	90
Anthracene	Maleimide	120
Anthracene	Anthracene	180

Utilizing the reversibility of the Diels-Alder reaction can allow for creation of materials with two distinct sets of physical properties. In this study, we will

synthesize materials that will go from a high-molecular weight state to a low-molecular weight state using this reaction as a switch. Utilizing this Diels-Alder adduct as a spacer in between the polymerizable monomer unit and the controlled radical polymerization initiator will allow the formation of a polymer that is highly cross-linked. Upon exposure to a thermal stimulus, the Diels-Alder adduct will dissociate into the constituent parts, causing the dissociation of the cross-links. Upon removal of the stimulus, the Diels-Alder equilibrium will shift back towards the cycloaddition product, or adduct, causing the cross-linking reaction to reoccur, essentially locking the polymer matrix in place.

The overall goal of this research is to create a Diels-Alder based cross-linked polymer matrix for use in the creation of non-linear optical materials. As addressed, the cross-linking will allow for the lifetime of the non-linear activity of the material to increase. Current poling lifetimes are insufficient for long-term use of these materials in environments where immediate repair and re-poling may not be a realistic possibility. Utilizing a matrix that is simply a high molecular weight polymer with no cross-linking can lead to the situation shown in Figure 1.5.

Figure 1.6: Chromophore incorporated into high molecular weight matrix (left) poling occurring due to exposure to electric field (green) in order to provide non-linear activity (middle), chromophore relaxing back to initial state due to Brownian motion (right).

The polymer shown in Figure 1.6 is high molecular weight or contains irreversible cross-links. While this high molecular weight matrix provides resistance to the mobility of the chromophore within the matrix, this also causes significant complications during the poling process of the chromophores. In order to align properly, the chromophores must be able to maneuver around the matrix to achieve the desired arrangement. In a high molecular weight matrix, this movement becomes almost impossible due to the high levels of chain entanglement present in the matrix. Since the chromophores are unable to move freely through the matrix, the poling process is not as effective as it could be, decreasing the non-linear activity of the material. Although the high molecular weight polymer is sufficient to prevent mobility of the chromophore, an ideal material would allow chromophore mobility on demand, while maintaining the rigidity of the high molecular weight matrix once the poling process was

completed. Creating this ideal material is the main focus of this research, and the overall goal can be summed up in Figure 1.7.

Figure 1.7: Matrix is exposed to thermal stimulus, causing the matrix to release cross-links (left). The lower molecular weight matrix allows chromophores the mobility necessary to assemble appropriately (middle). Upon removal of the thermal and electric stimuli, the chromophores are locked into place in an ideal position post poling (right).

The material proposed here can contain the excellent physical properties of a high molecular weight matrix with desirable additive mobility found in lower molecular weight matrices, effectively creating a material with two distinct sets of physical properties.

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Chapter 2: Preparation of a Diels-Alder Active Cross-Linker

2.1 Motivation

Non-Linear optical materials (NLOs) are valued for their unique ability to affect the properties of incident light, such as causing frequency doubling^[1]. This frequency doubling causes a subsequent decrease in wavelength, as evidenced by equation 2.1.

$$c = \lambda\nu \quad (2.1)$$

Where c is the speed of light, λ the wavelength and ν the frequency. While frequency doubling does cause an increase in the overall energy of the light, combining two photons decreases the intensity of the light. This has obvious applications in coatings technology in protective coatings for cameras and satellite lenses, which would require expensive maintenance and replacement if the lens was damaged by a laser attack.

While many NLOs require crystals in order to achieve these interesting properties, organic molecules can also be effective in this regard. These organic molecules possessing these properties, called chromophores, can either be incorporated into the backbone of a polymer or used as an additive in a polymer matrix. For these organic based NLOs to work properly, the chromophore moieties must be aligned properly^[2]. When the chromophore is incorporated into the polymer chain, the whole chain must move with the chromophore functionality in order to align, which can be extremely difficult to achieve. On the other hand, when the chromophore is loaded into a matrix, these chromophoric

molecules become easy to pole as they are much freer to move and rotate in the matrix; unfortunately, the chromophores retain this ability to move after alignment, causing a loss of non-linear optical properties. This can be a huge problem with long term application of these materials, as a loss of efficacy over time is unacceptable. To enhance the lifetime of these materials, new materials need to be developed that will inhibit the relaxation of these chromophores into a random orientation. Developing these materials is the focus of the current study.

To increase the lifetime of the poled chromophores, the rigidity of the matrix can be increased, causing less freedom of movement for the chromophores loaded within. This can easily be achieved by increasing the molecular weight through cross-linking or other means. While this solution will decrease the ability of the chromophore to relax, it will also inhibit the initial poling, as well as inhibit the ability of the chromophore to disperse uniformly. Compounded with this, Dalton *et al* reported that at high cross-link densities the non-linearity of the thin film is greatly inhibited^[3]. Since increasing the molecular weight or the cross-link density is not an effective way to reduce relaxation, different solutions are required.

2.2 Background Information

2.2.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a method of thermal analysis primarily used to study phase transitions. The technique was developed by E.S. Watson and M.J. O'Neill in 1960^[4]. DSC operates by measuring the heat flow

that is required to keep a sample and an inert reference at a zero temperature differential throughout a linear temperature ramp. This yields the instantaneous heat capacity at constant pressure (C_p) of the sample. Therefore when a sample undergoes an endothermic transition the amount of energy required to keep it at the same temperature as the reference is equivalent to the magnitude of the energy absorbed in the transition yielding a direct calorimetric measurement of the enthalpy of transition (ΔH_{cal}). This quantity is calculated by integrating the area under the C_p curve as shown by Equation 2.2.

$$\Delta H_{cal} = \int_{T_1}^{T_2} C_p dT \quad (2.2)$$

The same principle can be applied to an exothermic transition only with the amount of energy required to keep the reference at the same temperature indicating the enthalpy of transition. From the ΔH_{cal} measurement the entropy of the phase transition can be calculated as shown by Equation 2.3 where the melting temperature (T_m) is the temperature where C_p reaches its maximum.

$$\Delta S = \frac{\Delta H_{cal}}{T_m} \quad (2.3)$$

For the purpose of this research, DSC analysis was used both to learn the glass transition temperatures of polymer samples synthesized, which is a common use of DSC in the field of polymer chemistry, and also to investigate the effectiveness of the Diels-Alder linkages that had been incorporated into the polymer backbone. These transitions can both easily be seen using DSC, which

was also utilized to examine the overall reversibility of the samples prepared over several cycles.

2.2.2 Optical Clarity and Measurements

To effectively meet the goals of the project, the end result must be optically clear. Optical clarity is measured in three different ways; transmittance, haze, and clarity. Transmittance is defined as the amount of light that passes through the material relative to the total amount of light the material was exposed to. Haze and clarity are defined as the amount of light that is bent 2.5° more or less, respectively, after passing through the material relative to the total amount of light. These values are explained further in Figure 2.1.

Figure 2.1: Illustrated explanation of transmittance, haze, and clarity.

In an ideal material, it is desirable that transmittance and clarity near 100% and haze is kept at a minimum. For polymeric materials, an optically clear polymer such as polystyrene or poly(methylmethacrylate) would be a reasonable

baseline, although it is prudent to compare optical clarity measurements between similar samples. Processing conditions can also have an effect on the optical properties of a material^[5].

2.3 Experimental Strategy

In the present study a partially cross-linked matrix was developed utilizing Diels-Alder chemistry. This system allows the cross-links to be reversible, tailoring the properties of the matrix based upon the energy input into the sample. This will allow for better dispersion of the chromophore additive as well as being able to maintain rigidity much longer than a non-cross-linked matrix with minimal effect on non-linearity of the material. A detailed system design can be seen in Figure 2.2.

Figure 2.2: Polymer matrix shown with Diels-Alder adduct cross links (A, purple) falling apart into constituent pieces upon exposure to thermal stimulus (B, red and blue). This allows the additive (green) to migrate within the matrix upon mixing (C). Removal of the thermal stimulus, Diels-Alder linkages re-form, holding the additives in a well-dispersed state (D).

To achieve this type of a system, thermally reversible cross-links are required. As detailed earlier, the Diels-Alder reaction is an excellent choice for this application, and was easily incorporated into the matrix.

2.3.1 Synthesis of Thermally Responsive Cross-linking Agent (DA-Xlinkers 1 through 3)

Schemes 2.1 and 2.2 illustrate the synthesis of the cross-linker molecules. The active site of polymerization was varied between a tertiary site and a secondary site. This was done in order to affect the stability of the propagating radical, adjusting the rate at which the cross-linker was incorporated into the polymer chain.

Scheme 2.1: Synthesis of DA-Xlinker 1 (R=CH₃) and DA-Xlinker 3 (R=H)

In the synthesis of DA-Xlinkers 1 and 3, furfuryl alcohol and phenolic maleimide were allowed to stir in tetrahydrofuran at 50 °C overnight. The compound was then purified by rotary evaporation, dissolved in methylene chloride, and esterified using methacryloyl chloride or acryloyl chloride in the presence of triethylamine. Salts were then filtered out, and the compound was washed with water and sodium bicarbonate solution. Solvent was removed using rotary evaporation, and the product was placed under high vacuum to remove residual solvent. Structure and purity were confirmed using ¹HNMR spectroscopy.

Scheme 2.2: Synthesis of DA-Xlinker 2

In the synthesis of DA-Xlinker 2, furfuryl alcohol was reacted with methacryloyl chloride with triethylamine in methylene chloride. Salts were then filtered out, and the compound was washed with water and sodium bicarbonate solution. The product was then rotary evaporated and placed under high vacuum. The compound was then dissolved in tetrahydrofuran, and allowed to stir with phenolic maleimide overnight at 50 °C. This compound was rotary evaporated, dissolved in methylene chloride and reacted with acryloyl chloride in the presence of triethylamine. Salts were gravity filtered and removed, and the compound was washed with water and sodium bicarbonate solution. Solvent was removed using rotary evaporation, and the product was placed under high vacuum to remove residual solvent. Structure and purity were confirmed using ¹HNMR spectroscopy.

2.3.2 Synthesis of Thermally Responsive Poly(Methyl Methacrylate) (TR-PMMA)

The three DA-Xlinkers were then copolymerized with methyl methacrylate, as shown in Scheme 2.3.

Scheme 2.3: Synthesis of TR-PMMA

A simple free radical polymerization was performed, using azobisisobutyronitrile (AIBN) as an initiator in tetrahydrofuran. These reactions were performed at 60 °C and were allowed to proceed until gelation occurred. The Diels-Alder compounds were added in varying percentages ranging from 0.5% to 10% by total mole of monomer. The resulting polymer was then placed in an oven to drive off residual tetrahydrofuran and then analyzed by DSC. Gel Permeation Chromatography (GPC) was not performed on this compound as it was insoluble due to gelation and would swell as opposed to dissolve.

2.3.3 Processing of TR-PMMA into Useful Parts

The TR-PMMA samples created were then blended with commercially available high molecular weight acrylic using a DSM Xplore micro-compounder in a variety of ratios. The acrylic and TR-PMMA were allowed to mix for 10-15 minutes at 120 RPM to facilitate uniform properties of the resulting blend. Upon

completion of mixing, the polymer was extruded as a rod and allowed to cool. The blends were later molded into parts using a compression molder. These parts were then analyzed for their optical properties. The thermal responsiveness of the polymer and physical properties were also tested using DSC and dynamic mechanical analysis (DMA), respectively.

2.4 Results and Discussion

A variety of blends were successfully processed and analyzed for their thermal, optical, and mechanical properties. The results of the DSC analysis can be found in Figure 2.3.

Figure 2.3: DSC results of TR-PMMA blend with repeated cycles compared to results for unaltered PMMA. Samples were subjected to 5 min isotherm at 50 °C with a heating rate of 20 °C/min to 250 °C followed by a cooling ramp of 10 °C/min to 50 °C.

As mentioned, the temperature at which the retro Diels-Alder reaction occurs for a maleimide/furan system is 90 °C, and the glass transition temperature of PMMA occurs at 105 °C. This causes an unfortunate overlap in our thermograms, but relevant information can still be obtained from these results. As expected, when increasing the molecular weight average of the polymer sample being analyzed, the glass transition temperature increases by a small amount, which can be seen in the first upslope in heat flow. There is an additional endotherm in heat flow of the first cycle, and this endotherm is attributed to the Diels-Alder linkage being broken as temperature increases. Unfortunately, subsequent runs of the sample revealed that the Diels-Alder linkages were not reforming under the conditions and time frames assumed to be effective. To facilitate the reformation of cross-links, the temperatures at which the samples were annealed and the annealing time the samples were given were altered. The sample was then analyzed after a much longer annealing period, and results can be found in Figure 2.4.

Figure 2.4: Annealed TR-PMMA DSC results compared to 1st cycle TR-PMMA. Analysis conditions were a 5 min isotherm at 50 °C with a heating rate of 20 °C/min to 250 °C followed by a cooling rate of 10 °C/min to 50 °C.

This thermogram shows a very similar curve even after annealing has taken place, indicating a low percentage of Diels-Alder linkages reforming after exposure to thermal stimulus. While this is initially discouraging, in retrospect it is not surprising. The samples prepared utilizing these TR-PMMA blends were at most a 10% incorporation of cross-linker into PMMA, and were further diluted with commercially available acrylic into an even lower concentration. The Diels-Alder linkages were likely broken during processing due to the high shear forces and the high temperatures at which the samples were processed. To reform a Diels-Alder linkage, a furan functionality must be in close proximity to a maleimide group. Due to the rigidity of the polymer after removal of heat, the likelihood of these two groups finding each other in the polymer matrix is incredibly low. It is also clear from the literature, that the recovery of Diels-Alder linkages in self-healing materials requires a significant amount of time and

exposure to long-term heat. It is possibly that the conditions selected for the annealing experiment may not have been ideal to facilitate the reformation of these linkages. To completely understand this occurrence in the material, higher concentration cross-linked TR-PMMA would need to be synthesized. Due to synthetic limitations and initial processing complications, a better synthetic strategy was devised.

Optical clarity measurements were conducted on the processed parts made from the compression molder. The samples were subjected to clarity and haze measurements. Examples of the parts can be found in Figure 2.5.

Figure 2.5: From left to right, 0% TR-PMMA, 20% TR-PMMA, 40% TR-PMMA, and 67% TR-PMMA.

It is clear to see that as the percentage of TR-PMMA used in the sample increases, the test plates adopt a darker brown color. This is likely due to the additional Diels-Alder adducts, which appear as a dark brown color in pure form, present in the sample. The results of the haze and clarity measurements are shown in Table 2.1.

Table 2.1: Haze and clarity measurements of TR-PMMA blends and unblended PMMA.

Sample	Crosslinker	% Crosslinker	% TR-PMMA	Haze	Clarity
1	None	None	0	5.11	92.60
2	1	0.5	20	5.29	92.30
3	1	0.5	40	6.70	89.50
4	1	0.5	67	23.5	88.60
5	1	1.0	20	18.10	57.10
6	1	1.0	40	32.40	36.54
7	1	1.0	67	44.10	42.40
8	1	2.5	20	9.56	77.50
9	1	2.5	35	6.46	82.80
10	1	5	20	21.00	64.40
11	1	5	32	16.20	55.20
12	1	10	24	45.50	32.10
13	1	10	40	65.90	16.10
14	2	0.5	20	9.89	76.20
15	2	0.5	40	17.20	64.30
16	2	0.5	60	30.30	63.60

As the amount of cross-linker in a sample is increased, the clarity decreases while the haze increases. This strong correlation between amount of cross-linker and undesirable optical properties indicates the likely cause of this is the cross-linker, either due to the additional rigidity it causes in the matrix, or in the structure of the cross-linking molecule itself. While some of these results could also be caused by sample defects, the correlation seems strong enough to ignore experimental error as a potential cause for the trend.

Another cause for concern with this method is the inability to accurately determine the molecular weight of the polymer. The polymers were insoluble in solution, making GPC analysis impossible. Due to this, the polymer was analyzed utilizing ^1H NMR spectroscopy. To test the actual reversibility of the polymer, TR-PMMA samples were submerged in refluxing toluene to facilitate the retro Diels-Alder reaction. Even after significant time spent heating in solution, the polymer samples remained undissolved. This suggests uncontrolled and unintended side reactions are occurring that would lead to irreversible cross-

linking. To confirm this hypothesis, NMR spectra were taken of both the unheated TR-PMMA as well as the recovered refluxed TR-PMMA. The spectra can be seen in Figure 2.6.

Figure 2.6: NMR Spectra of both refluxed TR-PMMA (top) and initial TR-PMMA (bottom).

While the spectra contain a variety of unusual peaks due to the topology of the polymer, there are several important areas to note. There is a clear reduction in the intensity of peaks present around 3.25 ppm, which correspond to the protons attached to the bridgehead carbon of the Diels-Alder adducts. New peaks also appear at 5.2, 7.6, and 7.7 ppm, which are consistent with the free furan and maleimide groups. These suggest that the Diels-Alder linkages are indeed falling apart upon exposure to thermal stimulus. The side reactions forming permanent cross-links, causing the insolubility, are unknown at this time.

This method of synthesizing and creating these materials was determined to be inefficient for achieving the goals of the project, causing a different

synthetic method to be pursued. The proposed synthetic scheme, seeks to solve the problems encountered by this first method. The strategy here is to create linear polymers of furan and maleimide functionality with an acrylate pendant group. The synthesis for these monomers can be found in Scheme 2.4. Synthesis of these materials is being aided by Tristan Kleine and Christopher Pattillo of the Costanzo group.

Scheme 2.4: Synthesis of maleimide and furan based acrylic monomers.

An interesting aspect of this synthetic method is the protection of the maleimide and furan units by attaching protecting groups via Diels-Alder reactions. The goal of these protecting groups is to prevent cross-linking reactions from occurring between the polymer chains during polymerization. These monomers were prepared and then polymerized via free radical polymerization, shown in Scheme 2.5.

Scheme 2.5: Synthesis of polymaleimide and polyfuran protected polymers.

The desired outcome is that cross-linking occurs only after the chromophore has been successfully incorporated into the matrix, and not before, which could potentially limit the ability of the chromophore to disperse evenly. At the high temperatures and shear forces the polymers will experience during processing, the protecting group should fall off, leaving the maleimide and furan functionalities free to react. Unlike in the initial method, where the cross-linking moieties were few and far between, in the polyfuran and polymaleimide mixture, it is analogous to a very simple A-A B-B macromonomer coupling experiment. With the high amount of both furan functionality and maleimide functionality, the likelihood of successful cross-linking via Diels-Alder reaction is exponentially greater than that seen in the first system. The work in this area is ongoing, and

final synthesis, processing, and analysis will be performed by Tristan Kleine and Christopher Pattillo during the Summer of 2012 while working at the Army Research Laboratories in Aberdeen, MD.

2.5 Conclusions

A variety of TR-PMMA blends were successfully processed and molded into parts in order to be analyzed by DSC and for optical clarity. After analysis by DSC, it was found that the Diels-Alder linkages were not successfully reforming after the high temperature and force processing, even after extensive post-processing annealing. The desirable optical properties, as well as the ease of processing, were found to diminish as more cross-linker was added to the matrix. Other error may have been introduced due to the gelation of the TR-PMMA samples at lower conversions, causing inconsistencies between similar samples and potentially altering the amount of cross-linker that was actually incorporated into the matrix. These results lead to the project being taken in a new direction in which a furan based polymer and a maleimide based polymer were blended together during processing to facilitate a Diels-Alder A-A B-B cross-linking reaction. This new method is still being investigated and results are currently being collected.

2.6 Experimental

2.6.1 Materials

All materials and reagents were purchased from commercially available sources and no further purification was performed before use. Preparation of 4-maleimide phenol followed previously published methods.

2.6.2. Instrumentation

^1H and ^{13}C NMR spectroscopy were performed using either a 300 MHz or 600 MHz Bruker spectrometer in deuterated chloroform. All peaks are reported in $\delta(\text{ppm})$ relative to the residual solvent peak. Polymer processing was performed using a lab-scale DSM Xplore twin-screw compounder.

2.6.3 Synthetic Preparations

2.6.3.1 Synthesis of DA-Xlinker 1 and 3 (Step 1)

In a 250 mL round-bottomed flask equipped with magnetic stir bar, phenolic maleimide (5.0 g, 26.4 mmol) was dissolved in 100 mL of tetrahydrofuran. Furfuryl alcohol (2.59 g, 26.4 mmol) was then added to the solution. The solution was heated to 50 °C and allowed to stir overnight. Upon completion, the solution was rotary evaporated and exposed to high vacuum to dryness, yields were quantitative. The compound was analyzed via ^1H NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3 , δ): 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 5.35 (s, 1H), 4.18-4.24 (overlap of s from combination of exo

and endo product, 2H), 3.65 (s, 1H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H)

2.6.3.2 Synthesis of DA-Xlinker 1 and 3 (Step 2)

In a 250 mL round-bottomed flask equipped with magnetic stir bar, the phenolic maleimide/furfuryl alcohol Diels-Alder adduct (7.58 g, 26.4 mmol) was dissolved in 100 mL of methylene chloride. Triethylamine (3.18 g, 31.5 mmol) was then added simultaneously to the solution with acryloyl chloride (TSK Notebook) or methacryloyl chloride (3.18 g, 30.4 mmol). This solution was allowed to stir overnight at room temperature. The resulting solution was gravity filtered to remove salts, washed 3x with water and sodium bicarbonate solution, dried with magnesium sulfate and solvent removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR. ^1H NMR (300 MHz, CDCl_3 , δ): 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 6.27 (s, 1H), 6.10 (s, 1H), 6.05 (two overlapping singlets, 2H), 5.56 (two overlapping singlets, 2H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H)

2.6.3.3 Synthesis of DA-Xlinker 2 (Step 1)

In a 250 mL round-bottomed flask equipped with magnetic stir bar, phenolic maleimide (5.0 g, 26.4 mmol) was dissolved in 100 mL of methylene chloride. Triethylamine (3.18 g, 31.5 mmol) was then added drop wise

simultaneously with methacryloyl chloride (3.18 g, 30.4 mmol). This solution was allowed to stir overnight at room temperature. The resulting solution was gravity filtered to remove salts, washed 3x with water and sodium bicarbonate solution, dried with magnesium sulfate and solvent removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3 , δ): 7.38 (s, 1H), 6.38 (s, 1H), 6.31 (s, 1H), 6.08 (s, 1H), 5.52 (s, 1H), 5.09 (d, 2H), 1.90 (s, 3H)

2.6.3.4 Synthesis of DA-Xlinker 2 (Step 2)

In a 250 mL round-bottomed flask equipped with magnetic stir bar, the esterified phenolic maleimide (6.29 g, 25.8 mmol) was dissolved in 100 mL of tetrahydrofuran. Furfuryl alcohol (2.59 g, 26.4 mmol) was then added to the solution. The solution was heated to 50 °C and allowed to stir overnight. Upon completion, the solution was rotary evaporated and exposed to high vacuum to dryness, yields were quantitative. The compound was then analyzed via ^1H NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3 , δ): 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 5.35 (s, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.01 (s, 3H)

2.6.3.5 Synthesis of DA-Xlinker 2 (Step 3)

In a 250 mL round-bottomed flask equipped with magnetic stir bar, the DA-Xlinker 2 precursor (10.2 g, 25.8 mmol) was dissolved in 100 mL of

methylene chloride. Triethylamine (3.18 g, 31.5 mmol) was then added followed by acryloyl chloride (2.75 g, 30.4 mmol) added drop wise. This solution was allowed to stir overnight at room temperature. The resulting solution was gravity filtered to remove salts, washed 3x with water and sodium bicarbonate solution, dried with magnesium sulfate and solvent removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR. ^1H NMR (300 MHz, CDCl_3 , δ): 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 6.10 (s, 1H), 6.03 (s, 1H), 5.50 (s, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.01 (s, 3H)

2.6.3.6 Free Radical Polymerization of TR-PMMA

In a 50 mL round-bottomed flask equipped with magnetic stir bar. AIBN (19.5 mg, 115 μmol , 0.5%) was added to the solution, followed by the desired DA-Xlinker molecule (percentages ranged from 0.5% to 10%). Methyl methacrylate (percentages ranged from 99.5% to 90%) was then added to the solution, followed by 10 mL of tetrahydrofuran. The reaction vessel was then sealed using copper wire and rubber septum and purged under nitrogen gas for 10 minutes. The flask was then lowered into a temperature controlled oil bath set at 60 $^\circ\text{C}$ and allowed to stir until gelation began to occur. Upon gelation, the reaction was terminated via injection of air and diluted with solvent. The resulting solid was then dried in an oven to drive off residual tetrahydrofuran. The resulting sample was then analyzed by DSC to determine Diels-Alder activity.

2.6.3.7 Furan Monomer Synthesis (Step 1)

In a 100 mL Schlenk flask equipped with magnetic stir bar, sodium hydride (0.37 g, 15.3 mmol) was added. The flask was then exposed to vacuum and backfilled three times with nitrogen gas. Anhydrous tetrahydrofuran (10-15 mL) was then added to the flask and this slurry was allowed to stir for several minutes. Furfuryl alcohol (1.00 g, 10.2 mmol) was then added drop wise to the stirring solution, which was left for two hours. Upon completion of this time benzyl bromide (1.83 g, 10.7 mmol) was added and the reaction was allowed to stir overnight. The next day water was added slowly in order to quench residual sodium hydride and the product was extracted with diethyl ether. Solvent was then removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3 , δ): 7.67 (d, 1H), 7.38-7.45 (m, 5H), 6.47 (d of d, 1H), 6.39 (d, 1H), 4.55 (s, 2H), 4.48 (s, 2H)

2.6.3.8 Furan Monomer Synthesis (Step 2)

In a 50 mL round bottomed flask equipped with magnetic stir bar, the product of step 1 (1.15 g, 8.21 mmol) was added to the flask and dissolved in minimal tetrahydrofuran. Phenolic maleimide (1.55 g, 8.21 mmol) was then added to the solution. The solution was heated to 65 °C and left to stir for 48 hours. Solvent was removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR spectroscopy. ^1H NMR

(300 MHz, CDCl₃, δ): 7.25-7.45 (m, 5H), 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 5.35 (s, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 4.73 (s, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H)

2.6.3.9 Furan Monomer Synthesis (Step 3)

In a 50 mL round bottomed flask equipped with magnetic stir bar, the product from step 2 (3.08 g, 8.21 mmol) was dissolved in methylene chloride. The solution was then cooled to 0 °C. Triethylamine (1.00 g, 9.85 mmol) and methacryloyl chloride (0.94 g, 9.03 mmol) were then added drop wise simultaneously and allowed to stir for two hours at room temperature. The resulting solution was gravity filtered to remove salts, washed 3x with water and sodium bicarbonate solution, dried with magnesium sulfate and solvent removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ¹H NMR spectroscopy. ¹H NMR (300 MHz, CDCl₃, δ): 7.25-7.45 (m, 5H), 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 6.10 (s, 1H), 6.03 (s, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 4.73 (s, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.05 (s, 3H)

2.6.3.10 Maleimide Monomer Synthesis (Step 1)

In a 1000 mL round bottomed flask equipped with magnetic stir bar, 4-aminophenol (89.5 g, 800 mmol) was added and dissolved in acetone (500 mL). In a separate beaker, maleic anhydride (80.0 g, 815 mmol) was dissolved in acetone (300 mL). The maleic anhydride solution was then added drop wise to the stirring 4-aminophenol solution and was allowed to stir for two hours.

2.6.3.11 Maleimide Monomer Synthesis (Step 2)

In a 500 mL round bottomed flask equipped with magnetic stir bar, the product from step 1 (41.5 g, 200 mmol) was added and dissolved in dimethylformamide. Catalytic sodium acetate (1.00 g, 12 mmol) was then added, followed by acetic anhydride (44.9 g, 440 mmol). The reaction was then allowed to stir at 70 °C overnight. Upon completion, the product was precipitated into ice water and dried by vacuum filtration. Structure was confirmed by ^1H NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3 , δ): 7.45 (d, 2H), 7.26 (d, 2H), 7.04 (s, 2H), 2.31 (s, 3H)

2.6.3.12 Maleimide Monomer Synthesis (Step 3)

In a 100 mL round bottomed flask equipped with magnetic stir bar, the product from step 2 (5.53 g, 23.9 mmol) was added and then dissolved in tetrahydrofuran. Furfuryl alcohol (2.34 g, 23.9 mmol) was then added to the solution. . The solution was heated to 65 °C and left to stir for 48 hours. Solvent was removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR. ^1H NMR (300 MHz, CDCl_3 , δ): 7.12 (d, 2H), 6.93

(d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 3.65 (s, 1H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.31 (s, 3H)

2.6.3.13 Maleimide Monomer Synthesis (Step 4)

In a 100 mL round bottomed flask equipped with magnetic stir bar, the product from step 3 (7.17 g, 23.9 mmol) was dissolve in methylene chloride. The solution was then cooled to 0 °C. Triethylamine (2.90 g, 28.7 mmol) was added to the solution, followed by drop wise methacryloyl chloride (2.74 g, 26.8 mmol) and allowed to stir for two hours at room temperature. The resulting solution was gravity filtered to remove salts, washed 3x with water and sodium bicarbonate solution, dried with magnesium sulfate and solvent removed via rotary evaporation and high vacuum. The resulting compound was then analyzed via ^1H NMR spectroscopy. ^1H NMR (300 MHz, CDCl_3 , δ): 7.12 (d, 2H), 6.93 (d, 2H), 6.48 (s, 1H), 6.40 (s, 1H), 6.25-6.28 (overlap of d of d from combination of exo and endo product and s, 3H), 6.10 (s, 1H), 6.03 (s, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.31 (s, 3H), 2.05 (s, 3H)

2.6.3.14 Typical Polymerization of Polymaleimide and Polyfuran systems

In a 50 mL round bottomed flask equipped with stir bar, AIBN (0.05 mol%) was added and dissolved in toluene (40% total volume), followed by furan/maleimide monomer (10 mol%), and styrene (90 mol%). The solution was

then purged under nitrogen gas for 10-15 minutes and lowered into a temperature controlled oil bath set to 60 °C and allowed to stir for 30 minutes. The polymerization was terminated via introduction of air, diluted and precipitated into methanol. The polymer was vacuum filtered, allowed to dry and analyzed via GPC.

2. 7 References

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Chapter 3: Preparation of an Inimer Based Cross-Linking System

3.1 Motivation

Incorporating a high-percentage of a cross-linking monomer unit into a free radical polymerization caused considerable problems, especially if that polymerization is allowed to proceed to gelation. A non-uniform distribution of cross-linked sites, as well as an unknown amount of cross-links being incorporated into the gel make repeatability impossible. Cross-linkers are incorporated randomly, yielding low uniformity between samples, even holding reaction conditions identical, incorporation will not occur identically. In a large scale production of this polymer matrix, having samples of uniform quality can mean the difference between total failure of the NLO or successful activity of the material on incident light. This disparity between samples is an unacceptable risk in the creation of these materials. The method utilized to create these materials in Chapter 2 (Scheme 2.3) highlighted these risks as well as provided difficulty in processing and optical clarity issues. This non-uniformity and difficulty in processability was unacceptable, so the development of a new system that could incorporate cross-linker in a more uniform fashion was required.

3.2 Background Information

3.2.1 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a chromatographic technique utilized to separate samples in solution based on size. This technique was typically used to characterize TR-PMMA samples. Similar to other forms of

chromatography, there exists a mobile phase and a stationary phase. The mobile phase (or eluent) is a solvent the polymer is soluble in, such as THF, and the stationary phase consists of a porous gel. The purpose of this porous gel is at the heart of the effectiveness of GPC, and the pore size is carefully controlled in the columns. The gel serves to separate larger polymer chains from smaller polymer chains by allowing the smaller polymer chains to become stuck or trapped in the pores. Due to the size of the chains, smaller polymers are much more likely to become hindered or trapped by the pores in the gel than a higher molecular weight polymer. The amount of time required for a sample to travel through the column and past the detector is inversely proportional to the sample's molecular weight. There are a variety of detectors available for use with GPC, but the two main types utilize either light scattering or refractive index to measure the amount of polymer present in the eluent as it passes by the detector. The GPC must then convert the elution time of the TR-PMMA sample into meaningful molecular weight data. This is done using a universal calibration curve, carefully created using monodisperse samples of linear polystyrene to ensure accuracy^[1]. Using this calibration curve, it is a simple calculation to come to the average molecular weight of the TR-PMMA sample.

While GPC appears to separate samples by molecular weight, in reality a GPC separates samples by hydrodynamic volume, or the amount of space a sample takes up in solution. All of the above still holds true, since polymers with large hydrodynamic volumes will also be less likely to become trapped or hindered in the porous gel phase, but this can cause some interesting anomalies

in the cases of polymers that occupy a significant amount of space in solution but may not necessarily have a high molecular weight, and vice versa.

3.3 Experimental Strategy

While the goal of this method is identical to that covered in Chapter 2, the pathway in which the goal is achieved is different. An inimer system was utilized to better control the amount of cross-linker present during polymerization. This also provides a much better picture of the overall structure of the polymer matrix, as the distance between cross-linked sites is more likely to be much larger, due to an inability of the chain to easily wrap back upon itself. In addition, steric effects by the growing chain make the polymerizable monomer site on the inimer more difficult to access. This new method should cause an overall increase in uniformity of the matrix, potentially dealing with the optical clarity problems discussed at the end of Chapter 2. To preserve the over-arching goal of a reversibly cross-linked matrix, the inimer molecules must also be Diels-Alder adducts, and the two functionalities separated by the Diels-Alder linkage.

3.3.1 Synthesis of Inimers 1,2,3 and 4

Scheme 3.1: Synthesis of Inimer Systems

Using a phenolic maleimide/furfuryl alcohol Diels-Alder adduct identical to the work discussed in Chapter 2, the inimer molecules were synthesized utilizing similar esterification conditions. Compounds were added to methylene chloride with triethylamine and the desired acid halide to perform a simple esterification. Salts were removed by gravity filtration, and the resulting solution washed with water and bicarbonate, followed by removal of solvent. The isolated compounds were then analyzed by ^1H NMR spectroscopy in order to confirm structure and ensure purity. The amount of substitution around both the ATRP initiator and polymerizable moieties were varied to investigate the effect of the differing secondary and tertiary rates of incorporation on the cross-linking of the matrix. The differences between inimers 1 through 4 can be seen in Table 3.1.

Table 3.1: Number designations for the differently substituted inimer systems synthesized.

<u>Inimer</u>	<u>R₁ (Initiator)</u>	<u>R₂ (Monomer)</u>
1	H	H
2	H	CH ₃
3	CH ₃	H
4	CH ₃	CH ₃

3.3.2 ATRP of Inimer systems with Methylmethacrylate

Scheme 3.2: ATRP of inimer systems, and the resulting cleavage experiments.

The inimers were then used as an initiator for ATRP experiments. Using a variety of combinations of catalysts and ligand systems involving copper(I) bromide, copper(I) chloride, *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDETA), and 2,2'-bipyridine (bipy). The reaction times varied greatly depending on the ligand and catalyst system utilized, as PMDETA and copper(I) bromide typically allow for polymerization one order of magnitude faster than bipy and copper(I) chloride, respectively. The resulting polymers were isolated via precipitation into methanol, allowed to dry and then molecular weight was determined using GPC. In order to test the effectiveness of the Diels-Alder cross-links, the polymers were subjected to cleavage experiments, which can be seen in Scheme 3.3.

Scheme 3.3: Cleavage Experiments performed to confirm Diels-Alder cross-linking and reformation experiments

The cleavage experiments were performed at 110°C in toluene over 24h. Upon completion of the reaction time, these polymers were precipitated into methanol, allowed to dry and molecular weight was measured using GPC.

3.4 Results and Discussion

TR-PMMA samples were first synthesized and isolated for analysis, then subjected to cleavage experiments to observe the effectiveness of the Diels-Alder adducts breaking apart and subsequently reforming. Reaction conditions and experimental results can be found in table 3.2.

Table 3.2: Initial investigation polymer synthesis results.

Sample ^a	Inimer	Catalyst ^b	Time	Gel	Thermal Treatment
1	2	CuBr	19 hrs	N	Cleavage
2	3	CuBr	20 hrs	Y	Minimal cleavage
3	3	CuCl	20 hrs	Y	Minimal cleavage
4	3	CuBr	8 hrs	N	No cleavage

a: Conditions: 60 °C

b: if CuCl catalyst - 100:1:0.5:1 [M]:[I]:[Cu]:[L], if CuBr catalyst - 100:1:0.5:0.5 [M]:[I]:[Cu]:[L]

These reactions were allowed to proceed to gelation or very nearly to gelation. Allowing gelation to occur during polymerization created significant solubility problems when attempting to analyze the samples via GPC, as the samples were insoluble. To increase solubility, sonication was utilized, causing the TR-PMMA samples to dissolve. Unfortunately upon further research, this method was found to cleave Diels-Alder linkages due to the input of mechanical energy into the system, so while it appeared the samples were dissolving more readily due to sonication, the samples were dissolving more readily due to bond cleavage occurring in the matrix. Following this discovery, sonication was ceased and polymerization conditions were adjusted to stop reactions prior to gelation onset, allowing for easier isolation and analysis. The conditions and results of these reactions can be found in Table 3.3. It is also important to note whether or not the polymer underwent gelation during the polymerization. The only way the TR-PMMA samples could possibly gel is through extensive cross-linking occurring at the inimer functionalities. In the case of sample 4 in Table 3.2, there

was no gelation observed, and also no noticeable difference upon Diels-Alder linkage cleavage. This suggests that the reaction conditions were insufficient to allow the incorporation of the polymerizable unit on the inimer into the polymer. This is not surprising, considering inimer 3 utilized a tertiary initiator group and a secondary polymerizable monomer. This secondary group would be very slow to become incorporated into the polymer, and would slow the rate of polymerization greatly once incorporated, causing undesirable kinetics and larger molecular weight distributions.

Table 3.3: Adjusted polymerization conditions and results.

Sample ^a	Inimer	Catalyst ^b	Time	Gel
5	4	CuCl	4 h	N
6	4	CuCl	15 h	N
7	4	CuBr	4.5 h	Y
8	4	CuBr	3.75 h	Y
9	4	CuCl	21 h	N
10	4	CuCl	21 h	N
11	4	CuCl	21 h	N
12	3	CuBr	30 min	N
13	3	CuBr	30 min	N
14	2	CuCl	6h	N
15	1	CuCl	14 h	N
16	1	CuBr	13 h	N

a: Conditions: 60 °C

b: if CuCl catalyst - 100:1:0.5:1 [M]:[I]:[Cu]:[L], if CuBr catalyst - 100:1:0.5:0.5 [M]:[I]:[Cu]:[L]

It became clear early on in these experiments that the most useful inimer to investigate in this first study was inimer 4, containing both a tertiary site of initiation as well as a tertiary polymerizable unit. This was chosen to eliminate potential impacts on the cross-linking due to kinetic differences of a

polymerization going from a tertiary free radical to a secondary free radical and vice versa, as well as eliminate slow initiation that may have occurred. These samples were all synthesized successfully, isolated and analyzed without remark. Upon investigating the extent to which the polymer was actually cross-linking, the results became significantly more interesting. The samples were brought to reflux in toluene overnight in order to break apart the Diels-Alder adducts. The samples were precipitated, allowed to dry, and then analyzed by GPC in order to observe the change in molecular weight of the matrix. The results of these experiments can be found in Table 3.4.

Table 3.4: Post-cleavage GPC results compared to GPC results of samples before cleavage.

Sample	Inimer	Comments
5	1	Shift to higher Mn
6	1	Shift to higher Mn
8	1	Shift to higher Mn
9	1	Shift to higher Mn
12	2	Shift to higher Mn
13	2	Shift to higher Mn
14	3	Shift to higher Mn
16	4	Shift to higher Mn

Conditions: Samples dissolved in toluene refluxed 24h, precipitated into methanol.

Upon cleavage of main chain and cross-linking bonds, an apparent increase in the molecular weight of the TR-PMMA sample was observed, this result has never been documented in literature before. Regardless of the inimer system chosen for analysis, or the reaction conditions used, the result was always the same. A representative GPC trace can be seen in Figure 3.1.

Figure 3.1: GPC trace of the TR-PMMA sample before cleavage (solid black) and after cleavage (dotted black)

The samples nearly mirror each other in terms of molecular weight distribution. To observe that this was indeed caused by the Diels-Alder linkages cleaving and reforming, the cleaved samples were then dissolved and stirred to facilitate reformation of the Diels-Alder adducts. The resulting GPC trace is shown in Figure 3.2.

Figure 3.2: GPC trace of TR-PMMA samples before cleavage, after cleavage (solid black, dotted black respectively), and after reformation of the Diels-Alder adduct (solid black).

The samples show the same increase in molecular weight upon cleavage of the Diels-Alder adduct, which is to be expected, but upon facilitating the reformation of the Diels-Alder linkage, a further increase in molecular weight is seen, and a decrease in polydispersity. This is likely due to an inability of the polymer to reform all of the cross-links present in the sample because the polymer must assume an odd conformation. Since all cross-linkable sites are also the beginning of an active polymer chain, sterically it would be difficult to achieve the necessary conformation for the Diels-Alder reaction to occur after initial cleavage. The topology proposed for this polymer is one similar to a knotted up ball of yarn, or a rope ball, which has been seen before in self-

condensing vinyl polymerizations^{[2][3]}. A conceptual design can be found in Figure 3.3.

Figure 3.3: The proposed "rope ball" topology of the inimer based TR-PMMA.

We believe that the inimer polymers are occasionally able to loop back onto themselves, creating closed loops, and essentially tying the polymer chain into a compact knot. Upon exposure to thermal stimuli, the knot unties itself, expanding into a much more linear topology. This would explain the apparent increases in molecular weight seen in the GPC traces as well as provide more basis for why the Diels-Alder linkages do not reform completely. GPC measures molecular weight by hydrodynamic volume, or the amount of space that the polymer takes up in solution. When we are breaking the Diels-Alder linkages and allowing the rope ball to untie itself, we are not affecting the actual molecular weight of the polymer, but we are affecting the amount of space the polymer occupies in solution, since it is freer to expand without the reversible cross-links. To truly prove this topology, dynamic light scattering will need to be performed on this polymer, which is currently being performed by Dr. Dan Savin at the University of Southern Mississippi. Another interesting area to investigate would

be the intrinsic viscosity of the polymer. This would effectively provide a measurement of the overall density of the polymer topology, providing further insight into this unique occurrence.

3.5 Conclusions

Polymers were synthesized using a variety of inimer based systems and conditions. The polymers were easily isolated and analyzed. Upon testing the cleavage of the Diels-Alder linkages in the polymer main chain and cross-links, an apparent molecular weight increase was observed. This apparent molecular weight increase is something never before observed in the literature, and could be due to the unique topology of the inimer system. The unique topology is thought to be similar to that of a tangled ball of string, that upon cleavage of the Diels-Alder linkages the ball untangles itself into a linear topology. This leads to an apparent molecular weight increase when analyzed by GPC. Future work includes dynamic light scattering to confirm the rope ball topology hypothesis, as well as adjusting the various concentrations of inimer and types of inimer utilized in this preparation.

3.6 Experimental

3.6.1 Materials and Instrumentation.

All materials were purchased from commercially available sources. Methyl methacrylate (MMA) was dried over CaH_2 and distilled to remove inhibitor. Preparation of 4-maleimide phenol followed previously published methods. ^1H NMR spectra were recorded on a 300 MHz varian instrument in CDCl_3 . Chemical

shifts, δ (ppm), were referenced to the residual solvent signal. GPC analysis was conducted in THF at 25 °C with flow rate of 1.00 ml min⁻¹. Three Polymer Standards Service columns (100 Å, 1000 Å and linear) were connected in series to a Thermoseparation Products P-100 isocratic pump, autosampler, column oven, and Knauer refractive index detector.

3.6.2 Synthesis of 2-bromo-2-methyl propionic acid (2,5-dihydro-2,5-dioxo-1H-pyrrolo-1-yl)-phenyl ester (1).

A stir bar, 4-maleimide phenol (5.00 g, 26.5 mmol) and dichloromethane (150 mL) were loaded into a 300 mL round bottom flask and were cooled to 0 °C. Next, triethylamine (3.78 mL, 30.4 mmol) and 2-bromo-2-methylpropionyl bromide (3.60 mL, 29.2 mmol) were added concurrently to the flask, which was then allowed to warm to room temperature and stirred for 20 h. The reaction was then washed with H₂O (3x, 100 mL). The organic layer was collected and dried over anhydrous MgSO₄. Solvent was removed via rotary evaporation to yield compound 1 (7.32 g, 82 %) as a tan solid. ¹H NMR (300 MHz, CDCl₃, δ): 7.42 (d, 2H), 7.28 (d, 2H), 6.85 (s, 2H), 2.05 (s, 6H).

3.6.3 Synthesis of 2-bromo-2-methyl propionic acid [1-(hydroxymethyl)-10-oxatricyclo[5.2.1.0^{2,6}]dec-8-en-3,5-dione] phenyl ester (2).

A stir bar, compound 1, furfuryl alcohol and THF were loaded into a round bottom flask employing a one to one molar ratio of compound 1 to furfuryl alcohol. The reaction was allowed to stir at room temperature for 48 h. Solvent was removed via rotary evaporation to yield compound 2 in quantitative yield as

a tan solid. ^1H NMR (300 MHz, CDCl_3 , δ): 7.20-7.48 (m, 4H), 6.25-6.68 (overlap of d of d from combination of exo and endo product, 2H), 5.28 (t, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.05 (s, 6H).

3.6.4 Synthesis of 2-bromo-2-methyl propionic acid [1-(methyl methacryloyloxy)-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl]-phenyl ester (DA-Inimer).

A stir bar, compound 2 (11.8 g, 28.0 mmol), triethylamine (4.52 mL, 34.6 mmol) and dichloromethane (150 mL) were loaded into a 300 mL round bottom flask and were cooled to 0 °C. Next, methacryloyl chloride (3.02 mL, 30.8 mmol) was added to the flask, which was then allowed to warm to room temperature and stirred for 20 h. The reaction was then washed with H_2O (3x, 100 mL). The organic layer was collected and dried over anhydrous MgSO_4 . Solvent was removed via rotary evaporation to yield compound DA-Inimer (11.9 g, 85 %) as a brown solid. ^1H NMR (300 MHz, CDCl_3 , δ): 7.20-7.48 (m, 4H), 6.25-6.68 (overlap of d of d from combination of exo and endo product and s, 4H), 5.28 (t, 1H), 4.18-4.24 (overlap of s from combination of exo and endo product, 2H), 2.94-3.05 (overlap of d from combination of exo and endo product, 2H), 2.18 (s, 3H) 2.05 (s, 6H).

3.6.5 Typical ATRP of MMA with DA-Inimer.

A stir bar, Cu^{I} catalyst and bipy were loaded into a 20 mL scintillation vial and sealed with a rubber septum. The reaction flask that was vacuum/backfilled

with N₂ (3x). Next, purged MMA and a purged stock solution of DA-Inimer (20 wt% in THF) were added to the reaction flask via a purged syringe. The reaction was stirred at 100 °C for a specified time. See Tables 3.2 and 3.3 for experimental ratios, Cu^I catalyst selection, reaction times and GPC analysis. The resulting reaction mixture was then stirred over Dowex Marathon Exchange resin, followed by filtration through basic Al₂O₃ and precipitation into MeOH to yield TR-br-PMMA as a white powder.

3.6.6 Typical cleavage TR-br-PMMA.

A stir bar, TR-br-PMMA (400 mg) and toluene (2 mL) were loaded into a 5 mL round bottom flask and stirred at 120 °C for 24 h. The reaction was then cooled and precipitated into MeOH to yield TR-I-PMMA as a white powder.

3.6.7 Reformation of Diels-Alder linkages to prepare TR-re-PMMA.

A stir bar, TR-I-PMMA (500 mg) and THF (4 mL) were loaded into a 10 mL round bottom flask and stirred at 55 °C for 66 h. Samples were taken directly for GPC analysis.

3.7 References

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Chapter 4: Conclusions

A Diels-Alder based cross-linked polymer network was successfully synthesized for use as a matrix in non-linear optical materials. These materials utilized furan and maleimide functionality to provide a thermally reversible method of affecting matrix viscosity and composition. This was performed to achieve a network that would successfully allow incorporation of a chromophore into the material providing non-linear optical activity. To be an effective non-linear optical material, the chromophore molecules must remain in an organized state for as long as possible, and heavily cross-linked matrices help facilitate this rigidity. While the chromophore was successfully incorporated into the matrix, it was found that the cross-linking material was ineffective in reforming the Diels-Alder adducts upon exposure to thermal stimulus sufficient to break these bonds. This is likely caused by the low percentage of Diels-Alder linkages in the backbone of the polymer, as well as processing conditions making the furan and maleimide functionalities unlikely to encounter each other after initial bond severance was achieved. Other problems with the method included non-uniform properties occurring throughout the matrix, leading to a stick-slip occurrence that caused surface defects when creating molded parts. The polymers synthesized were also insoluble even after cleavage of the Diels-Alder linkages. This indicates uncontrolled side reactions had occurred, causing irreversible cross-links in the polymer backbone, leading to insolubility and large difficulties in analysis and characterization. These complications caused the direction of the

project to be reevaluated, and a method was proposed utilizing a polyfuran/polymaleimide mixture of polymers to make up the matrix. This system was chosen because it alleviates the issues faced in the original method as well as simplifying synthesis even further.

In another attempt to alleviate the problems presented by the initial method of creating these materials, an inimer based system was proposed. This controlled radical polymerization initiator was coupled with a polymerizable double bond separated by a Diels-Alder linkage, allowing for the cross-link to be cleaved at high temperatures. This system would allow for very precise control of the amount of cross-linker in the system, as well as much more control over the desired molecular weight of the polymer prior to cross-linking due to use of controlled radical polymerization techniques. Synthesis of this material was successful, and the resulting polymers were easily characterized using GPC. Upon testing the ability of the compound to maintain sufficient Diels-Alder linkages over several cycles of cleavage and reformation, It was found that upon cleavage of the Diels-Alder linkages present in the inimer, the apparent molecular weight of the polymer increased. This is an especially unusual result after cleavage of a main chain linkage. GPC measures the hydrodynamic volume of polymers in solution, essentially the amount of space the polymer takes up. When the polymers are heavily cross-linked, it is believed that they maintain a unique topology similar to a very tightly tangled "rope-ball". Upon exposure to thermal stimulus the linkages break, allowing for the polymer to unwind itself into a linear shape, occupying more space in solution and subsequently causing the

polymer to appear to have increased in molecular weight. This result was identified and repeated using a variety of inimer systems and polymerization conditions. To prove the "rope-ball" topology being proposed for this polymer system, dynamic light scattering experiments are being performed.