A Bisphenol-A-based Resin System that Cures via Triazole Ring Formation for Marine Composite Applications

Irene Elizabeth Gorman

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A BISPHENOL-A-BASED RESIN SYSTEM THAT CURES VIA TRIAZOLE RING FORMATION FOR MARINE COMPOSITE APPLICATIONS

by

Irene Elizabeth Gorman

Abstract of 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

May 2012
ABSTRACT

A BISPHENOL-A-BASED RESIN SYSTEM THAT CURES VIA TRIAZOLE RING FORMATION FOR MARINE COMPOSITE APPLICATIONS

by Irene Elizabeth Gorman

May 2012

Large composite panels, such as those utilized in marine applications, cannot be economically cured in an autoclave. For these structures the elevated temperatures necessary to achieve high crosslink density must come from the curing reaction itself. We are developing a resin system that cures via triazole ring formation (cycloaddition reaction of azides with terminal alkynes) instead of the traditional oxirane/amine reaction. The high exothermicity of the azido/alkyne reaction is expected to yield higher extents of reaction under ambient-cure conditions, making the resin system potentially suitable for "out-of-autoclave" curing processes. This work was conducted through a multi-tiered approach involving synthesis, kinetic studies, thermal characterization, and mechanical analysis. The difunctional azide-terminated resin, di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA), was selected as the baseline diazide. A number of alkyne crosslinkers were synthesized and characterized, including propiolate esters of di- and trifunctional alcohols, propargyl esters of di- and trifunctional carboxylic acids, propargyl ethers of di- and trifunctional alcohols, and N,N,N',N'-tetrapropargyl derivatives of primary amines. Commercially available tripropargylamine (TPA) was also studied. Curing energetics as a function of alkyne type and catalyst loading, investigated through a dynamic differential scanning calorimetry approach, displayed two distinct kinetic
profiles when considering propiolate and propargyl type crosslinkers. Those systems employing a propiolate-based alkyne were found to be much more reactive towards the Huisgen 1,3-dipolar cycloaddition than the propargyl species. Additionally, the mechanical and thermal properties of resin systems, both un-catalyzed and catalyzed, composed of DAHP-BPA and tripropargyl amine were investigated by compression and rheological studies, differential scanning calorimetry, and thermogravametric analysis. The moduli of both DAHP-BPA/TPA systems were found to be approximately 3500 MPa, comparable to the modulus of EPON-825/4,4'-DDS resin. Ultimately, the utility of the DAHP-BPA/polyalkyne resin system lies not only in its capability for low-temperature curing, but also in the ability to customize the reactivity, thermal properties, and mechanical properties of the system through the use of catalyst and choice of alkyne crosslinker.
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by

Irene Elizabeth Gorman

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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DEDICATION

To my husband Brian, whom I dragged along on this crazy adventure, and to my parents, Owen and Wendy, who couldn’t help but produce another scientist.
ACKNOWLEDGMENTS

I would like to express deep gratitude to my adviser Dr. Robson Storey for teaching me to think clearly and critically, and for helping me become a better scientist. I am also sincerely thankful for the help offered by my committed members, Dr. Sarah Morgan, Dr. Jeffrey Wiggins, Dr. Daniel Savin, and Dr. James Rawlins.

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CHAPTER I
INTRODUCTION

Composite Materials

Increased strength, reduced weight, longevity, reduced maintenance, environmental corrosion resistance, zero magnetic signature, and improved design flexibility are important driving forces for replacement of metals by advanced composite materials. Traditional polymer composites are characterized by the marriage of diverse individual parts: one or more discontinuous phases embedded in a continuous phase.\(^1\)

Typically, the discontinuous phase is the stronger material, referred to as the reinforcement, while the continuous phase is known as the matrix. The type of fibers found in composites include, but are not limited to, glass, graphite, boron, silica, and Kevlar, with diameters ranging from 5 to 500μm.\(^1,2\) Although fibers contribute the majority of the strength to composites, fibers cannot be used directly in an engineering material due to their small cross sectional dimension.\(^1,2\) Furthermore, fibers acting alone cannot transmit a load from one fiber to another, thereby sharing the load. The polymer matrix serves to bind the fibers together, protect the fibers from environmental damage, transfer the load to the fibers, and enable the formation of materials stronger than the individual parts.\(^1,2\) It follows that the overall properties of any given composite are greatly influenced by the physical properties of the constituent phases, their relative levels of incorporation, and the interactions between them.

To obtain a highly crosslinked matrix with properties suitable for composite materials, a high heat-of-cure is often necessary. As crosslinking progresses, the glass transition temperature rises until a point during cure, dependent upon molecular structure,
were reactive groups no longer possess the configurational freedom to form new bonds. Ultimately, high cure-temperatures are required to push the crosslink density and to reach the desired thermal and physical properties. However, as composites find their way into aerospace and nautical applications, new ambient-temperature curing mechanisms that do not require external heating become desirable, for the simple reason that one cannot fit a ship into an autoclave. If the temperature of a crosslinking system could be increased by virtue of a highly exothermic reaction, then higher crosslink density could be achieved prior to vitrification. Ideally, this might be done by changing the chemistry of the crosslinkages only, while maintaining a proven backbone chemistry that is broadly accepted. Here the development of a novel resin system that cures via triazole ring formation (cycloaddition reaction of azides with terminal alkynes), instead of the traditional oxirane/amine reaction, is explored. The high exothermicity of the azido/alkyne reaction is expected to yield higher extents of reaction under ambient-cure conditions, making the resin system potentially suitable for "out-of-autoclave" curing processes. The process will employ two industry standards as benchmarks: an epoxy/amine resin and a vinyl ester resin.

_Epoxy/Amine Resins_

Currently 90% of the matrix resin materials used in advanced composites are some type of epoxide system.³ Epoxide resins, as a class, have a number of advantages over other thermoset matrices: minimal viscosity for enhanced workability, low shrinkage during cure, excellent chemical resistance, high adhesion to a wide variety of fibers, and resistance to creep and fatigue. Generally, epoxide resins are low molecular weight oligomers containing at least two epoxide functional groups.⁴ The most widely
used epoxy resin is formed through the reaction of epichlorohydrin and bisphenol-A (BPA).\textsuperscript{5} The reaction of epoxy oligomers or prepolymer
s with curing agents gives rise to highly crosslinked systems, with the best results being obtained through a two-stage-cure process.\textsuperscript{4} During the first stage, small curing-agent molecules combine with the larger epoxy oligomers, resulting in chain extended “clusters” of oligomers with low degree of crosslinking. During the second stage, the temperature of the system is raised, and the individual clusters crosslink, forming one large molecule. Polyamines are the most commonly used curing agents, and they react through a ring opening addition reaction. Some common amine curing agents are diethylene triamine, triethylene, tetramine, 4-4′ diaminodiphenylmethane, and polyaminoamides.

\textit{Vinyl ester resins}

Vinyl ester resins are formed by end-capping epoxy resin oligomers with an unsaturated monocarboxylic acid. As a result, vinyl ester resins share many of the valuable characteristics afforded by epoxy/amine systems: excellent chemical resistance and high tensile strength. Crosslinking is achieved via a free radical process, where the end-capped epoxy oligomers are dissolved in a liquid vinyl monomer, such as styrene, vinyl toluene, or methyl methacrylate. For example, most industrial vinyl ester resins are composed of 40-50 weight % styrene. These co-monomer systems also offer the added advantage of being curable at room temperature. However, due the high vinyl monomer content, volumetric shrinkage of vinyl ester resins is in the range of 5-10%. They also exhibit only moderate adhesive strengths (as compared to epoxies). Overall vinyl ester resins offer easy handling, toughness, and high chemical resistance. Currently DERAKANE®, a vinyl ester resin from Ashland Chemicals, is the matrix resin of choice
for the Navy. DERAKANE® has been employed in a vacuum assisted resin transfer molding (VARTM) process to fabricate multi-story glass-filled composite panels for use in Zumwalt Class Destroyers.

Cycloaddition of Azides to Alkynes

*Organic Azides*

Aliphatic azides can be readily synthesized through the nucleophilic displacement of halogen with sodium azide, or in this case, through the nucleophilic ring opening of an epoxide ring.\(^6\) The reaction can be carried out as a biphasic system with the substrate dissolved in an organic solvent and sodium azide dissolved in water. The product-azide can be easily isolated directly or by extraction.\(^7\) Traditional methods employ DMF\(^8\)- or DMSO\(^9,10\)-water mixtures as the reaction medium, although there have been recent reports on the use of methanol\(^11\) as a single component medium. Organic azides, particularly those of low molecular weight, are highly energetic and potentially explosive. The convention in working with azides is that the ratio of nitrogen to (carbon + oxygen) should be at most 1:3 for neat isolation.\(^8\)

The synthesis of di(3-azido-2 hydroxypropyl) ether of bisphenol-A (DAHP-BPA) was first reported by Fokin, Finn, and coworkers\(^12\) and is based on proven bisphenol-A backbone chemistry (Figure 1). They reported the use of NaN\(_3\)/LiClO\(_4\) in acetonitrile at 90 °C overnight, followed by the addition of water, and extraction of the product into ethyl acetate. The extract was washed with water and the product isolated by the removal of the solvent. More recently, Kessler and coworkers\(^11\) reported the synthesis of DAHP-BPA by reaction of EPON 828 with NaN\(_3\)/NH\(_4\)Cl for 12 h in refluxing methanol. These authors reported that the azide group was substituted at C2 of the glycidyl group (attack...
of azide ion on the more substituted carbon of the epoxide ring) and that two
diastereomers were obtained (major and minor). Whether Kessler et al. actually obtained
a different regioisomer is questionable since the chemical shifts they reported for their
major isomer are identical to those observed by us and reported by Fokin et al. Both
DAHP-BPA and the EPON reactant should consist of a 50:50 mixture of two
diastereomers, \textit{i.e.}, a pair of enantiomers and a meso compound, since both compounds
contain two chiral centers but also a plane of symmetry. Nonetheless, only one set of
peaks is observed in NMR, apparently because the chemical shift differences between
diastereomers are too small.

\begin{figure}
\centering
\includegraphics[width=0.7\textwidth]{di3-azido-2hydroxypropylether.png}
\caption{Di(3-azido-2 hydroxypropyl) ether of bisphenol-A (DAHP-BPA)}
\end{figure}


\textit{Terminal Alkynes}

The two chemical building blocks most widely used to incorporate terminal
alkyne groups into molecules are propargyl and propiolate. The easiest way to synthesize
propargyl-containing compounds is through the displacement of halogen from a
propargyl halide. For example, a common reaction is the propargylation of phenols using
either propargyl chloride or bromide. Propiolate functionality is readily achieved through
the use of propiolic acid. For example, the appropriate polyol can react with a slight
excess of propiolic acid.
Huisgen 1,3-Dipolar Cycloaddition

The cycloaddition of an azide to a multiple bond (Figure 2) was first described in 1893 when Michael discovered the formation of a 1,2,3-triazole from phenyl azide and dimethyl acetylenedicarboxylate.\textsuperscript{13} Since then, this reaction class has remained the most widely used synthetic route to 1,2,3-triazoles and triazole derivatives. However, it wasn’t until the late 1950s and 60s that the mechanism of addition was known, when Huisgen systematically investigated a group of [3 +2] cycloadditions and coined the term 1,3-dipolar cycloaddition.\textsuperscript{14,15}

![Figure 1](image-url)  \textit{Figure 1.} The 1,3-dipolar cycloaddition of an azide and terminal alkyne to give 1,2,3-triazole. Thermal cycloaddition is non-regiospecific. The movement of electron pairs are added for clarity and do not indicate the concerted or non-concerted nature of the reaction.

The 1,3-dipolar cycloaddition of azides (dipole) to terminal alkynes (dipolarophile) is concerted, highly exothermic (-210 and -250 kJ/mol), and capable of producing two regioisomers, the 1,4- and 1,5-regioisomer.\textsuperscript{16} Bonding in the 1,3-dipolar cycloaddition occurs by interaction of the highest occupied molecular orbital (HOMO) of one component, either the dipolarophile or the 1,3-dipole, with the lowest unoccupied molecular orbital (LUMO) of the opposite component.\textsuperscript{17} Of the two possible combinations, the pair with the smallest energy gap bonds. Typically, the energy difference between the two possible HOMO/LUMO combinations in the 1,3-dipolar cycloaddition of azides to alkynes is negligible.\textsuperscript{18,19} Furthermore, the two partial rate
constants associated with each addition pathway, \( k_2(1,4) \) and \( k_2(1,5) \), are equally rapid, leading to a 50/50 mixture of the two regioisomers.\(^{20}\) However, manipulating the electron density of either the azide or alkyne can alter these partial reaction rates. For example, the more electron-withdrawing the substituent on the alkyne, the higher \( k_2(1,4) \) becomes for a given azide, relative to \( k_2(1,5) \).\(^{18,19}\) Electron withdrawing substituents on the azide have the opposite effect. In addition to rendering the reaction regioselective, the increase in either \( k_2(1,4) \) or \( k_2(1,5) \) can increase the overall reaction rate. For certain electrophilic alkynes, the activation barrier for reaction can be quite low, ca. 70 kJ/mol,\(^{21}\) and in such cases the reaction will occur at low temperatures, including room temperature, even without catalyst.

In 2001, Kolb, Finn, and Sharpless wrote a seminal paper describing a new “click” strategy for organic chemistry.\(^{22}\) The authors identified a handful of organic reactions that “are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform, and that require benign or easily removed solvent”.\(^{22}\) The Huisgen 1,3-dipolar cycloaddition reaction was among that select group of reactions. These attributes, combined with its extremely exothermic nature, the fact that no small molecule is evolved, and its ability to proceed at low temperatures and even room temperature, make the Huisgen 1,3-dipolar cycloaddition an excellent crosslinking chemistry for a novel low-temperature-cure composite material. Furthermore, the 1,2,3-triazole heterocycle formed during the cycloaddition has aromatic character, hydrogen bond accepting ability, and high chemical stability; it is largely inert to severe hydrolytic, oxidizing, and reducing conditions, even at high temperature.\(^{23,24}\)
Figure 2. Orbital level scheme for 1,3-dipolar cycloadditions. Bonding occurs by interaction of the highest occupied molecular orbital (HOMO) of one component, either the dipolarphile or the 1,3-dipole, with the lowest unoccupied molecular orbital (LUMO) of the opposite component. Of the two possible combinations the pair with the smallest energy gap bonds. Typically the energy difference between the two possible HOMO/LUMO combinations is negligible, leading to a 50/50 mixture of the two possible regioisomers. However, the electronic character of either the azide or the alkyne can alter this ratio; electron deficient alkynes render the reaction azide-LUMO controlled, favoring the 1,4-regioisomer, while electron deficient azides render the reaction azide-HOMO controlled, favoring the 1,5-regioisomer.
Copper Catalyzed Azide Alkyne Cycloaddition

In addition to the paper published by Sharpless and coworkers, simultaneous reports on the ability of copper (I) to catalyze the Huisgen 1,3-diolar cycloaddition, rendering the reaction both faster and regioselective, reignited interest in this chemistry.\textsuperscript{25,26} The Cu(I)-catalyzed cycloaddition of azides to terminal alkynes (CuAAC) has found utility in the synthesis of a wide variety of macromolecular architectures, such as linear block and star copolymers, dendrimers, bioconjugates, and hyperbranched materials.\textsuperscript{27-29} The reaction has also been beneficial to the design of crosslinked materials, such as degradable networks, liquid crystal gel networks, hydrogels, metal adhesives, propellant binders, self-healing materials, and polytriazole matrices suitable for advanced composite materials.\textsuperscript{10,18,23}

The copper catalyzed reaction was first described by Mendal et al. in Denmark, and Fokin and Sharpless of the Scripps Institute, in the United States. The use of copper (I) catalyst drastically alters the reaction mechanism of the Huisgen 1,3-dipolar cycloaddition, converting it from a concerted process to a sequence of discrete steps culminating in the formation of a 5-triazole copper intermediate.\textsuperscript{30} It also renders the reaction regioselective for the 1,4-regioisomer and increases the reaction rate by a factor of $10^7$, relative to the thermal process.\textsuperscript{31} Mendal et al. first utilized copper(I) in the synthesis of peptidotriazoles in organic solvents starting from alkynylated amino acids attached to solid supports, and they emphasized the need to immobilize the alkyne on a resin support for successful reaction.\textsuperscript{26} In comparison, the Scripps group used an aqueous solvent system for the straightforward “stitching” of virtually any moiety containing an
azide and terminal alkyne functionality.\textsuperscript{25} They found no need for the use of solid supports.

To date copper(I) remains the only metal capable of facilitating the reliable, facile, and 1,4-regiospecific catalysis of the azide-alkyne cycloaddition.\textsuperscript{30} Other metals known to catalyze various transformations of alkynes, such as Ag(I), Pd(0/II), Pt(II), Au(I/III), and Hg(II), have failed to yield effective catalysis of terminal alkynes to 1,4-substituted-1,2,3-triazololes.\textsuperscript{30} Cycloadditions catalyzed by these other metals suffer from low yields, sluggish reaction rates, and poor regioselectivity. The unique ability of copper to catalyze the reaction may be due to its ability to form both $\sigma$- and $\pi$-complexes with terminal alkynes, and its ability to exchange these and other ligands within its coordination sphere.\textsuperscript{30} One exception is ruthenium cyclopentadienyl, which in 2005 was found to catalyze the formation of the 1,5-regioisomer from azides and terminal alkynes, in addition to internal alkynes.\textsuperscript{32} As one would expect from these differences, the ruthenium-catalyzed-azide-alkyne cycloaddition is mechanistically quite distinct from the copper-assisted process. Furthermore, the reaction is more sensitive to solvents and steric hindrance of the azide substituents.\textsuperscript{33-35}

A variety of different copper(I) sources may be employed in the CuAAC reaction: copper(I) salts (iodide, bromide, chloride, acetate) and coordination complexes such as $[\text{Cu(CH}_3\text{CN})_4]\text{PF}_6$ and $\text{Cu(PPh}_3)_3\text{Br}$. Copper(II) species, which are oxidized in situ, may also be utilized as copper(I) sources. Cupric salts and coordination complexes are well-known oxidizing agents for organic compounds, including alcohols, amines, aldehydes, thiols, phenols, and carboxylic acids.\textsuperscript{36} During the oxidation process, cupric salts are readily reduced to the catalytically active copper(I) state. Especially relevant to
the CuAAC reaction is the family of oxidative acetylenic couplings catalyzed by copper(II), with the Glaser coupling reaction being the most widely studied example.\textsuperscript{37} Being that terminal acetylenes are a required component of CuAAC reactions, their oxidation is unavoidable, which in turn produces the catalytically active Cu(I) species.\textsuperscript{30} Additionally, reducing agents may be intentionally added to the reaction mixture, with sodium ascorbate being the mostly widely used example.\textsuperscript{30}

A detailed mechanism of the CuAAC reaction is difficult to determine. Though the coordination chemistry of organic azides is well understood, the precise nature of reactive alkynyl copper species is not, whether in the CuAAC reaction or in any of the many other reactions involving Cu(I) acetylide complexes. The primary obstacles to illuminating the reaction mechanism are the tendency for copper species to form polynuclear complexes and the great facility for ligand exchange at the copper center.\textsuperscript{38,39} This results in a mixture of terminal alkynes and other ligands in rapid equilibrium at the copper atom.

Through combined Discrete Fourier transform (DFT) and small molecule kinetic experimental techniques a complex catalytic cycle involving multiple equilibria, competing pathways, and off-cycle dead ends has been proposed by Fokin et al (Figure 4).\textsuperscript{30,40} Furthermore, under certain conditions it was found that the formation of dormant oligomeric copper acetylides becomes rate-limiting, where the re-entry rate of active copper acetylide into the catalytic cycle becomes the rate determining step.\textsuperscript{30} Appropriate solvents that encourage ligand exchange, such as water and alcohols, as opposed to apolar organic solvents, have been shown to limit aggregation.\textsuperscript{30} Of course, none of this control is afforded to reactions that take place in the bulk.
Figure 3. Detailed catalytic cycle proposed by Fokin, where several key equilibria and irreversible off-cycle pathways affect the CuAAC catalytic cycle. Formation of oligomeric copper acetylide can be particularly detrimental, and under certain conditions the rate of the re-entry of reactive copper acetylide into the catalytic cycle ($k_{-4}$) becomes the rate limiting step.
Polytriazoles from Bulk-Polymerization

Though the Huisgen 1,3-dipolar cycloaddition and the CuAAC reaction have found wide utility within the broad field of polymer science, here we choose to limit our discussion to bulk polymerizations of polytriazoles, as they pertain most directly to this research.

Triazoles as Metal Adhesives

Sharpless, Finn, and Fokin were the first to report the bulk polymerization of polytriazoles, where the chemistry was utilized in the development of metal adhesives. A series of di-, tri-, and tetra-functional azides and alkynes were employed to adhere two copper plates. The copper plates served as the source of catalytically active Cu(I) species. From the study they discovered two key features which influenced the strength of the azide/alkyne adhesive: monomer functionality (order) and the presence of an amine group. The first factor is related to crosslink density; the higher-order monomers are capable of forming greater crosslink density. Regarding the second factor, the researchers found that amines assist in the production of Cu-acetylide intermediates and contribute to productive chelating interactions with the metal center. As one will recall, the formation of Cu-acetylide intermediates is a key step in the catalytic cycle.

In a follow-up paper, focused on the glass transition temperature ($T_g$) of the adhesives following polymerization, Finn et al. discovered that the azide/alkyne adhesives were capable of displaying final $T_g$s up to 50—60 °C higher that the curing temperature, well above the normal range of 10—20 °C seen in neat step growth polymerization. Due to bulk effects, the heat produced by an exothermic reaction is capable of raising the temperature of the reacting mass above that of the surrounding
environment. Under typical conditions, this can increase the \( T_g \) of some thermosets (such as epoxies) up to 20 °C above the curing temperature. However, this could not explain the phenomenon observed by Finn; the polymers were cured as thin films (average 0.12 mm thickness) sandwiched between copper plates capable of acting as heat sinks. The authors attributed the abnormally high \( T_g \)s to the copper catalyst’s ability to diffuse through the system, even at high conversion.\(^{42}\) Triazoles have good thermodynamic affinity for Cu(I) ions and yet at the same time the Cu-triazole interaction is kinetically mobile.\(^{42}\) It follows that small molecule Cu ions should be able to diffuse from one triazole binding site to the next, in a similar fashion to radical diffusion in addition polymerizations.

In their final paper, the Finn et al. group added Cu(I) catalyst or Cu(II) pre-catalyst to the system, without solely relying on the copper plates as the source of catalytically active copper.\(^{12}\) The researchers found that the addition of either Cu(I) or Cu(II) increased both the reaction rate and the adhesive strength, with the later phenomenon attributed to an increase in crosslink density. The most effective Cu(I) catalyst was CuPF\(_6\) 4MeCN, with cupric triflate, a THF soluble form of Cu(II), also being very effective. Additionally they investigated the effect of the presence of \( \beta \)-hydroxyl groups versus \( \beta \)-acetate groups in the azide monomer structure. Although the presence of either \( \beta \)-hydroxyl or \( \beta \)-acetate did not affect the rate of the reaction, those monomers containing \( \beta \)-hydroxyl groups yielded higher adhesive strengths. It is suspected that the OH groups are either responsible for the formation of a more effective crosslinking, or for the formation of a more flexible network.
Triazoles for Matrix Materials

In 2006 Du et al. were the first to utilize a triazole network for the development of matrix materials; they employed \( p \)-xylene diazide (XDA) and \( N,N,N',N' \)-tetrapropargyl-\( p,p' \)-diaminodiphenyl methane (TPDDM), as shown in Figure 5.\(^{45} \) It should be noted that the azide-containing monomer, XDA, exceeds the relative nitrogen content of what is deemed safe in the synthesis of azide-containing molecules. The convention in working with azides is that the ratio of nitrogen to (carbon + oxygen) should be, at most, 1:3 for neat isolation.\(^{46} \) In practice, slightly lower ratios can be tolerated, but any ratio below 1:2 should be handled with extreme caution and never isolated to dryness. Even the slightest amount of heat or pressure could initiate an explosive reaction.\(^{30} \) Here, the authors have synthesized an azide molecule with a ratio of 1:1.3, with no mention of potential hazards. They simply state that the monomer was chemically dried and then isolated by distillation. It would certainly not be feasible to scale-up the synthesis of the XDA monomer, nor could it be used in the fabrication of very large composite panels.

**Figure 4.** Xylene diazide (XDA) and \( N,N,N',N' \)-tetrapropargyl-\( p,p' \)-diaminodiphenyl methane (TPDDM) monomers employed by Du et al. to form a polytriazole network that degrades at the N-CH\(_2\) linkages.
Regardless of the prudence of their monomer design, the group was able to successfully polymerize the two monomers using a multi-stage curing process. The system was initially cured at a temperature of 70 °C, with a post cure at 120, 150, 180, or 200 °C. The systems were found to be very exothermic, and the authors noted that curing at an initial, low temperature of 70 °C helped dissipate the evolved heat and prevented a violent exotherm. The ultimate $T_g$ and degradation temperature ($T_d$) at 5% weight loss were found to be 218 and 350 °C, respectively. Triazole rings are typically stable up to 400 °C, slightly higher than the reported degradation temperature. In a follow up paper the triazole degradation mechanism was determined to initiate at the CH$_2$-N bonds and not within the triazole ring. Additionally, the activation energy of the reaction was determined by employing the ASTM E698 method, which will be discussed later, and was found to be 83.7 kJ/mol. Finally, they utilized a linear equivalent to the TPDDM monomer, dipropargyl ether of bisphenol-A (DPEBPA), to investigate the regioselectivity of the reaction; the 1,5-regioisomer was favored over the 1,4-regioisomer by a ratio of 62:38.

**Bulk Polymerization Kinetics of Polytriazoles**

Most recently Kessler investigated the bulk kinetics of the CuAAC reaction for the design of self-healing materials. Three monomers were synthesized: a bisphenol-A based azide, a bisphenol-E based alkyne, and a tetraethylene glycol based alkyne. The monomers were combined such that the molar ratio of azide to alkyne was 1:1, and a catalyst was loaded at 0.5, 1.0, or 2.0 wt%, with respect to the mass of the diene. The catalyst used was bromotris(triphenylphosphine)copper(I) ($\text{Cu(PPh}_3)_3\text{Br}$). The isoconversional kinetic method developed by Ozawa was used to monitor the change in
activation energy \((E_a)\) with conversion \((\alpha)\). The exotherm of reaction was measured using differential scanning calorimetry (DSC), at several scan rates: 2, 5, 10, 15 or 20 °C. Typically for this method the resulting thermograms are Gaussian in shape, with the peak exotherm shifting to higher temperature as the scan rate increases. For the bisphenol-E diyne/bisphenol-A diazide system (B/B), the dynamic scan curve showed a shoulder at lower temperatures relative to the major exotherm, as can be seen in Figure 6.\(^{11}\) As the catalyst loading increased the shoulder became more pronounced. The authors attributed the major exotherm to the traditional, thermal, Huisgen 1,3-dipolar cycloaddition, while the minor peak was attributed to the catalyst controlled CuAAC reaction. The tetraethylene glycol based alkyne/bisphenol-A diazide (T/B) system did not follow the same trend; the major exotherm remained constant regardless of catalyst concentration. Generally, \(E_a\) was lower for the system employing the bisphenol-E diyne than for the system employing the tetraethylene glycol based alkyne (Figure 7). For the later system, \(E_a\) was found to remain constant throughout the polymerization. For the former system, the relationship between \(E_a\) and \(\alpha\) was reported to be more complicated. For the lowest loading level, \(E_a\) was found to increase with conversion, while for the higher loading levels, a concave shape was observed. The concaved shape evident at higher loading levels suggests two competing reaction pathways,\(^{52}\) perhaps thermal versus catalyst controlled.
Figure 5. Effect of catalyst concentration on the click polymerization of the bisphenol-E diyne/bisphenol-A diazide system (B/B), at a heating rate of 10 °C/min (exothermic direction up).

Figure 6. $E_a$ versus $\alpha$, for both the bisphenol-E diyne/bisphenol-A diazide system (B/B) and the tetraethylene glycol based alkyne/bisphenol-A diazide (T/B) system, at various catalyst loadings.
Kinetics by Differential Scanning Calorimetry

Though there has been quite extensive research on the kinetics of the Huisgen 1,3-dipolar cycloaddition and the CuAAC reaction in solution, there has only been a handful of kinetic studies conducted in the bulk. To our knowledge, those studies are limited to the paper published by Kessler\textsuperscript{11} and paper published by Du.\textsuperscript{49} The paper published by Du did not report the effect of catalyst loading and only determined the averaged $E_a$ of a single system. In comparison, Kessler looked at two different monomer combinations with varying amounts of catalyst loading. However, neither group investigated the effect of electronic character of the alkyne (i.e. electron deficiency or neutrality) on the reaction kinetics. As one may recall, electron withdrawing substituents on the alkyne can render the cycloaddition faster and regioselective, even without catalyst. Both Kessler and Du used DSC to measure the exotherm of reaction and later calculated the activation energy.

Isoconversional Methods

Thermal kinetic data are commonly fitted to a single–step reaction model that yields a single averaged value of the $E_a$ for the overall curing process. As a result, the data obtained do not reflect changes in the reaction mechanism or kinetics with temperature and extent of conversion. This is particularly problematic for multi-step curing processes, such as epoxy cures and those systems employing catalyst.\textsuperscript{53} Isoconversional methods, also known as model-free kinetics, are among the few techniques that successfully allow for characterization of complex systems where an exact reaction model is not known and are routinely employed in the characterization of network systems.\textsuperscript{54} The fundamental assumption of the isoconversional methods is that a
single-step equation is only applicable to a single extent of conversion. In other words, isoconversional methods describe the kinetics of a given process by using multiple single-step kinetic equations, each of which is associated with a certain extent of conversion. This allows for complex, multi-step processes to be detected by a variation in $E_a$ with $\alpha$. Comparatively, independence of $E_a$ with respect to $\alpha$ is an indication of a single-step process. The best known isoconversional methods were developed by Friedman (FR), Flynn-Wall-Ozawa (FWO), and Kissinger-Akahira-Sunose (KAS), and are listed in Table 1. As stated, these methods take their origin in the following single-step kinetic equation,

$$\frac{d\alpha}{dt} = A \exp \left( \frac{-E}{RT} \right) f(\alpha)$$

(Equation 1)

where $A$ and $E$ are the Arrhenius parameters (the pre-exponential factor and the activation energy, respectively), $f(\alpha)$ is the reaction model, $R$ is the gas constant, $T$ is the temperature, $t$ is the time, and $\alpha$ is the extent of conversion. However, they assume the isoconversional principle, which states that at constant extent of conversion, the reaction rate is only a function of temperature. This principle may be expressed as follows:

$$\frac{d \ln(d\alpha/dt)}{dT^{-1}} = -\frac{E_a}{R}$$

(Equation 2)

Simple rearrangement of Equation 1 yields,

$$\ln \frac{d\alpha}{dt} = \ln A \alpha f(\alpha) - \frac{E_a}{RT\alpha}$$

(Equation 3)
which is the foundation of the Friedman method, where the subscript $i$ denotes different heating rates. The Friedman method is a differential method and typically results in noisy data and thus unstable $E_a$ values. The disadvantage of numerical differentiation is avoided by using integral isoconversional methods, as described by either FWO or KAS.

For isothermal conditions, integration of Equation 1 yields,

$$g(\alpha) \equiv \frac{\alpha}{\int_0^t} \frac{d\alpha}{f(\alpha)} = A \exp \left( -\frac{E}{RT} \right) t$$

(Equation 4)

where $g(\alpha)$ is the integral form of the reaction model. Rearrangement of Equation 4 gives Equation 5.

$$-\ln t_{\alpha,i} = \ln \frac{A \alpha}{g(\alpha)} - \frac{E_a}{RT_i}$$

(Equation 5)

Under non-isothermal conditions, where the temperature is raised at a constant heating rate $\beta$, integration of Equation 1 involves solving the temperature integral $I(E,T)$,

$$g(\alpha) \equiv \frac{A}{\beta} \int_0^{\tau_{\alpha}} \exp \left( -\frac{E}{RT} \right) dT = \frac{A}{\beta} I(E,T)$$

(Equation 6)

which does not have a numerical solution. However, the equation can be solved by either using approximations or numerical integration. One of the simplest approximations by Doyle$^{58}$ gives rise to the following,
\[
\ln \beta = A' - \frac{1.052 E_a}{RT}
\]

(Equation 7)

where \(A'\) is a constant. Equation 7 is employed by the most widely used isoconversional method developed by FWO. The use of a more precise approximation by Coats and Redfern\(^5\) yields the following equation,

\[
\ln \frac{\beta}{T^2} = A' - \frac{E_a}{RT}
\]

(Equation 8)

which is known as the KAS method. By all methods, three or more experiments at different heating rates, typically between 1 and 20 °C/min, are required, as this is the only practical way to obtain data on varying rates at a constant extent of conversion. Typical dynamic DSC curves are Gaussian in shape, and the peak temperature \(T_{\text{max}}\) shifts to higher temperatures as the heating rate, \(\beta\), is increased (Figure 8). Conversion \((\alpha)\) versus temperature plots are constructed from the thermograms and used as the basis for the kinetic analysis by the different isoconversional methods. For each \(\alpha\), a corresponding value for \(T\) is extracted and used to plot \(\ln(\beta), \ln(\beta da/dT)\), or \(\ln(\beta/T^2)\) versus \(T^{-1}\) to determine \(E_a(\alpha)\) by the FWO, FR, and KAS isoconversional methods, respectively (Figure 9).
Figure 7. Typical Gaussian shaped thermograms where peak temperature ($T_{\text{max}}$) shifts to higher temperatures as the heating rate, $\beta$, is increased.
For each $\alpha$, a corresponding value for $T$ is extracted and used to plot $ln(\beta)$, $ln(\beta d\alpha/dT)$, or $ln(\beta/T^2)$ versus $T^{-1}$ to determine $E_a(\alpha)$ by the FWO, FR, and KAS isoconversional methods, respectively.

Isoconversional methods have been used extensively in determining the complex kinetics of crosslinking. Take, for example, the curing of diglycidal ether of bisphenol-A (DGEBA) with a polyfunctional primary amine. In the early stages of reaction, primary amine/oxirane reactions dominate. These reaction form secondary amines, which tend to be less reactive to a second oxirane group. Due to this difference in reactivity between primary and secondary amines, network formation typically occurs in two stages: chain extension through oxirane reaction with primary amines and then crosslinking through oxirane reaction with secondary amines. In addition to the chemical changes, curing is accompanied by dramatic physical changes. At early stages,
the reaction medium is a liquid composed of monomers and oligomers. As the reaction progresses the molecular weight of the forming network increases, leading to an increase in viscosity and \( T_g \). Crosslinking continues to progress as the polymer chains lose their ability to slip past one another, and the medium turns from flowing liquid to a solid. This dramatic decrease in molecular mobility can also affect the curing kinetics, as the reaction moves to a diffusion controlled process.\(^5\) A comparison of an isoconversional method with other kinetic methods demonstrated that the former is much more sensitive to detecting curing kinetic complexity.\(^5^3\) In their paper\(^6^0\) on the application of DSC isoconversional kinetic analysis to monitor epoxy cure, Vyazovkin and Sbirrazzuoli reported a decrease in the \( E_a \) values at the later stages of the curing process; from 60 to 40 kJ/mol at \( \alpha > 60\% \). The lower values of \( E_a \) are consistent with those for diffusion of a small molecule in a liquid-solid medium; the authors concluded that the reaction had switched to a diffusion controlled process above 60% conversion.\(^5^4\) This switch to diffusion control has been observed for a number of crosslinking systems, including dicyanate ester resins and phenol formaldehyde resins.\(^5^1\)

In addition to a decrease in \( E_a \) with conversion, a number of papers have reported an increase in \( E_a \) with conversion.\(^5^2\) This effect may indicate that the rate of crosslinking is limited not by diffusion of small molecules, but through the mobility of longer polymer chains. In the latter case, diffusion encounters a larger energy barrier associated with the cooperative nature of motion.\(^5\) Kessler and White\(^6^1\) studied the curing kinetics of polydicyclopentadiene by ring opening metathesis while employing three different concentrations of Grubbs catalyst. Through application of an isoconversional method \( E_a \) values were found to significantly increase above 60% conversion. This effect was
explained by the decrease in molecular mobility following gelation. Alternatively, an increase in $E_a$ during the final stages of curing is sometimes associated with chemical processes that are initiated at higher temperatures. This phenomena was recently reported by Dimier et al.\textsuperscript{62} in a study on the curing of a polyurethane in a three-component resin. The increase in $E_a$ was attributed to the formation and reaction of allophanate, which is known to occur above 140 °C.

\textit{ASTM E698 Method}

Falling somewhere between model-fitting and model-free methods, both in design and its ability to accurately predict $E_a$,\textsuperscript{53} is the ASTM E698\textsuperscript{63} method. This approach employs a variation of Ozawa’s method to estimate a conversion-averaged $E_a$, while the pre-exponential factor is evaluated on the assumption of a first-order reaction. The ASTM method is relatively simple and allows for quick determination of $E_a$; thus it is a valuable tool in surveying a large number of systems. The Ozawa approach assumes Arrhenius behavior, and that the extent of reaction at the peak exotherm is constant and independent of heating rate. In combination with Doyle’s approximation\textsuperscript{58} this approach yields the following equation,

$$\ln \beta = A' - \frac{1.052E_a}{RT_{max}}$$

where $\beta$ is the scan rate (K/min), $A'$ is a constant, $E_a$ is activation energy (J/mol), $T_{max}$ is the temperature at maximum exotherm (K), and $R$ is the universal gas constant (8.314 J/mol K). Again, three or more experiments at different heating rates, typically between 1 and 20 °C/min, are required. Here, the peak exotherm temperature, as opposed to conversion/temperature pairs, is employed to calculate $E_a$ from the slope of linear plots of $\ln(\beta)$ versus $1/T_{max}$. 
Table 1

*Isoconversional Kinetic Relationships*

<table>
<thead>
<tr>
<th>FR Method</th>
<th>FWO Method</th>
<th>KAS Method</th>
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<tr>
<td>( \ln \left( \frac{\beta d\alpha}{dt} \right) = \ln \alpha' - \frac{E_a}{RT} )</td>
<td>( \ln \beta = \alpha' - \frac{1.052E_a}{RT} )</td>
<td>( \ln \frac{\beta}{T^2} = \alpha' - \frac{E_a}{RT} )</td>
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CHAPTER II
SYNTHESIS

Introduction

The azide reactant used in this work, di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA), was based on proven epoxy backbone chemistry. Diglycidyl ether of bisphenol-A was modified to carry azide functionality through nucleophilic attack of the oxirane rings with azide ion. This molecule is not new, and modifications to existing literature procedures were used in its synthesis. Similarly the majority of the alkynes have been reported in literature and slight modifications to their reported syntheses were employed. The propiolate esters were the first class of alkynes species to be synthesized, followed by the propargyl esters, and then the propargyl ethers and amines. As a general summary, the propiolate esters were readily synthesized by condensing the appropriate polyol with a slight excess of propiolic acid in refluxing toluene and in the presence of a catalytic amount of p-toluene sulfonic acid. The propargyl esters were synthesized by the reaction of the appropriate acid chloride with a slight excess of propargyl alcohol in toluene using one equivalent of pyridine as an acid acceptor. The propargyl ethers were synthesized by reaction of the corresponding polyol with a large (2X) excess of propargyl bromide under forcing phase-transfer conditions. And finally, the propargyl amines were synthesized by reaction of the corresponding amine with only a slight excess of propargyl bromide to avoid formation of quaternary salts. The multifunctional alkyne curing agents used in this work are shown in Figure 10 and Figure 12 through Figure 23. Tripropargyl amine (TPA) is commercially available and was obtained from Sigma Aldrich. Finally, linear bulk polymerizations were
employed in a “proof-of-concept” study, where the reactivity of a number of alkynes

towards the DAHP-BPA monomer was ensured.

![Figure 10. Structure of tripropargyl amine, a commercially available liquid alkyne.](image)

**Materials**

All reagents were used without further purification. Tetra-\textit{n}-butyl ammonium bromide (TBAB, 98%) was purchased from Fluka Chemicals. The diglycidal ether of bisphenol-A (DGEBA, EPON 825) was donated by Hexion Specialty Chemicals. The remaining chemicals and all of the solvents were purchased from Sigma-Aldrich.

**Instrumentation**

\textsuperscript{1}H and \textsuperscript{13}C NMR spectra were obtained using either a Bruker AC-300 or a Varian UNITY-INOVA 500 MHz spectrometer with 5 mm o.d. tubes. Sample concentrations were approximately 25% (w/v) in CDCl\textsubscript{3}, CD\textsubscript{3}CN, or DMSO-d\textsubscript{6} containing 1% TMS as an internal reference.

Gel Permeation Chromatography (GPC) was conducted using a Waters Alliance 2695 Separations Module, an on-line multiangle laser light scattering (MALLS) detector (MiniDAWN\textsuperscript{TM}, Wyatt Technology Inc.) operating at 60mV and at a wavelength of 658nm, an interferometric refractometer (Optilab rEX\textsuperscript{TM}, Wyatt Technology Inc.) operating at a wavelength of 658 nm and at a temperature of 35 °C, and two mixed E (3 \textmu m beadsize) PL gel (Polymer Laboratories Inc.) GPC columns connected in series, heated to 35 °C. Freshly distilled THF served as the mobile phase at a flow rate of 1.0
mL/min. Sample concentrations were 5-20mg/mL in freshly distilled THF, with an injection volume of 100 μL. The detector signals were recorded using ASTRA™ software (Wyatt Technology Inc.) and molecular weights were determined using dn/dc calculated from the interferometric refractometer detector response and assuming 100% mass recovery from the columns.

**Azide Synthesis**

Sharpless and coworkers first reported the synthesis of DAHP-BPA in 2007. The structure of their product was identical to that shown in Figure 1 (attack of azide ion on the less substituted carbon of the epoxide ring). We used a modification of this procedure in which the acetonitrile was replaced with a mixture of 2-ethoxyethanol (Cellosolve) and water (3:1, v/v), with NH₄Cl charged to the reaction at the beginning to serve as a proton source and to help catalyze the epoxy ring opening. The pH was monitored over the course of the reaction to ensure it remained in a neutral range, ca. 6-9; typically, no adjustment was necessary. When outside of this pH range the reaction has been reported to become sluggish. Use of 2-ethoxyethanol enabled a higher reaction temperature (107 °C); this modification, coupled with the addition of ammonium chloride, lead to an increase in reaction rate. These conditions produced complete reaction in about 4 h, yielding a single product with ¹H and ¹³C NMR chemical shifts identical to those reported by Sharpless et al., as shown in Figure 11. This procedure was also successfully scaled to produce 2 kg of DAHP-BPA in a single reaction.
Figure 11. $^1$H NMR spectra of starting material diglycidal ether of bisphenol-A and product di(3-azido-2-hydroxypropyl) ether of bisphenol-A.
**Synthesis of Di(3-Azido-2-Hydroxypropyl) Ether of Bisphenol-A (DAHP-BPA)**

To a 500 mL round-bottom flask equipped with a magnetic stir bar were charged 85.1 g DGEBA epoxy resin (EPON 825) (0.25 mol), 65.7 g ammonium chloride (1.23 mol), 64.3 g sodium azide (1.0 mol), 167 mL 2-ethoxyethanol (Cellosolve), and 83 mL de-ionized (DI) water. The reaction was allowed to stir until the majority of the reagents had dissolved. The reaction was then brought to reflux by submersing the flask into an oil bath at a constant temperature of 130 °C. The internal temperature of the reaction reached 107 °C; the pH remained in the neutral range, ca. 7-8. The reaction was allowed to reflux for 4 h with continuous stirring. The reaction contents were then cooled and added to a separatory funnel. To the funnel was added 250 mL DI water, and the mixture was extracted with ethyl acetate (2 x 250 mL). The organic layers were combined and washed with brine (2 x 250 mL) and DI water (2 x 250 mL), dried with MgSO$_4$, filtered, and vacuum stripped using a wiped film evaporator to yield the final product. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 1.63$ (s, 6H, CH$_3$), 2.55 (s, 2H, OH), 3.51 (m, 4H, CH$_2$-N$_3$), 3.99 (d, 4H, O-CH$_2$), 4.15 (m, 2H, CH-OH), 6.82 (d, 4H, Ar-C$_{2,6}$-H), 7.12 (d, 4H, Ar-C$_{3,5}$-H) ppm. $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta = 31.00$ (CH$_3$), 41.76 (C-CH$_3$), 53.37 (CH$_2$-N$_3$), 68.97 (CH-OH), 69.33 (O-CH$_2$), 113.92 (Ar-C$_{3,5}$), 127.85 (Ar-C$_{2,6}$), 143.86 (Ar-C$_1$), 156.03 (Ar-C$_4$) ppm.

**Alkyne Synthesis**

Two basic building blocks were employed to create polyfunctional alkyne crosslinkers: propioloyl and propargyl. Syntheses for several of the propargyl and propiolate esters (DPA, TPTM, HDP, and TMPTP) were initially developed by Willer, Lin, and Baum at Fluorchem Inc., Azusa, CA, during development of triazole-cure
propellants. Two alkyne compounds are novel and previously undescribed: TPEDEA and TMBTP.

Synthesis of Oligo(Ethylene Glycol) Dipropiolates

\[
\text{n}=1, \text{diethylene glycol dipropiolate (DEGDP, liquid)}
\]
\[
\text{n}=3, \text{tetra(ethylene glycol) dipropiolate (TEGDP, liquid)}
\]
\[
\text{n}=3, \text{PEG-200 dipropiolate (PEGDP, liquid)}
\]

Figure 12. Structure of oligo(ethylene glycol) dipropiolates: diethylene glycol dipropiolate (DEGDP), tetra(ethylene glycol) dipropiolate (TEGDP), and PEG-200 dipropiolate (PEGDP).

A minor modification of the procedure of Miller was used to synthesize three oligo(ethylene glycol) dipropiolates: poly(ethylene glycol)-200 dipropiolate (PEGDP), di(ethylene glycol) dipropiolate (DEGDP), and tetra(ethylene glycol) dipropiolate (TEGDP). The synthesis of tetra(ethylene glycol) dipropiolate is representative: tetraethylene glycol (77.6 g, 0.40 mol) was weighed into a dry 1000 mL round bottom flask equipped with a magnetic stir bar, and dried by placing under high vacuum (< 0.5 Torr) for one hour at 60 °C. Propiolic acid (63 g, 95%, 0.85 mol), benzene (350 mL), and p-toluenesulfonic acid mono-hydrate (4.0 g) were added to the flask. A Dean-Stark trap and a condenser were attached, and the reaction was protected by a nitrogen bubbler. The mixture was heated at reflux for 20 h, and the water of condensation was separated (bath temp 110 °C). A total of 15.5 mL of water was collected (theory is 14.4 mL). The mixture was then cooled to below room temperature and transferred to a 1 L separatory funnel using two 200 mL diethyl ether rinses to insure complete transfer. The benzene-
diethyl ether solution was washed with 20 wt% sodium hydroxide solution (1 x 25 mL). The solution was then washed with brine (1 x 25 mL), dried over MgSO₄, and filtered, and the solvent was removed under reduced pressure. $^1$H-NMR (300 MHz, CDCl₃): δ = 3.00 (s, 2H, ≡C-H), 3.54 (s, 8H, CH₂-O), 4.25 (t, $J$ = 6.5 Hz, 4H, CH₂-CH₂-O-CO), 4.31 (t, $J$ = 6.5 Hz, 4H, CH₂-CH₂-O-CO) ppm. $^{13}$C-NMR (75 MHz, CDCl₃): δ = 65.19, 68.47, 70.53, 70.57 (CH₂-CH₂), 74.46 (C=), 75.38 (≡C-H), 152.59(C=O) ppm.

**Synthesis of 1,3,5-Tris(Methyl)Benzene Tripropiolate (TMBTP)**

![Structure of 1,3,5-tris(methyl)benzene tripropiolate (TMBTP), a solid at room temperature.](image)

**Figure 13.** Structure of 1,3,5-tris(methyl)benzene tripropiolate (TMBTP), a solid at room temperature.

First, 1,3,5-tri(hydroxymethyl)benzene was synthesized by the literature procedure developed by Moses. The melting point of the product was 75-76 °C (lit. 75 °C). Propiolic acid (2.45g, 0.035 mol) was then weighed into a dry 100 mL round-bottom flask equipped with a magnetic stirring bar. Toluene (50 mL), 1,3,5-tri(hydroxymethyl)benzene (1.68 g, 0.010 mol), and $p$-tolunesulfonic acid monohydrate(0.2 g) were added to the flask. A Dean-Stark trap and a condenser were attached, and the reaction was protected by a nitrogen bubbler. The mixture was heated to reflux for 4.5 h, and 0.7 mL of water was separated (theory is 0.54 mL). Most of the water came off in the first hour. When the production of water ceased, the mixture was cooled to room temperature and transferred to a 250 mL separatory funnel. The toluene solution
was washed with 5% sodium hydroxide solution (2 x 5 mL) and 10 mL of brine. It was then dried over MgSO4 and filtered, and the solvent was removed under reduced pressure. The product slowly crystallized while under vacuum. The yield of crude product was essentially quantitative. A small sample was recrystallized from methanol to give crystals melting at 62-64 °C. FT-IR (film, warm): 3404(w), 3253(vs), 2951(m), 2892(m), 2119(vs), 1712(vs), 1461(m), 1370(m), 1241(vs), 1029(m), 966(m), 955(sh), 913(w), 867(m), 756(s) and 710(m) cm⁻¹. ¹H-NMR (DMSO-d₆): δ = 4.60 (s, 3H, ≡C-H), 5.23 (s, 6H, CH₂-O), 7.41 (s, 3H, Ar-H) ppm. ¹³C-NMR (DMSO-d₆): δ = 67.35 (CH₂-O), 74.96 (C-≡), 79.95 (≡C-H), 128.89 (Ar-CH), 136.17 (Ar-C-), and 152.47 (C=O) ppm. HRMS (EI); C₁₈H₁₂O₆ [M]+: calcd. 324.0634; found 324.0635 amu.

**Synthesis of Trimethylolpropane Tripropiolate (TMPTP)**

![Structure of Trimethylolpropane Tripropiolate (TMPTP)]

*Figure 14.* Structure of trimethylolpropane tripropiolate (TMPTP), a solid at room temperature.

Propiolic acid (70.05g, 1.0 mol) was weighed into a dry 500 mL round-bottom flask equipped with a magnetic stirring bar. Toluene (250 mL), trimethylol propane (40.25 g, 0.30 mol) and p-tolunesulfonic acid mono-hydrate (3.0 g) were added to the flask. A Dean-Stark trap and a condenser were attached, and the reaction was protected by a nitrogen bubbler. The mixture was heated to reflux for 4.5 h and 21 mL water was separated (theory is 16.2 mL). Most of the water came off in the first hour. The mixture was cooled to room temperature and transferred to a 1 L separatory funnel. Ethyl acetate
(250 mL) was added to keep the product in solution. The toluene-ethyl acetate solution was washed with 5% sodium hydroxide solution (2 x 100 mL) and 100 mL of brine solution. It was then dried over MgSO₄ and filtered, and the solvents were removed under reduced pressure. The product slowly crystallized with a yield of 85.72g (0.296 mol, 98.5%), and a melting point of 71-73 °C. The product contained traces of toluene, which were removed by melting the product and casting it into teflon pans as thin sheets and drying the sheets in a vacuum oven. An analytical sample was obtained by recrystallization from acetone, and it had a melting point of 80-82 °C. FT-IR (film, warm): 3283(m), 2973(w), 2121(s), 1717(vs), 1466(m), 1387(w), 1219(vs), 990(m) and 752(m) cm⁻¹. ¹H-NMR (DMSO-d₆): δ = 0.83 (t, J = 7.5 Hz, 3H, -CH₃), 1.42(q, J = 7.5 Hz, 2H, CH₂-CH₃), 4.12 (s, 6H, CH₂-O), 4.58(s, 3H, ≡C-H) ppm. ¹³C-NMR (DMSO-d₆): δ = 7.5 (-CH₃), 22.87 (C- (CH₂)₄), 65.62 (-CH₂), 74.76 (C=C=), 80.08 (≡C-H), and 152.39 (C=O) ppm. Anal. calcd. for: C₁₅H₁₄O₆: C, 62.07; H, 4.86; Found: C, 62.27; H, 4.84 %.

Synthesis of 1,6-Hexane Dipropiolate (HDP)

![Structure of 1,6-hexane dipropiolate (HDP)](image)

Figure 15. Structure of 1,6-hexane dipropiolate (HDP), a solid at room temperature.

1,6-Hexane dipropiolate was prepared by the procedure of Wang et al.⁶⁸ The melting point was 44-45 °C (lit. 42-45 °C⁶⁸).
Synthesis of propiolate Ethoxylated Pentaerythritol (PEP)

Figure 16. Structure of propiolate ethoxylated pentaerythritol (PEP), liquid at room temperature.

Ethoxylated pentaerythritol (avg. ¾ ethoxylated, 25.04 g, 0.093 mole) was weighed into a dry 500 mL round bottomed flask equipped with a magnetic stirring bar. The material was dried by placing it under vacuum for approximately one hour. Propiolic acid (25.2 g, 0.41 mol), benzene (150 ml), and p-tolunesulfonic acid monohydrate (1.8 grams) are then added to the flask. A Dean-Stark trap and a condenser were attached, and the reaction was placed under a nitrogen blanket. The mixture was heated to reflux (bath temp 100 °C), and the water was collected. The mixture was allowed to reflux for approximately 40 h, cooled to room temperature, and transferred to a 500 ml separatory funnel. Diethyl ether was used to insure complete transfer. The benzene-diethyl ether solution was washed with 10 % sodium hydroxide solution (1 x 50 ml). The wash was checked to make sure the pH was basic. The solution was then washed with brine (1 x 50 ml). The cleaned solution was dried over MgSO₄, filtered, and the solvent removed by rotary evaporation. The propiolate ethoxylated pentaerythritol (PEP) yield was 45.4 g (101.8%). The discrepancy in yield is likely due to the variability in the
actual formula weight of the reagent. ATR-FTIR (liquid): 3233(s), 2877(s), 2116(vs), 1716(vs), 1452(m), 1352(m), 1230(vs), 1110(s), 1031(m), 954((m), 862(w), 755(m), 702(w) cm\(^{-1}\). \(^1\)H-NMR (DMSO-d\(_6\)): \(\delta = 3.52(s, \approx 8\ H,\ CH_2-C), 3.64(m,\ 6H,\ CH_2-O), 4.25(m,\ 6H,\ CH_2-CH_2-O-CO),\ 4.51(s,\ 3H,\ \equiv C-H)\) ppm. \(^{13}\)C-NMR (DMSO-d\(_6\)): \(\delta = 65.56,\ 68.22,\ 70.17\) (CH\(_2\)-O), 75.07 (C-\(=\)C=), 79.50 (=C-H), 152.66 (C=O) ppm.

**Synthesis of Dipropargyl Adipate (DPA)**

![Structure of dipropargyl adipate (DPA)](image)

*Figure 17. Structure of dipropargyl adipate (DPA), a liquid at room temperature.*

Propargyl alcohol (12.0 g, 0.214 mol), pyridine (16.0 g, 0.202 mol), and dry dichloroethane (100 mL) were charged to a 500 mL round-bottom flask. The resulting solution was maintained at 10 °C by means of a salt/ice/water bath. A solution of adipoyl chloride (18.3 g, 0.10 mol) in 100 mL of dry dichloroethane was added dropwise over 15 min. The solution was stirred overnight at room temperature and then transferred to a 1 L separatory funnel with the aid of a small amount of dichloroethane. The dichloroethane solution was washed with water (2 x 100 mL), 5% HCl (100 mL), and saturated sodium bicarbonate solution (100 mL). The dichloroethane solution was dried over MgSO\(_4\) and filtered, and the dichloroethane was removed under reduced pressure. The product was purified by vacuum distillation. The main fraction was collected at 0.7 Torr, boiling from 130 to 132 °C. The reported boiling point is 142-145 °C @ 4 Torr.\(^{69}\) FT-IR (film): 3290(vs), 2947(s), 2874(m), 2129(m), 1740(vs), 1436(s), 1418(sh), 1382(s), 1350(sh), 1311(sh), 1235(s), 1164(s), 1077(m), 1027(m), 996(m), 959(m), 935(m), 680(s) 647(s) cm\(^{-1}\). \(^1\)H-NMR (300 MHz, CD\(_3\)CN): \(\delta = 1.72\) (m, 4H, CH\(_2\)), 2.39 (m, 4H, CH\(_2\)-CO), 2.50
(t, 2H, \equiv\text{C-H}), 4.68 (d, 4H, O-\text{CH}_2) \text{ ppm.} \quad ^{13}\text{C-NMR (75 MHz, CD}_3\text{CN): } \delta = 24.04 (\text{CH}_2-\text{CH}_2), 33.42 (\text{CH}_2-\text{CO}), 51.82 (\text{O-CH}_2), 74.90 (\text{H-}\equiv\text{C}), 77.63 (\text{CH}_2-\equiv\text{C}), 172.30 (\text{C}=\text{O}) \text{ ppm.}

\textit{Synthesis of Tripropargyl Trimesate (TPTM)}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{structure}
\caption{Structure of tripropargyl trimesate (TPTM), a solid at room temperature.}
\end{figure}

Propargyl alcohol (18.0 g, 0.32 mol) and pyridine (24 g, 0.30 mol) were dissolved in 150 mL of anhydrous dichloroethane in a 500 mL round-bottom flask equipped with a magnetic stirring bar. This reaction was maintained at 10 °C by means of a salt/ice/water bath. A solution of trimesic chloride (26.6 g, 0.10 mol) in 100 mL of anhydrous dichloroethane was added drop-wise over 20 min. The solution was stirred overnight at room temperature. The next day the solution was transferred to a 1 L separatory funnel with the aid of a small amount of dichloroethane. The dichloroethane solution was washed with water (2 x 100 mL), 5% HCl (100 mL) and with 5% sodium hydroxide solution (100 mL). The dichloroethane solution was then dried over MgSO\textsubscript{4} and filtered, and the dichloroethane was removed under reduced pressure. The product was purified by recrystallization from acetone. The yield was 29.16 g (0.09 mol, 90%). The melting point was 82 °C. FT-IR (film): 3290(vs), 2947(s), 2874(m), 2129(m), 1740(vs), 1436(s), 1418(sh), 1382(s), 1350(sh), 1311(sh), 1235(s), 1164(s), 1077(m), 1027(m), 996(m),
959(m), 935(m), 680(s) 647(s) cm⁻¹. ¹H NMR (DMSO-d₆) δ = 3.65 (t, J = 2.4 Hz, 3H, ≡C-H), 5.03 (d, J = 2.4 Hz, 6H, O-CH₂), 8.62 (s, 3H, Ar-CH) ppm. ¹³C NMR (DMSO-d₆) δ = 51.84 (O-CH₂), 74.90 (H-C=), 77.64 (CH₂-C=), 124.05 (Ar-CH), 133.44 (Ar-C=), 172.33 (C=O) ppm. HRMS (EI); C₁₈H₁₂O₆ [M]+: calcd. 324.0634; found 324.0641.

**Synthesis of Trimethylolpropane Tripargyl Ether (TMPTPE)**

![Structural diagram of TMPTPE]

*Figure 19. Structure of trimethylolpropane tripargyl ether (TMPTPE).*

This compound was synthesized using a minor modification of the procedure of Mekni and Baklouti.⁷⁰ Trimethylolpropane (6.71g, 0.050 mol) was weighed into a dry 100 mL round bottom flask equipped with a mechanical stirrer, condenser, and septum. Sodium hydroxide (12 g 0.30 mol), water (1.0 mL) and TBAB (0.80 g) were added and the temperature of the solution was adjusted to 25 °C. The reaction was protected by a nitrogen bubbler. Propargyl bromide (45.0 g of 80 wt% solution in toluene, 0.30 mol) was added drop-wise over the course of 1 h, and then the temperature was slowly raised to 60 °C over the course of 1 h. During this time the reaction became homogeneous. The reaction mixture was stirred at 60 °C overnight. It was then cooled and diluted with 100 mL of methylene chloride and filtered to remove salts. The salts were extracted with two 100 mL portions of methylene chloride, and the extracts were filtered and combined with the main reaction. The crude product was observed to be contaminated with some very fine salts that went through the filter. The solvents were stripped, and the crude product
(yield = 15.01 g) was analyzed by $^1$H NMR. Except for small amounts of toluene and propargyl bromide, the product was quite pure. The remaining toluene and propargyl bromide were removed under high vacuum, and the product was distilled using a Kugelrohr apparatus (200 °C @ 0.40 Torr), to yield 10.5g (42.3 mmol, 84.6%) of purified product. NMR analysis indicated that the purified product was 90% tri- and 10% dipropargylated. $^1$H and $^{13}$C NMR chemical shifts were in excellent agreement with reported values.$^{71}$

FT-IR (film): 3294(vs), 2880-3000(b, vs), 1721(w), 1475(s), 1442(m), 1360(s), 1265(m), 1084(s), 1025(m), 975(m), 912(m) cm$^{-1}$. $^1$H-NMR (CDCl$_3$): δ = 0.88 (t, 3H, J = 4.2 Hz, -CH$_3$), 1.42 (q, 2H, J = 4.2 Hz, CH$_2$-CH$_3$), 2.42 (t, 3H, J = 2.4 Hz, ≡C-H), 3.40 (s, 6H, CH$_2$-O), 4.14 (d, 6H, J = 2.4 Hz, O-CH$_2$-C≡) ppm. $^{13}$C-NMR (CDCl$_3$): δ = 7.42 (-CH$_3$), 22.62 (CH$_2$-CH$_3$), 42.66 (C-(CH$_2$)$_4$), 58.48 (O-CH$_2$-C≡), 70.12 (O-CH$_2$-C), 74.19 (H-C≡), 80.09 (C-C≡) ppm.

**Synthesis of Oligo(Ethylene Glycol) Dipropargyl Ether**

Two compounds, tetra(ethylene glycol) dipropargyl ether (TEGDPE, liquid) and poly(ethylene glycol)-200 dipropargyl ether (PEGDPE, liquid), were made using a minor modification of the procedure of Mekni and Baklouti.$^{70}$ The synthesis of tetra(ethylene glycol) dipropargyl ether is representative: tetraethylene glycol (19.4 g, 0.10 mol) was weighed into a dry 250 mL three-neck round-bottom flask equipped with a mechanical
stirrer, septum and a condenser. Sodium hydroxide (16.0 g, 0.40 mol), water (2 mL) and TBAB (0.40 g) were added to the flask, and the reaction was protected by a nitrogen bubbler. The mixture was heated to 45 °C, and propargyl bromide (60 g of 80 wt% solution in toluene, 0.40 mol) was added drop-wise over 1 h. Following addition, the reaction temperature was raised to 60 °C and stirred for 6 h. The mixture was cooled and diluted with 100 mL of methylene chloride. The mixture was filtered to remove salts; the salts were extracted with methylene chloride (2 x 50 mL), and the combined solutions were stripped of solvents. FT-IR spectroscopy showed that no hydroxyl remained, indicating reaction completion. The yield of crude product was 32.28 g. The remaining toluene and propargyl bromide were removed under high vacuum, and the resulting product was Kugelrohr distilled at 200 °C @ 0.50 Torr in two batches. The reported boiling point was 110 °C @ 0.1 Torr. The yield of purified product was 26.46 g (98 mmol, 98%). FT-IR (film): 3251(m), 2870(s), 2113(w), 1458(w), 1350(m), 1270(w), 1250(w), 1102(vs), 1033(m), 919(w), 842(w) cm\(^{-1}\). \(^1\)H-NMR (300 MHz, CD\(_3\)CN): \(\delta=4.16 \text{ (d, } J=2.4 \text{ Hz, } 4\text{H, O-CH}_2\text{-C\(\equiv\)}}\), 3.60 (s, 8H), 3.40 (s, 8H), 2.74 (t, \(J=2.4 \text{ Hz, } 2\text{H, H-C\(\equiv\)}}\) ppm. \(^13\)C-NMR (75 MHz, CD\(_3\)CN): \(\delta=57.82, 69.05, 70.02, 70.25 \text{ (O-CH}_2\text{-C\(\equiv\)}}\), 74.94 (H-C\(\equiv\)), 80.08 (C-C\(\equiv\)) ppm.

**Synthesis of N,N,N',N'-Tetrapropargyl-2,2'-(Ethyleneoxy)Bis(Ethylamine) (TPEDEA)**

![Structure of TPEDEA](image)

**Figure 21.** Structure of N,N,N',N'-tetrapropargyl-2,2'-(ethylenedioxy)bis(ethylamine) (TPEDEA), a liquid at room temperature.
To a 3-neck 500 mL round-bottom flask, equipped with a mechanical stirrer, were charged 2,2′-(ethylenedioxy)bis(ethylamine) (14.82 g, 0.10 mol), water (40 mL), sodium hydroxide (17.6 g, 0.44 mol), dichloroethane (80 mL) and TBAB (0.322 g). A reflux condenser equipped with a nitrogen bubbler was attached, and a room temperature bath was placed around the flask. Propargyl bromide (65.46 g of 80 wt% solution in toluene, 0.44 mol) was added drop-wise over the course of 1 h, and the mixture was stirred overnight. The mixture was transferred to a 1 L separatory funnel with the aid of 400 mL of methylene chloride. The pH of the aqueous layer was checked and found to be slightly basic. The aqueous layer was separated, and the organic layer was dried over magnesium sulfate, filtered, and then solvent-stripped to yield the crude product (32.5 g). The crude product was chromatographed on 250 g of silica using an 80/20 solution of methylene chloride/ethyl acetate as the eluent; 150 mL fractions were collected. A very dark band eluted as fraction 3, with fractions 5-8 containing the desired compound. These fractions were combined and solvent-stripped to give 17 g (57 mmol, 57%) of a slightly yellow-brown product. Thin layer chromatography (TLC) showed that fractions 9 and 10 might also contain the desired compound. They were combined and solvent-stripped, yielding an additional 3.1 g (10 mmol, 10%). NMR analysis showed both products were the desired tetra-functional compound. FT-IR (film) = 3300 (vs), 2924(m), 2821(m), 2103(w), 1672(w), 1642(w), 1440(m), 1352(m), 1328(m), 1101(m), 1055(w), 977(w), 902(m), 832(w), 806(w), 636(s) cm\(^{-1}\). \(^{1}\)H-NMR (CDCl\(_3\)): \(\delta = 2.45 \text{ (t, } J = 2.4 \text{ Hz, } 4\text{H, H-C≡})\), 2.68 (t, \(J = 7 \text{ Hz, NCH}_2\text{-CH}_2\text{O}\)), 3.45 (d, \(J = 2.4 \text{ Hz, } 8\text{H, N-CH}_2\text{-C≡})\), 3.55 (s, 4H, OCH\(_2\text{CH}_2\text{O}\)), 3.60 (t, \(J = 7 \text{ Hz, } 4\text{H, NCH}_2\text{-CH}_2\text{O}\)) ppm. \(^{13}\)C-NMR (CD\(_3\)CN): \(\delta = 42.46 \text{ (N-CH}_2\text{-C≡), 52.40 (N-CH}_2\text{-CH}_2\text{), 69.51 (O-CH}_2\text{CH}_2\text{), 70.32 (O-CH}_2\text{CH}_2\text{), 73.73}\).
(H-\(\equiv\)), 79.41 (C-\(\equiv\)) ppm. HRMS (NCI): \(\text{C}_{18}\text{H}_{25}\text{N}_{2}\text{O}_{2}\) [MH]^+: calc. 301.1916; found 301.1904 amu.

**Synthesis of \(N,N,N',N'\)-Tetrapropargylethylenediamine (TPEDA)**

![Structure of N,N,N',N'-tetrapropargylethylenediamine (TPEDA)](image)

*Figure 22.* Structure of \(N,N,N',N'\)-tetrapropargylethylenediamine (TPEDA), a liquid at room temperature.

This compound was prepared using a minor modification of the procedure of Yamada and Aoki.\(^{72}\) To a 3-neck 500 mL round-bottom flask, equipped with a mechanical stirrer, were charged ethylene diamine (6.0g, 0.10 mol), water (40 mL), sodium hydroxide (17.6g, 0.44 mol), dichloroethane (80 mL) and TBAB (0.322g). A reflux condenser equipped with a nitrogen bubbler was attached, and a room temperature bath was placed around the flask. Propargyl bromide (65.46 g of 80 wt% solution in toluene, 0.44 mol) was then added drop-wise over 1 h, and the reaction was stirred for 22 h at room temperature. The mixture was then transferred to a 500 mL separatory funnel with the aid of 100 mL of dichloroethane and 100 mL of water. The pH of the aqueous layer was checked to ensure it was basic. A very stable emulsion formed; so the mixture was filtered through a fiberglass filter to remove any polymeric impurities before returning it to the separatory funnel. The organic layer was separated, dried over magnesium sulfate, filtered, and then solvent-stripped to give the crude product (28.2 g). TLC showed at least three products. The crude product was chromatographed on 200 g of silica using methylene chloride as the eluent, collecting 150 mL fractions. A very dark
band eluted at fractions 3 and 4 and contained a solid material, perhaps a quaternary salt. Fractions 6-11 contained the desired crude compound (8.5g). Fractions 6-11 were combined, solvent-stripped, and Kugelrohr distilled (175 °C@0.5 Torr) to give 5.9 g (28 mmol, 28%) of slightly yellow product. FT-IR (film) = 3300 (vs), 2924(m), 2821(m), 2103(w), 1672(w), 1642(w), 1440(m), 1352(m), 1328(m), 1124(m), 1101(m), 1055(w), 977(w), 902(m), 832(w), 806(w), 636(s) cm\(^{-1}\). \(^1\)H-NMR (CDCl\(_3\)): \(\delta = 2.21 (t, J = 2.4 \text{ Hz}, 4\text{H, H-C≡}), 2.68 (s, 4\text{H, CH}_2-\text{CH}_2), 3.45 (d, J = 2.4 \text{ Hz, 8H, N-CH}_2-\text{C≡}) \text{ ppm.} \^{13}\)C-NMR (CDCl\(_3\)): \(\delta = 42.47 (\text{CH}_2-\text{CH}_2), 49.89 (\text{N-CH}_2-\text{C≡}), 73.19 (\text{H-C≡}), 78.66 (\text{C-C≡}) \text{ ppm.} \) HRMS (Cl): C\(_{14}\)H\(_{17}\)N\(_2\) [MH\(^+\)]: calc. 213.1392; found 213.1383 amu.

**Synthesis of N,N,N′,N′-Tetra Propargyl Benzene Diamine (TPBDA)**

![Structure of N,N,N′,N′-tetra propargyl benzene diamine (TPBDA), a solid at room temperature.](image)

\(p\)-Phenylene diamine (0.040 mol, 4.33 g), propargyl bromide (0.18 mol, 26.78 g of 80 wt% solution in toluene), potassium carbonate (0.15 mol, 20.73 g), and DMF (150 mL) were charged to a 500 mL round bottom flask, and the reaction was refluxed at 100 °C for 24 h. The reaction mixture was cooled, combined with 400 mL of methylene chloride, washed with water, and dried over magnesium sulfate. The crude product was obtained as a viscous, slightly red liquid. TLC indicated predominantly tetra-substituted material. The crude product was chromatographed on 200 g of silica using dichloromethane as the eluent. Three recrystallizations in ethanol yielded 6.0 g of a cream colored crystal. NMR analysis showed that the product was the desired tetra-
functional compound. It was found that TPBDA should be stored under a nitrogen blanket and in the dark. The melting point was 74-75 °C. $^1$H-NMR (CDCl$_3$): $\delta = 2.70$ (t, 4H, H-C≡), 4.09 (d, 8H, CH$_2$-C≡), 6.98 (s, 4H, Ar-CH) ppm. $^{13}$C-NMR (CDCl$_3$): $\delta = 40.42$ (CH$_2$-C≡), 73.22 (H-C≡), 79.48 (C-C≡), 117.71(Ar-CH), 205.27 (Ar-CN) ppm. HRMS (Cl): C$_{14}$H$_{17}$N$_2$ [MH]$^+$: calc. 213.1392; found 213.1383 amu.

**Linear Bulk Polymerizations**

The reaction between azide modified epoxy resin and the alkyne curatives was initially investigated using difunctional alkynes in a “proof of concept” study, which yielded linear polymer products. Mixtures of two alkyne monomers, DEGDP and DPA, were used to create three different resin systems, all at a theoretical 1:1 azide:alkyne stoichiometric ratio, with either a relative alkyne ration of 50:50 or 65:35 for the DEGDP and DPA species, respectively. The systems were cured for 24 hrs at room temperature, followed by a post-cure at 100 °C for 2 hrs, or were immediately cured at 100 °C for 2 hrs. Molecular weight was impeded by limiting the time held at 100 °C in order to maintain solubility in common GPC solvents. Figure 24 shows gel permeation chromatograms of the starting epoxy resin, the azide-modified resin, and the chain-extended polymers. The chromatograms show that the addition of azide to the epoxy resin results in a significant increase in hydrodynamic volume, while the peak shape remains the same, indicating the lack of degradation, fractionation, or chain coupling/extension during reaction with the azide. For both the starting epoxy resin and the azide-modified resin a high molecular weight shoulder is observed. This shoulder is associated with chain extended impurities present in the starting material, as no purification was performed on the EPON-825. Upon polymerization the peaks shift to
shorter elution times, and broaden, clearly indicating an increase in molecular weight. Table 2 lists the quantitative results obtained from GPC-MALLS. Average degree of polymerization, $X_n$, was calculated as number average molecular weight, $M_n$, obtained from MALLS, divided by the average molecular weight of the structural units in the polymer (assuming that the propiolate and propargyl ester monomers entered the polymer in proportion to their relative abundances in the feed). The greatest $X_n$ was obtained for the system containing the higher proportion (65 mol%) of the more reactive propiolate monomer. The two systems formulated at equimolar ratio of propiolate/propargyl produced the same $X_n$, but the sample immediately reacted at 100°C produced a narrower distribution of degrees of polymerization.

![Figure 24. GPC chromatograms (differential refractometer) of epoxy resin (EPON 825), azide-modified epoxy resin, and three polymers obtained by reaction of azide-modified epoxy resin with a mixture of diethylene glycol dipropiolate (DEGDP) and dipropargyl adipate (DPA).](image-url)
Table 2

**GPC Results Comparing Linear Polymerization to the Modified and Unmodified Resins**

<table>
<thead>
<tr>
<th></th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w$ (g/mol)</th>
<th>PDI</th>
<th>Theor. $\bar{M}_n$ (g/mol)</th>
<th>$\bar{X}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. EPON 825</td>
<td>340</td>
<td>350</td>
<td>1.03</td>
<td>340.41</td>
<td>-</td>
</tr>
<tr>
<td>2. DAHP-BPA</td>
<td>450</td>
<td>460</td>
<td>1.02</td>
<td>426.47</td>
<td>-</td>
</tr>
<tr>
<td>3. Diethylene glycol dipropiolate (DEGDP)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>210.18</td>
<td>-</td>
</tr>
<tr>
<td>4. Dipropargyl adipate (DPA)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>222.24</td>
<td>-</td>
</tr>
<tr>
<td>5. DEGDP/DPA (50/50) 100 °C, 2 h</td>
<td>2,830</td>
<td>4,390</td>
<td>1.55</td>
<td>-</td>
<td>8.8</td>
</tr>
<tr>
<td>6. DEGDP/DPA (50/50), RT 12 h, 100 °C 2 h</td>
<td>2,900</td>
<td>6,100</td>
<td>2.11</td>
<td>-</td>
<td>9.0</td>
</tr>
<tr>
<td>7. DEGDP/DPA (65/35) 100 °C 2 h</td>
<td>3,720</td>
<td>6,730</td>
<td>1.81</td>
<td>-</td>
<td>11.6</td>
</tr>
</tbody>
</table>

$^a$GPC-MALLS

In addition to GPC studies, NMR was use to characterize the polytriazoles. Neat polymerizations were conducted by combining either TEGDP or TEGDPE with DAHP-BPA such that the molar ratio of azide:alkyne was 1:1. Each system was polymerized both with and without catalyst, either bromotris(triphenylphosphine)copper(I) (BTTPP) or copper(II) ethylhexanoate (CEH). The reactants were combined and mixed for 5 min, and then 0.5 g of the mixture was charged to a high density polyethylene vial. The vials were placed in a 70 °C curing oven for 2 or 12 h, for the systems employing TEGDP and TEGDPE, respectively. These conditions were chosen to limit molecular weight and maintain solubility of the product in common solvents. Where possible those shifts
associated with the 1,5-regioisomer have been denoted with an asterisk (*).

TEGDP/DAHP-BPA \(^1\)H-NMR (500 MHz, DMSO-d6): \(\delta = 1.58\) (s, 6H, CH\(_3\)), 3.42 (s, 8H, O-CH\(_2\)CH\(_2\)), 3.52-3.56 (m, 4H, CH\(_2\)CH\(_2\)-O-CO), 3.71 (m, 4H, CH\(_2\)CH\(_2\)-O-CO), 3.93 (m, 4H, OCH\(_2\)-CHOH), 4.26 (m, 2H, CH-OH), 4.39 (m, CH\(_2\)-O-CO=), 4.55* and 4.68 (m, 4H, CH\(_2\)-N), 5.46* and 5.61 (d, 2H, OH), 6.84 (d, 4H, Ar-C\(_{2,6}\)-H), 7.11 (d, 4H, Ar-C\(_{3,5}\)-H), 8.27* and 8.70 (2H, N-CH=:C) ppm. \(^{13}\)C-NMR (125 MHz, DMSO-d6): \(\delta = 30.86\) (C-CH\(_3\)), 41.25 (C-CH\(_3\)), 53.03 (CH\(_2\)-N), 63.82 (CH\(_2\)-O-CO-\(\equiv\)), 65.21 and 67.65* (CH-OH), 68.34 (CH\(_2\)CH\(_2\)-O-CO), 69.41 (OCH\(_2\)-CHOH), 69.79-69.86 (CH\(_2\)CH\(_2\)-O & CH\(_2\)CH\(_2\)-O-CO), 113.98 (Ar-C\(_{3,5}\)), 127.51 (Ar-C\(_{2,6}\)), 128.80* and 130.17 (N-CH=:C), 137.48* and 138.42 (N-CH=C), 142.98 (Ar-C\(_1\)), and 156.11 (Ar-C\(_4\)), 152.29 (O=\(\equiv\)C-CH), 158.16* and 160.39 (C=O) ppm. TEGDPE/DAHP-BPA \(^1\)H-NMR (500 MHz, DMSO-d6): \(\delta = 1.58\) (s, 6H, CH\(_3\)), 3.42 (s, 8H, O-CH\(_2\)CH\(_2\)), 3.50-3.54 (m, 4H, O-CH\(_2\)-CH\(_2\)), 3.71 (m, 4H, OCH\(_2\)-CHOH), 4.13 (m, CH\(_3\)C=CH), 4.21* and 4.24 (m, 2H, CH-OH), 4.43* and 4.56 (m, 4H, CH\(_2\)-N), 4.53 and 4.68* (m, 4H, OCH\(_2\)-C=), 5.51* and 5.57 (d, 2H, OH), 6.83 (d, 4H, Ar-C\(_{2,6}\)-H), 7.10 (d, 4H, Ar-C\(_{3,5}\)-H), 7.68* and 8.03 (2H, N-CH=:C) ppm. \(^{13}\)C-NMR (125 MHz, DMSO-d6): \(\delta = 30.78\) (C-CH\(_3\)), 41.24 (C-CH\(_3\)), 50.72* and 50.62 (CH\(_2\)-N), 57.54 (CH\(_2\)C=CH), 60.40* and 63.55 (OCH\(_2\)=C), 67.91 and 68.21* (CH-OH), 68.57 and 69.01 (O-CH\(_2\)CH\(_2\)), 69.23 (OCH\(_2\)-CHOH), 69.47-69.82 (O-CH\(_2\)CH\(_2\)), 113.97 (Ar-C\(_{3,5}\)), 127.50 (Ar-C\(_{2,6}\)), 124.95 and 133.14* (N-CH=C), 134.94* and 143.69 (N-CH=C), 142.94 (Ar-C\(_1\)), 156.14 (Ar-C\(_4\)) ppm.

As discussed previously, the 1,3-dipolar cycloaddition of terminal alkynes with azides can be rendered regioselective through the use of catalyst. In addition to kinetic
data, regioselectivity may also be used as a diagnostic indicator catalytic control. By integrating and comparing the proton peaks associated with the triazole ring at 7.68 and 8.03 ppm (Figure 25 & Figure 26), it was found that the TEGDPE/DAHP-BPA polymer contained 56% 1,4-regioisomer and 44% 1,5-regioisomer. Depending on the type of catalyst used and the loading amount, regioselectivity was found to increase in favor of the 1,4-regioisomer. As the loading levels of BTTPP increased from 0.012 mol % to 0.5 %, regioselectivity was also found to increase from 62:38, 87:13, 94:6, to 98:2, for loading levels 0.012, 0.12, 0.24 and 0.5%, respectively as shown in Figure 25. Similarly the CEH catalyst was found to increase the regioselectivity from 62:38, 85:15, 90:10, and 93:7 for loading levels 0.01, 0.1, 0.2, and 0.5%, respectively, shown in Figure 26. Both catalysts were able to effectively control the polymerization of TEGDPE and DAHP-BPA, with the regioselectivity increasing as the catalyst loading levels were increased. Ultimately the maximum regioselectivity was achieved by using 0.5% BTTPP; the system was 98% selective for the 1,4-regioisomer. This selectivity is especially high considering solvent was not employed to offer extra control over polymerization.
Figure 25. $^1$H NMR spectra of TEGDPE/DAHP-BPA with varying amounts of BTTPP catalyst: (A) 0.0%, (B) 0.012%, (C) 0.12%, (D) 0.24%, and (E) 0.5% loading. The labels (a) and (a’) denote the protons of the triazole ring for the 1,4- and 1,5-regioisomer, respectively, while the solvent peaks are marked with asterisks (*).
Figure 26. $^1$H NMR spectra of TEGDPE/DAHP-BPA with varying amounts of CEH catalyst: (A) 0.0%, (B) 0.01%, (C) 0.1%, (D) 0.2%, and (E) 0.5% loading. The labels (a) and (a’) denote the protons of the triazole ring for the 1,4- and 1,5-regioisomer, respectively, while the solvent peaks are marked with asterisks (*).
The un-catalyzed TEGDP system was found to contain 80% 1,4-regioisomer and 20% 1,5-regioisomer, 8.69 and 8.27 ppm, respectively, a much higher ratio than that found for the TEGDPE/DAHP-BPA system (Figure 27). When employing 0.1 mol % CEH catalyst that ratio was found to increase slightly to 89:11, and at 0.5 mol % BTTPP loading that ratio increased again to 93:7. From these results it is difficult to determine whether the catalyzed reaction is dominant over the thermal reaction. However, more insight can be gained by studying the kinetics of the reaction, which will be discussed in detail later. What can be concluded is that the DAHP-BPA/TEGDP system is thermally regioselective, as compared to the DAHP-BPA/TEGDPE system. The high thermal regioselectivity of the un-catalyzed system is indicative of the molecular orbitals involved in the 1,3-dipolar addition between TEGDP and DAHP-BPA. The Huisgen 1,3-dipolar cycloaddition is a concerted process where the highest occupied molecular orbital (HOMO) of one component reacts with the lowest unoccupied molecular orbital (LUMO) of the second component. Of the two possible combinations, the one with the smaller energy gap becomes the dominant reaction pathway. Generally, the energy difference between the two possible HOMO and LUMO combinations for the 1,3-dipolar cycloaddition of an azide to an alkyne is negligible, leading to little or no regioselectivity. This was observed for the un-catalyzed TEGDPE system, where the ratio of the two regioisomers was ca. 1:1. However, regioselectivity can be altered through the use of catalyst, ring strain, appropriate solvents, and by manipulating the electronic character of the azide and the alkyne groups. TEGDP contains an electron-withdrawing ester group adjacent to the alkyne, causing the system to favor the azide-HOMO controlled reaction and the 1,4-regioisomer. In an attempt to move away
from copper catalyst, particularly for electrical, optical, and biological applications, many researchers have begun to obtain regioselective Huisgen 1,3-dipolar cycloadditions through alternative means.\textsuperscript{74,75,79,80}

![Figure 27. \textsuperscript{1}H NMR spectra of TEGDP/DAHP-BPA with (A) 0.0% catalyst loading, (B) 0.01% CEH loading, and (C) 0.5% BTTPP loading. The labels (a) and (a’) denote the protons of the triazole ring for the 1,4- and 1,5-regioisomer, respectively, while the solvent peaks are marked with asterisks (*).](image)

**Conclusions**

An azide resin and a series of alkyne crosslinkers and chain extenders were readily synthesized, forming a toolbox of monomers capable of producing systems with a variety of reactivities, thermal properties, and physical properties. Linear systems were initially employed in a proof of concept study where a propargyl and propiolate monomer
were polymerized with DAHP-BPA at elevated temperatures. Linear polymerizations were also used to determine regioselectivity. As mentioned earlier, the thermal reaction tends to produce a 50/50 mixture of the 1,4- and 1,5-regioisomers, while the catalyst controlled reaction is selective for the 1,4-regioisomer. The propiolates were found to be thermally regioselective, favoring the 1,4-regioisomer over the 1,5-regioisomer at a ratio of 4:1. Unfortunately, because the system is thermally regioselective it was difficult to determine if any further increase in regioselectivity, following the addition of catalyst, was significant. Comparatively, the use of copper catalyst clearly increased the regioselectivity of a system employing a propargyl species. The regioselectivity increased from ca. a 1:1 regioisomer ratio for the un-catalyzed system to 50:1, 1,4- to 1,5-regioisomer, for a system employing 0.5 mol % BTTPP. Further information obtained from kinetic analysis will help fully characterize the effect of catalyst loading on propargyl and propiolate systems.
CHAPTER III

KINETICS

Introduction

The two structural building blocks employed, propiolate and propargyl, produced compounds with dramatic differences in reactivity. The initial class of alkyne species studied, the propiolates, was modeled after propellant binders, and was observed to be much more reactive than the propargyl class. This was attributed to the electron withdrawing character of the carbonyl group, which strongly increases the reactivity of the propiolate towards the Huisgen cycloaddition. In early studies, we found that care must be taken when mixing resin systems that consist exclusively or predominantly of propiolate alkynes; mixing more than 2 g of a propiolate/di(3-azido-2 hydroxypropyl) ether of bisphenol-A (DAHP-BPA) system resulted in an uncontrollable exotherm.

Although the propiolate species are too reactive when used as the sole alkyne in a resin system, when combined with the less reactive propargyl species, the reactivity of the system can be fine-tuned. The use of copper catalyst offers a second approach to manipulating the reactivity of the system; copper catalyst has been shown to not only render the reaction regioselective but has also been shown to increase the rate of reaction.

Here we directly compare the kinetics of the two classes of alkynes, propargyl and propiolate, through differential scanning calorimetry and rheological experimentation. The averaged activation energy and the change in activation energy with conversion will be explored through the ASTM E698 and Ozawa isoconversional method, respectively. Finally, effect of copper catalyst, oxidation state, type, and loading levels, is investigated.
Materials

Bromotris(triphenylphosphine)copper(I) (BTPP) and copper(II) ethylhexanoate (CEH) were purchased from Sigma-Aldrich, and used without further purification.

Instrumentation

Thermograms were recorded using a Q200 (TA Instruments) differential scanning calorimeter. The furnace atmosphere was defined by 50 mL/min of nitrogen. Polymer samples ranged from 5-12 mg and were analyzed in standard aluminum crucibles.

Viscosity of the resin system was measured using an ARES (TA Instruments) Rheometer at room temperature (RT) and a frequency of 1 Hz. Samples were loaded onto parallel 25 mm aluminum plates.

Comparison of DAHP-BPA System to Epoxy Standard

Samples were prepared by combining azide-modified epoxy resin DAHP-BPA and polyalkyne crosslinker(s) such that the ratio of azide to alkyne functionality was 1:1 and the total reaction mass was approximately 0.3 g. All systems were mixed for 5 min. Between 5-12 mg of the mixture was then charged to a standard, capped aluminum DSC pan. Once the pans were prepared either a DSC run was immediately conducted or the sample was stored at -10 °C until DSC was conducted. Those samples stored at -10 °C were run within 12 h.

In Figure 28, dynamic DSC scans, conducted at a scan rate of 10 °C/min, compare the curing rate of azide-modified epoxy resin with a representative alkyne of each type: TMBTP (propiolate ester type), TPTM (propargyl ester type), TMPTPE (propargyl ether type), and TPA (propargyl amine type), as well as a commercial aerospace resin system composed of EPON 825 and an amine crosslinker, 4,4’-diaminodiphenyl sulfone (4,4’-
DDS). The significantly higher reactivity of the propiolate type, as compared to the propargyl and the EPON825/4,4'-DDS system, is evident from the earlier (lower temperature) onset of the exothermic curing reaction. The initial propiolate ester exotherm occurred at a relatively low temperature of ca. 18 °C. In comparison, the three propargyl-based crosslinkers showed much lower reactivity and did not begin to exotherm until 75 °C, while the EPON825/4,4'-DDS system did not begin to exotherm until 150 °C. However the EPON825 system does have one advantage over the azide/alkyne systems, a broader exotherm. By spreading the evolved heat over a longer period of time the possibility of an uncontrollable exotherm is reduced, and doing just this is a current goal of the project. For all azide/alkyne polymerizations, the total heat of reaction was approximately the same, ca. 700 J/g. Comparatively the EPON825/4,4'-DDS total heat of reaction was ca. 375 J/g.
Figure 28. Dynamic DSC scans obtained at 10 °C/min (exothermal direction up), comparing the curing profiles of DAHP-BPA with a representative from each class of alkyne species: TMBTP (propiolate ester), TPTM (propargyl ester), TMPTPE (propargyl ether), and TPA (propargyl amine). The commercial aerospace resin system, EPON 825/4,4’-diaminodiphenyl sulfone is also shown for comparison.

Systematic Comparison of Propargyl and Propiolate

A systematic study was conducted to compare formulations containing varying amounts of propiolate and propargyl species, specifically HDP and DPA. These two alkynes were chosen because they have equivalent molecular weights. The samples were studied by dynamic DSC and though rheological measurements (Figure 29 & Figure 30). A total of 7 systems were investigated, containing relative ratios of DPA/HDP of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100, respectively. All systems were formulated
so that the molar ratio of total azide to total alkyne was 1:1, and the total reaction mass was approximately 0.3 g. HDA, a solid, was first combined with DPA, a liquid, by slightly warming the solution prior to combining with DAHP-BPA. All systems were mixed for 5 min. Between 5-12 mg of the mixture was then charged to a standard, capped aluminum DSC pan. Once the pans were prepared either a DSC run was immediately conducted or the sample was stored at -10 °C until DSC was conducted. Those samples stored at -10 °C were run within 12 h.

The DSC peak exotherm maxima ($T_{\text{max}}$) (Figure 29) shifted from ca. 138 °C for the system containing 100% DPA to ca. 89 °C for the system containing 100% HDP; all systems containing a mixture of the two alkyne species displayed a bimodal thermogram. In addition to the two exotherms observed at ca. 89 °C and 138 °C, a third exotherm was observed at ca. 250 °C for those systems incorporating the HDP alkyne. The exotherm at 250 °C increased as the HDA content increased, and was not observed in the system containing 100% DPA, indicating that HDA cures by a more complex mechanism. Overall, a very high rate of heat release can result in uncontrollable reactions, as seen in some propiolate systems. The bimodal curing profiles displayed by the DPA/HDP mixtures offer a potential solution to this problem by releasing the heat in two fractions.
Figure 29. Dynamic DSC scans obtained at 10 °C/min (exothermal direction up), comparing the curing rates of DAHP-BPA with various blends of DPA and HDP, ranging from 100 % DPA to 100 % HDP.

The same DPA/HDP blends were reacted with DAHP-BPA isothermally at room temperature and viscosity was monitored as a function of time (Figure 30). Viscosity of developing networks was measured using parallel plate rheometry. Uncured resin systems were mixed according to the above DSC specifications and carefully poured onto parallel 25 mm aluminum plates.

For the system containing 100% DPA, viscosity was found to remain relatively constant over the course of the experiment, with no appreciable increase. This indicated that resin compositions consisting of DAHP-BPA and propargyl-type alkynes are shelf-stable for long periods (days) in the absence of catalyst. In comparison the system utilizing 100% HDP was found to vitrify after ca. 600 min. The rheological profiles of
those systems containing a mixture of DPA and HDP fell between these two extremes, predictably in accordance with the propiolate/propargyl ratio.

![Diagram of Viscosity vs. time for mixtures of DAHP-BPA with various DPA/HDP blends](image)

**Figure 30.** Viscosity vs. time for mixtures of DAHP-BPA with various DPA/HDP blends, ranging from 100% DPA content to 100% HDP. Data were collected at 1 Hz and room temperature.

**Catalytic Activity**

Preliminary experiments were conducted on a variety of copper species to determine their ability to function as a catalyst within our neat system. Among the catalysts examined were two cuprous halides, CuCl and CuBr, as well as the coordination compounds, bromotris(triphenylphosphine)copper(I) (BTTPP) and copper(II) ethylhexanoate (CEH) (Figure 31). Samples were prepared by combining azide-modified epoxy resin DAHP-BPA and polyalkyne crosslinker(s) such that the ratio of azide to alkyne functionality was 1:1. The catalyst was first mixed with the alkyne component
before DAHP-BPA was added to the system. All systems were mixed for 5 min. For DSC studies, 5-12 mg of the mixture was charged to a standard, capped aluminum DSC pan. Once the pans were prepared either a DSC run was immediately conducted or the sample was stored at -10 °C until DSC was conducted. Those samples stored at -10 °C were run within 12 h.

![Chemical structures](image)

bromotris(triphenylphosphine)copper(I)  copper(II) ethylhexanoate

*Figure 31.* Coordination compounds bromotris(triphenylphosphine)copper(I) (BTTPP) and copper(II) ethylhexanoate.

The simple cuprous salts CuBr and CuCl were found to be immiscible within a system composed of DAHP-BPA and TPTM, both by visual inspection and through DSC analysis. There was no measured difference in $T_{max}$, catalyzed or un-catalyzed for those systems employing either CuBr or CuCl at loading levels up to 3.0 mol %. It was anticipated that the coordination complex, bromotris(triphenylphosphine)copper(I) (BTTPP) would be more miscible with our system due to the aromatic hydrocarbon nature of the triphenylphosphine ligands. BTTPP is widely used in CuAAC reactions in solution, and was also employed by Kessler\(^{11}\) in their bulk kinetic analysis. BTTPP was soluble within a system composed of DAHP-BPA and either TEGDP or TEGDPE.
Furthermore, BTTPP was found to reduce the $T_{\text{max}}$ by ca. 70-80 °C at 0.2 mol % loading. Unfortunately at higher loadings, 0.1 mol % and greater, bubbles formed during bulk polymerization. This could be problematic during the fabrication of composite parts where bubbles and voids are detrimental to the overall mechanical properties. CEH was also highly soluble within the DAHP-BPA/alkyne system, and was found to reduce the $T_{\text{max}}$ by ca. 30-40 °C at 0.2 mol % loading. Though this catalyst has an oxidation number of II, it is still highly active in the system, indicating in situ reduction. Furthermore, no bubbles were present following bulk polymerization, even at high loading levels.

Glaser Coupling

Cu(I) readily catalyzes the Huisgen click reaction, but Cu(II) presumably does not; however in situ reduction of Cu(II) to create active Cu(I) has been widely reported in literature. Cupric species are capable of catalyzing oxidative acetylenic coupling, with the Glaser coupling being the most widely known example. Being that terminal acetylenes are a required component of CuAAC reactions, their oxidation is unavoidable, which in turn produces the catalytically active Cu(I) species. In order to investigated the mechanism by which CEH is being reduced and to determine whether or not a propargyl versus propiolate species is more effective at reducing a copper(II) through Glaser coupling, TEGDPE and TEGDP were combined with 0.1 mol % CEH and were allowed to react at 70 °C for 12 and 2 h, respectively. These conditions were chosen in order to mimic the bulk polymerization conditions used in the regioselectivity study. Two additional systems were subjected to the heat profiles, but in the absence of catalyst, to act as controls.
During Glaser coupling the alkyne protons are lost, and it follows that if coupling were occurring in appreciable amounts one would expect a loss in relative concentration of that proton. By NMR no difference was found between the initial concentration of alkyne protons to the concentration found after exposure to heat and catalyst (Figure 32). This finding held true for both the catalyzed TEGDPE and TEGDP systems, and the controls. These results suggest that neither species is effective at initiating Glaser coupling, and therefore reduction must be occurring by a different mechanism.

Figure 32. $^1$H NMR spectra of pure TEGDPE and TEGDP compared to spectra of the same compounds after heating at 70° C for 12 and 2 h, respectively, in the presence of 0.1 mol % CEH catalyst. These conditions were chosen to mimic neat polymerization conditions. Ultimately no appreciable amount of Glaser coupling was detected; the relative concentration of alkyne protons remained constant.
Average Activation Energy as Determined by the ASTM E698 Method

The ASTM E698 method\textsuperscript{63} was applied to DAHP-BPA resin/alkyne crosslinker formulations derived from eleven alkyne crosslinker types, excluding \(N,N,N',N'\)-tetra propargyl benzene diamine (TPBDA) and propiolate ethoxylated pentaerythritol (PEP). This method is based on the variable program rate method of Ozawa, which requires three or more experiments at different heating rates, typically between 1 and 20 °C/min. The Ozawa approach assumes Arrhenius behavior, and that the extent of reaction at the peak exotherm is constant and independent of heating rate. Typical dynamic DSC curves are shown in Figure 33, and it can be seen that peak temperature, \(T_{\text{max}}\), shifts to higher temperatures as the heating rate, \(\beta\), is increased.

Samples were prepared by combining azide-modified epoxy resin DAHP-BPA and polyalkyne crosslinker(s) such that the ratio of azide to alkyne functionality was 1:1. All systems were mixed for 5 min. For DSC studies, 5-12 mg of the mixture was charged to a standard, capped aluminum DSC pan. Once the pans were prepared either a DSC run was immediately conducted or the sample was stored at -10 °C until DSC was conducted. Those samples stored at -10 °C were run within 12 h. Each sample was equilibrated in the DSC for 2 min at 0 °C and then heated to 300 °C at a pre-determined heating rate, \(\beta\). Each formulation was analyzed at five heating rates (\(\beta = 2, 5, 10, 15, \text{and} 20 \, ^\circ\text{C/min}\)), and each formulation/heating rate combination was analyzed in duplicate. A follow-up dynamic scan was conducted at 10 °C/min to ensure that there was no residual exotherm and that the curing reaction had gone to completion. The maximum exotherm temperature, \(T_{\text{max}}\), was determined for each run from curves similar to those in Figure 33. Linear plots of \(\ln(\beta)\) versus \(T_{\text{max}}^{-1}\) were then constructed and used to calculate \(E_a\) from the
slope (Figure 34 & Figure 35). For all samples the linear fit coefficient of determination (R²) was greater than 0.99. The kinetic values determined by the ASTM E698 method are tabulated in Table 3.

*Figure 33.* Dynamic DSC curves for the DAHP-BPA/TEGDPE system at heating rates of 2, 5, 10, 15, and 20 °C (exothermal direction up). The exotherm temperature maxima, \( T_{\text{max}} \), and \( \Delta H \) were determined.
Table 3

*Activation Energies and Other Kinetic Parameters by the ASTM E698 Method*

<table>
<thead>
<tr>
<th>Alkyne</th>
<th>$E_a$ (kJ/mol)</th>
<th>Avg ΔH (J/g)</th>
<th>Avg ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Propiolate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMBTP</td>
<td>69.2</td>
<td>-662.8±58.7</td>
<td>-213±19</td>
</tr>
<tr>
<td>HDA</td>
<td>70.0</td>
<td>-602.7±52.4</td>
<td>-195±17</td>
</tr>
<tr>
<td>TEGDGP</td>
<td>72.3</td>
<td>-651.6±8.1</td>
<td>-236±3</td>
</tr>
<tr>
<td>TMPTP</td>
<td>73.6</td>
<td>-851.1±10.2</td>
<td>-264±3</td>
</tr>
<tr>
<td>2. Propargyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPA</td>
<td>82.3</td>
<td>-775.3±20.7</td>
<td>-242±6</td>
</tr>
<tr>
<td>TMPTPE</td>
<td>82.5</td>
<td>-809.4±26.2</td>
<td>-248±8</td>
</tr>
<tr>
<td>TEGDPE</td>
<td>83.3</td>
<td>-704.2±6.4</td>
<td>-249±2</td>
</tr>
<tr>
<td>TPEDA</td>
<td>84.3</td>
<td>-926.1±35.3</td>
<td>-246±9</td>
</tr>
<tr>
<td>TPA</td>
<td>84.7</td>
<td>-956.4±42.9</td>
<td>-245±11</td>
</tr>
<tr>
<td>TPEDEA</td>
<td>85.9</td>
<td>-824.8±7.7</td>
<td>-238±2</td>
</tr>
<tr>
<td>TPTM</td>
<td>86.4</td>
<td>-737.4±9.7</td>
<td>-237±3</td>
</tr>
</tbody>
</table>
Figure 34. Ozawa plots of \( \ln(\beta) \) versus \( 1000/T_{\text{max}} \) for the propiolate class of alkynes. For all samples the linear fit coefficient of determination \( (R^2) \) was greater than 0.99.

Figure 35. Ozawa plots of \( \ln(\beta) \) versus \( 1000/T_{\text{max}} \) for the propargyl class of alkynes. For all samples the linear fit coefficient of determination \( (R^2) \) was greater than 0.99.
As expected, a propiolate compound, TMBTP, was determined to have the lowest averaged $E_a$ (69.2 kJ/mol) of all crosslinkers studied. Furthermore all propiolate-based crosslinkers displayed a similar averaged $E_a$, with values ranging from 69.2 to 73.6 kJ/mol. In contrast, TPTM crosslinker, a propargyl type, displayed the highest averaged $E_a$, 86.4 kJ/mol. All of the propargyl-type structures displayed relatively high values ranging from 82.3 to 86.4 kJ/mol. Although a distinct divide was evident between the propiolate and propargyl crosslinkers, no significant difference in $E_a$ was observed among the propargyl ether, propargyl amine, and propargyl ester subdivisions.

The normalized, total enthalpy of reaction, $\Delta H'$, was also determined for all systems by integration of the dynamic DSC peaks for each scan rate, and the taking the average of the ten runs (five scan rates in total were used for each formulation, and each scan rate was run in duplicate). The $\Delta H'$ values ranged from -195 to -264 kJ/mol. Determination of $\Delta H$ suffers from higher error, due in part to baseline selection and baseline irregularities, as compared to $T_{max}$ which is not significantly affected by baseline shifts. In general the determined $\Delta H'$ were within the predicted $\Delta H'$ range for the Huisgen 1,3-dipolar cycloaddition, -210 and -270 kJ/mol. These numbers indicate that the Huisgen reaction is extremely exothermic among organic reactions generally.

Kinetic Effect of Catalyst Loading as Determined by Isoconversional Analysis

TEGDP and TEGDPE were chosen as di-functional representatives of the two classes of alkynes for isoconversional kinetic analysis (Figure 36). They have similar molecular weights and their linear structures were expected to yield soluble products, enabling NMR analysis following polymerization. Isoconversional methods, also known as model-free kinetics, are among the few techniques that successfully allow for
characterization of complex systems where an exact reaction model is not known, and are routinely employed in the characterization of network systems.\textsuperscript{54} Here we employ the FWO method to follow the change in activation energy with conversion of the two systems; DAHP-BPA combined with either TEGDPE or TEGDP. Each system was polymerized both with and without catalyst, either BTTPP or CEH.

![Chemical structure](image)

**Figure 36.** Representative systems for isoconversional analysis; the reaction of di(3-azido-2-hydroxypropyl) ether of bisphenol-A (DAHP-BPA) with either tetraethylene glycol dipropiolate (TEGDP) or tetraethylene glycol dipropargyl ether (TEGDPE), both with and without catalyst, either copper(II) ethyl hexanoate (CEH) or bromotris(triphenylphosphine) copper(I) (BTTPP).

Samples were prepared by combining azide-modified epoxy resin DAHP-BPA and polyalkyne crosslinker(s) such that the ratio of azide to alkyne functionality was 1:1. When applicable either CEH or BTTPP was added to the reaction mixture. The catalyst was first mixed with the alkyne component before DAHP-BPA was added to the system. All systems were mixed for 5 min. For DSC studies, 5-12 mg of the mixture was charged to a standard, capped aluminum DSC pan. Once the pans were prepared either a DSC run was immediately conducted or the sample was stored at -10 °C until DSC was conducted. Those samples stored at -10 °C were run within 12 h. Each sample was equilibrated for 2 min at 0 °C and then heated to 300 °C at a pre-determined heating rate, $\beta$. Each formulation was analyzed at five heating rates ($\beta = 2, 5, 10, 15, \text{and } 20 \degree \text{C/min}$), and each
formulation/heating rate combination was analyzed in duplicate. A follow-up dynamic scan was conducted at 10 °C/min to ensure that there was no residual reaction, as noted by lack of residual exotherm. Conversion ($\alpha$) versus temperature plots were constructed from the thermograms and used as the basis for the kinetic analysis. This was done by determining the average total heat of the reaction, $\Delta H'$, for each formulation (average of ten runs), and then calculating conversion, $\alpha$, as a function of cure time, $t$, by taking the ratio between the heat released until time $t$ and $\Delta H'$. For each $\alpha$, a corresponding value for $T$ was extracted and used to plot $ln(\beta)$, versus $T^{-1}$ to determine activation energy as a function of conversion, $E_a(\alpha)$, by the FWO method. Beginning at $\alpha = 0.05$, $E_a$ was determined at 5% conversion increments up to $\alpha = 0.90$, yielding 18 linear plots per system. All plots had a linear fit coefficient of determination ($R^2$) greater than 0.99, with those plots for high conversions suffering from the greatest error. Finally a master plot of $\alpha$ versus $E_a$ was constructed for each system (Figure 37, Figure 38, Figure 40 & Figure 43).

Early isothermal studies employed CEH catalyst at ca. 0.1 mol % loading (Figure 37 & Figure 38). This catalyst was initially chosen because it is highly soluble in the alkyne crosslinkers. Though this catalyst has an oxidation number of II, it is still highly active in the system, indicating in situ reduction. For all four systems, DAHP-BPA combined with TEGDP or TEGDPE, both catalyzed and un-catalyzed, $E_a(\alpha)$ was found to vary with conversion. And as expected, the TEGDP systems were found to have lower $E_a(\alpha)$ than the TEGDPE systems.

There was little difference between the $E_a(\alpha)$ obtained for the un-catalyzed and catalyzed TEGDP systems, as can be seen in Figure 37, with the un-catalyzed system
having a slightly lower $E_a(\alpha)$. For the un-catalyzed TEGDP system, the $E_a(\alpha)$ was found to vary with increasing conversion in the range of 66.0-71.9 kJ/mol by the FWO method. The range of $E_a(\alpha)$ values for the un-catalyzed TEGDP system agreed with the averaged $E_a$ value obtained by the ASTM E698 method, 70.09 kJ/mol. Similarly for the catalyzed TEGDP system, the $E_a(\alpha)$ was found to vary with increasing conversion in the range of 69.7-70.2 kJ/mol. However taking into account experimental error, the two systems essentially had the same $E_a(\alpha)$ values, indicating no catalytic activity. The obtained $E_a(\alpha)$ values are similar to the values reported for the copper/azide catalytic cycle, and the lack of catalytic activity for this particular system may be due to the fact that the catalyst-assisted reaction did not offer a significant energy advantage.

![Figure 37](image-url)  
*Figure 37. Dependency of activation energy on conversion, estimated by the FWO method, for the representative systems, DAHP-BPA/TEGDP with and without 0.1% CEH catalyst.*
For the un-catalyzed TEGDPE system, the $E_a(\alpha)$ was found to vary with increasing conversion in the range of 83.7-97.2 kJ/mol, by the FWO method (Figure 38). The range of $E_a(\alpha)$ values for the TEGDPE un-catalyzed system agreed with the averaged $E_a$ value obtained by the ASTM E698 method, 83.3 kJ/mol. For the catalyzed TEGDPE system, the $E_a(\alpha)$ was found to vary with increasing conversion in the range 82.7-103.2 kJ/mol. The un-catalyzed TEGDPE system behaved similarly to the TEGDP systems, where $E_a(\alpha)$ gradually increased with conversion. However, for TEGDPE there was a significant difference between the $E_a(\alpha)$ profiles of the un-catalyzed and the catalyzed systems; the kinetic profile for catalyzed TEGDPE system was parabolic in shape as opposed to the gradual increase in $E_a(\alpha)$ with conversion. Here too the use of catalyst was found to increase $E_a(\alpha)$. 

Figure 38. Dependency of activation energy on conversion, estimated by the FWO method, for the representative systems, DAHP-BPA/TEGDPE with and without 0.12% CEH catalyst.
To confirm that the lack of catalytic activity observed in the DAHP-BPA/TEGDP system was not due to insufficient catalyst loading, 0.5, and 2.0 mol % CEH loading was employed in a follow up study. Ultimately it was found that at higher catalyst loadings \( E_a(\alpha) \) increased (Figure 40); indicating a possible competitive reaction, such as the formation of dormant oligomeric copper acetylides. \( E_a(\alpha) \) varied in the range of 69.6-88.5 kJ/mol, and 80.84-94.05 kJ/mol, for those systems employing 0.5, and 2.0 mol % CEH, respectively. At the highest loading level, 2.0 mol % CEH, the DSC curves became less Gaussian, with the peak becoming skewed towards the high temperature side (Figure 39). The \( T_{max} \) at 2.0 mol % were found to be ca. 10-20 °C lower than those values obtained for the un-catalyzed system and the systems with 0.1 mol % loading. Although the reaction was initializing at lower temperatures at 2% loading, a larger difference, as compared to the un-catalyzed system, was expected. In comparison, a 10-20 °C reduction in \( T_{max} \) was observed for just 0.2% loading of CEH in a system employing TEGDPE. Ultimately these results demonstrate that the lack of catalytic activity is not due to insufficient loading.
Figure 39. Dynamic DSC curves for the DAHP-BPA/TEGDP system with 2.0 mol % loading CEH (exothermal direction up). A high loading levels the peak becomes skewed towards the high temperature side.
A second follow up study was conducted using the Cu(I) catalyst, BTTPP, to determine whether the abnormal kinetic behavior observed with CEH was due to the use of copper (II) vs. copper (I). It was found that 0.5% copper (I) catalyst loadings also increased $E_a(\alpha)$ (Figure 40). At 0.5 mol % BTTPP loading $E_a(\alpha)$ was found to vary from 72.1 kJ/mol to 85.6 kJ/mol, as compared to 66.0 kJ/mol to 71.9 kJ/mol for the uncatalyzed system. Furthermore, all plots (0%, 0.1% CEH, 2.0% CEH, and 0.5% BTTPP) had the same general shape with the same slope. This indicates that there is no change in reaction mechanism,\textsuperscript{54} i.e. the switch from a catalyst controlled process to a thermally controlled process, as is seen for the TEGDPE system, which will be discussed shortly.

\textit{Figure 40}. Dependency of activation energy on conversion, estimated by the FWO method, for the representative systems, DAHP-BPA/TEGDP with various catalysts.
The lack of catalytic activity is not due to insufficient loading or due to the use of a copper (II) species.

The effect of increased catalyst loading on a DAHP-BPA/TEGDPE system was also investigated. Loading levels of 0.06, 0.16, and 0.22 mol % CEH were employed. With the highest loading level, 0.22 mol % CEH, a second dominating peak (peak [a]) emerges at lower temperatures (Figure 41). It is believed that the new peak is associated with the catalyst controlled reaction, as its presence is dependent on CEH loading, while the original peak (peak [b]) is associated with the thermal process. By analyzing the peak temperatures separately through the use of multiple-peak fitting, two distinct activation energies are obtained from the ASTM E698 method. Peak (a) was found to have an $E_a$ of 112.1 kJ/mol and peak (b) was found to have an $E_a$ of 98.3 kJ/mol (Figure 42). All kinetic profiles were marked by an initial increase in $E_a(\alpha)$ up to ca. 35-40% conversion at which point $E_a(\alpha)$ began to decrease (Figure 43), as was seen in 0.12 mol % loading. The parabolic shape of the kinetic plot was most pronounced for the system employing 0.2 mol % loading. At loading levels of 0.06, 0.16, and 0.22 mol % $E_a(\alpha)$ was found to vary from 93.9 to 90.0 kJ/mol, 91.1 to 118.5 kJ/mol, and 88.39 to 126.7 kJ/mol, respectively. These results are somewhat puzzling as catalyst typically functions by providing an alternative reaction pathway with a lower activation energy, and the lack of activity cannot be explained through an insufficient energy advantage. Here, although there is a perceived reaction rate increase, $E_a(\alpha)$ is calculated to increase. When employing CEH, the perceived increase in activation energy could be due to the reduction of Cu(II); the activation energy of azide/alkyne reaction was not being measured.
Figure 41. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.2 mol % loading CEH (exothermal direction up). The primary peak (a) has shifted from 145 °C to 100 °C.
Figure 42. Ozawa plots of \( \ln(\beta) \) versus \( 1000/T_{\text{max}} \) for peak (a) and peak (b) evident in the dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.2 mol % loading CEH. For both peaks the linear fit coefficient of determination (\( R^2 \)) was greater than 0.99. The spread between the two plots is attributed to the difference in temperatures at which the peak exotherms occur.
Figure 43. Dependency of activation energy on conversion, estimated by the FWO method, for the representative systems, DAHP-BPA/TEGDPE with various CEH loading amounts, from 0.0% up to 0.22%.

In a similar fashion to the experiments conducted using TEGDP, the copper (I) catalyst BTTPP was employed at various loadings within a DAHP-BPA/TEGDPE system, to determine whether the abnormal kinetic behavior was due to the use of copper (II) vs. copper (I). In this series, the BTTPP loading levels were 0.012, 0.12, 0.24, 0.5, and 1.0 mol %. At higher loading levels (0.12, 0.24 and 0.5%) the DSC curves were found to be non-Gaussian and composed of two overlapping peaks, which have been denoted (a) and (b) (Figure 44). At 1.0 mol % catalyst, the thermogram was composed exclusively of peak (a). Furthermore, as catalyst loading increased, peak (a) became
more pronounced, and at 1.0 % loading the thermogram was composed exclusively of peak (a) (Figure 45 through Figure 49). Kessler observed this same bimodal behavior in a system composed of DAHP-BPA and a bisphenol-E based diene (B/B system).\textsuperscript{11} Interestingly they did not see this behavior in their system composed of DAHP-BPA and a tetraethylene glycol diyne (T/B system), which is structurally very similar to our DAHP-BPA/TEGDPE system.\textsuperscript{11} When the averaged $E_a$ was calculated for the individual peaks by the ASTM E698 method, peak (a) was found to have an $E_a$ of 79.3 kJ/mol and peak (b) was found to have an $E_a$ of 63.4 kJ/mol (Figure 50). These results are counterintuitive, as one would expect peak (a) to have a lower $E_a$ as its presence and size is dependent on catalyst loading; however, similar results were observed by Kessler for their B/B system, where peak (a) was found to have a higher $E_a$ than peak (b), 74.5 and 58.4 kJ/mol, respectively, when 0.6 mol % BTTPP was employed.\textsuperscript{11} These results certainly point to the value in using isoconversional kinetics, as the reduction in $E_a$ is not evident until determined as a function of conversion.

To summarize, $E_a(\alpha)$ was found to vary from 76.1 kJ/mol to 84.4 kJ/mol for 0.012% catalyst loading, 59.5 kJ/mol to 83.4 kJ/mol for 0.12% catalyst loading, 57.9 kJ/mol to 78.3 kJ/mol for 0.24% catalyst loading, 60.6 kJ/mol to 79.3 kJ/mol for 0.5% catalyst loading, and 60.1 kJ/mol to 70.1 kJ/mol for 1.0% catalyst loading, as compared to 80.1 kJ/mol to 107.0 kJ/mol for the un-catalyzed system (Figure 51). For those systems employing either 0.12, 0.24, or 0.5 % catalyst loading, $E_a(\alpha)$ reached a minimum before gradually increasing with conversion. This minimum was reached at approximately 15% conversion for 0.12 mol % catalyst, 35% conversion for 0.24 mol % catalyst, and 55% conversion for 0.5 mol % catalyst. At 1.0% catalyst, $E_a(\alpha)$ gradually...
increased until a maximum was reached at ca. 25% conversion, after which $E_a(\alpha)$ gradually began to decrease, with the lowest $E_a$ being observed at 90% conversion. At the highest catalyst loadings, excessive catalyst may induce a competing reaction pathway, indicated by the initial increase in $E_a(\alpha)$.\textsuperscript{52} A minimum in the $E_a$ vs. $\alpha$ curve was also seen by Kessler et al. for their B/B system, where the conversion at which the minima occurred increased with catalyst loading.\textsuperscript{11} A slope change in the kinetic plot is typically indicative of a change in reaction mechanism; here that mechanism change could be a switch from a catalyst controlled reaction to a thermal reaction.

Figure 44. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.0, 0.012, 0.12, 0.24, 0.5, and 1.0 mol % BTTPP catalyst at a heating rates 10 °C (exothermal direction up), where (a) and (b) denote the overlapping peaks.
Figure 45. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.012 mol % loading BTTPP (exothermal direction up). The low temperature shoulder is not yet visible.

Figure 46. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.12 mol % loading BTTPP (exothermal direction up). A shoulder is beginning to emerge at lower temperatures.
Figure 47. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.24 mol % loading BTTPP (exothermal direction up). The shoulder is now clearly visible at all scan rates.

Figure 48. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.5 mol % loading BTTPP (exothermal direction up). The shoulder is beginning to dominate all thermograms.
Figure 49. Dynamic DSC curves for the DAHP-BPA/TEGDPE system with 1.0 mol % loading BTTPP (exothermal direction up). The shoulder now dominates all thermograms.
Figure 50. Ozawa plots of ln(β) versus 1000/T\textsubscript{max} for peak (a) and peak (b) present in the dynamic DSC curves for the DAHP-BPA/TEGDPE system with 0.12, 0.24, 0.5 and 1.0 mol % loading BTTPP. \(E_a\) could be calculated from any one of the four loading levels, although 0.24 mol % gave the best linear fit with a linear fit coefficient of determination (R\textsuperscript{2}) greater than 0.99. From all four systems \(E_a\) was determined to be 79.3 kJ/mol and 63.4 kJ/mol for peaks (a) and (b), respectively.
Figure 51. Dependency of activation energy on conversion, estimated by the FWO method, for the representative systems, DAHP-BPA/TEGDPE with various BTTPP loading amounts, from 0.0 up to 1.0 mol %.

Conclusions

Propiolate species are much more reactive towards the Huisgen 1,3-dipolar cycloaddition than the propargyl class, as evident by the comparative studies, and determination of $E_a$ by the ASTM E698 method and Ozawa’s isoconversional method. This behavior is due to the electron withdrawing character of the carbonyl group, which strongly increases the reactivity of the propiolate towards the Huisgen cycloaddition. Overall, the propiolate species were found to have $E_a$ in the range of 70-74 kJ/mol; while the propargyl species were found to have $E_a$ in the range of 82-87 kJ/mol. Though the
propiolate species proved too reactive on their own, they could be combined with the less reactive propargyl species to achieve reactivity and physical properties tailored to specific applications. Regardless of chemical structure, all systems studied were very exothermic, between -200 kJ/mol and -260kJ/mol.

In addition to an electron deficient alkyne, catalyst is also capable of increasing the reaction rate. Initially a number of catalysts were screened for activity within our system. Simple copper salts such as CuBr and CuCl were found to be insoluble and therefore ineffective as catalysts. The coordination compounds, BTTPP and CEH, were found to be soluble, effective catalysts and were used for in-depth isoconversional analyses.

Interesting kinetic profiles emerged for both systems, TEGDP and TEGDPE, from the isoconversional studies. For the TEGDP system $E_a(\alpha)$ was found to increase when catalyst was employed, regardless of the concentration of the catalyst or the oxidation state of copper. This is strange behavior as catalysts typically function by offering an alternative reaction pathway with a lower $E_a$. The $E_a(\alpha)$ values obtained for the TEGDP system are similar to the values reported for the copper/azide catalytic cycle, and the lack of catalytic activity for this particular system may be due to the fact that the catalyst-assisted reaction did not offer a significant energy advantage. Unfortunately the regioselectivity, as determined by NMR analysis, cannot confirm this hypothesis as the system is already thermally regioselective.

Comparatively for the TEGDPE system $E_a(\alpha)$ was found to increase when CEH was used and decrease when BTTPP was used. Here the abnormal kinetics observed with CEH could be indicative of an “induction” period, such as the reduction of Cu(II) to
Cu(I); the initial increase in $E_a(\alpha)$ is associated with the reduction of Cu(II), while decrease in $E_a(\alpha)$ is associated with the CuAAC reaction. It is not believed that the behavior is due to the lack of catalytic activity; regioselectivity increases as the loading of CEH increase, a second indicator of catalytic control. Furthermore, in gel point studies discussed later, time to gel was reduced by 20% for a crosslinking reaction at 65 °C when 0.2 mol % CEH was used. For those systems employing BTTPP $E_a(\alpha)$ was found to decrease, and at 0.12, 0.24, and 0.5 % loading levels $E_a(\alpha)$ reached a minimum before gradually increasing with conversion. A slope change in the kinetic plot is typically characteristic of a change in reaction mechanism; here that mechanism change could be a switch from a catalyst controlled reaction to a thermal reaction. Comparatively, at 1.0% BTTPP loading $E_a(\alpha)$ was found to initially increase up to a maximum before decreasing to a $E_a$ value of 60.1 kJ/mol at 90% conversion. This behavior could be indicative of a competitive reaction which is induced at high loading levels. To conclude both CEH and BTTPP are effective catalyst within systems consisting of DAHP-BPA and a propiolate crosslinker, while copper catalyst is ineffective for those systems utilizing propargyl crosslinkers.
CHAPTER IV
THERMAL AND MECHANICAL PROPERTIES

Introduction

Both the reactivity and physical properties of a triazole-cure (azido/alkyne) resin system can be varied by altering the type of alkyne crosslinker employed: propiolate vs. propargyl and aromatic vs. aliphatic. Here we explore the mechanical and thermal properties of a triazole resin system, and determine the effect network structure as a result of catalyst loading on these properties. Tripropargyl amine (TPA) has been identified as an excellent alkyne for large-scale resin mixtures and for the use in fabrication carbon composite materials. Those crosslinkers which are solid at room temperature proved troublesome to mix with the azide-modified epoxy resin, yielding formulated resins with higher than optimal viscosity for easy handling. Furthermore, the susceptibility to hydrolytic degradation of the ester linkage found in the propiolate and propargyl esters was of some concern. A number of the propargyl ether and propargyl amine compounds are liquid, circumventing both issues, including the commercially available TPA. In addition to its lack of ester linkages and low viscosity, TPA has a high functionality to molecular weight ratio which could lead to higher crosslink density. Furthermore, amine based alkynes were favored by Sharpless\(^4\) because amines assist in the production of Cu-acetylide intermediates during CuAAC polymerizations. As one will recall the formation of Cu-acetylide intermediates is a key step in the catalytic cycle.

Elevated temperatures, and not room temperature, will be used to cure the di(3-azido-2 hydroxypropyl) ether of bisphenol-A (DAHP-BPA)/TPA system, and the majority of systems discussed in this section. Though we have identified systems which
cure at room temperature, the propiolates, as currently designed they are too reactive to use on the large scale. Propargyl ethers, esters, and amines are less reactive but require elevated temperature and/or catalyst to achieve full conversion. Room temperature cure is still the ultimate goal of the project, but here we needed to understand the ultimate physical and thermal properties of our system, and the use of elevated cure temperatures is the easiest pathway to that information.

Materials

Copper(II) ethylhexanoate (CEH) and all solvents were purchased from Sigma-Aldrich. TPA was purchased from GFS Chemicals. DERAKANE® 510A-40 was donated by Ashland Chemical. All compounds were used without further purification.

Instrumentation

Dynamic mechanical analysis (DMA) was conducted using a TA Instruments Q800. Sample dimensions were approximately 12 mm by 6 mm by 1.5 mm. Measurements were taken in tensile mode.

Compression tests were conducted according to the ASTM 695-02a method. Cylinders were compressed at a displacement controlled test rate of 1.27 mm/min on a MTS Systems Corporation Model 810 servo-hydraulic universal test frame equipped with a low friction compression sub-press (Wyoming Test Fixtures Model CU-SP). Linear variable differential transformer compression data were recorded from MTS Testworks® software using a MTS 100 kN load cell at a sampling rate of 10 Hz.

Thermograms were recorded using a Q200 (TA Instruments) differential scanning calorimeter. The furnace atmosphere was defined by 50 mL/min nitrogen. Standard capped aluminum crucibles were loaded with 5-12 mg of cured resin, and the samples
were subjected to a temperature ramp of 10 °C/min from 30 °C to 225 °C. The samples were then held at 225 °C for 1 min before ramping 10 °C/min from 225 °C to 30 °C. The entire profile was repeated 3 times. The first cycle determined the extent of cure, and erased thermal history. The second two scans were used to determine the $T_g$ of a fully cured system.

Thermogravametric analysis (TGA) measurements were conducted on a Q50 (TA Instruments) thermogravimetric analyzer. The furnace atmosphere was defined by 60 mL/min nitrogen. TGA samples were prepared by loading a platinum sample pan with 10-20 mg of cured resin. The samples were subjected to a temperature ramp of 10 °C/min from 35 °C to 400 °C. The degradation temperature was determined from the 5% weight loss point.

Tan δ, storage modulus ($G'$), and loss modulus ($G''$) of the developing network were measured by an ARES (TA Instruments) Rheometer equipped with a heating oven set to 65 °C. All tests were conducted in dynamic mode. Uncured resin systems were mixed according to the above specifications and carefully poured onto parallel 25 mm aluminum plates. Initial strain sweeps were made to identify the linear viscoelastic region of the sample. Once the sample showed a linearly viscoelastic response, measurements were made at 0.5, 1.0 and 5.0 rad/s at 0.1% strain using the ARES MultiWave mode. Tests were run every three minutes until the samples were well into vitrification. Gel point ($t_{gel}$) was determined from the $G'/G''$crossover point at 1.0 rad/s.

A CD-1510 Lab Style Drum Winder, with a drum diameter of 18 inches and a drum width of 12 inches, was used to impregnate single fiber tow for the fabrication of carbon fiber composites.
Tan Delta Variation

In addition to reactivity, crosslink density and resulting physical properties can be shifted through selective blending of different alkyne types; in particular, glass transition temperature of the resulting network can be directly affected by incorporation of linear polyethylene glycol-based alkyne species. Figure 52 displays plots of tan δ versus temperature, obtained by DMA, of DAHP-BPA cured with various mixtures of poly(ethylene glycol)-200 dipropiolate (PEGDP) and trimethylolpropane tripropiolate (TMPTP). A total of 5 systems were investigated, containing relative ratios of PEGDP/TMPTP of 100/0, 80/20, 70/30, 60/40, and 50/50. The systems were stirred for 5 min, molded, and allowed to react at 70 °C for 2 h. All systems were formulated so that the molar ratio of total azide to total alkyne was 1:1.

Figure 52. Tan δ vs. temperature of DAHP-BPA cured using various mixtures of PEGDP and TMPTP. Samples were equilibrated and held for 5 min at 35 °C, and then heated at a rate of 2 °C/min to 200 °C.
For each curve, the peak maximum represents the glass transition temperature ($T_g$) of the cured resin at that particular composition. The data show that as the proportion of trifunctional alkyne is increased, the resulting tan δ peak increases. For the system containing 100% PEGDP the tan δ peak was found at 56 °C; while the system containing a 50/50 mixture of the two alkynes was found to have a tan δ peak at 90 °C.

The propiolate esters, due to their high reactivity, and the fact that they are typically solids or high viscosity melts at room temperature, are not always suitable for use as the sole curative in a practical resin formulation. If the desired $T_g$ is below ca. 100-110 °C, we have found that a mixture of a dipropiolate, e.g., tetra(ethylene glycol) dipropiolate, and a tri- or tetrapropargyl ether, e.g., trimethylolpropane tripropargyl ether, produces an excellent formulation for a room temperature or slightly elevated temperature cure. The dipropiolate initiates a linear chain-extension reaction, raising the temperature of the reacting mass without gelation or vitrification, and the rising temperature then activates the slower propargyl ether crosslinking reaction.

Compression Modulus

Compression samples were prepared using DAHP-BPA and TPA; combined so that the ratio of azide functionality to alkyne functionality was 1:1.05. DAHP-BPA and TPA were mixed by hand for approximately 5 min before degassing the solution. Polypropylene 1 ml vials were charged with the resin system, and placed in a room temperature vacuum oven for 45 min. The degassing process was used to minimize the possibility of bubble formation during curing. Next the vials were place in a 60 °C oven for 24 h. The oven temperature was then raised to 135 °C, and the samples were cured for an additional 0.5, 1.0, 2.0, 2.5, or 4.0 h. Five samples were prepared for each curing
schedule. A five percent excess of TPA and an initial low curing temperature were used to prevent excessive loss of the monomer during the curing process, which boils at ca. 80 °C. A second set of samples was prepared with the addition of 0.05 mole percent CEH. CEH was chosen over BTTPP because bubbles tend to form during crosslinking when the later catalyst is used. The catalyzed samples were prepared in the same manner as the un-catalyzed samples and were cured at 60 °C for 24 h, and 135 °C for 0.5, 1.0, 1.5, 2.0, 2.5, or 3.0 h. Again five samples were prepared for each curing schedule. The averaged modulus, strain at yield, stress at yield, and when applicable $T_g$, for each curing schedule are listed in Table 4 and Table 5.

Table 4

*Average Values for Modulus, Stress, Strain, and $T_g$ of the Un-catalyzed DAHP-BPA/TPA Compression Cylinders*

<table>
<thead>
<tr>
<th>Cure time</th>
<th>Avg Modulus (MPa)</th>
<th>Avg Strain @ Yield (%)</th>
<th>Avg Stress @ Yield (MPa)</th>
<th>Avg $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>3580 ± 30</td>
<td>7.43 ± 0.09</td>
<td>136.9 ± 0.8</td>
<td>--</td>
</tr>
<tr>
<td>1 hr</td>
<td>3520 ± 30</td>
<td>7.84 ± 0.03</td>
<td>137 ± 1.0</td>
<td>--</td>
</tr>
<tr>
<td>2 hrs</td>
<td>3540.0 ± 20</td>
<td>8.1 ± 0.1</td>
<td>141 ± 1.0</td>
<td>130.4</td>
</tr>
<tr>
<td>2.5 hrs</td>
<td>3590 ± 60</td>
<td>8.0 ± 0.2</td>
<td>141 ± 1.0</td>
<td>130.0</td>
</tr>
<tr>
<td>4 hrs</td>
<td>3400 ± 170</td>
<td>8.4 ± 0.3</td>
<td>141 ± 1.4</td>
<td>131.3</td>
</tr>
</tbody>
</table>

*T_g values are listed for fully cured systems.*
Table 5

*Averaged Values for Modulus, Stress, Strain, and T_g of the Catalyzed DAHP-BPA/TPA Compression Cylinders*

<table>
<thead>
<tr>
<th>Cure time</th>
<th>Avg Modulus (MPa)</th>
<th>Avg Strain @ Yield (%)</th>
<th>Avg Stress @ Yield (MPa)</th>
<th>Avg T_g (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>3600 ± 100</td>
<td>6.7 ± 0.1</td>
<td>131 ± 1.5</td>
<td>--</td>
</tr>
<tr>
<td>1 hr</td>
<td>3570 ± 50</td>
<td>7.6 ± 0.1</td>
<td>134 ± 1.0</td>
<td>--</td>
</tr>
<tr>
<td>1.5 hrs</td>
<td>3600 ± 70</td>
<td>7.89 ± 0.08</td>
<td>136 ± 1.5</td>
<td>--</td>
</tr>
<tr>
<td>2 hrs</td>
<td>3540 ± 20</td>
<td>7.7 ± 0.2</td>
<td>135 ± 1.0</td>
<td>129.4</td>
</tr>
<tr>
<td>2.5 hrs</td>
<td>3540 ± 20</td>
<td>7.7 ± 0.2</td>
<td>137 ± 1.5</td>
<td>128.9</td>
</tr>
<tr>
<td>3 hrs</td>
<td>3520 ± 20</td>
<td>7.72 ± 0.08</td>
<td>135.9 ± 0.8</td>
<td>128.2</td>
</tr>
</tbody>
</table>

*T_g values are listed for fully cured systems.

The stress/strain curves for both the uncatalyzed and catalyzed DAHP-BPA/TPA systems exhibited strain softening, *i.e.*, a characteristic decrease in stress after the yield point (Figure 53 & Figure 54). Stress was found to drop by ca. 10 MPa (7%) for both systems. The average modulus values for the two systems were also found to be very similar, in the range of ca. 3500 MPa. For example, the modulus value found after a 2 h cure at 135 °C for the uncatalyzed and catalyzed systems was 3540 MPa. These data demonstrate that regiospecificity of the azide/alkyne linkage does not affect the compression strength of the cured matrix. The uncatalyzed system contained approximately equal amounts of the kinked 1,5-regioisomer and the more linear 1,4-regioisomer, while the catalyzed system contained predominantly the 1,4-regioisomer. It was thought that the 1,4-regioisomer would have a higher modulus; it
was hypothesized that the linear structure would be better at distributing load. However, the catalyzed system consistently displayed a lower strain at yield than the un-catalyzed system, at the same cure schedule, though the resulting values are within experimental error (Figures 55 through Figure 58).

Figure 53. Stress/strain curve for un-catalyzed DAHP-BPA/TPA compression cylinders cured at the elevated temperature of 135°C for varying amounts of time. Cylinders were compressed at a displacement controlled test rate of 1.27 mm/min.
Figure 54. Stress/strain curve for catalyzed DAHP-BPA/TPA compression cylinders cured at the elevated temperature of 135°C for varying amounts of time. Cylinders were compressed at a displacement controlled test rate of 1.27 mm/min.
Figure 55. Direct comparison of modulus data collected for the uncatalyzed and catalyzed DAHP-BPA/TPA system cured at the elevated temperature of 135°C for 0.5 hours.

Figure 56. Direct comparison of modulus data collected for the uncatalyzed and catalyzed DAHP-BPA/TPA system cured at the elevated temperature of 135°C for 1.0 hour.
Figure 57. Direct comparison of modulus data collected for the uncatalyzed and catalyzed DAHP-BPA/TPA system cured at the elevated temperature of 135°C for 1.5 hours.

Figure 58. Direct comparison of modulus data collected for the uncatalyzed and catalyzed DAHP-BPA/TPA system cured at the elevated temperature of 135°C for 2.0 hours.
The DAHP-BPA/TPA systems, both catalyzed and un-catalyzed, were compared to two industry-standard resin systems, DERAKANE® epoxy vinyl ester resin and EPON-825 cured with 4,4'-diaminodiphenyl sulfone (4,4'-DDS) resin (Figure 59 through Figure 62). DERAKANE® 510A-40 was combined with 1.0 weight percent methyl ethyl ketone peroxide and 0.2 weight percent cobalt naphthenate (6%), and allowed to cure for 24 h at room temperature, while the EPON-825/4,4'-DDS samples were prepared by combining epoxy and amine in a ratio of 2:1 (mol:mol) and curing at 125 °C for 5 h and 200 °C for 2 h. Following compression testing, the triazole systems were found to display a higher modulus than both the EPON-825/4,4'-DDS system and the DERAKANE® system. The higher modulus achieved by the DAHP-BPA/TPA systems could be due to the additional aromaticity introduced by triazole ring formation, or perhaps the DAHP-BPA/TPA systems display higher densities than the two industry standards. The strain at yield for both DAHP-BPA/TPA systems, cured at 135 °C for 2.0 h, was slightly lower than the strain at yield for EPON-825/4,4'-DDS, but higher than the DERAKANE® system. Finally the stress at yield for the DAHP-BPA/TPA systems was found to be comparable to EPON-825/4,4'-DDS, and higher than DERAKANE®. Overall the results indicate that the mechanical properties of the DAHP-BPA/TPA system are comparable to the EPON-825/4,4'-DDS system, and superior to the DERAKANE® system (Table 6).
Figure 59. Comparison of stress/strain curves for industry standards EPON 825/4,4'-DDS and DERAKANE®, to those plots obtained for the uncatalyzed and catalyzed DAHP-BPA/TPA systems cured at 135° C for 2.0 h.

Figure 60. Zone I comparison of stress/strain curves for industry standards EPON 825/4,4'-DDS and DERAKANE®, to those plots obtained for the uncatalyzed and catalyzed DAHP-BPA/TPA systems cured at 135° C for 2.0 h.
Figure 61. Zone II comparison of stress/strain curves for industry standards EPON 825/4,4'-DDS and DERAKANE®, to those plots obtained for the uncatalyzed and catalyzed DAHP-BPA/TPA systems cured at 135° C for 2.0 h.

Figure 62. Zone III comparison of stress/strain curves for industry standards EPON 825/4,4'-DDS and DERAKANE®, to those plots obtained for the uncatalyzed and catalyzed DAHP-BPA/TPA systems cured at 135° C for 2.0 h.
Table 6

Modulus, Stress at Yield, and Strain at Yield for DAHP-BPA/TPA,\textsuperscript{a} EPON 825/4,4’-DDS,\textsuperscript{b} and DERAKANE\textsuperscript{c}® Resin Systems

<table>
<thead>
<tr>
<th></th>
<th>Modulus (MPa)</th>
<th>Strain at Yield (%)</th>
<th>Stress at Yield (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAHP-BPA/TPA cat</td>
<td>3540</td>
<td>7.8</td>
<td>135</td>
</tr>
<tr>
<td>DAHP-BPA/TPA</td>
<td>3540</td>
<td>8.2</td>
<td>141</td>
</tr>
<tr>
<td>EPON 825/4,4’-DDS</td>
<td>2900</td>
<td>10.3</td>
<td>145</td>
</tr>
<tr>
<td>DERAKANE®</td>
<td>3000</td>
<td>4.5</td>
<td>80</td>
</tr>
</tbody>
</table>

\textsuperscript{a}cured at 65°C for 24 h and 135°C for 2.0 h, \textsuperscript{b}cured at 125°C for 5.0 h and 200°C for 1.0 h, \textsuperscript{c}cured at RT for 24 h

Thermal Properties

\textit{DAHP-BPA/Tripropargyl Amine}

Extent of cure and $T_g$ of the DAHP-BPA/TPA system were determined by DSC for the compression samples discussed in the previous section. Sample pans were loaded with 5-12 mg of cured resin and were subjected to a temperature ramp of 10 °C/min from 30 °C to 225 °C. The samples were then held at 225 °C for 1 min before ramping 10 °C/min from 225 °C to 30 °C. The entire profile was repeated 3 times. The first cycle determined the extent of cure and erased thermal history. The second two scans were used to determine the $T_g$ of a fully cured system. A fully cured system was reached after 2 h at 135 °C, as evident by the lack of residual exotherm, and was found to have a $T_g$ of ca. 130 °C, regardless of catalyst loading.

Thermal gravimetric analysis (TGA) was used to determine the degradation temperature ($T_d$) of the cured DAHP-BPA/TPA resin. Approximately 30 mg of sample
was loaded into a platinum TGA pan. The sample was then subjected to a temperature ramp of 20 °C up to 400 °C. The $T_d$ is defined as the temperature at 5% weight loss, and was determined to be ca. 340 °C (Figure 63).

![Graph of degradation temperature](image)

**Figure 63.** Degradation temperature of a DAHP-BPA/TPA resin system. The degradation temperature is defined at 5% weight loss.

Comparing the $T_g$ and $T_d$ values determined for the DAHP-BPA/TPA system to those values obtained by Du et al. for their system composed of $p$-xylene diazide (XDA) and $N,N,N',N'$-tetrapropargyl-$p,p'$-diaminodiphenyl methane (TPDDM), the $T_g$ of DAHP-BPA/TPA is much lower than the $T_g$ of XDA/TPDDM, 130 °C versus 218 °C, while the $T_d$’s are comparable, 340 °C versus 350 °C. The discrepancies in $T_g$ could be due to the aromatic nature of both azide and alkyne monomer employed by Du. Certainly inspiration could be taken from their alkyne component, when designing systems with higher $T_g$s, but as mentioned earlier, because of XDA’s compact structure it cannot be isolated safely, and it would not be practical for scale up or fabrication of large composite
panels. Triazole rings are typically stable up to 400 °C, slightly higher than the reported degradation temperature. The similar $T_d$’s indicate that degradation of both systems initiate at the CH$_2$-N bonds and not within the triazole ring.

**DAHP-BPA/Tripropargyl Trimesate**

A current goal of the project is to raise the $T_g$ of our resin system. One approach, as mentioned above, is to increase the aromaticity of the alkyne components. Tripropargyl trimesate (TPTM) is an aromatic, solid material with a high melting point, and, unfortunately, low solubility in DAHP-BPA. In order for TPTM to dissolve in DAHP-BPA, the system must be heated to 95 °C. At this temperature the system begins to crosslink, leaving a limited time window between achieving a homogeneous system and vitrification. Additionally, following achievement of a homogenous system, if the mixture is exposed to 95 °C for longer than 5 mins, the system tends to exotherm in an uncontrollable manner, producing a hard black foam. Furthermore, because of the above challenges it is very difficult to produce “bubble-free” cylinders.

Fortunately bubbles do not affect DSC measurements, and $T_g$ of the system has been determined. The two components were mixed and heated to 95 °C to achieve a homogeneous sample. The sample was then cured at 75 °C for 2.5 h, 90 °C for 2 h, and 165 °C for 2 h. The system was not immediately cured at 165 °C for fear of an uncontrollable exotherm; this was observed when the system was exposed to 95 °C for too long while mixing. An aluminum DSC sample pan was loaded with 6.4 mg of cured resin, and the sample was subjected to a temperature ramp of 10 °C/min from 30 °C to 225 °C. The sample was then held at 225 °C for 1 min before ramping 10 °C/min from 225 °C to 30 °C. The entire profile was repeated 3 times. The first cycle determined the
extent of cure, and erased thermal history. The second two scans were used to determine
the $T_g$ of a fully cured system. The DAHP-BPA/TPTM system was found to be fully
cured and to have a $T_g$ 10 °C higher than that of the DAHP-BPA/TPA system, 140 °C
versus 130 °C, respectively. This is not quite to the goal of 150 °C, but it does
demonstrate that increased aromaticity raises the $T_g$ of our system.

*DAHP-BPA/N,N,N',N'-Tetra Propargyl Benzene Diamine*

In the above study utilizing TPTM, $T_g$ was found to increase by employing an
aromatic polyalkyne. Unfortunately in order for TPTM to dissolve in DAHP-BPA, the
system must be heated to 95 °C. At this temperature the system begins to crosslink,
leaving a limited time window between achieving a homogeneous system and
vitrification. A second aromatic alkyne, N,N,N',N'-tetra propargyl benzene diamine
(TPBDA) was found to have a lower melting point and higher solubility in DAHP-BPA,
as compared to TPTM. The compound melts at 74-75 °C and is soluble in DAHP-BPA
at 55 °C. This allows for easier molding and handling before the onset of vitrification
and decreases the potential of an uncontrollable exotherm.

Thanks in part to the relatively low solubility temperature, a successful molding
 technique was developed for the DAHP-BPA/TPBDA system. DAHP-BPA was initially
warmed in a 60 °C oil bath, and degassed by applying direct vacuum. Vacuum was then
removed, TPBDA was added, and the system was stirred for 5 min. The warm,
homogeneous system was then pipetted into 1 mL polypropylene vials. During this
pipetting process the system cools and changes from a clear viscous liquid to an opaque
thick paste. The vials were next placed in a vacuum oven heated to 60 °C. The system
was allowed to change back to a clear liquid before pulling vacuum for approximately 45
min. The system was finally cured at 70 °C for 24 h and 160 °C for 2 h. It was found that immediately heating the system to 160 °C caused the system to uncontrollably exotherm.

After curing the system it was noticed that any resin over-spill and the resin found at the top of the molded cylinder, had turned a deep, dark brown. The cured resin found at the bottom of the molded cylinder, that part not exposed to atmosphere, was amber in color. This amber coloration is consistent with cured samples produced from DAHP-BPA/TPA. It seems that the system oxidizes when exposed to high temperature (the dark coloration is not noticed after the 24 h 70 °C cure segment). In fact the starting material, p-phenylene diamine, used in the synthesis of TPBDA, is known to readily oxidize when exposed to atmosphere. Several things can be done to prevent or reduce oxidation. First, it is essential to start with very pure TPBDA that has not been exposed to the atmosphere or light for extended periods of time. Second, the system could be cured under a nitrogen atmosphere. And third, the system could be cured using a temperature ramp. These solution, however, may not be practical for the fabrication of large composite panels; prepreg material, and uncured resin mixtures, would need to be stored under nitrogen, in addition to the curing occurring under nitrogen.

Putting the oxidation issues aside, the $T_g$ of the system is very promising (Figure 64). An aluminum DSC sample pan was loaded with 6.4 mg of cured resin, and the sample was subjected to a temperature ramp of 10 °C/minute from 30 °C to 225 °C. The sample was then held at 225 °C for 1 min before ramping 10 °C/min from 225 °C to 30 °C. The entire profile was repeated 3 times. The first cycle determined the extent of cure, and erase thermal history. The second two scans were used to determine the $T_g$ of a
fully cured system. The DAHP-BPA/TPBDA system was found to be fully cured and to have a $T_g$ 20 °C higher than that of the DAHP-BPA/TPA system, 150 °C versus 130 °C, respectively. This study further demonstrates the value in using aromatic alkynes. However, it may prove difficult to identify a structure which introduces aromaticity, yet remains easy to handle and one that is not susceptible to oxidation. Perhaps TPBDA and TPA could be used in tandem, so as to prevent an excess increase in the overall viscosity, and to help limit oxidation.

![Figure 64. Determination of $T_g$ for a system composed of DAHP-BPA and TPBDA. The sample was subjected to a temperature ramp of 10° C/min from 30° C to 225° C, was held at 225° C for 1 minute, and then subjected to a second ramp of 10° C/min from 225° C to 30° C. The cycle was repeated 3 times. The first cycle was used to determine the extent of cure and to erase thermal history, and the second and third cycles were used to determine $T_g$.](image)
Gel Point Determination

In order to fully characterize the DAHP-BPA/TPA system, the gel point was determined for a reaction temperature of 65 °C. This temperature was selected to prevent excessive evaporative loss of TPA, which has a boiling point of ca. 85 °C. Samples were prepared in the traditional manner where DAHP-BPA and TPA were combined so that the ratio of azide functionality to alkyne functionality was 1:1.05. DAHP-BPA and TPA were mixed by hand for approximately 5 min before degassing. Both catalyzed and uncatalyzed systems were investigated; when applicable 0.1 or 0.2 mol % CEH was added.

The values of time to gel ($t_{gel}$) were determined from the crossover point of the storage modulus ($G'$) and loss modulus ($G''$) versus time curves at a frequency of 1.0 radian/second and a temperature of 65 °C (Figure 65, Figure 66, & Figure 67). The uncatalyzed system was found to gel at 40,200 s ($\approx 11$ hours), while the catalyzed systems were found to gel at 39,000 s and 32,500 s for 0.1 and 0.2 mol % CEH loading, respectively. The value of $t_{gel}$ was reduced by 15 min when 0.1 mol % catalyst was employed, with the affect being more drastic at 0.2 mol % loading, where $t_{gel}$ was reduced by 2 h. Although catalyst has been shown to be particularly valuable following vitrification, where the small catalyst molecules maintain mobility over the large polymer molecules, here we have demonstrated that catalyst loading can also lead to a reduction in $t_{gel}$. Ultimately loading levels greater than 0.2 mol % will need to be employed if a significant decrease in gel time is desired.
Figure 65. Evolution of the storage modulus ($G'$) and loss modulus ($G''$) for uncatalyzed DAHP-BPA/TPA system at a frequency of 1.0 rad/sec and a temperature of 65° C.

Figure 66. Evolution of the storage modulus ($G'$) and loss modulus ($G''$) catalyzed DAHP-BPA/TPA system employing 0.1 mol % CEH at a frequency of 1.0 rad/sec and a temperature of 65° C.
Figure 67. Evolution of the storage modulus ($G'$) and loss modulus ($G''$) catalyzed DAHP-BPA/TPA system employing 0.2 mol % CEH at a frequency of 1.0 rad/sec and a temperature of 65° C.

Composite Fabrication

Fabrication of Carbon-Fiber Reinforced Composite

Carbon composite panels were fabricated using a system composed of DAHP-BPA and TPA. The two components were mixed at an azide/alkyne ratio of 1:1.05 and diluted with acetone by achieve either 60 or 80 wt % solids. The drum-winder was utilized to impregnate carbon fabric, and a hand layup procedure, 0°- 90° fiber orientation, was used to fabricate the panels.

The first panel was fabricated using the 80 wt % solids solution in acetone. However, when using the drum-winder it was noticed that too much resin was impregnating the fibers. For this reason the second panel was fabricated using the 60 wt
% solids solution. Both panels were cured at 45 °C for 24 h, 60 °C for 10 h, 75 °C for 10 h, and 135 °C for 2 h.

The resin content of the second composite panel was determined using TGA. Approximately 8 mg of composite sample was loaded into a platinum TGA pan. The sample was then subjected to a temperature ramp of 20 °C/min up to 800 °C. The resin content was defined as the total fractional weight loss over the course of the ramp. It was determined that the composite panel was composed of 15 wt % resin and 85 wt % carbon (Figure 68). Unfortunately, the drum winder method does not produce composite materials capable of producing high quality test coupons for mechanical analysis; the fiber orientation is slightly off from zero degrees. However, this endeavor demonstrated the processability of the DAHP-BPA/TPA for the fabrication of carbon composite panels.

![Figure 68. The resin content of the carbon composite panel, defined as the weight loss over the course of the reaction. Temperature was increased at a rate of 20 °C/min up to 800 °C.](image-url)
DAHP-BPA, TEGDP, and propiolate ethoxylated pentaerythritol (PEP), were combined at a theoretical 1:1 azide:alkyne stoichiometric ratio with the two alkynes added in a ratio of 4:1, respectively. The solution was mixed and degassed at room temperature for 5 min. Four sheets of glass fiber weave were cut to dimensions of 3x3 inches. The resin blend was used to make a hand lay-up sample on top of a polyethylene sheet with alternating portions of resin and glass fiber; through this process (alternating the weave pattern of the glass fiber) all four sheets were placed. Then a second polyethylene sheet was placed over the lay-up, and the system was pressed very lightly using a mechanical press. A similar procedure was used to prepare a control composite panel from DERAKANE® 510A-40, formulated with 1.0 weight percent methyl ethyl ketone peroxide and 0.2 weight percent cobalt naphthenate (6%). Both panels were allowed to cure at room temperature for 36 hours. Dogbone samples (ASTM D638-03 Type V) were cut from the panels using a water jet cutter.

Cured thermosets obtained from the azide-modified epoxy resin displayed adhesion to glass fiber that was significantly better than epoxy vinyl ester resin (Figure 69). The DAHP-BPA system shows breakage of the glass fibers directly at the fracture surface with no indication of fiber pull-out, behavior similar to tradition epoxy resins. In contrast, the DERAKANE® shows extensive fiber pull-out and comparatively poor resin/fiber adhesion.
Conclusions

We have demonstrated that our tool box of crosslinkers is not only capable of producing systems with a wide range of reactivities, but also systems with a variety of mechanical and thermal properties. By varying the relative incorporation of an aromatic and an aliphatic alkyne, tan δ increased ca. 35 °C for an azide/alkyne resin mixture containing 50% aromatic crosslinker as compared to a system containing 100% aliphatic crosslinker. This allows for the tailoring of mechanical and thermal properties to a desired application.

If $T_g$s below ca. 100 °C are desired, several room temperature-cure systems have been identified, though care must still be taken when mixing large quantities. One such system composed of DAHP-BPA, TEGDP, and PEP was shown to have enhanced adhesion to
glass as compared to DERAKANE®. However, for these systems to find utility in the fabrication of composite panels for aeronautical applications, formulations that are safe to mix in large quantities and that yield ultimate $T_g$s in the range of 130-150 °C, are required.

Because of its commercial availability, low viscosity and low equivalent weight, TPA was identified as a promising alkyne for the fabrication of large composite panels. Initially the compression modulus of a system composed of DAHP-BPA and TPA, both catalyzed and un-catalyzed and cured elevated temperatures, was determined. With a compression modulus of ca. 3500 MPa the DAHP-BPA/TPA systems were found to have a higher modulus that both industry standards, DERAKANE® epoxy vinyl ester resin and EPON-825/4,4'-DDS resin. $T_g$s of the fully cured systems, both the uncatalyzed and catalyzed systems, were found to be 130.44 °C and 129.36 °C, respectively. Additionally the $t_{gel}$ of the DAHP-BPA/TPA system was studied, both catalyzed and uncatalyzed. The results showed that catalyst levels greater than 0.2 mol % will be required if a significant decrease in gel time is desired.

The $T_g$ displayed by the DAHP-BPA/TPA system was slightly lower than the aerospace target of 150 °C. For this reason the thermal properties of DAHP-BPA cured with two aromatic alkynes, TPTM and TPBDA, were studied. The resulting $T_g$s were found to be 140 °C and 150 °C, for the system employing TPTM and TPBDA, respectively. However both compounds are solids and proved difficult to mix with the already viscous DAHP-BPA monomer. Furthermore TPBDA was found to oxidize at high curing temperatures. It may be challenging to identify a structure which introduces aromaticity, yet remains easy to handle and one that is not susceptible to oxidation.
Perhaps TPBDA and TPA could be used in tandem, so as to prevent an excess increase in the overall viscosity, and to help limit oxidation.

Finally the DAHP-BPA/TPA system was used in the fabrication of composite panels. Although the panels were not sophisticated enough for mechanical testing, the ease of fabrication demonstrated the potential of this novel resin system for use in aerospace and nautical composite applications. Ultimately, the utility of this resin system for composite applications lies not only in the potential for low-temperature-cure, but in the ability to customize the reactivity, thermal properties, and mechanical properties through the use of catalyst and a variety of alkyne crosslinkers.
CHAPTER V
CONCLUSIONS AND FUTURE WORK

With the goal of developing a low-temperature-cure composite resin system, we have designed a modified epoxy resin, derived directly from commercial DGEBA-type resins, e.g., EPON 825, that cures via triazole ring formation (Huisgen 1,3-dipolar cycloaddition reaction) rather than the traditional oxirane/amine reaction. A series of di-, tri-, and tetra-functional alkynes, of various types, including propargyl esters, ethers, and amines, and propiolate esters, were synthesized to serve as chain extenders/crosslinkers for the di(3-azido-2 hydroxypropyl) ether of bisphenol-A (DAHP-BPA) resin.

A distinct divide was evident in the reactivities of the propargyl class and the propiolate class of alkynes, with the propiolates being much more reactive. This enhanced reactivity was attributed to the electron withdrawing character of the carbonyl group, which strongly increases the reactivity of the propiolate towards the Huisgen cycloaddition. Certain propiolate/azide combinations were found to cure at room temperature, but if more than 2 g were mixed an uncontrollable exotherm resulted. It would certainly not be feasible to use these combinations to fabricate the very large composite panels required by marine applications. Though the propiolate species proved too reactive on their own, they could be combined with the less reactive propargyl species to achieve tailorable reactivity. Regardless of chemical structure, all systems studied were very exothermic, between -200 kJ/mol and -260kJ/mol. In fact this behavior represents the greatest challenge of the research, controlling the very exothermic azido/alkyne click reaction.
The enhanced reactivity displayed by the propiolate systems lead to unique kinetic behavior, where catalyst was found to be ineffective by isoconversional analysis; the catalytic pathway did not offer a significant energy advantage. For the systems employing tetraethylene glycol dipropiolate (TEGDP) activation energy as a function of conversion \( E_a(\alpha) \) was found to increase when catalyst was employed, regardless of catalyst concentration or oxidation state. Comparatively for the tetraethylene glycol dipropargyl ether (TEGDPE) system \( E_a(\alpha) \) was found to increase when copper(II) ethylhexanoate (CEH) was used and decrease when bromotrifluoromethyl(triphenylphosphine)copper(I) (BTTPP) was used. Here the abnormal kinetics observed with CEH could be indicative of an “induction” period, such as the reduction of Cu(II) to Cu(I); the initial increase in \( E_a(\alpha) \) is associated with the reduction of Cu(II), while decrease \( E_a(\alpha) \) is associated with the Cu(I) controlled azide/alkyne reaction. It is not believed that the behavior is due to the lack of catalytic activity; regioselectivity increases as the loading of CEH increase, a second indicator of catalytic control. Furthermore, in gel point studies, time to gel was reduced by 20% when 0.2 mol % CEH was used. To conclude both CEH and BTTPP are effective catalyst within systems consisting of DAHP-BPA and a propiolate crosslinker, while copper catalyst is ineffective for those systems utilizing propargyl crosslinkers.

Finally, we have demonstrated that our tool box of crosslinkers is not only capable of producing systems with a wide range of reactivities, but also systems with a variety of mechanical and thermal properties. By varying the relative incorporation of aromatic and aliphatic alkynes both the crosslink density and the resulting glass transition temperature \( T_g \) can be varied. Ultimately formulations that are safe to mix in large
quantities and that yield $T_g$s in the range of 130-150 °C are required in the fabrication of composite panels for aeronautical applications. Because of its commercial availability, low viscosity and low equivalent weight, TPA was identified as a promising candidate. With a compression modulus of ca. 3500 MPa the DAHP-BPA/TPA system was found to have a higher modulus that both industry standards, DERAKANE® epoxy vinyl ester resin and EPON-825/4,4’-DDS resin. Additionally, the DAHP-BPA/TPA system was readily used to fabricate composite panels. Although the panels were not sophisticated enough for mechanical testing, the ease of fabrication demonstrated the potential of this novel resin system for use in aerospace and nautical composite applications.

The majority of the work presented focused on the reactivity of the various alkyne species in combination with DAHP-BPA, both with and without catalyst. Although this specific emphasis area could benefit from more traditional kinetic analysis by spectroscopic methods, the primary focus of future studies should be on the mechanical and thermal properties of crosslinked networks, and on the development of sophisticated composite materials suitable for mechanical testing. Here we changed the crosslinking chemistry only, while maintaining a proven backbone chemistry. It could be assumed that the DAHP-BPA system would display similar mechanical, chemical, and thermal properties to its parent epoxy system. However, as already discussed the compression modulus of the DAHP-BPA/TPA system was higher than the EPON-825/4,4’-DDS system. Work needs to be done in order to understand how the triazole linkages alter the crosslinked network and its resulting properties. This includes determining crosslink density, thermo-oxidative stability, weatherability, chemical resistance, and shrinkage during cure. Additionally, development of B-staged, carbon-filled composites as well as
fully cured carbon-filled composites for mechanical testing is a crucial next step.

Although the azide/alkyne reaction is highly exothermic, it is not exergonic; the reaction has a higher activation energy than the epoxy amine reaction. Currently B-staged epoxy composites have a limited shelf life, even when stored at low temperatures. Propargyls, when combined with DAHP-BPA/TPA, are stable at low temperatures, even room temperature. Their use in fabrication of B-staged composites could lead to materials with a longer shelf life. This project was inspired by the need for ambient cure resin materials, but the azide/alkyne reaction and the resulting triazole linkages may prove to have many advantages in addition to exothermicity.


65. Willer, R. L.; Lin, W.; Baum, K., Final Report for Contracts. In N00014-02-M-0150 (ONR), N68936-02-P-0468 (NAWC), and N00014-03-C-0384 (ONR).


