THE ENGINEERING OF REVERSIBLE THERMOSET RESINS BASED ON THE
REVERSIBLE PHOTODIMERIZATION OF COUMARIN

by

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ABSTRACT

This dissertation details the development of new UV light triggered reversible thermoset polymers utilizing the reversible photodimerization of coumarin. Thermoset polymers like epoxy resins are widely used for their many favorable properties including high dimensional stability, strength, and the ability to be cured from nonvolatile liquid precursors. However, the insolubility and intractability of these crosslinked polymers limit their use in applications where removability and repairability are necessary features. To address this limitation, our research explores the use of coumarin to create thermosets with photo-reversible crosslinks. The molecule coumarin is capable of forming a dimer when exposed to long wavelengths of UV light, and when exposed to short UV wavelengths this dimer is cleaved back into monomeric form, offering a promising way to make or break polymer crosslinks on-demand. In this research, three complementary approaches are taken to create materials that take advantage of three functions provided by coumarin: photodimerization, dimer photocleavage, and dimer thermal cleavage. Special attention is paid to the design of UV-reversible adhesives.

In Chapter 1, a review of coumarin’s fundamental photochemistry is presented, followed by a discussion of how this chemistry can be utilized to engineer light-responsive polymers.

Chapter 2 describes the design, synthesis, and evaluation of a new liquid photocurable resin using coumarin photodimerization. An epoxy-functionalized coumarin monomer was reacted with diamines to produce tetrafunctional precursor materials, leading to a liquid precursor resin that could be photocrosslinked and utilized as a photocurable adhesive. Adhesive strength was shown to increase with exposure time as a direct consequence of photodimerization. Inefficiencies in the network forming ability of the material were studied,
suggesting that photooxidative chain scission and intramolecular dimerization are partly responsible for limiting efficient photocuring of the material.

In Chapter 3, pre-assembled coumarin dimers bearing epoxy groups were used to create resins that could be cured like a conventional epoxy resin. Upon irradiation with 254 nm UV light, the coumarin dimers could be efficiently photocleaved and the thermoset network broken into fragments, yielding a liquid at the surface being irradiated. Irradiation with 254 nm light was demonstrated to release an adhesive bond to a UV transparent substrate within minutes of exposure. The adhesive strengths of these coumarin dimer epoxy resins were comparable to those made with the conventional epoxy resin, diglycidyl ether of bisphenol-a.

In Chapter 4, the thermal cleavage of coumarin dimers and its potential use in reversible thermoset polymers was studied. Coumarin dimers are known to undergo cycloreversion back to monomers at high temperatures, but this has never been studied in detail. Kinetic parameters for the thermal cleavage of syn head-to-head and syn head-to-tail 4-methyl-7-glycidyloxycoumarin dimers were measured, allowing the behavior of materials crosslinked by coumarin dimers to be predicted at high temperatures. The syn head-to-tail dimer was found to be significantly more thermally robust than the syn head-to-head dimer. The epoxy resins developed in Chapter 3 were used to demonstrate that thermal dissociation of coumarin dimers is an effective way to break crosslinks in a thermoset polymer; upon heating the polymer was reverted to liquid, releasing adhesive bonds.
1. Introduction

Thermosetting polymers are a class of materials comprised of a fully crosslinked polymer network.¹ Unlike thermoplastics, their crosslinked structure makes them intractable upon curing; they do not melt when heated, nor are they soluble in solvents. Thermosets are typically made from the reaction of small molecules or oligomers that can be liquid before curing, and this makes them useful in applications such as adhesives, encapsulants, and composite matrices which require liquid precursors free of volatile components. Although the crosslinked structure is useful in permanent applications, it presents difficulties in applications where removability, repairability, and reworkability are necessary features. There has been much interest from researchers in designing materials with the advantages of thermosets, but with properties that can be reversed or modified upon application of some external stimulus. In this dissertation, the reversible photodimerization of coumarin is explored as a means of both making and breaking bonds in a polymer in response to ultraviolet light, allowing the design of thermoset polymers with reversible crosslinks.

There are a number of chemistries researchers have explored that could be used for crosslinks that are reversible in a controlled way. These chemistries require the application of a thermal, chemical, or photochemical stimulus to make or break bonds in a polymer system, and thereby modify structure, induce phase changes, and alter material properties on demand.²⁻⁵
Figure 1.1 – Illustrated structures of a) thermoplastics, comprised of linear chains of repeating units, b) thermosets, comprised of an interconnected network of repeating units, and c) a reversible thermoset with stimuli-responsive reversible crosslinks, capable of being broken into processable fragments.

Thermally responsive polymers utilize chemistry triggered by the addition of heat to a system. For example, the Diels-Alder reaction can be used to form bonds in a polymer which break upon heating above a certain ceiling temperature, but reform upon cooling below it (Figure 1.2a). When the crosslinks of a thermoset are comprised of a diene-dienophile cycloadduct, the thermoset can be reverted to small molecules above the retro-Diels-Alder temperature. Other methods have been used, for example the reversible homolysis of alkoxyamines.
Figure 1.2 – Examples of thermally, chemically, and photochemically responsive reversible covalent bonds. a) Diels-Alder cycloaddition, b) alkoxyamine homolysis, c) disulfide oxidation/reduction, d) reversible hydrazone bond, e) [2+2] photocycloaddition

Chemically responsive materials are designed to change in response to the introduction of a catalyst or reagent. For example, it is possible to create a polymer crosslinked by disulfide bonds, which can be cleaved into two thiol groups upon addition of a reducing agent, and reformed (Figure 1.2c). Materials can be designed which contain crosslinks that cleave upon a change in pH or by introduction of fluoride. These systems have the disadvantage of requiring the addition of some external reagent which may have to diffuse through a solid for full modification of the material, therefore granting limited control of the process. This approach has therefore been widely used in polymer gels, but rarely in solvent-free thermosets.

Using light as a stimulus offers the unique ability to impart change to materials from a distance without contact, and with precise spatial and temporal control. Bonds can be formed
through photoinitiated free-radical mechanisms, as is utilized in commercially important photopolymerizations. However, the formation of reversible covalent bonds suitable for reversible crosslinks can be achieved by photocycloaddition reactions (Figure 1.2c). Molecules including coumarins, cinnamates, anthracenes, thymines, stilbenes, maleimides, and others are capable of undergoing a cycloadditions upon absorption of ultraviolet (UV) light, forming dimers. These photodimers can also often be cleaved upon exposure to shorter wavelengths of UV light. This reversibility is very appealing for polymer scientists interested in creating bonds which can be made and broken on demand.

**Figure 1.3** – The reversible photodimerization of coumarin

In this dissertation, the reversible photodimerization of coumarin, illustrated in Figure 1.3, is investigated as a means of making and breaking bonds in thermoset network polymers. Among photodimerizing molecules, coumarin is particularly appealing for a number of reasons. It undergoes a [2+2] cycloaddition upon exposure to UV wavelengths greater than 300 nm to form a cyclobutane-linked dimer, and this dimer can be symmetrically cleaved upon exposure to short wavelengths less than 300 nm. Unlike cinnamates and stilbenes, the photocleavage reaction is always symmetrical, meaning that the cyclobutane structure cleaves the same way it forms. This gives the system potential for a high degree of reversibility. Unlike thymine, whose photodimerization and photocleavage require short wavelengths under 300 nm, the wavelengths required for coumarin are accessible by common UV lamps. Photodimerization is commonly
performed with 313 nm and 365 nm lines from medium or high-pressure mercury vapor lamps, while photocleavage is performed with the 254 nm line of a low-pressure mercury lamp. The absorption spectrum of coumarin also means that it is unlikely to react unintentionally in the presence of visible wavelengths of light, unlike anthracene whose absorption spectrum approaches visible wavelengths. Coumarin is also appealing from a synthetic standpoint. 7-Hydroxycoumarin, the most widely used starting material, can be readily functionalized for incorporation into polymers by various methods. For these reasons, coumarins have been widely used to impart UV-responsive behavior in polymeric materials. To date, coumarin has been used to create light responsive materials for diverse applications including photoresists, liquid crystal displays, drug delivery systems, hydrogels, self-healing polymers, and materials with tunable viscoelasticity, refractive index, and porosity.

The purpose of this review is to highlight information relevant to the engineering of reversibly crosslinked materials utilizing the reversible photodimerization of coumarin. It begins by covering fundamental photochemistry, covering aspects of photodimerization in greater detail than what is currently available in the literature. The scope of this review is limited to the utilization of [2+2] photocycloaddition of coumarin and photocleavage of coumarin dimers to change material properties. It should be noted that coumarin derivatives have been used in materials for a wide range of other purposes, most notably as dyes for fluorescent labeling, as laser dyes, as emissive components in electroluminescent devices, and as absorbing species in polymers for light-harvesting applications. More recently, coumarin-4-yl methyl ester groups have seen a rise in popularity as UV-photocleavable groups. However, these uses are outside the scope of this review.
1.2 Coumarin Small Molecule Photochemistry

Coumarin photodimerization is one example of a great many possible \([2+2]\) photocycloadditions.\(^{25}\) Coumarin is capable of forming the four isomers shown in Figure 1.4: syn head-to-head, syn head-to-tail, anti head-to-head, and anti head-to-tail. The efficiency of the photodimerization and the dimers which arise depend strongly on the conditions of the photoreaction; they are affected by solvent, concentration, substituents on the molecule, the presence of triplet sensitizers, Lewis acids, and conditions which may cause pre-arrangement of the coumarin molecules such as crystal structure in solid state photoreactions, micellar media, and various supramolecular assemblies. For the purpose of materials design it is very helpful to understand how different isomers can be synthesized; different isomers have different chemical reactivities, as will be discussed in section 1.2.2.2.

![Figure 1.4 - The four possible coumarin dimers](image)

1.2.1 Coumarin Photodimerization

1.2.1.1 History and Mechanism of Coumarin Photodimerization

The photodimerization of coumarin was first discovered by Ciamician and Silber in 1902,\(^{26}\) who isolated the coumarin dimer after irradiation in alcohol solution for nearly one year in sunlight. The cyclobutane structure was first proposed in 1924,\(^{27}\) but it was some time before
the structure could be proved. In 1950 Schönberg et al. proved that the dimer had to have a
cyclobutane structure after showing that 3-phenycoumarin could be dimerized, thus eliminating
any other structural possibilities.28 Anet later determined the structure of the syn head-to-head
dimer by NMR spectroscopy and comparison to cinnamic acid dimers, and synthesized the anti
head-to-tail coumarin dimer from o-hydroxy-trans-cinnamic acid.29,30

Throughout the 1960’s and early 70’s the mechanism of photodimerization was studied.
Schenck et al. first studied the photosensitized dimerization of coumarin.31 They found that
irradiation of coumarin in the presence of the triplet sensitizer benzophenone in ethanol and
especially benzene solutions resulted in efficient formation of anti head-to-head dimer with trace
anti head-to-tail. Syn head-to-head, in contrast, was only formed from sensitizer-free direct
irradiation of coumarin in ethanol. They proposed that sensitized irradiation created a diradical
photoadduct intermediate from which the anti head-to-head dimer arose.

Hammond et al. proposed a simpler mechanism, that syn HH arises from the reaction of
an excited singlet state coumarin with a ground state coumarin and anti HH arises from the
reaction of a triplet state with ground state coumarin.32 This explained why anti HH arises from
triplet sensitization with benzophenone, and was supported by the observation that irradiation
in benzene at low concentration yields anti HH. They observed that anti HH dimer was still
formed with high specificity even when very low concentrations of benzophenone were used
and very little light could be absorbed by benzophenone. To explain this, they proposed a
double energy transfer mechanism where an excited singlet state coumarin transferred energy to
benzophenone, which then underwent intersystem crossing to the triplet state, which could then
excite another coumarin into the triplet state from which an anti HH dimer could form. This
mechanism was later disproven, and this observation is an artifact of the fact that the quantum yield of dimerization without sensitizer is orders of magnitude less efficient than with sensitizer.

The important role solvent plays in the photodimerization reaction was studied in more detail by Krauch, Farid, and Schenck.\textsuperscript{33} They found that syn dimers could only be formed in polar solvents at high concentration (0.5 M), while anti HH was the dominant product at low concentrations (0.01 M) and in nonpolar solvent at any concentration. Additionally, photoreactions performed in frozen solutions of dioxane or acetic acid produced much higher yields of syn HH dimer and total dimer conversion than liquid solutions. These results led them to propose that the product distributions are a result of associations in solution.

In contrast, Morrison et al. proposed that syn dimers proceed from an excited singlet state excimer.\textsuperscript{34} They refuted the hypothesis that ground state associations might be involved, noting that no deviation in Beer’s law could be observed with changing concentration, and showing no evidence of aggregation using vapor pressure osmometry measurements.\textsuperscript{35} They hypothesized that a “heavy atom” effect might result in enhanced intersystem crossing in halogenated solvents and lead to an increase in anti HH formation. Heavy atom solvents did result in a small increase in anti HH dimer formation, but intersystem crossing efficiency was not changed. Instead, the heavy atom solvents appeared to increase the efficiency with which already-formed triplet state coumarins proceeded to form dimers. The position that syn dimers arise from singlet state excimers was supported by the requirement for polar solvent, which would likely stabilize such an excimer.
Since the 1960’s the consensus has been that syn dimers arise from singlet state coumarins and anti dimers arise from a triplet state. In 2004, however, Wolff and Görner made a somewhat provocative proposal that both syn and anti dimers arise from triplet states.\cite{36} If this is true, a number of aspects of the photoreaction remain to be explained, including why anti dimers are markedly preferred when irradiated at low concentrations, why the formation of anti dimers (but not syn dimers) can be selectively quenched by piperylene,\cite{35} why the benzophenone sensitized photoreaction results in such highly selective formation of anti dimers, and the fact that there are no examples of photoreactions in which the yield of syn dimers has been increased by the presence of a triplet sensitizers. The authors suggested that perhaps a higher energy triplet state may be responsible for the formation of syn dimers, but this has not been investigated. Regardless of the multiplicity of the excited state, it is clear that anti dimers arise from a very different state than syn dimers.

The conditions favoring the formation of each dimer for parent coumarin are summarized in Table 1.1.
Table 1.1 – Summary of the four parent coumarin dimer isomers and conditions favoring their formation

<table>
<thead>
<tr>
<th>Dimer</th>
<th>Structure</th>
<th>Conditions</th>
</tr>
</thead>
</table>
| Syn head-to-head       | ![Syn head-to-head Structure](image) | • Direct irradiation in polar (especially protic) solvent at high concentration  
                           • Enhanced at low temperature                                                    |
| Syn head-to-tail       | ![Syn head-to-tail Structure](image) | • Polar solvent at high concentration (minor product)                        
                           • Lewis acid catalyzed photoreaction (major product)                          |
| Anti head-to-head      | ![Anti head-to-head Structure](image) | • Triplet sensitized photoreaction                                           
                           • Nonpolar solvents                                                            |
                           • Low concentrations in polar or nonpolar solvent                           |
| Anti head-to-tail      | ![Anti head-to-tail Structure](image) | • Triplet sensitized photoreaction (trace product)                          |

1.2.1.2 Effect of Triplet Sensitizers

The addition of benzophenone to the photolysis solution results in the efficient and selective formation of anti head-to-head dimer.\textsuperscript{31,32,34,35} The triplet sensitized reaction appears to be more efficient in nonpolar solvents than in polar solvents.\textsuperscript{31,35}

Photodimerization by direct irradiation is a highly inefficient process, due to a very short excited singlet state lifetime ($\tau_s < 0.1$ ns\textsuperscript{37}), and a low quantum yield for intersystem crossing to the longer lived triplet state ($\phi_{isc} = 0.007$ in acetonitrile\textsuperscript{35}). However, benzophenone undergoes highly efficient intersystem crossing ($\phi \approx 1$) and energy transfer to coumarin, raising the quantum yield orders of magnitude. Table 1.2 summarizes data by Hoffman, Wells, and Morrison,\textsuperscript{35} showing the dramatic effect of benzophenone on the reaction.
Table 1.2 – Quantum yields for direct and benzophenone sensitized photodimerization in various solvents with 0.3 M coumarin concentration. Data from Hoffman et al.\textsuperscript{35}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Benzophenone concentration (M)</th>
<th>Dimer quantum yield $\phi_{syn\ HH}$</th>
<th>$\phi_{anti\ HH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>0</td>
<td>$4.4\times10^{-4}$</td>
<td>$4.4\times10^{-4}$</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>0</td>
<td>-</td>
<td>$5.3\times10^{-4}$</td>
</tr>
<tr>
<td>toluene</td>
<td>0</td>
<td>-</td>
<td>$1.5\times10^{-3}$</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0</td>
<td>-</td>
<td>$3.5\times10^{-3}$</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>0.1</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>0.1</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>toluene</td>
<td>0.1</td>
<td>-</td>
<td>0.23</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.1</td>
<td>-</td>
<td>0.30</td>
</tr>
</tbody>
</table>

\subsection*{1.2.1.3 Lewis Acid Catalyzed Photodimerization}

Lewis discovered that Lewis acid complexation of parent coumarin has a remarkable effect on its photodimerization, catalyzing the reaction and causing highly selective formation of the syn head-to-tail dimer.\textsuperscript{38,39} Dimerization proceeds from the reaction of an excited singlet state coumarin-BF$_3$ complex with a ground state noncomplexed coumarin. This was confirmed by the observation that dimerization is most efficient using 0.125 equivalents BF$_3$ relative to coumarin, and that efficiency drops when higher BF$_3$ concentrations are used. When boron trifluoride diethyl etherate is used as the BF$_3$ source, the optimum quantity is about 1 equivalent because the presence of diethyl ether shifts the equilibrium away from the coumarin complex.

The quantum yield of photodimerization is increased from 0.0036 for direct irradiation of a 0.35 M coumarin solution in dichloromethane to 0.81 for 0.4 M solution with 0.05 M BF$_3$. The authors attributed the increase in quantum yield to a longer-lived excited singlet state for the complex, and an increase in the electrophilicity of the excited state. The inefficiency of direct irradiation has been attributed to the presence of a low-lying n, $\pi^*$ state which facilitates rapid
decay of the lowest $\pi, \pi^*$ state. This nonradiative relaxation pathway is eliminated by complexation of coumarin’s carbonyl nonbonding electrons.

The ability of Lewis acids to catalyze photodimerization of other coumarin derivatives has not been widely studied. Shim et al. showed that BF$_3$OEt$_2$ actually decreased the quantum yield of dimerization for 5,7-dimethoxycoumarin, and completely quenched the reaction at high concentrations.$^{40}$ Lewis claimed that the $\pi, \pi^*$ state lies below the $n, \pi^*$ state in this molecule, so the mechanism responsible for the increase in efficiency of parent coumarin would not be relevant.$^{39}$ In contrast, Zhao et al. demonstrated that the BF$_3$ catalyzed photodimerization of 7-allyloxycoumarin results in efficient and selective formation of syn head-to-tail dimer.$^{41}$ This suggests 7-alkoxy substituted coumarins might behave similarly to parent coumarin in this regard, and Lewis acid catalysis may be a useful synthetic tool for the synthesis of dimers of related coumarin derivatives.

In 2008 Wolff and Görner attempted to reinterpret the Lewis acid catalyzed photodimerization of coumarin using their triplet-only hypothesis.$^{42}$ They examined the photodimerization of 6-methylcoumarin and the coumarin analog n-methyl-2-quinolone. Like parent coumarin, complexation with BF$_3$ resulted in increased conversion to syn head-to-tail dimer, but anti head-to-head remained the predominant product.
1.2.1.4 Photochemistry of Substituted Coumarins

![Coumarin Structure]

**Figure 1.6** – The numbering scheme of coumarin

To have some understanding of how coumarins might behave in polymer systems it is important to first understand how substituents affect the photodimerization reaction. Although substituted coumarins have not been studied in as much detail as parent coumarin on a fundamental level, it is clear from the literature that substituents have a dramatic effect on photodimerization. For example, 6-methoxycoumarin has been found to dimerize only from the triplet state to form anti head-to-head dimer,\(^\text{43}\) while 7-methoxycoumarin has been found to dimerize only from the singlet state to form syn head-to-tail as the major product.\(^\text{44}\)

Substitutions at the 3 or 4 position tend to promote formation of head-to-tail dimers. Rao et al. in a study of various 3 and 6 substituted coumarins found that 3-substituted coumarins consistently formed head-to-tail dimers (although they were unable to determine if they were syn or anti dimers).\(^\text{43}\) 4-methylcoumarins, commonly used in many polymer systems, also preferentially form head-to-tail dimers. For example, Chen and Chen performed benzophenone sensitized photoreactions of 7-acetoxycoumarin and 4-methyl-7-acetoxycoumarin in dichloromethane, finding that 7-acetoxycoumarin gave anti head-to-head while 4-methyl-7-acetoxycoumarin gave anti head-to-tail, both in high yield.\(^\text{45}\) Substituents at both 3 and 4 positions, however, appear to inhibit photodimerization.\(^\text{46}\) It seems that electron donating groups at the 3 or 4 position are capable of increasing photodimerization efficiency.
The effect of a 4-methyl group is of particular interest, since 4-methylcoumarins are commonly used in polymer systems. While it is clear that this substituent makes head-to-tail dimers favored under most conditions, there are few studies directly comparing coumarins with and without the 4-methyl group, and its effect on efficiency is not clear. Chen and Chou performed an experiment looking at the photodimerization of 7-propionyloxycoumarin and 7-palmitoyloxycoumarin with and without 4-methyl groups when dispersed in poly(vinyl acetate) films. Analysis of the data shows the results are mixed; 4-methyl-7-palmitoyloxycoumarin dimerized about 170 times faster than 7-palmitoyloxycoumarin, but 7-propionyloxycoumarin dimerized nearly 4 times faster than 4-methyl-7-propionyloxycoumarin. It is likely that the results were due to differences of solubility in the polymer matrix and possibly pre-orientation of the molecules.

The photochemistry of 7-substituted coumarins is especially relevant to polymer applications, since 7-hydroxycoumarin is very widely used as a starting material. 7-Hydroxycoumarin is readily synthesized by Pechmann condensation, and it is easily derivatized for attachment to polymers by ester or alkoxy linkages. 7-Methoxycoumarin (also called herniarin) was found by Leenders et al. to produce 75% syn HT and 25% syn HH when irradiated at the relatively dilute concentration of 0.05 M in dichloromethane. Parent coumarin at this concentration and in this solvent would be expected to form only anti HH dimer. 7-acetoxycoumarin, in contrast, did not dimerize with direct irradiation in DCM in a range of concentrations, but did form anti head-to-head upon benzophenone sensitized irradiation. These results were reproduced by Muthuramu and Ramamurthy, who observed no dimerization from direct irradiation in DCM or from direct or sensitized irradiation in aqueous micellar suspensions. This raises the question of whether coumarins linked to a polymer chain through
a phenyl ester group might photodimerize less efficiently than those connected by an alkoxy group at the 7-position.

A relatively large amount of work has gone into the study of 5,7-dimethoxycoumarin, largely because it is an analog of furocoumarins and displays photobiological activity. Its photodimerization behavior is similar to parent coumarin, showing a preference for syn products in polar solvents and anti products in nonpolar solvent or with photosensitizer. Unlike parent coumarin, however, the predominant dimer when irradiated in polar solvent is syn head-to-tail, with a quantum yield of about 0.07 at 0.1 M in acetonitrile.\(^{50}\)

The photodimerization of 6-methylcoumarin was studied in detail by the group of Wolff.\(^{51}\) In all organic solvents, anti HH was the dominant product. The results were largely similar to what would be expected from parent coumarin, but with a stronger inclination towards anti HH. The fraction of syn products is increased in polar solvents (with the exception of acetone and cyclohexanone, which likely act as triplet sensitizers, and resulted in 100% anti HH), the addition of benzophenone increases yield of anti HH, complexation with BF\(_3\) increases the yield of syn HT (though retaining a large fraction of anti HH), low concentrations favor anti products, and overall yields are increased at low temperatures.

While there is ample evidence showing that a large number of coumarin derivatives are capable of photodimerization, the effect of various substituents on quantum yield is not well understood and remains an opportunity for more research as it might provide one pathway for optimization of coumarin-based light-responsive materials.

1.2.1.5 Solid State Dimerization

Like many other molecules capable of [2+2] photocycloadditions,\(^{52}\) various coumarin derivatives are capable of dimerizing from their crystalline form. The dimerization of 7-
methoxycoumarin was first discovered by accident after crystals were left under ambient lighting, and later this dimer was found to be syn head-to-tail. Parent coumarin does not readily photodimerize when exposed in the crystalline form. Later, Ramamurthy et al. reported their studies of the solid state photodimerization of various coumarin derivatives in a series of papers. Electronic and steric effects on the photoreaction were generally found to be minor compared to crystal structure. 7-acetoxy coumarin, which was previously found to be unable to dimerize from direct irradiation in solution, could be dimerized to syn HH in high yield in the solid state owing to its favorable structure. Generally, dimerization can occur from the solid state from topochemically favorable structures, that is, when the reactive double bonds of coumarin are parallel in the crystal lattice with separation within about 4.2 Å. However, notable exceptions to this rule were found. In 7-methoxycoumarin, for example, the double bonds are rotated 65° away from each other, but dimerization proceeds giving syn HT dimer with high efficiency, indicating a degree of orientational flexibility within the lattice. 4-chlorocoumarin, 4-methyl-6-chlorocoumarin, and 7-methylcoumarin were found to dimerize from non-topochemically favored structures, and likely arose as a result of lattice defects. Solid state dimerization can be a useful tool to synthesize dimers not otherwise accessible by solution state photoreactions, potentially in high yield.

1.2.1.6 Photodimerization with Topochemical Pre-Arrangement

Beyond the arrangement that occurs in a crystal lattice, researchers have also attempted to direct photoreactions via other environments, including micelles and guest-host inclusion complexes.

Micellar systems have been used for regio- and stereoselective control of many photochemical reactions, including photocycloadditions, via pre-orientation of the reactive
species. In the 1980’s Ramamurthy et al. attempted to find a pre-orientational effect on coumarin photodimerization via micelles. A series of coumarins were synthesized with 7-alkoxy groups comprised of a range of alkyl chains and irradiated in micellar systems using sodium dodecyl sulfate. In all cases, no clear effect of the micellar system on the regiochemistry of the photoproducts was observed.\textsuperscript{49,63--65} In 2003, however, Yu et al. found what might be a micelle effect in 6-alkyl coumarins.\textsuperscript{51} Those derivatives with larger alkyl chains appeared to exhibit a preference for both syn and anti head-to-head dimers, however it is not unequivocally a preorientation effect because the 6-alkylcoumarins naturally prefer HH dimers.

The interest in regio and stereoselective control of photodimerization has also led to many investigations of photodimerization in supramolecular guest-host inclusion complexes.\textsuperscript{66,67} Moorthy et al. first studied the photodimerization of coumarins in cyclodextrin guest-host complexes.\textsuperscript{68} Cyclodextrin, a starch-derived cyclic oligosaccharide, is capable of forming complexes with small molecules within the less-hydrophilic center of its ring. Complexes of various coumarin derivatives with $\beta$- or $\gamma$-cyclodextrin were identified, and the resulting photoproducts were strongly dependent on the nature of the complex. Brett et al. studied the photodimerization of coumarins in $\beta$-cyclodextrin, obtaining detailed information about the structure of the complexes.\textsuperscript{69--71} More recently, the group of Sivaguru studied the photodimerization of coumarins confined in cucurbiturils.\textsuperscript{72--75}

Like with solid state photodimerizations, it remains unclear how supramolecular pre-arrangement affects the quantum yield of photodimerization compared to solution state reactions.
1.2.2 Coumarin Dimer Properties

1.2.2.1 Photocleavage of Coumarin Dimers

The photocleavage of coumarin dimers was first reported by Krauch, Farid, and Schenck in their 1966 paper. They observed that exposure through a Solidex glass filter (a borosilicate similar to Pyrex, transparent up to 280 nm) resulted in the splitting of all four coumarin dimers to monomeric coumarin. Since then, coumarin dimer photocleavage has been more extensively studied. In 1972 Hasegawa et al. studied the photocleavage of anti head-to-head coumarin. Exposure to 277 nm light in dilute chloroform solution gave original monomeric coumarin as the sole product. However, exposure of the lactone ring-opened anti HH dimer in alkaline aqueous solution resulted in near quantitative asymmetric photocleavage of the dimer, yielding trans-2,2'-dihydroxystilbene and fumaric acid. Amides and esters of ring-opened syn HH dimer, however, photocleaved both symmetrically and asymmetrically.

In more recent years, the group of Hampp studied the photocleavage of coumarin dimers and applied two-photon excitation to the reaction. Two-photon excitation by a Q-switched 532 nm Nd:YAG laser was effective in causing dimer photocleavage, and this technique can be used to effect photocleavage in materials which would otherwise block short wavelength UV.

The photocleavage of coumarin dimers is efficient, with a quantum yield in the range of 0.15 to 0.3. Quantum yields from the literature are listed in Table 1.3. Photocleavage efficiency does not appear to strongly depend on solvent, but does depend on the dimer. Jiang et al. showed that photocleavage is most efficient for anti HH dimers, followed by syn HH, and then syn HT.
Table 1.3 – Photocleavage quantum yields for coumarin and various coumarin derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dimer</th>
<th>Solvent</th>
<th>Concentration (M)</th>
<th>λ (nm)</th>
<th>( \Phi_{\text{photocleavage}} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coumarin</td>
<td>anti HH</td>
<td>acetonitrile</td>
<td>2x10^{-3}</td>
<td>266</td>
<td>0.21</td>
<td>78</td>
</tr>
<tr>
<td>Coumarin</td>
<td>anti HH</td>
<td>acetonitrile</td>
<td>~3x10^{-3}</td>
<td>280</td>
<td>0.20 ± 0.010</td>
<td>82</td>
</tr>
<tr>
<td>Coumarin</td>
<td>syn HH</td>
<td>acetonitrile</td>
<td>~3x10^{-3}</td>
<td>280</td>
<td>0.171 ± 0.012</td>
<td></td>
</tr>
<tr>
<td>Coumarin</td>
<td>syn HT</td>
<td>acetonitrile</td>
<td>~3x10^{-3}</td>
<td>280</td>
<td>0.151 ± 0.012</td>
<td></td>
</tr>
<tr>
<td>Coumarin</td>
<td>syn HT</td>
<td>CCl₄</td>
<td>-</td>
<td>290</td>
<td>0.15</td>
<td>83</td>
</tr>
<tr>
<td>6-methylcoumarin</td>
<td>anti HH</td>
<td>cyclohexane</td>
<td>-</td>
<td>254</td>
<td>0.28</td>
<td>83</td>
</tr>
<tr>
<td>6-methylcoumarin</td>
<td>anti HH</td>
<td>chloroform</td>
<td>-</td>
<td>254</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>6-methylcoumarin</td>
<td>anti HH</td>
<td>dichloromethane</td>
<td>-</td>
<td>254</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>6-methylcoumarin</td>
<td>anti HH</td>
<td>acetonitrile</td>
<td>-</td>
<td>254</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>6-dodecylcoumarin</td>
<td>anti HH</td>
<td>CCl₄</td>
<td>-</td>
<td>254</td>
<td>0.18</td>
<td>83</td>
</tr>
<tr>
<td>7-(tert-butyldimethylsilyloxy)coumarin</td>
<td>anti HH</td>
<td>acetonitrile</td>
<td>3.6x10^{-4}</td>
<td>266</td>
<td>0.36</td>
<td>79</td>
</tr>
<tr>
<td>7-(3-(tert-butyldimethylsilanyloxy)propoxy)coumarin</td>
<td>anti HH</td>
<td>PMMA</td>
<td>~ 0.1</td>
<td>266</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>7-(3-(tert-butyldimethylsilanyloxy)propoxy)coumarin</td>
<td>anti HH</td>
<td>acetonitrile</td>
<td>3.0x10^{-4}</td>
<td>266</td>
<td>0.16</td>
<td>80</td>
</tr>
<tr>
<td>7-(3-(tert-butyldimethylsilanyloxy)propoxy)coumarin</td>
<td>anti HH</td>
<td>PMMA</td>
<td>~ 0.1</td>
<td>266</td>
<td>0.13</td>
<td></td>
</tr>
</tbody>
</table>

One point which remains unclear is the extent to which exposure to wavelengths causing photocleavage of coumarin dimers can also result in simultaneous photodimerization of monomeric coumarins. This has important implications for the cyclability of materials utilizing dimer photocleavage, but is not well understood.

1.2.2.2 Chemical and Thermal Stability of Coumarin Dimers

One important and often overlooked consideration is that coumarin dimers are reactive. The lactone rings of head-to-head dimers, and especially anti head-to-head are reactive towards nucleophiles. It has long been known that the dimers hydrolyze in alkaline conditions to give diacids, and that the ring-opened syn head-to-head dimer relactonizes readily at room temperature while diacids of anti head-to-head and anti head-to-tail are quite stable and requires dehydration at high temperatures to relactonize. Hasegawa et al. studied the reactivity of
coumarins, finding that both syn and anti head-to-head dimers reacted with amines and alcohols to form amides and esters.\(^\text{84}\)

In their studies of 6-methylcoumarin, the group of Wolff compared the reactivity of syn HH and anti HH 6-methylcoumarin dimers.\(^\text{51}\) The results are summarized in Table 1.4. Anti head-to-head is the least stable, hydrolyzing quickly under acidic and basic conditions, forming esters with alcohols, and degrading on silica gel and alumina chromatographic media. These results appear to be consistent with what has been observed for dimers of parent coumarin and other 6- or 7-substituted coumarins. Syn head-to-tail appears to be the most chemically stable dimer.\(^\text{85}\)

**Table 1.4** – Summary of 6-methylcoumarin dimer reactivity results by Yu et al.\(^\text{51}\)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Syn HH</th>
<th>Anti HH</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% HCl</td>
<td>Stable</td>
<td>56% monoacid</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>60% monoacid</td>
<td>100% diacid</td>
</tr>
<tr>
<td>Water, reflux, 3 hr.</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>MeOH, room temp.</td>
<td>40% monoester, 6% diester</td>
<td>73% monoester, 9% diester</td>
</tr>
<tr>
<td>24 hr (syn HH), 1 hr (anti HH)</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>MeOH, reflux, 2 hr.</td>
<td>62% monoester</td>
<td>100% diester</td>
</tr>
<tr>
<td>Silica gel, ethyl acetate, 1 week</td>
<td>Stable</td>
<td>Mono and diacid</td>
</tr>
<tr>
<td>Alumina, ethyl acetate, 1 week</td>
<td>100% decomposition</td>
<td>100% decomposition</td>
</tr>
</tbody>
</table>

The thermal dissociation of coumarin dimers is another often overlooked behavior. Since the very first studies of coumarin dimers, it has been known that many dimers cleanly dissociate into their respective monomers upon heating to around 200 °C.\(^\text{27,28,46}\)

Similar thermal cleavage occurs in other cyclobutane-linked photodimers and in anthracene dimers,\(^\text{86}\) however this behavior has not been well studied for coumarins. It is not known whether different coumarin dimers possess different thermal stabilities, or whether this
might impact the stability of coumarin-based light responsive materials in use at elevated temperatures or over long periods of time.

Coumarin dimers may also be cleavable in response to mechanical stimuli. In one interesting work, Kean et al. utilized mechanochemical cleavage of coumarin dimers in a polymer. Ultrasonication of a coumarin dimer-containing polymer generated monomeric coumarin which was used as a fluorescent indicator of damage.

1.3 Coumarin in Polymers

Since the last major review of coumarins in polymers by Trenor et al. in 2004, there has been a tremendous rise in interest in adopting photodimerization reactions for photoresponsive materials. Researchers have synthesized a tremendous range of polymers for applications including photoresists, liquid crystal photoalignment, hydrogels, adhesives, self-healing polymers, shape memory polymers, and materials with tunable viscoelasticity, refractive index, and porosity. In recent years, there has been a surge of interest in photodimerization reactions for light responsive micelles and nanoparticles, primarily motivated by interest in developing targeted drug delivery systems. The widespread adoption of controlled radical polymerization techniques such as ATRP have led to new architectures such as block copolymers which self-assemble into micelles.

Most reviews on this topic have followed an application-oriented approach. This section will instead examine the design of photocrosslinkable polymers utilizing coumarin photodimerization, and how design parameters such as composition and architecture influence the properties of the resulting materials.
1.3.1 Effects of Architecture

To generate a photocrosslinkable material, the starting material must have greater than two functional groups capable of forming intermolecular bonds. To accomplish this, researchers have synthesized polymers with coumarin groups as pendants on linear polymer backbones, as endcaps to arms on star and hyperbranched polymers, or as in-chain units within a linear polymer backbone, as illustrated in Figure 1.7.

\[ \text{Figure 1.7} \] – Three common architectures for photocrosslinkable materials; a) a linear backbone with pendant coumarins, b) star polymers with coumarin end caps, and c) polymers with in-chain coumarin groups

1.3.1.1 Linear Polymers with Coumarin Pendants

Of these architectures, the use of coumarin pendants on a linear polymer backbone is by far the most common approach (Figure 1.7a). Coumarin pendants may either be added to a polymer backbone possessing reactive groups, or may be incorporated by copolymerization of a coumarin containing monomer, as is commonly done for vinyl polymers. Radical polymerization of vinyl monomers such as 7-acryloxy coumarin is possible because coumarin’s 3,4 double bond is not particularly reactive during free radical polymerization. Coumarin has been reported to
undergo copolymerization with n-vinyl pyrrolidone\textsuperscript{112} and styrene,\textsuperscript{113} but the reaction is inefficient and only likely to occur in trace amounts.

This architecture was used in the very first photocrosslinkable polymers to utilize coumarin. In the 1960’s Delzenne and Laridon investigated coumarin photodimerization for photoresists.\textsuperscript{88,114} Drawing from the design of the photoresist poly(vinyl cinnamate),\textsuperscript{115} they described the synthesis of poly(7-acryloxy coumarin), it’s copolymer with ethyl acrylate, and their use as photoresists (Figure 1.8a). They also reported a number of hydroxyl-containing polymers, including poly(vinyl butyral) and poly(bisphenol-a-co-epichlorohydrin), which were modified with coumarin acid chlorides to produce polymers with pendant coumarin groups. These polymer films were mixed with Michler’s ketone as a photosensitizer, which was found to reduce the irradiation time required to make the films insoluble. Increasing the concentration of coumarin groups in the polymer was also found to reduce required irradiation time.

![Figure 1.8 – Polymers with coumarin pendants. a) Poly(7-acryloxy coumarin) by Delzene and Laridon\textsuperscript{88,114} b) Coumarin modified polyoxazoline hydrogels by Chujo et al. \textsuperscript{93}](image)

The use of coumarins for photocrosslinking of polymers was not revisited until 1990 when Chujo et al. reported hydrogels from polyoxazolines modified with pendant coumarin groups.\textsuperscript{93} This paper is in many ways foundational to many efforts which would follow. The coumarin modified polyoxazolines were irradiated as films and made insoluble and swellable in
water. Dimer conversion up to 95% could be achieved, and degree of swelling was found to decrease with increasing crosslink density; degree of swelling varied from 1.9 for 14% coumarin substitution to 20.7 for 1% coumarin substitution. Photocleavage of the coumarin dimer crosslinked gel was also demonstrated, resulting in a soluble polymer. However only 55-60% of the dimers reverted to monomer. Similar polymers were later made using anthracene with similar photogelation results, although photocleavage was not investigated and instead a reduction-cleavable disulfide bond was built into the polymer to provide reversibility.116

The length of the pendant group has some influence on photodimerization. Longer spacers between the coumarin group and the main chain tend have been shown to increase the rate of photodimerization,91 likely because they afford the coumarin chromophore greater mobility and opportunity for dimer formation during the limited lifetime of the excited state coumarin.

The use of pendant groups on a linear polymer offers the possibility of highly functional materials with high concentrations of crosslinkable groups. This may be an advantage when photocuring is the principal goal, like in a photoresist. However high concentrations of chromophores come with the tradeoff that UV transmission through the material is limited to thin layers by absorption. There is also the possibility that reversibility of the crosslinks by photocleavage is limited at high concentrations, as will be discussed in section 1.3.5.

1.3.1.2 Star and Branched Polymers with Coumarin End-Caps

In a star architecture, three or more arms radiate outward from a central branching point (Figure 1.7b). The functionality of the precursor is typically well defined, and molecular weights of the arms may range from small molecules to large oligomers. Compared to linear polymers of comparable molecular weight, star polymers tend to have lower viscosities. This may be an
advantage since mobility of the coumarin group is strongly correlated with photodimerization efficiency. Star architectures have been used for applications including shape memory and self-healing polymers. This architecture has also been used in anthracene-containing polymers.\textsuperscript{117}

For example, Banerjee et al. reported an innovative three-armed star polymer of polyisobutylene endcapped with coumarin groups intended for use as a healable sealant material.\textsuperscript{98} Up to 95\% dimerization conversion was possible, and of this 91\% of dimers could be photocleaved back to monomer. Healing ability was only studied on the micro-scale; atomic force microscopy (AFM) was used to make scratches and measure changes in scratch depth after photocleavage and re-photodimerization cycles. Photocleavage of the crosslinked films apparently allowed the material to flow back into the channel made by the scratch, although it is not clear to what extent heating from the UV lamps might have enabled this flow. The polyisobutylene-based polymer was shown to be an excellent gas and water vapor barrier. The polymers were later tested as sealants for encapsulation of organic photovoltaic devices.\textsuperscript{118} Lower molecular weight prepolymers with higher coumarin concentration were found to result in slower degradation in device performance, indicating that higher crosslink densities produced better barrier materials.

\begin{center}
\includegraphics[width=0.7\textwidth]{figure19.png}
\end{center}

\textbf{Figure 1.9} – Four-arm star polycaprolactone by Defize et al.\textsuperscript{102}

Recently, Defize et al. created a shape-memory material from a four-armed star polycaprolactone with 4-methylcoumarin groups end-capping each arm, as illustrated in Figure 1.9.\textsuperscript{102} Films of the polymer were photocured with and without benzophenone as a sensitizer,
which was found to dramatically decrease time required for insolubilization from 360 minutes neat to 30 minutes with 50 mol% benzophenone. Photodimerization in the material was monitored using Raman spectroscopy, reaching conversions up to 94%. However, irradiation with a 256 nm laser only caused up to 50% of dimers to cleave. This group not only found that the photocrosslinked polymer had good shape-memory behavior, retaining a temporary shape by deforming at 60° and cooling, but they were able to alter the permanent shape by photocleaving the coumarin dimer crosslinks and re-crosslinking in a new shape.

1.3.1.3 Coumarin Groups In-Chain

Photocrosslinkable polymers have also been made which utilize coumarin groups within the polymer chain itself (Figure 1.7c). Polymers with this design were first studied only as photoluminescent materials, but later found to be capable of photodimerization.

Nechifor created aromatic polyamides with coumarin units in-chain. Films and solutions of the material did exhibit photodimerization, although relatively slowly. About 60% conversion was reached after 25 minutes exposure to a 500 W high pressure mercury lamp. The rigid nature of the polymer likely slowed the photodimerization. Photocleavage was not attempted, but the strongly UV absorbing nature of the polymer suggests that it was unlikely to be successful.

Joy and coworkers reported polyesters with in-chain coumarin groups substituted at the 4 and 7 positions. Photodimerization of the in-chain coumarin units was observed to occur upon irradiation with 350 nm light, but so was cleavage of the coumarin-4-yl methyl ester. Coumarin-4-yl methyl ester groups are known to cleave upon UV irradiation, and this has been widely used as a photolabile protecting group. With 350 nm irradiation, ester cleavage was slow enough that photodimerization dominated and a crosslinked structure was produced, while
254 nm irradiation resulted in efficient cleavage of both coumarin dimers and the ester as shown in Figure 1.10. Because these polymers contain coumarin groups substituted at the 4 position, it is expected that dimerization would yield predominantly head-to-tail dimers, although this was never confirmed. Subsequent studies examined the kinetics of these processes in more detail.123

![Diagram of polyesters](image)

**Figure 1.10** – Polyesters by Joy et al.121 containing in-chain coumarin groups which undergo both photodimerization and chain scission.

Research by Ling et al. on coumarin-containing polyurethanes offers a comparison between the performance of coumarin pendants with in-chain coumarin groups.96,97 Their first material, structure shown in Figure 1.11a, featured pendant 4-methylcoumarin groups.96 Studying photodimerization/photocleavage in thin films using UV-vis revealed that the polymer had good photodimer reversibility, with up to 80% conversion to dimer upon 350 nm irradiation and return to near original levels of coumarin monomer after 254 nm irradiation. Cut films were able to be re-joined by a cycle of 254 nm irradiation followed by 350 nm irradiation, and the films repaired thusly retained up to 70% their original strength. The group later created another
polyurethane containing in-chain 4-methylcoumarin units rather than pendants (Figure 1.11b) for the purpose of preventing branching and gelation that can arise from the use of the triisocyanate used in the previous work. However, this polymer showed reduced reversibility with only up to 40% of dimers being photo-cleavable, and repaired strengths up to 64% of the original film were achieved after one healing cycle, and much less after multiple repair cycles.

Figure 1.11 – Self healing polyurethanes by Ling et al. a) with coumarin pendants\textsuperscript{96,124} b) with in-chain coumarin groups\textsuperscript{97}

While in-chain coumarin groups can be used for interesting effects, including strong luminescence and polymer chain scission as shown by Joy et al., they generally result in polymers with less efficient photodimerization than pendant groups. The bifunctional nature of the coumarin unit reduces the degrees of freedom available to the chromophore, meaning an excited state coumarin has lower probability of colliding with a ground state coumarin and forming a dimer.

1.3.2 Dimer First – Coumarin Dimers as Polymer Building Blocks

While most materials studied to date contain monomeric coumarins which undergo photodimerization in-situ, research has also investigated materials which utilize an isolated coumarin dimer as a building block for polymers. This approach has the advantage of exploiting the efficient photo-cleavage as a means to break bonds on demand starting from a controlled and
well characterized polymer structure, bonds which have the capability for re-dimerization in a subsequent step. The photocleavage of coumarin dimers is an appealing way to break covalent bonds in polymers because it requires no catalyst or co-reactant, nor does it produce any small molecule byproducts or generate reactive intermediates capable of unwanted side reactions.

1.3.2.1 Polymers from Ring-Opening of Coumarin Dimers

Hasegawa first studied in detail the tendency of the strained lactone rings in both syn and anti head-to-head coumarin dimers to react with nucleophiles. The dimers were found to react with amines and alcohols to form amides, imides, and esters. This reactivity was utilized to create new polyamides from the condensation of the coumarin dimer with various diamines. The reaction of anti head-to-head with diamines produced high molecular weight polymers, but syn head-to-head produced only low molecular weight products due to its lower reactivity and tendency to form imides as well as diamides. Irradiation of ring-opened coumarin dimers with 277 nm light was found to result exclusively in asymmetric photocleavage, and no scission of the polymer chain occurred, as illustrated in Figure 1.12. Similar polymers were also made from anti head-to-head 7-hydroxycoumarin dimer.

The anti head-to-head dimer is also the only coumarin dimer which possesses two enantiomers. The pair was able to be separated and used to synthesize optically active polyamides.

Figure 1.12 – Synthesis and asymmetric photocleavage of polyamides from anti head-to-head coumarin dimer by Hasegawa et al.
1.3.2.2 Materials with Photocleavable Coumarin Dimers

Polymers using non-ring opened coumarin dimers as photocleavable linkages have also been reported. These materials emphasize the utility of the photocleavage reaction.

In 1997 Chen and Chen reported the first and only example of a linear polymer utilizing coumarin dimers as a photocleavable linkage.\textsuperscript{45} They reported the synthesis of photocleavable polyurethanes from anti HH 7-hydroxycoumarin dimer and anti HT 4-methyl-7-hydroxycoumarin dimer reacted with diisocyanates (Figure 1.13a). Photocleavage of the polymers was performed in solution and monitored by UV absorption. Their approach used benzophenone sensitized irradiation to produce anti head-to-head or head-to-tail dimers selectively in high yield, an approach which would later be followed by researchers for other materials.

In 2006 Zhao et al. reported the synthesis of bridged polysilsesquioxane particles utilizing a syn head-to-tail coumarin dimer as the bridging group.\textsuperscript{137} Sol-gel polymerization of the coumarin dimer bridged bistriethoxysilane yielded a gel comprised of spherical nanoparticles. These nanoparticles were found to “melt” upon irradiation with 254 nm light while being observed by SEM, and this was linked to photocleavage of the dimers by UV-Vis and FTIR spectroscopy.

In a subsequent paper\textsuperscript{41}, Zhao noted the important observation that the chemical instability of anti dimers made them unsuitable in this application (see section 1.2.2.2). It was found that only the syn head-to-tail dimer could be easily isolated without degradation during silica column chromatography, and that it was unaffected by aqueous acid used in the sol-gel polymerization. Spin coated films of the bridged polysilsesquioxane were exposed with 254 nm
light to create fluorescent patterns and patterns with varying refractive index, as the photocleavage of coumarin dimers resulted in an increase in refractive index.

![Diagram](image)

**Figure 1.13** – Polymers using pre-assembled coumarin dimers as building blocks. **a)** polyurethanes from anti head-to-head 7-hydroxycoumarin dimer**45**. **b)** Polysilsesquioxanes with syn head-to-tail coumarin dimer bridge**137**. **c)** Coumarin dimer containing PMMA for phototriggered drug release**138**. **d)** Acrylates crosslinked with 7-methacyryloxy coumarin dimer**139**.

Polymers utilizing isolated coumarin dimers have also been investigated as a way to release small molecule drugs. Hampp et al. reported a material using the coumarin dimer as a pendant group along a poly(methyl methacrylate) backbone, with one half of the dimer attached to the polymer and the other half attached to a drug molecule which could be released from the polymer backbone upon photocleavage of the dimer via two-photon excitation (Figure 1.13c).**138**. The group later performed a more fundamental study of the photocleavage of a similar anti head-to-head coumarin dimer, measuring the quantum yield in solution and in films.**80**. From this they were able to estimate the rate of unintentional photocleavage an intraocular lens might experience with exposure to ambient sunlight, finding that 10% unintentional photocleavage of the dimer would take approximately 322 years. This shows the great potential for high selectivity for materials designed to utilize two-photon absorption triggered photocleavage.
Coumarin dimers have also been used as photocleavable crosslinking agents in polymers. The group of Saito described the use of anti head-to-head 7-methacryloyloxycoumarin dimer as a crosslinking agent for acrylate polymers. The crosslinker was synthesized from anti head-to-head 7-hydroxycoumarin dimer using the approach by Chen, and was copolymerized with butyl methacrylate, methyl acrylate, hexyl methacrylate, or ethyl acrylate. Although photocleavage and photodimerization conversions were not measured in absolute terms, exposure to 254 nm light lowered glass transition temperatures from 7% (for hexyl methacrylate) to 26% (for butyl methacrylate), while re-photodimerization increased the Tg’s to about 5% less than their original values. Vicker’s hardness measurements showed that hardnesses were reduced between 10 and 18% after photocleavage and returned to about 92% of their original values after re-photodimerization. These changes allowed healing of scratches in films after a photocleavage and re-photodimerization cycle. A maximum of 5 mol% of the coumarin dimer crosslinker was used, which raises the question of whether greater property changes might be possible in a more highly crosslinked thermoset containing greater concentrations of the photocleavable dimer.

Materials utilizing pre-assembled coumarin dimers as building blocks reveal that photocleavage is a powerful, efficient means of material modification. Selection of the appropriate dimer is important when designing the material; anti dimers are easily synthesized in high yield using sensitized irradiation, but due to chemical instability may be difficult to purify and can undergo unwanted reactions with nucleophiles in later synthetic steps.
1.3.3 Effects of Polymer Composition on Photoresponse

The properties of the polymer backbone to which coumarin groups are attached has a significant influence on the photodimerization reaction, and thus the ability to create efficient photoresponsive materials. The chemical nature of the polymer itself determines factors such as glass transition temperature (\(T_g\)), crystallinity, solubility, UV transmissivity, and susceptibility to photooxidative degradation. A wide range of polymers have been used as the basis for photoresponsive materials, including acrylates, polyesters, polyamides, polyurethanes, polyethers, polysiloxanes, polycarbonates, polysaccharides, polyphosphazenes, poly(ferrocenylsilanes), polybenzoxazines, and many others.

Studies comparing different acrylate copolymers reveal that the mobility of coumarin groups within a polymer plays a crucial role in the efficiency of photodimerization. Chen and Geh produced copolymers of 7-acryloxy-4-methylcoumarin with methyl methacrylate, methyl acrylate, ethyl acrylate, and butyl acrylate. Copolymers of ethyl acrylate and butyl acrylate with low concentrations of the coumarin comonomer produced low \(T_g\) polymers, and that those copolymers with the lowest \(T_g\) photocrosslinked the fastest. Lower \(T_g\)'s are correlated to higher segmental mobility of polymer chains, suggesting that the mobility of coumarin groups in a polymer has a strong influence on photodimerization.

Huyck et al. also performed a study on acrylate copolymers with coumarin pendants. Various acrylate and methacrylate monomers were copolymerized with 10 mol\% hydroxyethyl acrylate, and the copolymers post-functionalized with 7-chlorocarbonylmethoxycoumarin. Those polymers with \(T_g\) below the irradiation temperature (30-40\(^\circ\)) dimerized significantly faster than those with high \(T_g\)’s.
These studies show that mobility of the coumarin chromophore within a polymer environment appears to be the greatest factor affecting the rate of photodimerization. Other factors which may influence photodimerization are less clear. For example, solvent polarity has a strong effect on photodimerization of small molecule coumarins in solution, but it remains unknown whether polarity in a polymeric environment plays any significant role.

The composition of the polymer and its susceptibility to UV degradation is one factor which has been overlooked by many researchers. A successful photoresponsive material must have photodimerization and photocleavage reactions which occur in a time scale faster than unwanted degradation. Chen in one of the early studies of coumarin pendant containing acrylates found evidence of Honda et al., for example, found that their four-armed star poly(n-butyl acrylate) degraded after long UV exposures, with evidence of Norrish type I and II reactions in NMR spectra. Degradation from photolysis or photooxidation has been studied carefully by few researchers in the context of materials photocrosslinked by dimerization, and the competition between photodimerization and degradative processes is not well understood.

1.3.4 Liquid-to-Solid Transitions via Photocrosslinking

The design of polymers capable of undergoing a liquid-to-solid transition by photodimerization of coumarin groups has proven to be a challenge. There are relatively few examples of materials reported to accomplish this. In order to produce a room temperature liquid, a material must not crystallize, must not be glassy, and must have sufficiently low viscosity to allow flow in reasonable time scales. Generally speaking, crystallization can be inhibited by using mixtures of miscible components, such as multiple stereoisomers, constitutional isomers, and varying molecular weights. Non-glassy polymers and pre-polymers
can be made by using groups with high backbone mobility (polydimethylsiloxane, for example) or by the addition of groups which disrupt packing of polymer chains and effectively plasticize the polymer (poly(n-butyl acrylate), for example).

Matsuda et al. created liquid polyesters from ring-opening copolymerization of ε-caprolactone with trimethylene carbonate, which were end-capped with coumarin groups to form bi-, tri-, or tetrafunctional polymers. Here, a liquid photocurable precursor was important because these materials were intended to be used for stereolithographic formation of biodegradable parts. Polycaprolactone is a low T\textsubscript{g} polymer but which crystallizes with a melting point at about 60 °C. The copolymer with trimethylene carbonate effectively inhibits crystallization, resulting in a liquid polymer. Molecular weights ranged from 2200 to 13000, resulting in coumarin concentrations ranging from approximately 0.3 to 0.9 M. The materials were reported to cure into rigid solids. To produce higher functionalities, copolymers were also made using an oligohydroxyethylmethacrylate backbone, but these products were solids unless molecular weights were kept very small. These materials demonstrate that a low T\textsubscript{g}, noncrystallizing polymer backbone can result in liquid coumarin-functionalized materials.

**Figure 1.14** – Liquid polyesters by Matsuda et al., star shaped copolymers of poly(ε-caprolactone-co-trimethylene carbonate), where R is a two, three, or four functional polyol

However, the use of a noncrystallizing, low T\textsubscript{g} polymer backbone does not guarantee a liquid product once coumarins are integrated. Fawcett et al. produced silicones with pendant coumarin groups (Figure 1.15), and found that the addition of the coumarin groups transformed the liquid silicones to thermoplastic elastomers and even brittle solids, depending on the
concentration of coumarin. Coumarin groups were found to form associations within the polymer that served as noncovalent, physical crosslinks. The authors argued this effect was due to 1:1 associations via pi-stacking interactions, rather than phase separation into hard and soft blocks. This shows that strong intermolecular forces can exist between coumarins, and probably especially when the environment is a poor solvent for coumarin, as is likely the case with silicons. Later, photocuring of these materials was also studied, and photodimerization of pendant coumarins caused increases in modulus and tensile strength in all materials with different coumarin concentrations. Although the associations causing the physical crosslinking could have an interesting effect on photodimerization, the irradiations in these experiments were conducted at elevated temperatures in a melt and it is not clear what role they might play. It is possible that these physical associations may be overcome with sufficient dilution, or perhaps by an environment that sufficiently solvates the coumarin groups, but this remains an opportunity for more study.

![Coumarin functionalized polydimethylsiloxanes](image)

**Figure 1.15** – Coumarin functionalized polydimethylsiloxanes by Fawcett et al. Noncovalent interaction of coumarin groups created physical crosslinks that turned liquid silicons into solids.

### 1.3.5 Designing for Photoreversibility

The reversibility of coumarin dimerization is an important issue. In small molecule studies of coumarin dimer photocleavage in solution (see section 1.2.2.1) photocleavage has
been found to proceed in near quantitative yield, but in polymers this is not always the case. Typically, photocleavage results in regeneration of monomeric coumarin groups to between 50 and 90% of the original concentration. The precise reasons why some polymer systems see photocleavage go to high yield, while others photocleave partially remain unclear. Chen first suggested that irradiation with 254 nm light may cause both photocleavage and photodimerization simultaneously,\textsuperscript{141,166} a claim which has been repeated by other authors,\textsuperscript{102} but which has not been proven unequivocally. Such a mechanism appears unlikely considering the quantum yields for photocleavage are orders of magnitude greater than those for photodimerization. Nonetheless, this effect has important implications for the photoreversibility of a polymer crosslinked by coumarin dimers.

For a highly functional polymer such as a linear polymer with a large number of coumarin pendants per macromolecule, incomplete photocleavage might prevent a photocrosslinked material from reverting to an uncrosslinked state. For example, Chujo, Sada, and Saegusa in their study of coumarin functionalized polyoxazoline hydrogels found that irradiation of the gel with 254 nm light did not result in quantitative photocleavage of coumarin dimers, but only reverted 55-60% of dimers to monomer, as measured by UV-vis spectroscopy.\textsuperscript{93} This same behavior was observed when the polymer was embedded in a silica gel matrix.\textsuperscript{167} Those polymers which were photocrosslinked to a high degree by 350 nm irradiation could not be photo cleaved to a soluble form even after long irradiation times with 254 nm light.

From this we see that there is a competition between photocuring ability and photocleavage-induced reversibility. If photocrosslinking is the only concern for the material, then it is desirable to have a highly functionalized polymer so that gelation occurs quickly after a
relatively low conversion. However, if the functionality is too high, and photocleavage is only capable of reverting a fraction of dimers to monomer, then decrosslinking of the polymer may be impossible.

According to Flory the gel point conversion for a thermoset with $f$ number of equally reactive bond-forming functional groups can be predicted by the equation:

$$\alpha_c = \frac{1}{f-1}$$

If the monomer or pre-polymer fragments contain 10 coumarin groups, giving them a functionality of 10, then the material will only cross the gel point and become soluble by photocleavage if less than 11% of coumarin groups are dimer. Therefore, photocleavage must go to at least 89% completion for reversal of the thermoset network. To create an easily reversible thermoset, it is therefore desirable to use a monomer with low functionality.

### 1.3.6 Mechanical Change Through Coumarin Photodimerization

The reversible photodimerization of coumarin has been widely studied in applications like photoresists, hydrogels, light-triggered drug delivery systems, and light-tunable nanoparticles; applications in which the properties modified by photodimerization are primarily related to solubility. However, in recent years it has also begun to be studied as a way of changing the mechanical properties of materials.

One of the first studies to examine the effect of coumarin dimerization on mechanical properties was by Ohkawa et al., who made and tested polypeptide fibers with pendant coumarin groups. Poly(α,L-lysine) and poly(α,L-ornithine) fibers were made, and those with greater coumarin concentrations had greater tensile strength. UV exposure for 30 minutes
increased the strength of the poly(α,L-lysine) fiber by 71%, from 294 MPa to 486 MPa. For the poly(α,L-ornithine), strength was increased by 35%, from 279 MPa to 376 MPa. However, irradiation longer than 30 minutes had a detrimental effect on strength as the polymers degraded. This demonstrated that photocrosslinking can be quite effective at increasing strength and stiffness.

In soft, low T_g polymers, crosslinking by photodimerization most often tends to increase strength and modulus. For example, Fawcett et al. measured the tensile strength of polysiloxanes with pendant coumarin groups. The silicones were identical except for the concentration of coumarin groups, and as expected all materials showed an increase in tensile strength and modulus upon photodimerization (although absolute tensile strengths and moduli were not reported).

![Chemical structures](image)

**Figure 1.16** – a) polyurethane by Seoane Rivero et al. with polycaprolactone soft segments, where photodimerization increased strength and elasticity. b) polyester by Nagata et al. with polycaprolactone segments, where photodimerization decreased tensile strength

Seoane Rivero et al. studied the effect of photodimerization on the mechanical properties of polyurethanes. A polyurethane containing coumarin pendant groups in a polycaprolactone soft segment, polymerized with hexamethylene diisocyanate (Figure 1.16a), was found to transform from a soft and weak material to a tough elastomeric material by UV
exposure. Tensile strength was increased from 1.9 MPa to 6.7 MPa, and remarkably strain at break was increased from 2.1% to over 430%. Photodimerization appears to have significantly reduced the degree of crystallinity of the polycaprolactone segments, allowing this transformation to occur.

However, photocrosslinking does not uniformly increase strength in all cases. Nagata and Yamamoto reported polyesters with coumarin pendants made from a polycaprolactone diol and coumarin-containing diacid, designed as shape-memory polymers (Figure 1.16b)\textsuperscript{100} When these materials were irradiated with UV they exhibited a significant loss of tensile strength, despite photodimerization forming effective crosslinks that lent the material good shape-memory properties. A polyester with $M_n = 10,000$ polycaprolactone segments decreased in strength from 29 MPa to 12 MPa after 30 minutes UV exposure. Another with $M_n = 3000$ polycaprolactone segments, and correspondingly higher coumarin concentration, decreased from 15.6 MPa to 11.0 MPa after 15 minutes exposure. Elastic moduli and elongation at break decreased in both materials by similar proportions. The reason for this behavior was unfortunately not discussed, but it is possible photodimerization caused a loss of crystallinity like that observed by Seoane Rivero,\textsuperscript{170} and that the relatively low concentration of coumarin groups in these polymers produced insufficient crosslink density to overcome this loss of cohesion.

Beyond simply modulating the mechanical properties of polymer films, photodimerization has also been explored as a way to repair cuts, cracks, and scratches using light as a stimulus.\textsuperscript{171,172} These studies offer some insight into the ability of coumarin to make mechanical bonds whose properties depend on the photodimerization reaction.
Ling et al. synthesized and studied coumarin-containing polyurethanes for the purpose of creating repairable materials. In the polyurethane whose structure shown in Figure 1.17a, featured pendant 4-methylcoumarin groups. Repairability was tested by cutting a free-standing film of already photocrosslinked polymer with a razor, irradiating the cut surface with 254 nm light to photocleave coumarin dimer crosslinks, then joining the two halves and irradiating with 350 nm light to re-crosslink the polymer. After one such repair cycle, the tensile strength of the films was reduced from 2.3 MPa to about 1.6 MPa; the repaired film retained up to 70% the original strength. This was not simply a thermal effect, as films repaired only by heating to 40 °C retained only 17% of their original strength. In a later study, the effect of different molecular weight PEG soft segments in the polyurethane was examined. It was found that shorter PEG segments led to reduced coumarin-dimer reversibility, but the increased coumarin concentration resulted in higher strength repairs with up to 87% the strength of the original film.
The ability to repair bonds by photodimerization is not limited to soft, linear polymers, however. Kiskan and Yagci created polybenzoxazines from 4-methyl-7-hydroxycoumarin and Jeffamine polyetheramines (Figure 1.17b). Films of the resins were thermally cured and reported to show photo-repairability; two halves of a cracked sample were held together, irradiated with 300-350 nm light, and reportedly retained up to 44% of the tensile strength of the original film. This is a remarkable result considering the coumarin units were present in an already crosslinked thermoset, although the repairability was likely hindered by the rigid aromatic polymer segments generated by the curing of the benzoxazine.

In a recent example, Abdallh et al. reported a simple four-armed star monomer from the ester of pentaerythritol and 11-bromoundecanoic acid, which was then end-capped with 7-hydroxycoumarin (Figure 1.17c). Films of the material showed dimerization with up to 79% conversion, creating a free standing films, and photocleavage caused absorbance of the films to return to 97% of their original coumarin concentration – a very high degree of photocleavage ability compared to similar coumarin-based materials. In this work, the material’s mechanical response was characterized using Vickers hardness. Photocleavage of the photocrosslinked network reduced hardness from 21.1 to 13.9 HV, and re-photodimerization increased it back to 19.3 HV. The hardness of the photocrosslinked material is comparable to poly(methyl methacrylate). Most notably, films of this polymer were able to be adhered together photochemically. Two films were irradiated with 254 nm light, joined together, then photodimerized with 365 nm light to produce a joined film. Although the strength of this bond was not measured, it demonstrates the ability of coumarin photodimerization to create mechanical bonds.
These examples show that not only can photodimerization be used to modulate the mechanical properties of polymer films, but that it is also a viable means of repairing materials. The light-triggered chemical bonds created by photodimerization can lead to effective mechanical bonds between polymeric solids.

1.4 Conclusions

Coumarin photodimerization and photocleavage has proven itself to be a versatile tool for making and breaking bonds in polymeric materials in response to ultraviolet light. Recent years have seen a rapid expansion in the types of materials and applications this chemistry has been applied towards, especially in micro and nanostructured materials and phototriggered release systems for drug delivery, but also for macro scale materials including shape memory polymers and repairable self-healing materials.

Understanding the fundamental photochemistry of the coumarin system is important to the design of light responsive materials. It is hoped that the information reviewed here will provide a more accurate understanding of the photodimerization and photocleavage reactions relevant to polymer scientists than what is currently available in the literature. Despite the reaction being known for nearly 120 years, there are still many aspects of the photoreaction that are not well understood, and which would aid the design and synthesis of materials. For example, effects of various substituents on the dimerization quantum yield remain unclear, as do the relative contributions of electronic effects, steric effects, and associations in either ground state or excited states on the efficiency of dimerization and regiochemistry of the products. The chemical and thermal stability of the dimers of various coumarin derivatives also remains an area
for more study, as this may dictate the range of applications coumarin dimer-based
photoresponsive materials might be suitable for.

From the literature, we see several trends that can be used to guide the design of new
light responsive polymer materials using coumarin. To create an efficient, fast curing material,
there is an advantage to using soft, non-glassy materials which confer high mobility to coumarin
groups. There are also numerous tradeoffs to consider in the design of these polymers. For
time example, higher concentrations of coumarin may result in faster crosslinking materials and
higher crosslink densities, but come at the cost of limited UV penetration depth due to strong
absorption. Use of high functionality starting materials can produce materials that easily and
rapidly gel into a crosslinked network, but will also make reversibility by photocleavage require a
high degree of conversion before the network can be broken apart.

The potential of the reversible photodimerization reaction make it appealing for new
applications which have not yet been explored. One of the primary motivations of the work
presented in this dissertation was interest in designing a coumarin-based photoresponsive
polymer system that could function as a reversible, reworkable adhesive. A necessary
requirement for an adhesive is the ability to start from a liquid precursor which can wet the solid
surface to which it is applied and then cure to a solid. As we have seen, there are relatively few
examples of coumarin-based monomers or pre-polymers which are room temperature liquids
capable of a liquid-to-solid transition upon photocrosslinking (or vice-versa via photocleavage),
and new methods of creating liquid materials are needed. Although coumarin photochemistry
has proven itself to be capable of making crosslinks in a wide range of polymers, it also remains
unclear the extent to which coumarin photochemistry is capable of both making and breaking
strong mechanical bonds between solids.
It is hoped that this work presented here will give insight into the capabilities and limitations of the reversible photodimerization approach to light-responsive materials and drive further refinement toward ever more efficient and responsive materials.
CHAPTER 2: PHOTOCURING AND ADHESION OF DIAMINES MODIFIED WITH 4-METHYL-7-GLYCIDYLOXYCOUMARIN

Figure 2.1 – Formation of a reversible crosslinked network via coumarin photodimerization, converting liquid precursors into a solid

2.1 Introduction

The reversible photodimerization of coumarin offers an attractive means of imparting UV-responsive behavior in polymers. It provides the ability to make and break bonds within a material on demand in response to irradiation wavelength. There has been interest in utilizing this photochemical reaction in polymers for a wide range of purposes, but relatively little investigation of coumarin for mechanical purposes such as adhesion. The aim of this work was to design, synthesize, and evaluate a new liquid coumarin functionalized material capable of photocrosslinking into a solid that would create a robust mechanical bond, as illustrated in Figure 2.1.

The hypothesis central to this work is that the photodimerization of coumarin is capable of forming a crosslinked thermoset network, causing a transition of a liquid precursor to a solid polymer that can create an adhesive bond. Coumarin photodimerization has been used successfully for healable materials in which scratches can be healed by photocleavage and
photodimerization cycles,\textsuperscript{98} and where cut or cracked surfaces can be joined by photocrosslinking.\textsuperscript{96,99} Photocrosslinking has also been used to deactivate pressure sensitive adhesives by reducing their tack.\textsuperscript{95} However there are relatively few examples of coumarin-based polymers capable of transitioning from a liquid to a solid by means of photodimerization such that might be suitable for a photocurable adhesive. Examples include Matsuda et al., who created room temperature liquid polyesters.\textsuperscript{162} Recently, the group of Joy utilized coumarin dimerization to crosslink polyesters intended for use as underwater adhesives,\textsuperscript{142} serving to transform a viscous polymer into a nonflowing one. However, the photocuring process was not studied in detail. The relatively few examples of liquid-to-solid transitions suggest there may be obstacles to the synthesis of such polymers.

To evaluate the practicality of reversible photodimerization in reversible thermoset adhesives, a number of questions need to be answered. Firstly, the network forming ability afforded by coumarin dimerization is not well understood. Few studies have carefully examined processes which might hinder efficient photocuring, such as intramolecular cyclization or photooxidative degradation. Secondly, it is not clear whether the kinetics of photodimerization are practical for an adhesive, and what light intensities and time scales might be required to cure such a polymer. Conventional photocured adhesives most commonly use photoinitiators to start a free radical chain reaction. In this process the quantum yield of bond formation is greater than 1 due to its chain reaction nature; one photon absorbed by the photoinitiator may result in the formation of many bonds. With coumarin dimerization, each photon absorbed can result in a maximum of one bond. The quantum yield of coumarin dimerization in solution is low, about $\sim 10^{-4}$ for parent coumarin,\textsuperscript{35} and has never been measured in polymer systems. It is not clear whether this would make a polymer impractically slow to cure using common UV light sources.
It also remains unclear how thick of a film can be effectively cured by photodimerization, considering the strong absorption of coumarin chromophores. Answers to these questions would give valuable insights aiding the design of future light-responsive polymers utilizing [2+2] photocycloaddition.

Several fundamental criteria were identified to guide the design of the prototype photocurable materials. Firstly, the monomer or prepolymer must be a room temperature liquid which can be applied to surfaces to be adhered. Secondly, the noncoumarin components of the precursor should have excellent UV transparency at wavelengths required for both photodimerization (300-370 nm) and photocleavage (250-300 nm). Thirdly, the material should be photostable enough that unwanted degradative side reactions do not compete with photocuring.

Lastly, the liquid precursor must cure to a solid which will not flow under stress. To achieve this, the precursor should have a functionality of at least three coumarin units. A bifunctional monomer, for example, would be capable of forming high molecular weight polymer only approaching 100% conversion of its reactive groups, a target unlikely to be achieved by photodimerization. By using a multifunctional precursor, the system will reach a critical conversion, called the gel point, at which the growing polymer forms an interpenetrating network throughout its volume, and the polymer begins to show solid-like properties.

The approach taken to this problem was to synthesize a prepolymer analogous to an epoxy resin. 4-methyl-7-glycidyloxycoumarin was used as a versatile building block that could be reacted with many polyamines to serve as a backbone for the coumarin functionalized prepolymer, as shown in Scheme 2.1. Use of a diamine can result in a tetrafunctional precursor, thus providing enough bonds to result in a fully crosslinked polymer network. This approach is
advantageous because it allows a variety of commercially available amines to be used to build the backbone of the precursor, and thus the material can be tailored to meet the criteria listed above. The approach of using diamines has been used previously for thermally reversible Diels-Alder based thermosets.\textsuperscript{173}

\textbf{Scheme 2.1} – The general approach to a photocurable precursor taken in this work. 4-methyl-7-glycidyl oxycomarin is reacted with a diamine to produce a tetrafunctional prepolymer which can be photocured into a crosslinked thermoset network.

Importantly, this approach was also taken to compliment the work described later in Chapter 3. In Chapter 3 a system is created which takes essentially the reverse approach reported here; coumarin dimers are first dimerized, isolated, and then thermally cured with the diamine, thus creating a resin which can be reverted to a liquid by photocleavage of the dimer crosslinks. The results of the present chapter identified a diamine that remained liquid when fully functionalized with coumarin groups, and therefore identified a curing agent for the epoxy resin of Chapter 3 known to form a liquid upon photocleavage.

Experiments were performed to evaluate the network forming ability of the candidate photocurable resins, measure the adhesive strength of the polymer as a function of irradiation, and determine the origins of processes detrimental to the photocuring ability of the material.
The results of this study are hoped to yield insights which can improve design of future photocurable adhesives.

## 2.2 Results and Discussion

### 2.2.1 Synthesis

The first stage of this work was to produce a coumarin functionalized liquid precursor resin. The system was modeled after an epoxy resin as shown in Scheme 2.1, where 4-methyl-7-glycidyloxycoumarin (MGOC) was reacted with a diamine to produce a tetrafunctional precursor material which would later be photocured (the synthesis of 4-methyl-7-glycidyloxycoumarin is detailed in Chapter 3). The first task was to select a diamine which would afford a material with the required properties: a liquid at room temperature, low color, excellent UV transparency over the range of wavelengths needed for both coumarin dimerization and dimer photocleavage. The candidate polyamines investigated are listed in Table 2.1. Diamines bridged by aliphatic groups, polyethers, and siloxanes were chosen as the most promising candidates. All were colorless liquids. Aromatic amines, for example, were not investigated due to a tendency to absorb ultraviolet, to discolor strongly upon oxidation, and for their tendency to produce rigid polymers.

The coumarin functionalized polyamines were synthesized by heating the amine with a 20% excess of 4-methyl-7-glycidyloxycoumarin in alcohol. Initially the reaction was attempted by heating both components in solution with an aprotic solvent, but this resulted in incomplete reactions even after long reaction times. It was found that refluxing in an alcohol (in this case methanol) with a small excess of the coumarin monomer greatly accelerated the reaction, resulting in near complete substitution after 24 hours. The use of alcohols as accelerants in the
reaction between epoxides and amines is documented. The structures of the diamines and descriptions of the resulting products are summarized in Table 2.1.

The first diamines to be investigated were Jeffamine polyether diamines, produced by Huntsman Corporation. Two polypropylene glycol (PPG) based diamines with different molecular weights were examined: D-400 and D-2000. D-400 when reacted with 4-methyl-7-glycidyloxy coumarin (D400-MGOC) became a brittle, amorphous solid which melted from 55-65 °C. D-2000 when reacted with 4-methyl-7-glycidyloxy coumarin (D2000-MGOC) formed a viscous liquid. Both possessed a light yellow color. The conversions were determined from 1H NMR data by comparing the integrations of the methyl groups from the poly(propylene glycol) backbone with the coumarin 4-methyl groups, and both these diamines were found to have reacted with greater than 98% conversion.

Table 2.1 – List of diamines reacted with MGOC, and description of the reaction product

<table>
<thead>
<tr>
<th>Name</th>
<th>Diamine structure</th>
<th>Product of reaction with MGOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jeffamine D-400</td>
<td>H₂N&lt;sub&gt;n&lt;/sub&gt; O&lt;sub&gt;n&lt;/sub&gt; NH₂ n ≈ 6.2</td>
<td>Brittle, amorphous solid m.p. 55-65 °C</td>
</tr>
<tr>
<td>Jeffamine D-2000</td>
<td>H₂N&lt;sub&gt;n&lt;/sub&gt; O&lt;sub&gt;n&lt;/sub&gt; NH₂ n ≈ 31</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td>1,6-hexanedi amine</td>
<td>H₂N</td>
<td>Brittle solid</td>
</tr>
<tr>
<td>2,2,4(2,4,4)-trimethyl-1,6-hexanedi amine</td>
<td>H₂N</td>
<td>Brittle, amorphous solid m.p. 85-100 °C</td>
</tr>
<tr>
<td>1,2-bis(aminopropyl) tetramethyldisiloxane</td>
<td>H₂N</td>
<td>Brittle solid m.p. 65-75 °C</td>
</tr>
<tr>
<td>Gelest DMS-A11 (aminopropyl terminated PDMS)</td>
<td>H₂N&lt;sub&gt;n&lt;/sub&gt; Si&lt;sub&gt;n&lt;/sub&gt; O&lt;sub&gt;n&lt;/sub&gt; Si&lt;sub&gt;n&lt;/sub&gt; NH₂ n = 9.1-9.8</td>
<td>Soft, rubbery solid</td>
</tr>
</tbody>
</table>
The use of small molecule aliphatic diamines with 4-methyl-7-glycidyloxycoumarin exclusively produced brittle solids. 2,2,4(2,4,4)-trimethyl-1,6-hexanediameine (from the commercial product EpoTek 301) is itself a low viscosity liquid. This diamine is a mixture of two isomers, which was hypothesized to reduce the melting point of the product. However, the properties of the coumarin substituted product are dominated by the coumarin groups.

Two diamines containing siloxane bridging groups were also investigated. Silicones are appealing for this application since they tend to be very UV transparent over a wide wavelength range, and resistant to photooxidative degradation. 1,2-bis(aminopropyl)tetramethylene disiloxane, like the small molecule aliphatic diamines, produced a rigid brittle solid. An aminopropyl-terminated polydimethylsiloxane, Gelest DMS-A11, was similarly reacted with MGOC. It produced a soft rubbery material, but not a flowing liquid.

From these results it is evident that substantial intramolecular forces between coumarin groups make it difficult to create liquids from small molecules, and even from polymers unless they are sufficiently diluted. There are reports of similar behavior when coumarin groups are incorporated into polymers. Fawcett et al. reported that when pendant coumarin groups were added to polydimethylsiloxane, the liquid silicones were transformed to thermoplastic elastomers or rigid solids as a result of noncovalent associations between coumarins.165

Ultimately, Jeffamine D-2000 was the only diamine to produce a room temperature liquid. The long PPG chain provided sufficient dilution to disrupt packing of coumarin groups. It is also conceivable that the polymer environment plays a role in solvating the coumarin groups. Assuming that D2000-MGOC possesses a number average molecular weight of 2909 g/mol, a density of approximately 1 g/cm³, and a functionality of 4 coumarins per molecule, the
concentration of coumarins in the liquid material is approximately 1.3-1.4 M. For comparison, this concentration is greater than those of the silicones described by Fawcett,\textsuperscript{165} which are estimated to have coumarin concentrations ranging from 0.3 to 1.2 M, all producing solids. D2000-MGOC also has a coumarin concentration greater than liquid polyesters by Matsuda et al.,\textsuperscript{162} one of the few reported examples of liquid coumarin-based polymers, which are estimated to range from 0.3 to 0.9 M.

D2000-MGOC, fulfilling the minimum requirements for a photurable adhesive, was investigated further along with D400-MGOC to see the effects of a higher coumarin concentration in a similar material.

\subsection*{2.2.2 Photocuring of Thin Films}

The photocuring ability of the coumarin modified diamines was first studied in thin films. This allowed the photoreaction’s progress to be monitored photometrically by examining coumarin’s absorption peak at 320 nm as a function of irradiation time. Assuming absorbance of the film is directly proportional to the concentration of coumarin chromophores, and knowing that pure coumarin dimer has zero absorbance at 320 nm, the conversion of coumarin to coumarin dimer could be calculated. Figure 2.2 shows the typical spectral change for a thin film of D2000-MGOC with exposure. Photocuring was also monitored by ATR-FTIR spectroscopy to examine chemical changes, and by measuring the solubility of the films. The purpose of these experiments was to determine the rate of photodimerization in a typical UV curing apparatus, and determine what conversions are necessary to effect gelation.

In thermosetting polymers, the gel point occurs when enough functional groups have reacted that an interconnected network forms throughout the volume of the polymer. At this
point, viscosity increases precipitously, the polymer transitions from liquid-like to solid-like behavior, and some fraction of the material becomes insoluble in solvent, called the gel fraction.¹

**Figure 2.2** – Typical absorption spectra for D2000-MGOC thin films, showing decrease in absorption of coumarin units with UV exposure time

Thin films of D400-MGOC and D2000-MGOC on fused quartz substrates were exposed to the light of a metal halide lamp first in air, then in a borosilicate glass tube flushed with argon. The two conditions were used to determine if oxygen played a detrimental part in photocuring, since oxygen can quench excited state chromophores and/or lead to photooxidative degradation of the material. The results of the exposures of D400-MGOC and D2000-MGOC under both air and argon are shown in Figure 2.3, where monomer-to-dimer conversion as determined from the change in absorbance is plotted against exposure time.
The first clear trend from the data in Figure 2.3 is that dimerization proceeds faster in the liquid D2000-MGOC than it does in the solid D400-MGOC. Despite D400-MGOC possessing a little over twice the concentration of coumarin groups of D2000-MGOC, the solid phase appears to slow dimerization. This suggests that the mobility of coumarin groups in the polymer has a greater influence on the photodimerization rate than their concentration.

The next clear trend in this data is that coumarin groups in both D400-MGOC and D2000-MGOC dimerize more slowly under argon than under air in the early stages of irradiation. This result was unexpected, as it was originally hypothesized that the presence of oxygen may quench excited state coumarins and slow the dimerization rate. This observation is likely explained by the difference in the two exposure conditions; the samples exposed under argon were performed in a borosilicate glass tube while those exposed under air were not, and reflection losses from the glass would cause a small loss in light intensity reaching the film.
Although the samples exposed under argon dimerize more slowly, they are capable of reaching higher conversions than those exposed under air. D2000-MGOC reaches a plateau of about 80% conversion under air, but 86% conversion under argon. D400-MGOC reaches a plateau at 74% conversion under air, and higher under argon.

To explain why the maximum possible conversion was higher for those exposed under argon than those exposed under air, it was hypothesized that the glass tube used for the inert gas exposures provided additional filtering of short wavelength light that may cause photo cleavage of dimers. If trace amounts of <300 nm light were transmitted through the borosilicate glass filter, it would result in a photodimerization-photocleavage steady state, and reduce the maximum possible conversion. Because the transmission cutoff of borosilicate glass is very close to 300 nm, the additional layer of glass provided by the tube would absorb a greater amount of short wavelength light, and result in a higher maximum conversion plateau. This hypothesis was tested by setting up an experiment to examine the effect of different filters on the photoreaction (these results are detailed in section 2.2.4.2).

To evaluate the ability of photodimerization to result in formation of a crosslinked network, the solubility of the exposed films was studied. Table 2.2 summarizes these results. The exposed specimens were placed in a beaker filled with acetone, a good solvent for the material, and after 24 hours the specimens were dried and masses of the films were recorded. By measuring the solubility of the coated slides as a function of conversion determined by UV-vis absorption, it was possible to determine at what conversion gelation was reached. In all samples there was a certain exposure threshold after which an insoluble portion of film was left on the slide. The insoluble fraction was detectible by mass change, visible to the eye, and detectable by UV-vis spectroscopy. At conversions under this threshold the polymer dissolved completely,
leaving no measurable remnant on the slide. This threshold was taken to correspond to the gel point.

**Table 2.2 – Summary of thin film exposure results**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Maximum conversion</th>
<th>Time to max conversion (min)</th>
<th>Gel point conversion</th>
<th>Maximum gel fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-400 Air</td>
<td>74%</td>
<td>10</td>
<td>66%</td>
<td>0.21 ± 0.055 (6 min)</td>
</tr>
<tr>
<td>D-400 Argon</td>
<td>74%</td>
<td>12</td>
<td>60%</td>
<td>0.38 ± 0.10 (10 min)</td>
</tr>
<tr>
<td>D-2000 Air</td>
<td>80%</td>
<td>4</td>
<td>78%</td>
<td>0.11 ± 0.052 (10 min)</td>
</tr>
<tr>
<td>D-2000 Argon</td>
<td>86%</td>
<td>8</td>
<td>70%</td>
<td>0.38 ± 0.053 (8 min)</td>
</tr>
</tbody>
</table>

For both D400-MGOC and D2000-MGOC, those samples exposed under air required higher conversions to reach a gel point than those exposed under argon, indicating that air caused a detrimental effect on curing. Those exposed under air also possessed a lower maximum gel fraction than those under argon. In all cases, however, the gel fraction was quite small, with no specimens retaining more than 40% of the original film mass remaining after soaking in solvent.

This series of experiments raised a number of questions. It is clear that the photocuring of the material was inefficient, requiring high conversion for gelation and resulting in low gel fractions. This prompted a more detailed investigation of the reasons for this behavior.

Unmodified Jeffamine D-2000 was spin coated onto fused quartz slides and exposed to look for evidence of oxidative degradation of the PPG backbone when exposed in films similar in thickness and for similar time scales as the rest of the thin film exposures. Three samples were
prepared; one unexposed, one exposed 12 min under air, and one exposed 12 min under nitrogen. IR spectra were taken via ATR. No new peaks were observed in the infrared spectra.

UV-vis spectra were also collected on the unmodified Jeffamine (Figure 2.4). No change was observed after UV exposure, except for a slight increase in short wavelength absorption for the sample exposed under air. This supports the assumption that the spectral changes observed in D200-MGOC and D400-MGOC upon irradiation (Figure 2.2) can be entirely attributed to photodimerization, and there are no side processes occurring that would lend doubt to the conversion calculations.

**Figure 2.4** – UV-vis spectra of unmodified Jeffamine D-2000 before exposure and after 12 minutes exposure under air and nitrogen. No significant change observed after irradiation.

The thin film exposure experiments indicated a gel point conversion of 60-66% for D400-MGOC, and 70-78% for D2000-MGOC. These conversions are higher than expected for a tetrafunctional monomer. According to Flory-Stockmayer theory\(^\text{168}\) the gel point conversion for a multifunctional monomer is given by:

\[
\alpha_c = \frac{1}{f-1}
\]
Where $f$ is the functionality of the monomer. Therefore, for a tetrafunctional monomer in which all groups can be assumed to react equally, the gel point conversion can be predicted to be 0.33. Gel point conversions determined by the thin film exposure experiments (Table 2.2) are at least twice this conversion, which raises questions about the photocuring process resulting from photodimerization.

Possible reasons for the higher-than-expected gel point conversion include intramolecular dimerization, and photooxidative chain scission of Jeffamine D-2000’s PPG backbone.\textsuperscript{175} The higher gel point conversions and lower overall gel fractions for the specimens exposed under air provide some evidence to suggest that photooxidative degradation might be a significant contribution. It was also hypothesized that since the gel point conversion and ultimate gel fraction of those samples exposed under argon still indicated inefficient curing, the formation of intramolecular dimers which do not contribute to crosslink density may also be occurring. These hypotheses are discussed in sections 2.2.4 and 2.2.5.

2.2.3 Effects of Lamp Filtering on Photodimerization

After these experiments had been performed, a new study examined the effect of lamp filtering on the photocuring of D2000-MGOC. The previous experiments looked at the photocuring of thin films under a metal halide lamp filtered by a sheet of borosilicate glass, and it was discovered that D2000-MGOC exposed while in a borosilicate glass tube under an argon atmosphere reached higher conversions than D2000-MGOC exposed in the open air. Figure 2.3 shows that in both D400-MGOC and D2000-MGOC the initial rate of dimerization was faster for the samples exposed under air than those exposed under argon, which was unexpected since it was hypothesized that oxygen could act as a quencher of excited state coumarins, thus retarding the photoreaction. The slower initial dimerization rate under argon might be explained
by a small loss in transmission resulting from reflection at the extra interface provided by the
glass tube, but this does not explain why the maximum conversion was higher under argon. It
was hypothesized that the extra layer of borosilicate glass between the sample and the lamp
added to the filtering of the lamp’s light. Because the transmission cutoff of borosilicate glass is
very close to 300 nm, the conversion plateau of the sample exposed under air may be a result of
a steady state between photodimerization and photocleavage caused by trace amounts of <300
nm light not absorbed by the filter.

To test this hypothesis, new films were exposed under three different filtering
conditions; soda-lime glass, borosilicate glass, and no filter, providing wavelength cutoffs at
approximately 310 nm, 280 nm, and 240 nm respectively (spectra are shown in Figure 2.7). The
effect on conversion was measured by UV-vis spectroscopy. Films of D2000-MGOC were
prepared on fused quartz slides as before. Due to the difficulty of maintaining a constant
temperature under the lamp without a filter to attenuate the high flux of infrared radiation,
specimens were placed on a hollow aluminum block through which water was circulated. This
was effective at maintaining a constant temperature for all three conditions.

![Figure 2.5](image.png)

**Figure 2.5** – Effect of lamp filters on conversion in D2000-MGOC films
Figure 2.5 shows the monomer to dimer conversion as a function of exposure time for all three filter conditions. With no filter, wavelengths down to 240 nm are transmitted, dimerization is rapid, and conversion plateaus at 59% conversion. With borosilicate glass, wavelengths down to 280 nm are transmitted, and dimerization plateaus at 80% conversion, consistent with the samples exposed in the previous experiment (see Figure 2.3). With the even higher wavelength cutoff provided by the soda-lime glass filter, dimerization is much slower as a result of the diminished UV intensity near coumarin’s absorption peak, but conversions greater than 80% are possible. Conversion reached 86% after 10 minutes exposure.

![Chemical structures showing monomer to dimer conversion](image)

**Figure 2.6** – Steady state between dimer and monomers resulting from simultaneous photodimerization and photocleavage due to trace <300 nm light. This steady state is responsible for the dimer conversion plateau observed in D2000-MGOC films.

This result indicates that the maximum attainable conversion is limited by a steady state between photodimerization and photocleavage in the film, as illustrated in Figure 2.6. With the borosilicate glass filter, the amount of light under 300 nm is very small, but a steady state between photodimerization and photocleavage is possible due to the much higher quantum yield of photocleavage ($\phi \approx 0.2^{82}$) compared to photodimerization ($\phi \approx 10^{-3} - 10^{-4}$).\(^{35}\) The importance of light source filtering has been largely overlooked by researchers utilizing photodimerization for polymer crosslinking. One important consequence of this conversion plateau is that it would be expected to hinder the photobleaching effect of coumarin.
photodimerization; greater concentrations of residual monomeric coumarin will absorb light and reduce the depth UV light is able to penetrate into a film.

![Emission spectra of the CureZone 2 metal halide lamp in the UV region.](image)

**Figure 2.7** – Emission spectra of the CureZone 2 metal halide lamp in the UV region. Intensities are normalized to allow direct comparison of the three filter conditions. (Additional spectra are given in supplementary data section 2.5.4, highlighting the region near 300 nm.)

The solubilities of the films exposed in this experiment were measured. Unexpectedly, all of these films exposed under air were nearly completely soluble within the uncertainty of the measurements, leaving very little if any insoluble fraction behind after soaking in acetone. The increased conversion afforded by the soda-lime glass filter did not lead to more insoluble films. This prompted further study to determine what mechanisms might be hindering photocrosslinking.
2.2.4 Evaluation of Photooxidative Degradation

2.2.4.1 Analysis of IR Spectra

Fourier transform infrared spectroscopy (FTIR) was performed with thin film exposures to examine chemical changes with exposure. This was analyzed to determine if photooxidation might be a factor in the low curing efficiency of the polymer, and why virtually all the films exposed outside of a glass tube were nearly completely soluble, even at high conversions.

According to Mailhot et al.\textsuperscript{175} who performed an IR study on the degradation of Jeffamine D-2000 cured with DGEBA, if photooxidation occurred in the PPG backbone, we would expect to see the formation of aliphatic formates and a corresponding peak at 1725 cm\(^{-1}\). If photooxidation occurred at an aromatic ether linkage where coumarin attaches to the amine, phenyl formates form with a corresponding peak at 1739 cm\(^{-1}\). Unfortunately, both these carbonyl peaks overlap with the coumarin and coumarin dimer peaks at 1718 cm\(^{-1}\) and 1755 cm\(^{-1}\) respectively. Quantification of the spectra obtained is very difficult due to inconsistencies in the performance of the ATR system, which produced inconsistent baselines. IR data collected from the thin films remains inconclusive due to lack of sensitivity, and inability to deconvolve any peaks indicative of photooxidative degradation which overlap with the coumarin peaks.

2.2.4.2 Thick Film Photocuring and Photoproduct Characterization

The thin film samples allowed dimerization conversion to be measured by UV-Vis spectroscopy, but the very small amount of material in these films precluded sensitive measurements of solubility and characterization of chemical information. From these studies it remained uncertain the extent to which photooxidation might play a role in the higher than expected gel point conversion and high solubilities of exposed films. A series of exposures were performed on films drop cast onto glass slides, producing films approximately 1 mm thick. After
soaking in acetone at room temperature for 24 hours, the mass change was measured. The results are shown in Table 2.3.

**Table 2.3 – Solubilities of exposed D2000-MGOC thick films**

<table>
<thead>
<tr>
<th>Exposure time (hr)</th>
<th>Filter</th>
<th>Conditions</th>
<th>Insoluble (gel) fraction</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (control)</td>
<td>-</td>
<td>-</td>
<td>0.6%</td>
<td>0.9%</td>
</tr>
<tr>
<td>1</td>
<td>Borosilicate glass</td>
<td>Air, in tube</td>
<td>5.5%</td>
<td>0.9%</td>
</tr>
<tr>
<td>1</td>
<td>Borosilicate glass</td>
<td>N₂, in tube</td>
<td>18.0%</td>
<td>0.9%</td>
</tr>
<tr>
<td>4</td>
<td>Borosilicate glass</td>
<td>Air, in tube</td>
<td>30.3%</td>
<td>0.6%</td>
</tr>
<tr>
<td>4</td>
<td>Borosilicate glass</td>
<td>N₂, in tube</td>
<td>71.3%</td>
<td>0.7%</td>
</tr>
<tr>
<td>4</td>
<td>Soda lime glass</td>
<td>Air, in tube</td>
<td>17.2%</td>
<td>0.6%</td>
</tr>
<tr>
<td>4</td>
<td>Soda lime glass</td>
<td>N₂, in tube</td>
<td>58.0%</td>
<td>0.9%</td>
</tr>
<tr>
<td>4</td>
<td>Soda lime glass</td>
<td>Air, open</td>
<td>0.0%</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

In all cases, the films exposed under nitrogen retained a greater insoluble fraction than those exposed under air, demonstrating that this was not an effect of additional filtering by the borosilicate glass tube used for the exposures under inert gas. The material exposed in open air without a glass tube surrounding it was completely soluble, dissolving completely within minutes of immersion in acetone. These results suggest photooxidative degradation is a strong contributor to the inefficient photocuring of this material, at least at long exposure times.

**2.2.4.2.1 NMR Analysis of Soluble Fractions**

The relatively large amount of material afforded by this experiment allowed for more sensitive chemical characterization of the soluble fraction of the exposed polymers. NMR analysis of the soluble extracts was able to show the fraction of monomer and dimer units in the polymer, as well as the types of dimers formed during exposure.

By comparing exposed spectra to the dimer assignments determined from exposure of 4-methyl-7-methoxycoumarin, we see a nearly complete lack of syn head-to-head dimers as
evidenced by the lack of aromatic protons at 6.36 and 6.48 ppm, and a predominance of either the syn or anti head-to-tail dimer.

Figure 2.8 – Downfield region of $^1$H NMR spectra of the soluble extracts of the exposed thick films. 1) D2000-MGOC, unexposed. 2) D2000-MGOC exposed in glass tube, under air. 3) D2000-MGOC exposed in glass tube under nitrogen. 4) D2000-MGOC exposed under open air outside the glass tube. Small peak at 8.07 ppm for the samples exposed under air suggests formation of aliphatic formates, and PPG chain scission.

Figure 2.8 shows $^1$H NMR spectra in the downfield region for the extracts of the exposed thick films. The spectra show a predominance of syn head-to-tail dimer in the exposed films, evidenced by the aromatic peaks at 7.04, 6.64, and 6.05 ppm, with trace amounts of the syn head-to-head dimer evidenced by small broad peaks at 6.37 ppm. Of special interest is the very small peak at 8.07 ppm, which can be found in both samples exposed under air, but not in that exposed under nitrogen. This peak is consistent with the aldehyde of an aliphatic formate.
an expected product of the oxidation of PPG,\textsuperscript{175} and may be evidence of photooxidative chain scission in the PPG backbone of the polymer as illustrated in Figure 2.9.

![Figure 2.9](image)

**Figure 2.9** – The products of one possible photooxidation pathway in the PPG backbone of Jeffamine D-2000, resulting in chain scission and formation of acetate and formate groups. R represents coumarin groups.

### 2.2.5 Evaluation of Intramolecular Dimerization

Besides photooxidative degradation, it was also hypothesized that intramolecular dimerization could contribute to the low gel point conversion and low gel fraction of the cured polymer. Because the prepolymer is constructed with two coumarin units closely adjacent at each amine group, it was speculated that this could create a pre-assembly condition favorable for the formation of intramolecular dimers which would reduce the crosslink density of the cured polymer. This possibility is illustrated in Figure 2.10.

![Figure 2.10](image)

**Figure 2.10** – Hypothesized intramolecular dimerization between adjacent coumarin groups – a potential explanation for inefficient photocuring. Syn head-to-head and syn head-to-tail dimers are possible. Both anti head-to-head and anti head-to-tail dimers are improbable due to very high strain configurations.
Of the possible dimers that could result from intramolecular dimerization, it is believed syn head-to-head would present the lowest strain configuration and the most likely to form. To evaluate the possibility of intramolecular dimerization, the materials were exposed in solution where the concentration is diluted and the probability of intramolecular dimerization is increased.

### 2.2.5.1 NMR Monitoring of Photodimerization in Solution

Solutions of the D400-MGOC and D2000-MGOC were exposed and examined by NMR to determine which dimers were likely to form and compare to the composition of dimers extracted from the photocured films. Simple experiments were performed in NMR tubes with the prepolymer dissolved in CDCl₃. Samples of 35 mg of each were dissolved in 0.75 mL of deuterochloroform in NMR tubes. Assuming a number average molecular weight of approximately 2900 g/mol for D2000-MGOC, this would yield a solution with an approximate concentration of coumarin units of 0.06 M. The tubes were flushed with argon, but no rigorous degassing of the solutions was performed. The solutions were irradiated directly in the NMR tubes with unfiltered light from the metal halide lamp of the CureZone2. Figure 2.11 shows the ¹H NMR spectra of D400-MGOC as the photoreaction progresses.
Figure 2.11 – Downfield region of $^1$H NMR spectra of D400-MGOC exposed in solution in NMR tube. Blue highlighted peaks correspond to monomer (7.47, 6.87, 6.78, and 6.11 ppm). Red highlighted peaks correspond to syn HT dimer (7.08, 6.66, and 6.07 ppm). Syn HH peaks expected at 6.66, 6.52, and 6.36 ppm, but not found in significant quantity. Peak assignments made in agreement with Stitchell et al.\textsuperscript{177} and Muthuramu et al.\textsuperscript{49}

The NMR data shows that the dimers formed after 90 minutes of irradiation are at least 90% syn HT. The ratios are similar for both D400-MGOC and D2000-MGOC. It was initially hypothesized that intramolecular dimerization would favor syn HH dimers, but the NMR results suggest that if intramolecular dimerization is occurring, this is not the case. In fact, this photoreaction gives an even greater fraction of syn HT than might be expected for photodimerization of a monomeric 4-methylcoumarin (see Chapter 3, section 3.2.1.3.2, for example).

To evaluate the possibility of intramolecular dimerization interfering with network formation, we can compare this system to the work of Leenders et al. who studied the intramolecular dimerization of polymethylene bridged bis-coumarins.\textsuperscript{44} Intramolecular
dimerization was found to be the dominant path for 7,7'-polymethylenedioxycoumarins with 2 to 11 methylene units between coumarins when irradiated in dichloromethane solutions at concentrations from 0.01 to 0.1 M. In all bis-coumarins with a methylene chain greater than n=2, intramolecular syn head-to-tail dimer was the major product. One 4-methyl coumarin was studied, 7,7'-pentamethylenedioxy bis(4-methylcoumarin), and was found to produce 97% syn head-to-tail dimer when exposed at 0.01 M. This molecule (where coumarins are separated by 7 atoms) might be considered comparable to the chain ends of D2000-MGOC and D400-MGOC, where the two coumarin groups are separated by 9 atoms. The results by Leenders et al. show that there is indeed no preference for a head-to-head dimer by intramolecular dimerization, unless the separation between coumarin groups is much smaller than it is here. Therefore, the syn head-to-tail dimer seen in the spectra of irradiated D2000-MGOC and D400-MGOC may be either intramolecular or intermolecular, and the experimental evidence here can neither prove nor disprove the occurrence of intramolecular dimerization.

Evaluating the possibility of intramolecular dimerization in the film state is an even more difficult task. Leenders et al. found that the amount of intramolecular dimerization decreased with increasing concentration. The highest concentration studied was 0.1 M, and this was found to produce 65% intramolecular dimers. For comparison, the concentration of coumarins in D2000-MGOC is over an order of magnitude greater, approximately 1.4 M (calculated assuming a D2000-MGOC has number average molecular weight of 2900 g/mol, 4 coumarins per macromolecule, and a density of approximately 1 g/cm³). While we might expect intermolecular dimerization to predominate at this concentration, intramolecular dimerization cannot be discounted, and is likely to occur to some extent that cannot be quantified at this time.
2.2.6 Lap-Shear Adhesion Results

To evaluate the ability of D2000-MGOC to form an adhesive bond and determine whether photocuring is capable of forming a mechanical bond, an experiment was devised to test adhesion using a lap-shear method. The method was derived from ASTM D1002,\textsuperscript{178} a standard test method for adhesive strength. In place of metal coupons as specified in the standard, borosilicate glass microscope slides were bonded together. Two glass slides were adhered with D2000-MGOC and exposed with UV (\(\lambda > 300\ \text{nm}\)) using the CureZone2 metal halide lamp. After exposure, the glass slides were pulled under tension until yield.

![Graph showing average lap shear strength vs. exposure time for D2000-MGOC.](image_url)

**Figure 2.12** – Average lap shear strength vs. exposure time for D2000-MGOC

Figure 2.12 shows the strength of the bond as a function of exposure time. With no exposure, the sample behaved exactly like a fluid; the liquid D2000-MGOC flowed under the shear stress and glass slides separated with little resistance. After only a short exposure time different behavior began to emerge. With five minutes exposure, a clear yield point could be observed. Figure 2.13 shows representative stress-extension curves of the lap shear samples. In
the exposed samples, there is a clear yield point at which the lap-shear bond is broken. After they are extended beyond this point, the samples exhibit a slowly decaying response typical of a viscous fluid, a result of the excess material at the edges of the specimens which remained only partially cured due to the thickness of the material in these regions. After 20 minutes exposure, an average lap-shear strength of 0.93 ± 0.15 MPa was achieved.

Figure 2.13 – Representative shear stress vs extension curves for photocuring of D2000-MGOC

These results demonstrate the ability of photodimerization to cure a liquid into a nonflowing solid, suitable as an adhesive. Although excess liquid remained uncured at the edges of the samples, the material within the thin layer between glass slides cured to a soft and rubbery yet nonflowing solid. This suggests that photooxidative degradation, which had previously hindered a liquid-to-solid transition in D2000-MGOC films exposed under open air, was mitigated by the polymer layer being sandwiched between two impermeable glass slides.
D2000-MGOC is effective as a photocurable adhesive. From the trend observed in Figure 2.12, it appears likely that stronger bonds could be made with longer exposure times. Unfortunately, it became difficult to reproducibly measure lap shear strengths for samples exposed longer than 20 minutes because the glass substrates tended to break under tension. The maximum possible adhesive strength of the material therefore remains unknown. Nonetheless, the lap-shear strength that was achieved in these experiments, nearly 1 MPa, is comparable to that of other elastomeric adhesives. For example, RTV silicone adhesives bonded to metal substrates commonly exhibit lap-shear strengths on the order of 1 MPa.\(^{179}\)

The unoptimized adhesive strength of D2000-MGOC is also greater than that of a photocrosslinkable adhesive reported by Joy et al.,\(^{142}\) the only other example of an adhesive cured by coumarin photodimerization reported to date. Here, liquid polyesters containing pendant coumarin, catechol, and aliphatic groups were found to produce lap-shear strengths up to 0.8 MPa on glass surfaces. D2000-MGOC in comparison displays strengths up to 0.93 MPa, and this small but statistically significant difference may be a result of D2000-MGOC’s higher concentration of coumarin groups, lending the cured polymer a correspondingly higher crosslink density.

2.3 Conclusions

Photocurable resins were synthesized by the reaction of 4-methyl-7-glycidyloxycoumarin (MGOC) with diamines. The product of MGOC with Jeffamine D-2000 (D2000-MGOC) was found to meet the requirements for a photocured adhesive; the product is a viscous liquid at room temperature with excellent UV transparency down to 250 nm. Smaller molecular weight diamines produced only solid materials, but the relatively long poly(propylene glycol) (PPG)
chain in Jeffamine D-2000 was sufficient to disrupt interaction of coumarin groups and produce a liquid.

D2000-MGOC was found to be a viable photocurable adhesive for UV-transparent substrates. Lap-shear testing using glass microscope slides revealed that UV exposure causes a transition from liquid to a soft yet nonflowing solid, and a rapid increase in adhesive strength. Lap-shear strengths of nearly 1 MPa were achieved after 20 minutes of irradiation. This represents one of the first demonstrations of a photocurable adhesive utilizing coumarin photodimerization. The only material to be used in a similar way was reported by the group of Joy, where photodimerization of coumarin pendants on a polyester achieved lap-shear strengths up to 0.8 MPa.

More detailed study of the photocuring process revealed inefficiencies in the network forming ability of these polymers. Photocuring of D2000-MGOC and D400-MGOC was first studied in thin films, where photodimerization was monitored by UV-vis spectroscopy. Gelation was reached after 70-78% conversion, higher than expected for a four-functional system, prompting an investigation of the causes of this inefficient photocuring.

Use of different filters on the UV lamp revealed that the UV spectrum used to irradiate films has a strong effect on photodimerization. Films exposed under borosilicate glass filtered light ($\lambda > 280$ nm) reached lower conversion than soda-lime glass filtered light ($\lambda > 310$ nm), indicating a photodimerization-photocleavage steady state. This important effect has often been overlooked by researchers. However, the increased dimerization conversion afforded by the soda-lime glass filter did not necessarily result in better network formation. All specimens exposed under open air remained highly soluble in organic solvent, suggesting photooxidative degradation plays a role.
Photocuring of thick films of D2000-MGOC drop cast onto glass slides gave more sensitive measurements of solubility, revealing that photocuring strongly depends on the atmosphere the material is exposed under. Exposure under inert atmosphere produces solid, insoluble films, but exposure under open air results in completely soluble films. Analysis of the soluble fractions extracted from these films provided no evidence of photooxidation by IR spectroscopy, however NMR spectroscopy revealed signals consistent with aliphatic formates, a result consistent with photooxidative chain scission of the PPG backbone of Jeffamine D-2000.¹⁷⁵

Due to the close proximity of the two coumarin groups on the ends of the PPG diamine backbone, it was hypothesized that intramolecular dimerization may contribute another source of inefficiency in the photocuring process. It was hypothesized that syn head-to-head dimer might be the preferred product of an intramolecular dimerization, being a lower strain configuration than syn head-to-tail, but exposures in solution revealed that syn head-to-tail is always the dominant product even when diluted. Intramolecular dimerization resulting in syn head-to-tail dimers remains a possibility, but the degree to which of this process occurs in the film form is not precisely known.

In conclusion, coumarin photodimerization has proven itself to be a viable means of curing a light-responsive adhesive. Due to the reversible nature of coumarin dimers, this material has the unique capability for reversal by photocleavage. We can surmise that the photocuring inefficiency of this material is in part due to photooxidative degradation of the poly(propylene glycol) backbone of the resin, and that intramolecular dimerization likely plays a role that remains not yet well understood.
In the following chapter, a complimentary system is presented. Here, pre-assembled dimers of MGOC will be mixed with Jeffamine D-2000 and cured by heating, much like a conventional epoxy resin is cured. From the results of the work in this chapter, we expect that photocleavage of the coumarin dimers in the thermally cured resin will revert it to a liquid material essentially identical in structure to the photocurable resin described here.

2.4 Experimental

2.4.1 Materials and Instrumentation

Jeffamine D-400 and D-2000 were donated by Huntsman Corporation and used as received. 2,2,4(2,4,4)-trimethyl-1,6-hexanediardiamine was obtained as the part B component of Epotek 301, a commercial epoxy resin. 1,6-hexanediardiamine was purchased from Alfa Aesar, and sublimed before use. 1,2-bis(aminopropyl)tetramethyldisiloxane was purchased from Manchester Organics. DMS-A11 (an aminopropyl terminated polydimethylsiloxane) was purchased from Gelest. Methyl amine was purchased from Sigma Aldrich. Methanol and dichloromethane were purchased from Fisher Chemical. Anhydrous ethanol was purchased from Decon Labs, Inc. Chloroform and ethyl acetate were purchased from EMD Millipore. All solvents were ACS grade or better and used as received unless otherwise noted.

Fused quartz slides were purchased from GM Associates, Inc. A Novascan Technologies PSD-UV was used for ozone cleaning of slides. A Laurel Technologies Model WS-400B-6NPP/LITE was used for spin coating. NMR spectra were taken on a Bruker AVIII-400 spectrometer or Bruker DRX-500. $^1$H NMR spectra are reported with chemical shift relative to a TMS internal standard, and $^{13}$C spectra are reported with chemical shift relative to the CDCl$_3$ signal at 77.16 ppm. IR spectra were taken with a Thermo Nicolet Avatar 360 FTIR equipped
with a Harrick MVP-Pro ATR accessory. UV-vis spectroscopy was performed with an HP 8453 spectrophotometer. UV exposures were performed with a UV Process Supply, Inc. CureZone 2 equipped with a 400 W metal halide lamp and filtered through borosilicate glass (Borofloat 33, 3.3 mm thickness) unless otherwise noted. The spectral irradiance of the lamp was measured by a calibrated Ocean Optics HR2000 equipped with a 600 µm fiber optic cable and cosine corrector, and determined to produce an irradiance of 19 mW/cm² from 300-370 nm at the same location under the lamp where exposures were performed. Lap shear testing was performed using an MTS Criterion Model 42.

2.4.2 Synthesis

2.4.2.1 4-methyl-7-glycidyloxy coumarin Synthesis

The detailed synthesis procedure for 4-methyl-7-glycidyloxy coumarin can be found in Chapter 3, section 3.4.2.1.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{O} \quad \text{NH}_2 \\
\text{D-400: } n & = 6.2 \\
\text{D-2000: } n & = 33
\end{align*}
\]

2.4.2.2 Synthesis of D400-MGOC

4-Methyl-7-glycidyloxy coumarin (1.161 g, 5 mmol) and Jeffamine D-400 (0.435 g, 1 mmol) were measured in a 25 mL round bottom flask, and 6 mL of methanol was added. The flask was equipped with a condenser, flushed with nitrogen, and the colorless turbid mixture inside was
stirred with a magnetic stir bar while heated to reflux over a heating mantle – about 65 °C. After about 4 hours the opaque mixture turned completely transparent. The solution was refluxed for 24 hours. The resulting solution was rotary evaporated, then redissolved in 5 mL chloroform. Excess monomer was removed by elution through a silica plug with a 1:1 mixture of ethyl acetate and chloroform, and the desired product was collected by eluting with a 1:4 mixture of methanol in chloroform. The solution was rotary evaporated and dried further by heating to 40 °C under high vacuum for 24 hours. When cooled, the material was a light yellow, hard, brittle solid. 1.209 g. 89% yield. Melting point: 55-65 °C. 98% coumarin substitution.

\[\text{\(^1\)H NMR (400 MHz, CDCl}_3\): } \delta 0.96 (m, 1H), 1.02 (m, 0.5H), 1.13 (m, 4H), 2.39 (s, 3H), 2.59-3.01 (m, 2H), 3.16 (m, 0.5H), 3.26-3.77 (m, 5H), 3.91-4.22 (m, 4H), 6.11 (s, 1H), 6.70-6.91 (m, 2H), 7.47 (m, 1H)\]

2.4.2.3 Synthesis of D2000-MGOC

The reaction of Jeffamine D-2000 with 4-methyl-7-glycidyloxycoumarin was conducted identically to the reaction with D-400, except 1.980 g (1 mmol) of D-2000 was used as the starting material. The resulting material was a light yellow, viscous liquid. 2.498 g. 86% yield. 98% coumarin substitution.

\[\text{\(^1\)H NMR (400 MHz, CDCl}_3\): } \delta 0.97 (m, 1.1H), 1.03 (m, 0.4H), 1.13 (m, 24H), 1.29 (m, 0.2H), 1.82 (s, 0.8H), 2.39 (s, 3H), 2.55-3.03 (m, 2H), 3.08-3.75 (m, 26H), 3.91-4.21 (m, 4H), 6.12 (m, 1H), 6.75-6.90 (m, 2H), 7.48 (m, 1H). \text{\(^{13}\)C NMR (100 MHz, CDCl}_3\): } \delta 17.5, 17.6, 18.8, 73.1, 73.51, 73.53, 75.3, 75.47, 75.50, 75.7, 77.2, 101.8, 112.2, 112.3, 112.5, 125.67, 125.71, 152.6, 155.3, 161.4, 161.8\]
4-Methyl-7-glycidyloxyccoumarin (0.581 g, 2.5 mmol) was measured in a 10 mL round bottom flask, and 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine (Epotek 301 part B) (0.079 g, 0.5 mmol) was added by pipette. Methanol (3 mL) was measured and added, and the mixture was stirred with a magnetic stir bar. The mixture was heated under reflux while stirring with a magnetic stir bar under nitrogen for 24 hours, then the solvent was removed by rotary evaporation. The desired product was isolated using a silica plug; the crude product was dissolved in chloroform and loaded onto a silica plug, then eluted with a 1:1 mixture of chloroform and ethyl acetate until monomer was completely removed, and then eluted with a 1:1 mixture of chloroform and methanol. The product was rotary evaporated and dried further under high vacuum to leave a colorless, white foamed solid (0.521 g, 96% yield). Coumarin substitution is estimated to be 86%, determined by comparing the integration of the coumarin aromatic peak at 7.44 ppm to that of the diamine’s combined methyl peaks at 0.85-1.12 ppm. MP: 85-100 °C

$^1$H NMR (400 MHz, CDCl$_3$): 0.85-1.12 (m, 2.6H), 1.36-1.66 (m, 1.2H), 2.36 (s, 3H), 2.42-2.91 (m, 3H), 4.02 (m, 2H), 4.16 (m, 1H), 6.09 (m, 1H), 6.73 (m, 1H), 6.84 (m, 1H), 7.44 (m, 1H)
1,6-Hexanediame (HMDA-MGOC)

1,6-Hexanediame was sublimed before use. 1,6-Hexanediame (0.232 g, 2 mmol) and MGOC (2.79 g, 12 mmol) were measured in a 25 mL round bottom flask. Ethanol (7 mL) was added, the flask was fitted with a condenser, and flushed with argon. The solution was heated under reflux for 24 hours while stirring with a magnetic stir bar, then rotary evaporated. To isolate the product, the crude material was dissolved in dichloromethane, loaded atop a small silica gel column, and eluted with ethyl acetate until all monomer and byproduct was removed. The column was then eluted with a 1:1 mixture of methanol and dichloromethane to recover the desired product. The solution was rotary evaporated, and solvent removed under vacuum at 40 °C, leaving a white solids.

$^1$H NMR (400 MHz, CDCl$_3$): 1.35 (m, 1H), 1.54 (m, 1H), 2.36 (s, 3H), 2.47-3.00 (m, 3H), 3.65-4.30 (m, 4H), 6.09 (m, 1H), 7.64 (m, 1H), 6.84 (m, 1H), 7.44 (m, 1H)
### 2.4.2.6 1,3-bis(aminopropyl)tetrabytesdisiloxane (BAPTMDS-MGOC)

![Chemical Structure]

1,3-Bis(aminopropyl)tetrabytesdisiloxane (0.249 g, 1 mmol) and MGOC (1.16 g, 5 mmol) were measured in a 50 mL round bottom flask. Methanol (5 mL) was added to the flask, and the flask was flushed with nitrogen for about 20 minutes. The flask was heated under reflux under nitrogen for 24 hours. The solution was rotary evaporated, then dissolved in a small amount of dichloromethane and loaded onto a silica gel plug. The plug was eluted with ethyl acetate until excess monomer and byproduct was removed, then eluted with a 1:1 mixture of methanol and dichloromethane to recover the desired product. The solution was rotary evaporated, and the product was dried further by heating under vacuum, leaving a yellow foamed solid. 0.817 g, 69% yield. Melting point: 65-75 °C.

### 2.4.2.7 Gelest DMS-A11 (aminopropyl terminated PDMS) (DMS-A11-MGOC)

![Chemical Structure]

For DMS-A11, the amine hydrogen equivalent weight was taken to be 225 g/eq based on the molecular weight specifications provided by the manufacturer. 4-methyl-7-glycidyloxycoumarin
(2.322 g, 0.01 equivalents) and DMS-A11 (1.50 g, 0.0067 equivalents) were measured in a 25 mL round bottom flask. 6 mL of ethanol was added, and the mixture stirred with a magnetic stir bar. The flask was fitted with a condenser, flushed with nitrogen, and heated to a boil under reflux for 24 hours. The solution was rotary evaporated. The product was isolated on a silica column; the sample was dissolved in dichloromethane, loaded onto a column containing 50 g of silica gel, eluted with 1:1 mixture of dichloromethane and ethyl acetate to remove excess monomer, then a 1:1 mixture of dichloromethane and methanol to recover the product. After rotary evaporation, the product was a light yellow rubbery solid. 1.76 g. 58% yield.

2.4.2.8 Methylamine-MGOC (Model Compound)

4-Methyl-7-glycidyloxycoumarin (0.761 g, 3.28 mmol) was measured in a 25 mL round bottom flask. Methylamine (0.114 mL of 40 wt% solution in water) was measured by micropipette and added to the flask, giving a 1:2.5 ratio of methylamine to 4-methyl-7-glycidyloxycoumarin. The flask contents were dissolved in 2 mL chloroform and 0.5 mL ethanol, the flask was fitted with a condenser, flushed with argon, and heated to a gentle boil under reflux while stirring with a magnetic stir bar for 24 hours. The product was isolated by loading onto a silica gel column with chloroform, eluting with ethyl acetate to remove excess monomer and byproducts, then eluting with a 1:1 mixture of methanol and dichloromethane to recover the product. The solvent was removed by rotary evaporation, then further dried under vacuum. Mass recovered: 0.640 g, 98% yield.
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 2.39 \text{ (dd, } J = 1.8, 1.2 \text{ Hz, } 6\text{H}), \ 2.49 \text{ (d, } J = 8.2 \text{ Hz, } 3\text{H}), \ 2.83 - 2.64 \text{ (m, } 4\text{H}), \ 3.67 \text{ (br s, } 2\text{H}), \ 4.12 - 3.97 \text{ (m, } 4\text{H}), \ 4.22 - 4.15 \text{ (m, } 2\text{H}), \ 6.12 \text{ (dq, } J = 2.5, 1.2 \text{ Hz, } 2\text{H}), \ 6.78 \text{ (dd, } J = 8.2, 2.5 \text{ Hz, } 2\text{H}), \ 6.87 \text{ (ddd, } J = 8.8, 4.1, 2.5 \text{ Hz, } 2\text{H}), \ 7.48 \text{ (dd, } J = 8.8, 3.5 \text{ Hz, } 2\text{H}). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 161.63, 161.62, 161.33, 161.32, 155.23, 155.21, 152.68, 125.78, 125.78, 114.07, 114.04, 112.52, 112.49, 112.29, 112.27, 101.80, 101.76, 77.16, 70.70, 70.67, 67.15, 66.89, 61.15, 60.41, 43.86, 43.27, 18.80.

### 2.4.3 Thin Film Preparation, Exposure, and Testing

Fused quartz slides were cleaned by ultrasonication in a solution of 1% Liquinox detergent in water, DI water, and ethanol for 30 minutes each, followed by ozone treatment for 30 minutes. For D-400, an 8 wt% solution in cyclohexanone was prepared and filtered through a 0.45 µm PTFE syringe filter. 80 µL of the solution was cast onto slides by dispensing at 700 rpm for 8 seconds, then spinning at 1200 rpm for 1 minute. For D-2000, a 12 wt% solution in cyclohexanone was prepared and filtered, and cast onto slides by dispensing at 700 rpm and spinning at 1000 rpm for 1 minute. After spin coating, the slides were dried under high vacuum overnight.

A UV Process Supply, Inc. CureZone 2 equipped with a 400 W metal halide lamp was used for UV exposures. The lamp was filtered with a sheet of borosilicate glass (Borofloat 33, 3.3 mm thick) unless otherwise noted. The spectral irradiance of the lamp was measured by a calibrated Ocean Optics HR2000 equipped with a 600 µm fiber optic cable and cosine corrector, and determined to produce an irradiance of 19 mW/cm\(^2\) from 300-370 nm at the distance to the lamp samples were exposed from. Lamp emission spectra are shown in Supplementary Data section 2.5.4.
A fan was used to cool inside of the CureZone2 apparatus to approximately 40 °C, as measured by a thermocouple. To maintain samples at a constant temperature throughout the exposure, slides were placed on a glass plate and heated to 40 °C on a hot plate prior to exposure. UV-vis absorption spectra were measured for each slide before and after irradiation to measure dimerization conversion.

To measure solubility, the coated and irradiated slides were placed in a beaker filled with 30 mL of acetone at room temperature overnight, then removed, air dried, and massed.

### 2.4.4 Preparation and Irradiation of Thick Films

Glass microscope slides were cleaned by ultrasonication in a bath of 1% liquinox detergent in DI water for 30 minutes, then rinsed thoroughly with DI water, oven dried, and massed. A 20 wt% solution of D2000-4M7EPC in chloroform was prepared and pipetted onto the glass slide. The material was allowed to dry in the air for one hour, then dried under vacuum overnight, and massed. Samples were exposed using the CureZone2 one of three ways; in a borosilicate glass tube sealed with a rubber stopper and flushed with nitrogen, in the same glass tube but under air, or outside the glass tube. Exposure temperature was monitored with a thermocouple and maintained at approximately 40 °C using fans to cool the apparatus. UV absorption spectra of the thick films could not be measured due to excessively high absorbances.

### 2.4.5 Adhesion Testing

Adhesive strength was tested using a lap shear method adapted from the procedures specified in ASTM D1002-10\textsuperscript{178} using glass microscope slides as a substrate. 1 in x 3 in x 1.0 mm borosilicate glass slides were cleaned in an ultrasonic bath of 1% Liquinox detergent in DI water and thoroughly rinsed with DI water. D2000-MGOC was applied to the glass slides with an
overlap length of 0.5 in (12.7 mm), with an excess of material extending 0.25 in (6.35 mm) beyond the overlap region. The samples were held together with binder clips at during assembly and UV irradiation. The binder clips were attached at the very edges of the glass slides to minimize light obstruction. 4 sets of 6 samples each were prepared and exposed for 0, 5, 10, or 20 minutes. The unexposed control was heated to 70 °C in an oven for 5 minutes to replicate conditions inside the UV cure apparatus. Lap shear strengths were measured using an extension rate of 0.13 cm/min.

2.5 Supplementary Data

2.5.1 NMR Spectra

(continued on next page)
Figure 2.14 – $^1$H NMR Spectrum of 4-methyl-7-glycidyloxycoumarin (MGOC)

![H NMR Spectrum](image)

Figure 2.15 – $^{13}$C NMR Spectrum of 4-methyl-7-glycidyloxycoumarin (MGOC)

![C NMR Spectrum](image)
Figure 2.16 – $^1$H NMR Spectrum of Jeffamine D-400

Figure 2.17 – $^{13}$C NMR Spectrum of Jeffamine D-400
Figure 2.18 – $^1$H NMR Spectrum of D400-MGOC
Figure 2.19 – $^1$H NMR Spectrum of Jeffamine D-2000

Figure 2.20 – $^{13}$C NMR Spectrum of Jeffamine D-2000
Figure 2.21 – $^1$H NMR Spectrum of D2000-MGOC

Figure 2.22 – $^{13}$C NMR Spectrum of D2000-MGOC
Figure 2.23 – $^1$H NMR Spectrum of 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine (TMHDA)

$\text{H}_2\text{N} \bigg\| \bigg\| \text{H}_2\text{N}$

Figure 2.24 – $^{13}$C NMR Spectrum of 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine (TMHDA)

$\text{H}_2\text{N} \bigg\| \bigg\| \text{H}_2\text{N}$
Figure 2.25 – $^1$H NMR Spectrum of TMHDA-MGOC
Figure 2.26 – $^1$H NMR Spectrum of methylamine-MGOC

Figure 2.27 – $^{13}$C NMR Spectrum of methylamine-MGOC
2.5.2 Infrared Spectra

Figure 2.28 – IR spectrum of Jeffamine D-400 (unmodified)

Figure 2.29 – IR spectrum of Jeffamine D-2000 (unmodified)
Figure 2.30 – IR spectrum of 4-methyl-7-glycidyloxycoumarin

Figure 2.31 – IR spectrum of D400-MGOC
Figure 2.32 – IR spectrum of D2000-MGOC

2.5.3 UV-Vis Absorption Spectra

Figure 2.33 – UV absorption spectrum of neat Jeffamine D-2000 cast onto a fused quartz slide
2.5.4 Lamp Emission Spectra

Lamp emission spectra were measured with an Ocean Optics Jaz spectrometer with a 3 ms integration time and 100 scans averaged. Lamps were warmed up a minimum of 30 minutes before spectra were taken. Spectra for the metal halide lamp of the CureZone2 are normalized to the area of the 579 nm peak to allow comparison of the relative intensities for the different filters.

**Figure 2.34** – Emission spectra of CureZone2 metal halide lamp with three different filter conditions, full spectra

![](image1)

**Figure 2.35** – Emission spectra of CureZone2 metal halide lamp with three different filter conditions, zoomed in to UV region

![](image2)
**Figure 2.36** – Emission Spectra of CureZone2 metal halide lamp with three different filter conditions, zoomed in to region critical for photocleavage.
CHAPTER 3: PHOTOCLEAVABLE COUMARIN DIMER-BASED EPOXY RESINS

3.1 Introduction

Epoxy resins are a class of thermosetting polymer widely used as adhesives. Upon curing, an epoxy resin forms an intractable thermoset network which cannot be melted upon heating nor dissolved by solvent. This limits their utility in special applications where repairability and reworkability are desirable qualities. To eliminate the need for labor intensive mechanical removal, there is interest in creating polymers incorporating weak links which can be triggered by an external stimulus so that the adhesive can be removed or reworked on-demand without damage to the substrate being adhered. An ideal adhesive might retain the favorable properties of epoxy resins, including liquid precursors, solvent-free application, low shrinkage upon curing, and strong adhesion to a wide variety of surfaces, but with an added stimuli-responsive component allowing easy removal of the polymer. In this work, photocleavable coumarin dimers were used to create an epoxy resin capable of being debonded from an adherend using ultraviolet light as a stimulus.

There have been numerous approaches to creating such stimuli responsive polymers which could be incorporated into an epoxy resin or similar adhesive. Many approaches utilize dynamic bonds which change around an equilibrium condition, e.g. supramolecular interactions or dynamic covalent bonds. However, unless the system is carefully designed, such bonds can lead to creep in response to mechanical stress. Polymers have been made which utilize thermal, chemical, or photochemical stimuli to trigger chemistry which breaks a chemical bond or otherwise imparts a physical change to the material and make it removable. Of these possible stimuli, light is appealing in its ability to be applied with precise control in space and time.
The approach taken in this work was to utilize the photocleavage of coumarin dimers to break bonds in a crosslinked epoxy network. Of the possible photochemical approaches to thermoset reversibility, coumarin dimer photocleavage offers a way to break bonds upon UV irradiation without the need for any catalyst or co-reactant, and also a way to potentially repair bonds through subsequent photodimerization. The photodimerization of coumarin is well known\textsuperscript{181}; upon irradiation with UV wavelengths greater than 300 nm, coumarins can bond via a [2+2] cycloaddition to yield a dimer. This dimer can then be cleaved symmetrically back to monomeric coumarin upon exposure to UV wavelengths shorter than 300 nm. Photocleavage of the coumarin dimer is an efficient photochemical reaction, with quantum yields of 0.15 to 0.2.\textsuperscript{82}

While coumarin has primarily been used in polymers for its forward photodimerization reaction, there are also examples where pre-assembled coumarin dimers have been used as cleavable polymer building blocks. Chen et al. created polyurethanes containing photocleavable anti head-to-head coumarin dimers.\textsuperscript{45} Zhao et al. used coumarin dimers to create photoresponsive polysilsesquioxanes, nanoparticles of which could be deformed upon irradiation\textsuperscript{137}, and films of which could be patterned with varying thickness and refractive index upon dimer photocleavage.\textsuperscript{41} Recently, Abdalllh et al. created various polyacrylates containing a coumarin dimer bridged bis methacrylate crosslinker in which scratches could be healed by a cycle of photocleavage and photodimerization.\textsuperscript{139} Although these examples show the potential of coumarin dimer photocleavage for modification of materials, it remains to be seen whether this approach might be effective in modifying macro-scale mechanical bonds.

The object of this work was to utilize coumarin dimers to create a resin which can be cured like a conventional epoxy resin, but which exploits the efficient photocleavage of the coumarin dimers to enable reversion to a liquid form upon irradiation with short wavelength UV
light. From this material, the efficacy of coumarin dimer photocleavage for reversal of an adhesive can be evaluated. It is hypothesized that photocleavage of coumarin dimer units making up the crosslinks of a thermoset polymer network offers an efficient means of reverting a solid polymer to liquid fragments, and thereby enabling adhesive bonds to be released.

Scheme 3.1 – Overview of synthesis, curing, and photocleavage of a coumarin dimer-based epoxy resin

In this work, dimers of 4-methyl-7-glycidyloxycoumarin were synthesized, isolated, and used as a diepoxide which could be cured with a diamine to produce a thermoset polymer, as illustrated in Scheme 3.1. Jeffamine D-2000, a diamine with a polypropylene glycol backbone, was selected as the curing agent on the basis of the work in Chapter 2. When all amines of D-2000 were reacted with monomeric 4-methyl-7-glycidyloxycoumarin the product was found to remain a viscous liquid. Therefore, an epoxy formed from the coumarin dimer diepoxide cured
with D-2000, when photocleaved with short wavelength UV light, is expected to become a viscous liquid nearly identical to the photocurable resin studied in Chapter 2.

A series of experiments were developed to probe the curing of the epoxy resin and the capacity of photocleavage to induce debonding. Once a viable method of synthesizing and isolating the 4-methyl-7-glycidyloxycoumarin dimer was discovered, the curing behavior of epoxies cured with D-2000 was studied by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Adhesive strengths were measured using a standard lap-shear test with the epoxies used to adhere aluminum coupons. Lastly, the photocleavage ability of the epoxies was evaluated using a novel experiment in which fused quartz slides were adhered in a lap-shear configuration, pulled under a constant tension, and irradiated with 254 nm light until the lap-shear joint began to flow and eventually debond.

3.2 Results and Discussion

3.2.1 Synthesis

3.2.1.1 4-methyl-7-glycidyloxycoumarin (MGOC) Synthesis

![Figure 3.1 – 4-methyl-7-glycidyloxycoumarin (MGOC)](image)

The initial approach taken towards synthesizing the coumarin dimer diepoxide was to synthesize 4-methyl-7-glycidyloxycoumarin (Figure 3.1), photodimerize it, and then isolate the dimer photoproduct. The first step was therefore to synthesize the monomer. 4-methyl-7-
glycidyloxy coumarin synthesis was first attempted using the method reported by Jiang et al. However, the procedure was found to be irreproducible; it resulted in almost exclusive formation of the bis-coumarin shown in Figure 3.2.

![Figure 3.2 – bis-coumarin byproduct of MGOC synthesis](image)

Synthesis of the monomer was successful using a large excess of epichlorohydrin in ethanol, using potassium hydroxide to deprotonate phenolic hydroxycoumarin (Scheme 3.2). This process is not unlike the industrial process used for the large scale synthesis of diglycidyl ether of bisphenol-a (DGEBA), the most widely used conventional epoxy resin. The reaction is greatly accelerated by the use of a protic solvent, in this case ethanol.

![Scheme 3.2 – Synthesis of 4-methyl-7-glycidyloxy coumarin](image)

Traces of the bis-coumarin byproduct were removed completely by sublimation, and high purity was achieved after recrystallization in ethanol or toluene.

### 3.2.1.2 Early attempts at 4-methyl-7-glycidyloxy coumarin dimer synthesis

The first attempts to synthesize dimers were made by direct UV irradiation of the monomer. Although this produced moderate yields of product, preliminary efforts to isolate...
dimers from the reaction mixture proved to be very difficult. Photolysis of the monomer in solution afforded a mixture of syn head-to-head, syn head-to-tail, and anti head-to-tail dimers, trace byproducts, and residual monomer. Crystals could not be grown from this mixture, and chromatography on a silica gel column was unsuccessful due to very close retention factors of all components of the mixture.

It was therefore decided to pursue an approach which would synthesize a coumarin dimer derivative which could be made in high yield, isolated easily, and converted to the glycidyloxycoumarin dimer. The first such approach is shown in Scheme 3.3; the objective was to synthesize the anti head-to-tail 4-methyl-7-hydroxycoumarin dimer according to the procedure reported by Chen and Chen⁴⁵, and from this synthesize the glycidyloxycoumarin dimer using epichlorohydrin in the same fashion as monomeric 4-methyl-7-glycidyloxycoumarin.

![Scheme 3.3](image.png)

**Scheme 3.3** – Attempted synthesis of 4-methyl-7-glycidyloxycoumarin dimer from anti head-to-tail 4-methyl-7-hydroxycoumarin dimer

Synthesis of the anti head-to-tail hydroxycoumarin dimer was successful, however the reaction with epichlorohydrin was not. The reaction was attempted with numerous bases and
solvents, but in all cases a complex mixture of byproducts was formed. It was only later discovered that nearly this same approach had been attempted unsuccessfully and was reported in the dissertation of Zhao.\textsuperscript{85} The anti dimers of coumarin are unstable under alkaline conditions, and the phenolic hydroxycoumarin dimer cannot be deprotonated without rapid degradation of the molecule.

Furthermore, anti dimers are especially susceptible to opening of their lactone rings by nucleophiles.\textsuperscript{84} This suggests that if amines were used as a curing agent for such an epoxy they would be likely to react with lactones in competition with the epoxide as illustrated in Figure 3.3. This side-reaction would have two effects. Firstly, the maximum crosslink density of the polymer would be reduced, since the reaction would form an amide which is unable to readily react with a second epoxide. Secondly, this would likely hinder the photo-reversibility of the polymer, since ring-opened coumarin dimers are reported to preferentially photocleave asymmetrically.\textsuperscript{77}

![Figure 3.3 - Possible reactions of coumarin dimers with amines](image)

Figure 3.3 – Possible reactions of coumarin dimers with amines; (a) the intended reaction of each amine with two epoxide groups, and (b) undesired lactone ring opening of anti dimers by amines, which would compete with the intended reaction and allow asymmetric photocleavage. To avoid this possibility, syn dimers were selected instead of anti.

It thus became clear that syn dimers would be necessary for use in an epoxy resin cured by amines. The next approach attempted was similar to one reported by Zhao.\textsuperscript{85} Coumarin
dimerization can be catalyzed by the presence of boron trifluoride and other Lewis acids.\textsuperscript{38,39} The Lewis acid forms a complex with the coumarin carbonyl which has the effect of increasing coumarin’s excited singlet state lifetime, thereby greatly increasing the quantum yield of photodimerization and selectively forming the syn head-to-tail dimer, which could be readily isolated by crystallization. This approach could not be used on glycidyloxyoumarin directly however, due to the tendency of Lewis acids to induce ring opening polymerization of epoxy groups. Instead, 4-methyl-7-allyloxyoumarin could be dimerized in the presence of BF\textsubscript{3} and the allyl group of the resulting syn head-to-tail dimer could be epoxidized to the glycidyloxyoumarin dimer using a peroxide such as meta-chloroperoxybenzoic acid (m-CPBA). This approach is outlined in Scheme 3.4.

\textbf{Scheme 3.4} – Attempted synthesis of syn head-to-tail 4-methyl-7-glycidyloxyoumarin by allyloxyoumarin route. Lewis acid catalyzed photodimerization was unsuccessful.

4-methyl-7-allyloxyoumarin was synthesized according to the procedure by Zhao.\textsuperscript{85} An approximately 0.2 M solution was prepared with dry and degassed dichloromethane, and BF\textsubscript{3}•OEt\textsubscript{2} was added by syringe under inert gas. The solution was irradiated for 72 hours in a Rayonet photochemical reactor. After irradiation, the solution was washed with water, dried, and evaporated, but \textsuperscript{1}H NMR of the product revealed that no dimerization had taken place. Because
the Lewis acid catalyzed photodimerization of a 4-methyl substituted coumarin has not been reported before, the photoreaction was repeated with 7-allyloxycoumarin as in the literature. Unexpectedly the reaction again yielded no photoproducts, and only unchanged 7-allyloxycoumarin could be recovered.

Lewis acid catalyzed photodimerizations have only been reported using water-cooled immersion well type photoreactors, therefore it is hypothesized that the elevated temperature inside the Rayonet photochemical reactor (40 °C) may interfere with the complexation of the coumarin by BF$_3$, or increase the rate of quenching of the excited singlet state. More work is needed to determine the exact reason why these photoreactions were unsuccessful.

From these results it became clear that direct irradiation would be the best way to obtain the desired syn dimers, and that an improved purification method would be necessary to isolate them.

3.2.1.3 Photodimerization and isolation of 4-methyl-7-glycidyloxycoumarin dimers

3.2.1.3.1 Solid State Photodimerization of 4-methyl-7-glycidyloxycoumarin

It was hypothesized that solid state photodimerization might offer an efficient method of synthesis of the coumarin dimers. Solid state photodimerizations of various coumarin derivatives have been well studied. 4-methyl-7-methoxycoumarin is reported to undergo dimerization from the solid state, producing syn head-to-head dimers as the major product and syn head-to-tail as the minor product. It was therefore hypothesized that 4-methyl-7-glycidyloxy coumarin might offer similar behavior in the solid state.

Solid MGOC previously crystallized in toluene was irradiated with the metal halide lamp in glass ampoules flame sealed under argon. A series of samples were irradiated between 3 and 48 hours, and the products analyzed by $^1$H NMR. Figure 3.4 shows the composition of each
sample plotted as a function of irradiation time. Early in the exposure the syn head-to-head dimer predominates, unlike in solution state exposures where syn head-to-tail is the dominant product. This suggests that syn head-to-head is the topochemically preferred product arising from the crystal structure of the starting material, and that the syn head-to-tail dimer, which is preferred in all other circumstances, arises as a result of defects in the structure which increase with prolonged exposure.

![Graph](image)

**Figure 3.4** – Evolution of photoproducts from solid state irradiation of MGOC, determined by $^1$H NMR spectroscopy

Figure 3.4 shows the fraction of each component in the irradiated samples as a function of time as determined from integrations of their respective $^1$H NMR peaks. Unexpectedly, the fraction of syn head-to-head dimer not only decreases in rate of formation as irradiation progresses, but the absolute quantity of syn head-to-head decreases in favor of syn head-to-tail. This would suggest that during irradiation there existed a steady state between photodimerization and photocleavage, where some fraction of syn head-to-head already formed was cleaved to monomer and subsequently re-dimerized into the increasingly favorable syn
head-to-tail. However, the irradiation was performed with the lamp equipped with a soda-lime glass filter which filtered nearly all measurable light of wavelength less than 300 nm (Figure 3.27, in section 3.7 - Supplementary Data). This surprising result highlights the high quantum efficiency of the photoeleavage reaction compared to dimerization.

X-ray diffraction (XRD) was performed to determine the crystal structure of 4-methyl-7-glycidyloxycoumarin. Data from this measurement can be found in Supplementary Data section 3.5.5. The crystal was determined to have an orthorhombic structure with coumarin units aligned parallel in a head-to-head configuration. This explains the topochemical preference for the syn head-to-head dimer. The reactive double bonds are situated 4.13 Å apart, indicating the reaction is consistent with the topochemical principles promulgated by Schmidt. The formation of syn head-to-tail dimer therefore occurs at defect sites in the crystal, which increase in number as photodimerization continues and disrupts the structure of the lattice. Similar behavior was observed by Moorthy and Venkatesan in 4-methyl-7-methoxycoumarin, where the non-topochemically preferred syn head-to-tail dimer increases in proportion to the topochemically preferred syn head-to-head dimer as the reaction progresses. The decrease in the overall quantity of syn head-to-head dimer was not observed in 4-methyl-7-methoxycoumarin, however.
3.2.1.3.2 Solution State Photodimerization of 4-methyl-7-glycidyloxycoumarin

Scheme 3.5 – Photodimerization of 4-methyl-7-glycidyloxycoumarin by direct irradiation in acetonitrile solution, 0.3 M, for 140 hours

Direct irradiation in solution turned out to be convenient and produce high yields after long irradiation times. A 0.3 M solution in acetonitrile was irradiated in a Rayonet photochemical reactor with 350 nm lamps (emission spectrum shown in Supplementary Data section 3.5.3, Figure 3.28) for 5 days and 20 hours, resulting in approximately 87% conversion of the monomer. Analysis of the $^1$H NMR spectrum of the crude photoproduct mixture revealed 67% syn head-to-tail, 16% syn head-to-head, approximately 4% anti head-to-tail, and 13% monomer.

3.2.1.3.3 Isolation of 4-methyl-7-glycidyloxycoumarin dimers

Isolation of the MGOC dimers was achieved using flash chromatography on a silica gel column in an automated flash chromatography system. Numerous eluents were screened using thin layer chromatography, until it was found that a mixture of 1 part acetone with 2 parts hexanes produced much better separation than any other solvent or solvent combination. This produced a $\Delta R_f$ of 0.12 between the monomer and syn head-to-tail spots, with clear definition of three major products. An automated flash chromatography system with high resolution 25-40
µm silica gel columns was used. Syn head-to-head was able to be isolated with good purity. Syn head-to-tail was isolated with approximately 98% purity, containing traces of anti head-to-tail dimer, which eluted at nearly the exact same rate as syn head-to-tail.

### 3.2.2 Curing of Coumarin Dimer Epoxy Resins

The coumarin dimer diepoxides thus synthesized could in principle be cured with any conventional epoxy curing agent in which they are soluble. Jeffamine D-2000, a diamine with a polypropylene glycol backbone, was selected as the principal curing agent to be studied. It possesses excellent UV transparency at 254 nm, and previous experiments described in Chapter 2 showed that when all amines are completely reacted with monomeric 4-methyl-7-glycidyloxycoumarin, it remains a viscous liquid. It was expected that this same liquid product would be generated by photocleavage of the fully cured epoxy network, and that this reversion to liquid would enable the release of an adhesive bond.

**Figure 3.5** – The expected product of syn HH MGOC cured with Jeffamine D-2000

Because syn head-to-head and syn head-to-tail dimers were isolated separately by chromatography, it was decided to prepare resins from both dimers separately to determine
whether the dimer structure would influence the properties of the epoxy. Initial attempts at mixing the coumarin dimers with Jeffamine D-2000 found that both dimers were poorly soluble in the liquid diamine at room temperature. When heated to 100 °C, however, the coumarin dimer solids melted and dissolved, reprecipitating into solids when cooled back to room temperature. This indicated that D-2000 would make a suitable curing agent. To homogenize the resin mixtures, the coumarin dimer-based resins were dissolved in dichloromethane prior to application, which left the dimer uniformly dispersed in the curing agent as fine particles after evaporation of the solvent.

The time-temperature schedule required to adequately cure the resin into a crosslinked network was determined using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) experiments.

3.2.2.1 DMA Results

Dynamic mechanical analysis was used to determine a cure schedule for the epoxy resins. An apparatus designed for paste samples was used in which the cylindrical probe was partially immersed in a small sample of the liquid resin, and linear oscillation was applied. Due to a complex combination of compressive and shear forces resulting from the probe immersed in resin, the measurements were not calculated using a proper geometric factor, and therefore the reported moduli are only relative measurements. However, the experiment provided useful information regarding transitions and the evolution of the material’s stiffness. Using this method, the gel point could be determined by the onset of the storage modulus, $E'$, which shows the material beginning to show solidlike behavior. Gel points were determined using the peak of $\tan \delta$, which is equal to the ratio of the storage modulus $E'$ and the loss modulus, $E''$. 
Preliminary experiments using the conventional epoxy resin diglycidyl ether of bisphenol-a (DGEBA) showed that Jeffamine D-2000 produces very slow curing epoxy resins. This is likely because of the high dilution of reactive amines as a result of the large PPG backbone of the diamine, and to a lesser extent due to a degree of steric hinderance from methyl groups adjacent to the amines. The mixed resin left at room temperature did not gel after many days, but the resin eventually cured to a soft, rubbery solid.

Results of DMA curing experiments are shown in Figure 3.6, where $E'$ is the storage modulus and $E''$ is the loss modulus. DGEBA cured with D-2000 at 100 °C resulted in gelation after 5 hours 27 minutes (Figure 3.6A). The storage modulus $E'$, which appears at the onset of gelation, steadily increases over the course of 48 hours. Syn HT MGOC showed very different behavior, gelling after only 2 hours 32 minutes (Figure 3.6B), and reaching a plateau in stiffness much faster than DGEBA.

Figure 3.6 – DMA results for curing of (A) DGEBA and (B) syn HT MGOC with Jeffamine D-2000 in paste apparatus at 100 °C over 48 hours using 1 Hz oscillation. Gel point occurred at 5 hours 27 minutes for DGEBA, and 2 hours 32 minutes for syn HT MGOC. (Moduli $E'$ and $E''$ are relative measurements due to undefined sample geometry.)
3.2.2.2 DSC Results

Thermograms of all three resins for both uncured resin mixtures as prepared and resins cured at 100 °C for 12 hours are shown in Figure 3.7. To get a sense of the extent of reaction after this cure cycle, the integrations of the exotherm taken from 80 to 300 °C for the uncured and cured DGEBA-based resins were compared, revealing approximately 90% conversion. The cure exotherms for the coumarin dimer-based epoxy resins could not be quantified directly due to extra features, but the largely unchanging slope in the region of the exotherm indicates the reaction has progressed nearly to completion.

The thermograms for syn HH and syn HT MGOC containing epoxy resins show some noteworthy features. In syn HH at about 60 °C and in syn HT at 94 °C there are small endotherms attributable to the melting of the dimer solids dispersed in the D-2000 curing agent. In syn HH there is an exotherm at 230 °C, which can be attributed to the thermal cleavage of the coumarin dimer. This exotherm is not present in the syn HT-based resin, although the beginnings of an exotherm are visible near 300 °C which may indicate the onset of thermal cleavage for this dimer. This suggests the syn HT is more thermally robust than syn HH. (A detailed study of the thermal cleavage phenomenon is reported in Chapter 4.)

The thermograms also reveal the glass transition temperatures of both the uncured mixture and cured polymer, reported in Table 3.1. The $T_g$'s are all well below room temperature, as expected for the soft rubbery polymers produced by D-2000. The $T_g$ increases upon curing for all materials with the exception of syn HH, which unexpectedly does not change upon curing.
Figure 3.7 – DSC thermograms of epoxy resins before and after curing at 100 °C for 12 hours. Run with 5 °C/min ramp rate. Thermograms are plotted exotherm down.
Table 3.1 – Glass transition temperatures for epoxies mixed with Jeffamine D-2000 before and after curing. Measured by DSC with 5 °C/min heating rate.

<table>
<thead>
<tr>
<th></th>
<th>Uncured T_g (°C)</th>
<th>Cured T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA</td>
<td>-64</td>
<td>-47</td>
</tr>
<tr>
<td>Syn HH</td>
<td>-50</td>
<td>-51</td>
</tr>
<tr>
<td>Syn HT</td>
<td>-54</td>
<td>-48</td>
</tr>
</tbody>
</table>

3.2.2.3 FTIR Analysis of Cured Resins

One concern for curing of the resin was that coumarin dimers are capable of ring opening with nucleophiles like amines, as illustrated in Figure 3.3. Although this reaction could still allow the polymer to cure into a crosslinked network, it would both reduce ultimate crosslink density and harm the reversibility of the cured resin because ring opened coumarins are known to preferentially photocleave asymmetrically. Both anti and syn head-to-head dimers are known to undergo lactone ring opening, with anti reacting more readily than syn. This reaction has not been reported with head-to-tail dimers nor with 4-substituted coumarin dimers like the 4-methyl coumarin used here, therefore it was unknown how these derivatives would behave.

The cured polymers were analyzed using FTIR spectroscopy. Lactone ring-opening of syn head-to-head coumarin dimer by a primary amine would result in the formation of amides or imides. Amides would be expected to be found in the region 1630-1690 cm\(^{-1}\). FTIR spectra were obtained on the cured materials, and no evidence of these reactions could be found (Figure 3.8). The IR spectra do not show any new signals not present in the original dimers. Therefore, it can be concluded that no significant lactone ring-opening occurred in competition with the epoxy reaction. Additional IR spectra of the epoxy resins can be found in Supplementary Data section 3.5.2.
3.2.3 Lap Shear Adhesion Testing of Epoxy Resins

Adhesive strengths of the epoxy resins were determined using a single lap-shear method, according to ASTM D1002. This test allowed the epoxies to be evaluated as adhesives and allowed a direct comparison of the mechanical performance of the coumarin dimer-based epoxies with those prepared from the conventional diglycidyl ether of bisphenol-a (DGEBA).

Figure 3.8 – Carbonyl region of the IR spectra of syn HH and syn HT MGOC cured with Jeffamine D-2000. No new peaks indicative of lactone ring-opening are present.

Figure 3.9 – Average lap shear strengths of epoxy resins cured with Jeffamine D-2000
The lap shear strengths for the three epoxy resins are shown in Figure 3.9, and representative stress-extension curves are shown in Figure 3.10. This data is tabulated in Table 3.2. Syn HH MGOC produced the strongest bond, followed by DGEBA, with syn HT MGOC producing the weakest bond.

**Table 3.2** – Average lap shear strengths of epoxy resins cured with Jeffamine D-2000

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>Lap shear strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syn HH MGOC</td>
<td>3.99 ± 0.80</td>
</tr>
<tr>
<td>Syn HT MGOC</td>
<td>2.30 ± 0.35</td>
</tr>
<tr>
<td>DGEBA</td>
<td>2.83 ± 0.40</td>
</tr>
</tbody>
</table>

The results were somewhat unexpected. It might be expected that the coumarin dimer-based epoxies would produce weaker resins, since they were applied with solvent which might create bubbles and defects if traces of the solvent remained during curing. However, the
strength of syn HT and DGEBA were comparable, and syn HH produced a stronger bond than both.

There is a significant difference between syn HH and syn HT dimers. After curing the resins, it was noticed that those containing syn HT were softer and more flexible than syn HH. This does not appear to be a result of a difference in reactivity between the two monomers; DSC measurements demonstrated that conversions were essentially identical for identical cure schedules.

Overall, the soft, elastomeric polymer resulting from the long flexible PPG backbone of D-2000 results in a relatively weak adhesive bond. For comparison, the strengths here are nearly ten times weaker than those of a rigid, densely crosslinked epoxy previously tested in our lab by the same method. The lap shear strength of a DGEBA cured with 2,2,4(2,4,4)-trimethyl-1,6-hexanediamine, a short aliphatic diamine, was found to be 27 MPa. However, these results suggest that there is no reason to expect that coumarin dimer diepoxide should not form bonds with comparable strength to DGEBA-based resins should a different curing agent be used.

### 3.2.4 Photocleavage Testing of Coumarin Dimer Epoxy Resins

A preliminary experiment was performed to observe coumarin dimer photocleavage spectroscopically in the cured polymer itself. Two fused quartz plates were clamped together with syn HT-MGOC-D2000, cured, and irradiated with 254 nm light, with UV-vis spectra taken every minute. The spectra are shown in Figure 3.11. These spectra show the appearance of the characteristic absorption peak of the monomeric coumarin at 320 nm, confirming the occurrence of dimer photocleavage. The rate of photocleavage is very nearly constant over 10 minutes of irradiation. Interestingly, the spectra also show that the absorbance at 254 nm, the wavelength of irradiation, is nearly constant during this exposure.
Figure 3.11 – UV-Vis spectra of cured syn HT-MGOC-D2000 showing spectral change with 254 nm irradiation. Each spectrum taken one minute apart.

An experiment was devised to study the effect of photocleavage on an adhesive bond made by the coumarin dimer epoxy resin. The coumarin dimer epoxy was used to adhere two fused quartz microscope slides in a lap-shear configuration. After the lap-shear samples were assembled and cured, they were placed in an Instron mechanical tester with tension clamps, and a constant force of 10 N in tension was applied to the sample. While under tension, the sample was irradiated with short wavelength ultraviolet light from a 4 W lamp (lamp spectrum can be found in Figure 3.28 in Supplementary Data). The apparatus is shown in Figure 3.12. It was hypothesized that after a certain amount of irradiation, photo cleavage would break a number of bonds such that the degree of crosslinking was lower than the gel point. Because Jeffamine D-2000 gives the polymer a glass transition temperature well below room temperature, once the gel point is passed the polymer was expected to become a liquid and viscous flow would begin, and this would be apparent as an extension of the crosshead of the Instron.
Specimens made from syn HH MGOC-D2000, syn HT MGOC-D2000, and DGEBA-D2000 as a control were tested. Before irradiation, all specimens were held under constant tension over the course of one hour, during which time no extension occurred, indicating complete cure to a solid. The control, DGEBA-D2000, was exposed to 254 nm light under tension for one hour and no extension was observed. The two coumarin dimer resins when irradiated began to show very small deformations very early on in the exposure. Within minutes, substantial extension could be measured. The slides slowly flowed apart at an increasing rate as shear area decreased and presumably as the viscosity of the polymer at the interface decreased. Both syn HH and syn HT completely debonded within 10 minutes of exposure. The results of this experiment are tabulated in Table 3.3.
Figure 3.13 – Extension vs time for the lap shear samples exposed with 254 nm light while pulled under tension. The onset of extension indicates the point at which the bond is released and viscous flow begins, i.e., the point at which the epoxy network is photocleaved into liquid fragments.

Table 3.3 – 254 nm irradiation times required for onset of adhesive debonding (time required for 1% extension) and complete debonding (time required for 100% extension).

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>Avg. time to 1% extension (min)</th>
<th>Avg. time to complete debonding (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syn HH MGOC</td>
<td>4.7 ± 0.3</td>
<td>9.9 ± 1.1</td>
</tr>
<tr>
<td>Syn HT MGOC</td>
<td>3.8 ± 0.3</td>
<td>6.7 ± 1.2</td>
</tr>
<tr>
<td>DGEBA</td>
<td>∞</td>
<td>∞</td>
</tr>
</tbody>
</table>

Syn HH based resin took on average 595 s (9 min 55 s) for complete debonding. Syn HT took on average 400 s (6 min 40 s), a much shorter exposure time. The discrepancy between the two recalls the trend observed in the lap-shear adhesive strength measurements. Syn HT produced a noticeably softer and more elastic polymer upon curing, and gave lower strength adhesion, and this is likely related to the reason why it debonded more rapidly with photocleavage. From the literature we do not expect the quantum yield for photocleavage of syn
HT to be greater than syn HH; both dimers should photocleave at comparable rates. Together, these results would be expected if syn HT epoxy possessed a lower crosslink density than syn HH to begin with. This cannot be explained by a difference in reactivity between the two coumarin dimer diepoxides; DSC experiments showed no significant difference between the two. The precise reason for the difference between syn HH and syn HT remains unclear.

Specimens for photocleavage were prepared with a thin wire spacer between the fused quartz slides to determine whether the thickness of the adhesive joint had an effect on the debonding of the joint. It was hypothesized that due to strong absorption of the 254 nm light, photocleavage was only likely to occur in a thin layer close to the surface being irradiated. If this were the case, we would expect the time required for debonding to be essentially independent of the thickness of the epoxy layer. In all samples, when the slides separated the side closest to the UV lamp was left relatively clean, while the slide on the opposite side of the lamp retained the remainder of the epoxy film. This indicates that photocleavage had indeed only taken place only at the surface incident to the 254 nm light.

This brings up one of the limitations of this material and of this general approach to reversible adhesives. The reversibility of this material is limited chiefly by the finite transmissibility of short wavelength UV light through both the epoxy and the substrate to which it is adhered. Because of strong absorption of 254 nm light, photocleavage is only capable of occurring in a thin layer at the surface being irradiated. If the molar absorptivity of the coumarin dimer is 4540 M$^{-1}$cm$^{-1}$ at 254 nm (see Figure 3.31 in Supplementary Data section 3.7.4), and assuming the concentration of coumarin dimers in the material is approximately 0.7 M (as estimated from the density of material and the molecular weight of its repeating units) we can calculate that 99% of 254 nm light is absorbed within 6.2 μm of the surface. While this is
perfectly suitable for releasing adhesive bonds made directly to a UV transparent window, it means that thick layers of the epoxy cannot be readily reverted into liquid.

Furthermore, the requirement for UV wavelengths shorter than 300 nm limits the types of substrates from which this epoxy can be effectively debonded. Everyday materials including most common glasses and polymers are typically opaque to these wavelengths. However, there are still many materials transparent below 300 nm, including fused silica, quartz, sapphire, diamond, BaF₂, CaF, MgF₂, SrF, CsBr, CaCO₃ (calcite), YAG (undoped), some polyolefins, and numerous salts (KCl, KBr, NaF, NaCl, and LiF). Some borosilicate glasses are partially transparent down to 280 nm. Considering that many of these materials are used for specialty optical applications, it is conceivable that a photo-reversible epoxy like this could be useful for reversible assembly of optical components.

### 3.2.5 Repair of Photo-Debonded Epoxy Resins by Photodimerization

Photocleavage of coumarin dimers was found to effectively debond the adhesive, presumably leaving a population of monomeric coumarins at the interface exposed to 254 nm light as coumarin dimer crosslinks are broken. This raised the question of whether the adhesive bond might be capable of being re-formed by re-dimerization of monomeric coumarins with long wavelength UV exposure. To test this, preliminary experiments were conducted in which the photo-debonded specimens were reassembled, clamped with binder clips, and irradiated with UV (λ > 300 nm) using the CureZone 2 for 30 minutes. After long wavelength irradiation, the samples were placed back in the Instron and 10 N of tension was applied. After one hour under constant tension, no movement could be measured. This indicated that the photocleaved epoxy re-formed into a solid, nonflowing crosslinked network by photodimerization, and the adhesive bonds released by photocleavage are photo-repairable.
3.3 Conclusions

Coumarin dimer diepoxides were synthesized that were capable of reacting with diamines to produce crosslinked epoxy resins. This was achieved via direct irradiation of 4-methyl-7-glycidyloxycoumarin (MGOC) in solution, resulting in syn HH MGOC and syn HT MGOC dimers which were isolated by flash chromatography. Syn dimers were deemed necessary for the application to avoid the possibility of anti dimers undergoing lactone ring-opening with the diamines.

The diamine Jeffamine D-2000 was selected as a curing agent to produce resins that could be reverted to liquids upon decrosslinking by photocleavage. Both coumarin dimers were insoluble in D-2000 at room temperature, but dissolved upon heating to 100 °C. The reaction of the dimer diepoxides with Jeffamine D-2000 produced soft, flexible crosslinked polymer.

Lap shear testing was performed to evaluate the epoxies as adhesives. Although the polymers produced by D-2000 are relatively weak adhesives compared to more densely crosslinked epoxies, the strengths of the epoxies made from coumarin dimers are comparable to those made with the conventional epoxy resin diglycidyl ether of bisphenol-a (DGEBA). Syn HH MGOC produces an even stronger bond than DGEBA. The two dimers were found to produce epoxies with surprisingly different mechanical properties; Syn HT MGOC was notably softer than syn HH and produced weaker adhesive bonds. The reason for this difference remains unclear; both resins cured to a high degree of conversion, and no evidence of unintended side reactions such as lactone ring opening in the coumarin dimers could be detected.

Using coumarin dimers as building blocks for an epoxy resin has been demonstrated to be effective means of imparting photo-triggered reversibility in an adhesive material. To
demonstrate photoreversibility, fused quartz slides adhered with the epoxy were irradiated with 254 nm UV light while pulled under tension. Photocleavage was found to revert the cured polymer to liquid in a thin layer at the surface being irradiated, allowing the slides to slide apart until the adhesive joint was completely debonded. A small 4 W handheld UV lamp was capable of causing complete debonding of the epoxy joins in under 10 minutes. Repair of the photocleaved specimens was also demonstrated; photo-debonded specimens were rejoined and irradiated with long wavelength UV light to induce photodimerization of the new monomeric coumarins, which successfully re-formed a solid adhesive bond.

In conclusion, coumarin dimers serving as crosslinks in an epoxy resin is a viable means of creating a photoreversible thermoset adhesive. The resin, a mixture of a coumarin dimer diepoxide and a diamine, can be cured by heating like a traditional epoxy resin, creating adhesive bonds which can be later broken by photocleavage of the coumarin dimers by exposure to 254 nm light.
3.4 Experimental

3.4.1 Materials and Instrumentation

4-Methyl-7-hydroxycoumarin (4-methylumbelliferone) was purchased from Gold Biotechnology and used as received. 7-Hydroxycoumarin (umbelliferone) was purchased from Chem Impex Intl Inc. and recrystallized in ethanol before use. Epichlorohydrin was purchased from Acros Organics. Sodium acetate, benzophenone, allyl bromide, and boron trifluoride diethyl etherate were purchased from Sigma Aldrich. Acetic anhydride was purchased from EMD Millipore, and pyridine from Mallinckrodt. Diglycidyl ether of bisphenol-a (equivalent to D.E.R. 332) was purchased from Sigma Aldrich. Jeffamine D-2000 was received as a donation from Huntsman Corporation. Dichloromethane, toluene, and acetone were purchased from Fisher Chemical. Ethyl acetate, glacial acetic acid, and acetonitrile were purchased from EMD Millipore. Anhydrous ethanol was purchased from Decon Labs Inc., and diethyl ether was purchased from J.T. Baker. All solvents were ACS grade or better and used as received unless otherwise noted.

Solid state photodimerizations were performed with a UV Process Supply, Inc. CureZone 2 equipped with a 400 W metal halide lamp, filtered through soda lime glass. Solution state photodimerizations were performed using a Rayonet RPR-100 photochemical reactor equipped with 16 RMR-3500A lamps. For photocleavage experiments, a UVP UVGL-25 4 watt compact UV lamp was used. The emission spectra of these lamps were measured with an Ocean Optics Jaz portable spectrophotometer and can be found below in Section 3.5.4. Purification of coumarin dimers was performed with a Yamazen Corporation W-Prep 2XY automated flash chromatography system using size 2L Yamazen Universal Premium silica columns and size M injection columns. Melting points were measured in capillary tubes using a Stanford Research
Systems EZ-Melt, unless otherwise noted, and reported uncorrected. Differential scanning calorimetry (DSC) was performed with a TA Instruments Discovery DSC 25. Dynamic mechanical analysis (DMA) curing experiments were performed with a Netzsch DMA 242 E Artemis using the paste sample accessory. NMR spectra were taken with either a Bruker AVIII 400 MHz spectrometer or a Bruker DRX 500 spectrometer. Tetramethylsilane (TMS) was used as the internal standard for $^1$H spectra and CDCl$_3$ as the standard for $^{13}$C spectra. Infrared spectra were taken using a Thermo Nicolet Avatar 360 FTIR with a Harrick MVP-Pro ATR accessory. UV-vis spectra were taken with an HP 8453 spectrophotometer. X-Ray diffraction was performed using a Bruker APEX-II CCD diffractometer, with the crystal kept at 100 K during data collection, and the structure solved using Olex2$^{186}$ with the ShelXT$^{187}$ structure solution program using intrinsic phasing and refined with the ShelXL$^{188}$ refinement package using least squares minimization. An MTS Criterion Model 42 mechanical tester was used for lap-shear adhesion experiments. An Instron 5540 Series mechanical tester equipped with tension clamps was used for photocleavage experiments.

### 3.4.2 Synthesis

#### 3.4.2.1 Synthesis of 4-methyl-7-glycidyloxycoumarin (MGOC)

![Chemical structure of 4-methyl-7-glycidyloxycoumarin (MGOC)]

4-Methyl-7-hydroxycoumarin (15.00 g, 85.1 mmol) was measured in a 1000 mL three neck flask. The flask was fitted with a condenser, drying tube, and thermometer. 450 mL of a solution of 10 wt% potassium hydroxide in ethanol was added to the flask, dissolving the colorless solids and
forming a bright yellow solution. The solution was stirred at room temperature for 1.5 hours, during which time the solution became turbid. Epichlorohydrin (100 mL, 1.28 mol) was then added, and the solution was heated to 79 °C under reflux. After 3 hours the mixture was allowed to cool to room temperature and rotary evaporated to leave behind yellow solids. The solids were dissolved in 400 mL dichloromethane and washed with 300 mL deionized water three times, turning the organic layer colorless and clear. The organic layer was separated, dried with anhydrous magnesium sulfate, vacuum filtered, and rotary evaporated to produce white solids. The product was purified by sublimation at 125°C and 0.070 torr, yielding 16.845 g (72.5 mmol) of pure white product. 85% yield. Melting Point: 129-130 °C (lit. 133 °C<sup>189</sup>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 2.40 (d, J = 2.0 Hz, 3H), 2.79 (dd, J = 4.8, 2.6 Hz, 1H), 2.94 (dd, J = 4.8, 4.1 Hz, 1H), 3.38 (ddt, J = 5.9, 4.1, 2.7 Hz, 1H), 3.97 (dd, J = 11.1, 5.9 Hz, 1H), 4.33 (dd, J = 11.0, 2.8 Hz, 1H), 6.14 (q, J = 1.25 Hz, 1H), 6.82 (d, J = 2.50 Hz, 1H), 6.89 (dd, J = 8.79, 2.52 Hz, 1H), 7.50 (d, J = 8.79 Hz, 1H). 13<sup>C</sup> NMR (100 MHz, CDCl<sub>3</sub>): 18.80, 44.66, 49.91, 69.32, 101.78, 112.38, 112.70, 114.14, 125.77, 152.57, 155.28, 161.28, 161.50. FTIR: 1717, 1619, 1393, 1377, 1345, 1285, 1266, 1207, 1157, 1141, 1133, 1072, 1032, 1017, 1032, 1017, 982, 912, 862, 848, 829, 807, 763 cm<sup>-1</sup>

### 3.4.2.2 Synthesis of 7-glycidyloxycoumarin (GOC)

![](image)

7-Hydroxycoumarin (1.03 g, 6.35 mmol) was added to a 50 mL three neck flask fitted with a condenser, drying tube, and magnetic stir bar. A solution of 0.8 % (w/v) of sodium hydroxide in
ethanol was prepared and 40 mL of this solution was added to the flask. Upon addition of the base, the pale yellow solids formed a bright yellow solution. After stirring at room temperature for one hour, 6 mL (77 mmol) of epichlorohydrin was added to the flask. The clear yellow solution was heated to boiling under reflux for 3 hours. After cooling to room temperature, the hazy yellow solution was rotary evaporated. The remaining yellow solids were dissolved in 40 mL dichloromethane and washed with 30 mL of 5 wt% potassium carbonate in water, then washed twice with 30 mL deionized water. The colorless solution was dried with anhydrous sodium sulfate, vacuum filtered, and rotary evaporated to leave white solids. The impure solids were purified by sublimation at 110 °C and 0.1 torr, followed by recrystallization in ethanol yielding 0.778 g of small, colorless, needle-like crystals. 56% yield. Melting Point: 113-114.5 °C

$^1$H NMR (400 MHz, CDCl$_3$): 2.79 (dd, $J = 4.8$, 2.6 Hz, 1H), 2.94 (dd, $J = 4.9$, 4.1 Hz, 1H), 3.38 (ddt, $J = 5.9$, 4.1, 2.7, 2.7 Hz, 1H), 3.97 (ddd, $J = 11.1$, 5.9 Hz, 1H), 4.33 (ddd, $J = 11.1$, 2.8 Hz, 1H), 6.26 (d, $J = 9.5$ Hz 1H), 6.82 (d, $J = 2.5$ Hz 1H), 6.88 (ddd, $J = 8.6$, 2.5 Hz 1H), 7.37 (ddd, $J = 8.6$, 0.3 Hz, 1H), 7.63 (d, $J = 9.5$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 44.66, 49.89, 69.39, 101.79, 113.02, 113.08, 113.60, 128.99, 143.42, 155.90, 161.16, 161.68. FTIR: 1711, 1613, 1513, 1403, 1354, 1284, 1231, 1211, 1158, 1127, 1027, 1002, 991, 895, 845, 797, 764, 754

$^1$H NMR spectrum identical to that reported by Lee and Kim.
3.4.2.3 Synthesis of 4-methyl-7-acetoxy coumarin

To a 500 mL round bottom flask was added 30.024 g of 4-methyl-7-hydroxycoumarin, 22.829 g of sodium acetate, 108 mL acetic anhydride, and several drops of pyridine. The mixture was heated under reflux for 7 hours after which the mixture turned brown with white solids throughout. The flask was allowed to cool to room temperature, then rinsed with chilled water and ethanol and filtered through filter paper. The solids were collected and recrystallized in ethanol twice, producing a mat of colorless thread-like crystals. 28.917 g, 78% yield. Melting point: 150-152 °C (lit. 150-152 °C).

$^1$H NMR (400 MHz, CDCl$_3$): δ 2.34 (s, 3H), 2.43 (d, 3H), 6.26 (d, 1H), 7.08 (m, 2H), 7.60 (d, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 18.84, 21.23, 110.58, 114.63, 117.97, 118.21, 125.51, 152.04, 153.16, 154.28, 160.61, 168.87

3.4.2.4 Synthesis of anti head-to-tail 4-methyl-7-acetoxy coumarin

Dichloromethane (720 mL) dried by distillation over CaH$_2$ was poured into a 1000 mL round bottom flask and bubbled with dried nitrogen for one hour. To this flask was added 28.863 g of 4-methyl-7-acetoxy coumarin and 5.15 g of benzophenone. This solution was bubbled with argon for 20 minutes, then placed in a Rayonet photochemical reactor with 6 lamps emitting a
peak wavelength of 350 nm and exposed for a total of 11 days and 4 hours. The solvent was removed by rotary evaporation, and the yellow residue left behind was washed with diethyl ether. The remaining solid was recrystallized in glacial acetic acid. Mass: 18.034 g, 62% yield. Melting point: 195°C (lit. 192-193 °C)  

1H NMR (400 MHz, CDCl₃): δ 1.30 (s, 3H), 2.33 (s, 3H), 3.44 (s, 1H), 6.89 (d, J = 2.2 Hz, 1H), 6.99 (dd, J = 8.5, 2.3 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 21.24, 26.37, 45.15, 46.97, 111.54, 118.77, 120.53, 127.89, 151.20, 151.46, 165.53, 168.99

### 3.4.2.5 Synthesis of anti head-to-tail 4-methyl-7-hydroxycoumarin

![Chemical Structure](image)

Anti head-to-tail 4-methyl-7-acetoxy coumarin dimer (18.00g), ethanol (336 mL), and 336 mL of 4M HCl(aq) were added to a 1000 ml flask. The vessel was purged with N₂ gas and heated under reflux for 5 hours, after which the solvent was removed by rotary evaporation. Deionized water (240 mL) was added to the flask and the mixture was extracted with 1 L of ethyl acetate. The solid remaining after rotary evaporation of the organic layer was mixed with 75 mL glacial acetic acid and heated under reflux for 5 hours. Upon cooling to room temperature the solid was filtered through a fritted funnel and dried under vacuum. Mass: 13.993 g, 96% yield. Decomposition point: 220 °C (lit. dp 229-240 °C)  

¹H NMR (400 MHz, DMSO): δ 1.10 (s, 3H), 3.38 (s, 1H), 6.45(d, 1H), 6.65 (dd, 1H), 7.17 (d, 1H), 9.84 (s, 1H). ¹³C NMR (100 MHz, DMSO): δ 26.24, 44.03, 45.81, 103.17, 112.46, 113.82, 129.01, 150.98, 157.81, 166.09
4-Methyl-7-allyloxy coumarin was synthesized according to the procedure reported by Zhao for 7-allyloxy coumarin.\textsuperscript{85} 4-Methyl-7-hydroxy coumarin (5.30 g, 30 mmol), anhydrous potassium carbonate (5.67 g, 41 mmol), and acetone (150 mL) were added to a 250 mL 3-neck flask. Allyl bromide (5.7 mL, 66 mmol) was measured with a syringe and added to the flask dropwise over the course of an hour. The flask was heated to a boil under reflux under nitrogen while stirred with a magnetic stir bar for five hours. When cool, the mixture was filtered to remove residual potassium carbonate, the filtrate rinsed with additional acetone, and the solution was rotary evaporated to leave yellow-brown solids of crude product. The solids were recrystallized in methanol (solution turned dark blue upon methanol addition), and crystals were filtered and dried under vacuum to produce colorless crystals. Mass: 4.112 g, 58% yield. Melting point: 104-105 °C

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.49 (d, $J = 8.8$ Hz, 1H), 6.87 (dd, $J = 8.8$, 2.5 Hz, 1H), 6.82 (d, $J = 2.5$ Hz, 1H), 6.13 (q, $J = 1.2$ Hz, 1H), 6.04 (ddt, $J = 17.2$, 10.6, 5.3 Hz, 1H), 5.44 (dtd, $J = 17.3$, 1.7, 1.3 Hz, 1H), 5.34 (dq, $J = 10.5$, 1.4 Hz, 1H), 4.60 (dt, $J = 5.3$, 1.5 Hz, 2H), 2.39 (d, $J = 1.2$ Hz, 3H)

Spectra identical to those reported by Zak et al.\textsuperscript{191}
3.4.2.7 BF: Catalyzed photodimerization of 4-methyl-7-allyloxy coumarin

4-Methyl-7-allyloxy coumarin (1.08 g, 5 mmol) was measured in a 25 mL Pyrex round bottom flask. The flask was capped with a rubber septum and flushed with argon. Dichloromethane (25 mL), previously dried over 3Å molecular sieves and degassed by bubbling with nitrogen, was measured by syringe added to the flask under inert gas. Boron trifluoride diethyl etherate (0.62 mL, 5 mmol) was then measured by syringe and added to the flask under inert gas. The flask was again flushed with argon, and placed in the Rayonet photochemical reactor with 16 350 nm lamps and exposed for 72 hours, by which time the solution had turned yellow. The temperature was approximately 40 °C throughout the exposure. The crude photoprodut was transferred to a separatory funnel and washed with a 5% aqueous sodium chloride solution twice, then dried with anhydrous magnesium sulfate, filtered, and rotary evaporated. 1.04 g of white-yellow solid was recovered. ¹H NMR revealed that the product was comprised entirely of unchanged starting material, and no photodimerization had taken place.

3.4.2.8 Synthesis of 7-allyloxy coumarin

7-Allyloxy coumarin was synthesized following the method used for 4-methyl-7-allyloxy coumarin. 7-Hydroxycoumarin (2.43 g, 15 mmol), anhydrous potassium carbonate (2.83 g, 20.5 mmol), and acetone (75 mL) were added to a 100 mL 3-neck flask. Allyl bromide (2.9 mL, 33 mmol) was then measured with a syringe and added dropwise to the flask. The mixture was heated under reflux while stirred with a magnetic stir bar for five hours. When cool, the mixture was filtered to remove residual potassium carbonate, and the solution rotary evaporated.
The solids were recrystallized in methanol, then vacuum filtered to yield faintly yellow crystals. 69% yield. Melting point: 84-85 °C. (lit. 82-83 °C^85)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 (d, $J = 9.5$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 1H), 6.86 (dd, $J = 8.5$, 2.4 Hz, 1H), 6.82 (d, $J = 2.5$ Hz, 1H), 6.25 (d, $J = 9.5$ Hz, 1H), 6.04 (ddt, $J = 17.2$, 10.6, 5.3 Hz, 1H), 5.44 (dq, $J = 17.3$, 1.6 Hz, 1H), 5.34 (dq, $J = 10.5$, 1.4 Hz, 1H), 4.60 (dt, 5.3, 1.5 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.90, 161.30, 155.96, 143.50, 132.27, 128.88, 118.68, 114.39 (weak), 113.33, 113.25, 112.78, 101.87, 69.41

**3.4.2.9 BF$_3$ catalyzed photodimerization of 7-allyloxycoumarin**

7-Alllyloxycoumarin (2.02 g, 10 mmol) was measured in a 50 mL Pyrex pear-shaped flask. The flask was capped with a rubber septum and purged with argon. Dichloromethane (50 mL) previously dried with 3Å molecular sieves and degassed by freeze-pump-thaw cycles was added to the flask by cannula transfer. Boron trifluoride diethyl etherate (1.2 mL, 10 mmol) was measured by syringe and added to the flask. The solution was placed in the Rayonet photochemical reactor and exposed for 72 hours. The photochemical reactor was approximately 40 °C throughout the exposure. After irradiation the solution was dark yellow. The solution was washed with 50 mL of 5% sodium chloride three times in a separatory funnel, then rinsed with deionized water, dried with anhydrous magnesium sulfate, filtered, and rotary evaporated. 2.03 g of yellowish solid was recovered. $^1$H NMR of the crude product revealed that, like with 4-methyl-7-methoxycoumarin, no dimer was recovered and the starting material was unchanged.
3.4.2.10 Synthesis of 4-methyl-7-glycidyloxycoumarin dimers

Small Scale Solid State Photodimerization:

4-Methyl-7-glycidyloxycoumarin was recrystallized in toluene prior to use, yielding small colorless needle-like crystals. For small scale solid state exposures, 10 mg of 4-methyl-7-glycidyloxycoumarin was measured in six 2 mL borosilicate glass ampoules. The ampoules were evacuated, flushed with argon, evacuated again, and flame sealed under vacuum. The ampoules were exposed with the 400 W metal halide lamp of the CureZone2 filtered through soda-lime glass. The samples were fan cooled to 36-38 °C throughout the exposure as measured by a thermocouple. Samples were irradiated for 0, 3, 6, 12, 24, and 48 hours, after which the ampoules were broken, the samples dissolved in CDCl$_3$, and $^1$H NMR spectra taken.

Preparative Solid State Photodimerization:

4-Methyl-7-glycidyloxycoumarin (0.4 g) previously crystallized in toluene was measured in a borosilicate glass tube. The tube was evacuated, flushed with argon, and flame sealed under vacuum. The tube was placed in the CureZone2, cooled with a fan to 35 °C, and irradiated for 72 hours, turning periodically over the course of the irradiation.

Solution Photodimerization:

Acetonitrile was dried with 3Å molecular sieves and distilled prior to use. A 0.3 M solution was prepared by measuring 3.48 g (15.0 mmol) of 4-methyl-7-glycidyloxycoumarin in a
50 mL volumetric flask and filling to volume with acetonitrile. The coumarin was not completely soluble at this concentration at room temperature, but dissolved fully when warmed slightly above room temperature. The solution was transferred to a 50 mL round bottom flask, sealed with a stopcock valve, and degassed by five freeze-pump-thaw cycles. The flask was suspended in the Rayonet photochemical reactor equipped with 15 350 nm lamps, and irradiated for 5 days, 20 hours, and 28 minutes (140.5 hours), after which the solution was golden yellow. $^1$H NMR of the crude reaction mixture revealed about 87% conversion of the monomer to dimers; 12.9% monomer, 67.1% syn head-to-tail, 16.1% syn head-to-head, and 4% anti head-to-tail, as determined by the integrations of the methyl signals.

Purification of 4-methyl-7-glycidoxyxoumarin Dimers:

The photoproducts from solution photodimerization were isolated by flash chromatography using a Yamazen W-Prep 2XY automated flash chromatography system using Yamazen Universal Premium 2L silica columns and a gradient of hexane and acetone. Batches of approximately 500 mg at a time could be separated with good resolution. A typical procedure is as follows: 0.5 g of crude photoproduct was measured and dissolved in 2 mL of dichloromethane and loaded onto a medium sized injection column. The main column was equilibrated with 77% hexanes, 23% acetone then eluted with this mixture for 5 minutes, followed by a linear gradient from this mixture to 56% hexanes, 44% acetone over 16 minutes, then held at this final mixture for 14 minutes. The Yamazen chromatography system utilized a UV detector to monitor elution based on 254 nm absorption, but the intensity of the light used by the detector was small enough that any photocleavage of the dimers was negligible. Fractions were collected in 20 mL intervals. Fractions for monomer, syn head-to-tail dimer, and syn head-to-head dimer from multiple batches were combined in round bottom flasks, rotary evaporated,
and the remaining solvent removed by heating to 40 °C under vacuum overnight. The dimers both formed foams, then melted and solidified into transparent, glassy solids. Small crystallites were observed to form in solids of syn head-to-tail MGOC after 7 months at room temperature. NMR peak assignments were made in agreement with the assignments published by Stitchell et al.\textsuperscript{177} and Muthuramu et al.\textsuperscript{49} for 4-methyl coumarin dimers.

*Syn head-to-head 4-methyl-7-glycidyloxycoumarin dimer (syn HH MGOC)*

A light yellow, brittle, translucent solid.

0.517 g combined (92% of expected), 14.9% yield from total starting material.

Melting Point: 62 °C (determined by DSC) 73-80 °C (visually in capillary tube). Purity: >98%.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.67 (dt, $J = 8.7, 1.7$ Hz, 2H), 6.53 (dt, $J = 8.7, 2.6$ Hz, 2H), 6.36 (dd, $J = 5.1, 2.6$ Hz, 2H), 4.18 (ddd, $J = 10.6, 7.3, 2.8$ Hz, 2H), 3.82 (m, 2H), 3.62 (s, 2H), 3.32 (m, 2H), 2.90 (t, $J = 4.5$ Hz, 2H), 2.74 (m, 1H), 1.59 (s, 6H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 164.88, 164.86, 159.19, 159.18, 151.78, 128.44, 115.66, 115.64, 112.23, 112.21, 102.72, 102.65, 69.02, 68.98, 49.98, 49.96, 46.94, 44.69, 44.66, 44.61, 23.46

FTIR: (3073, 2974, 2932, (weak), sp3 C-H) 1762, 1622, 1584, 1508, 1421, 1266, 1244, 1196, 1176, 1120, 1095, 1046, 1022, 908, 839
Syn head-to-tail 4-methyl-7-glycidyloxycoumarin dimer (syn HT MGOC)

A colorless, brittle, transparent solid.

2.071 g combined (89% of expected), 59.5% yield from total starting material.

Melting Point: 54 °C (determined by DSC) 60-70 °C (visually in capillary tube). Purity: 98%.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.08 (d, J = 8.7\ \text{Hz, 2H}), 6.66 (m, 2H), 6.07 (m, 2H), 4.12 (m, 2H), 3.74 (m, 2H), 3.42 (s, 2H), 3.27 (m, 2H), 2.88 (m, 2H), 2.70 (m, 2H), 1.67 (s, 6H)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 164.69, 159.22, 150.40, 127.73, 114.52, 114.48, 112.57, 112.54, 112.38, 112.33, 102.78, 102.75, 102.59, 69.04, 55.34, 49.92, 49.90, 44.60, 44.57, 41.25, 31.78

FTIR: 1752, 1623, 1584, 1508, 1421, 1360, 1267, 1244, 1222, 1193, 1167, 1125, 1096, 1070, 1028, 1004, 912, 835, 771

3.4.3 Preparation of Coumarin Dimer and DGEBA-Based Epoxy Resins
All epoxy resins in this study were prepared using Jeffamine D-2000 as the curing agent using a stoichiometry of one amine for every two epoxide equivalents. The amine hydrogen equivalent weight (AHEW) of Jeffamine D-2000 was taken to be 495 g/eq based on the analysis provided by the manufacturer, and the epoxy equivalent weight of the coumarin dimers were taken to be 232.24 g/eq – half the molecular weight of the coumarin dimer. In a typical preparation, 58.1 mg (0.125 mmol, 0.25 meq) of syn HH or syn HT MGOC solids were measured in a vial, and 124 mg (0.25 meq) Jeffamine D-2000 was added by pipette. The MGOC dimers and D-2000 were found to be immiscible at room temperature, but miscible upon melting of the coumarin dimer at about 100 °C. Dichloromethane (50 wt%) was added to homogenize the mixture. For adhesion testing, the dichloromethane solution was dropped onto the substrate and the solvent allowed to evaporate in a fume hood. For DSC samples, the solution was dropped into a DSC pan and solvent removed under vacuum at room temperature for 24 hours before testing. For control specimens prepared with diglycidyl ether of bisphenol-a (DGEBA), the epoxy equivalent weight was taken to be 172 g/eq based on the manufacturer’s analysis. Unlike the coumarin dimer-based epoxies, DGEBA and Jeffamine D-2000 were found to be miscible, and no solvent was used in the mixing or application of these resins.

To determine the cure time and temperatures, dynamic mechanical analysis (DMA) was performed using a Netzsch DMA 242E Artemis equipped with sample holder for powdery and pasty samples (part DMA2420CA52.040-00). The sample holder was filled with 100 mg of prepared resin, and the DMA probe was lowered into the resin so that it was 1 mm from the bottom of the sample holder. For DMA analysis, syn HT MGOC was first ground into a fine powder using a Wig-L-Bug ball mill and stirred directly with Jeffamine D-2000 instead of casting.
the mixture from solvent, as was done for other samples. All DMA curing studies were performed using 1 Hz oscillation.

3.4.4 Lap-Shear Adhesion Testing

Lap shear tests were performed to evaluate the performance of the epoxy resins as adhesives. The procedure was performed in accordance with ASTM D1002\textsuperscript{178}. Aluminum coupons measuring 1” x 4” x 0.064” were used as the test substrate. Coupons were degreased with acetone, then etched with chromic acid according to ASTM D2651.\textsuperscript{192} Coupons were etched in chromic acid at 65 °C for 15 minutes, then thoroughly rinsed with deionized water and dried in a 60 °C oven. Three different epoxies were tested: syn HH MGOC, syn HT MOGC, and a diglycidyl ether of bisphenol-a (DGEBA) – all cured with Jeffamine D-2000. The two components were measured as described above to give stoichiometric ratios.

Six specimens were prepared for each epoxy formulation. The specimens were prepared for an overlap of 0.5 inches (12.7 mm), with adhesive applied 0.25 inches (6.35 mm) beyond the overlap (illustrated in Figure 3.14). DGEBA-D2000 was mixed and applied directly to the coupons. Because both coumarin dimer diepoxides were insoluble in D-2000 at room temperature, these mixtures were first dissolved in 0.4 mL dichloromethane and then applied to the test coupons with a syringe. Evaporation of the solvent left behind a thin white film with the coumarin dimer component uniformly distributed in the curing agent as a fine precipitate. Coupons were left to dry in a fume hood for several hours, after which no mass loss could be measured with a balance. The coupons were then assembled and held together with binder clips and cured in an oven at 120 °C for 12 hours.

Tensile testing of the prepared lap-shear samples was performed on an MTS Criterion Model 42, with the specimens clamped 1” from the edge of the test grips. Specimens were
pulled under tension using a crosshead extension rate of 0.13 cm/min. Lap shear strengths were determined from the peak load at the failure point divided by the overlap area, and reported in units of megapascals (MPa).

**Figure 3.14** – Illustration of lap-shear samples viewed from top and side. Blue region represents overlap area (0.5 in., 12.7 mm). Light blue represents adhesive application area (0.25 in., 6.35 mm). Dark grey regions represent area gripped by tension clamps (1 in., 25.4 mm).

### 3.4.5 Photocleavage Testing of Cured MGOC Dimer-D2000 Epoxy Resins

An experiment was devised to study the photo-reversibility of the coumarin dimer resins, in which two fused quartz slides were adhered in a single lap-shear configuration and the bond was irradiated with 254 nm light while under tension in a mechanical tester.

Fused quartz slides were cleaned by ultrasonication in a detergent solution (1% Liquinox detergent in DI water), followed by thorough rinse and ultrasonication in deionized water. Because syn HH MGOC and syn HT MGOC are not soluble in Jeffamine D-2000 without heating, the two components were dissolved in dichloromethane (DCM) prior to application to the slide. After being left to evaporate overnight, the coumarin dimer component was left uniformly dispersed in the Jeffamine D-2000 across the slide. Thin tungsten wires (nominal diameter 0.0035 in, 89 μm) were used as spacers to create a film with controlled thickness between the slides.

The two slides were assembled with a 0.5 inch (12.7 mm) overlap, clamped together using binder clips, and the samples were cured at 100 °C for 12 hours. After curing, the wire
spacers were removed, and excess resin was removed from the edges of the samples with a razor blade so that the lap-shear joint was bonded only by the 1” x 0.5” overlap area.

The cured samples were loaded into the tension clamps of an Instron mechanical tester, and a constant tension of 10 N was applied (producing a shear stress of approximately 31 kPa). Before UV irradiation, the samples were held under constant tension for one hour to confirm that the samples were fully cured and no flow was occurring. A portable UV lamp (UVP UVGL-25 4-watt compact UV lamp) was used for photocleavage. The lamp was allowed to warm up at least 30 minutes prior to the start of the experiment while blocked with a thick black cardboard shutter, and a small fan was used to cool the lamp to help stabilize the intensity of the 254 nm emission over the course of the exposure. An Ocean Optics Jaz spectrometer was used to monitor the emission transmitted through the sample during the course of the irradiation. The load was applied and shutter removed simultaneously so that the beginning of data recording corresponded to the start of irradiation. All photocleavage experiments were performed in triplicate.

For repair of photocleaved samples, the two halves of the debonded slides were held together in their original position with binder clips at their edges, and the samples were irradiated with the CureZone 2 metal halide lamp for 30 minutes. The samples were then loaded into the Instron, binder clips removed, and a constant tension of 10 N was applied over the course of one hour to look for evidence of flow under shear.

### 3.5 Supplementary Data

#### 3.5.1 NMR Spectra
Figure 3.15 – $^1$H NMR Spectrum of 4-methyl-7-glycidyloxycoumarin

Figure 3.16 – $^{13}$C NMR Spectrum of 4-methyl-7-glycidyloxycoumarin
Figure 3.17 – $^1$H NMR Spectrum of Syn Head-to-Head 4-methyl-7-glycidyloxy coumarin

Figure 3.18 – $^{13}$C NMR Spectrum of Syn Head-to-Head 4-methyl-7-glycidyloxy coumarin
Figure 3.19 – $^1$H NMR Spectrum of Syn Head-to-Tail 4-methyl-7-glycidyloxycoumarin

Figure 3.20 – $^{13}$C NMR Spectrum of Syn Head-to-Tail 4-methyl-7-glycidyloxycoumarin
Figure 3.21 – $^1$H NMR spectrum of 4-methyl-7-allyloxycoumarin

![H NMR spectrum](image)

Figure 3.22 – $^{13}$C NMR Spectrum of 4-methyl-7-allyloxycoumarin

![C NMR Spectrum](image)
Figure 3.23 – $^1$H NMR spectrum of 7-allyloxycoumarin

Figure 3.24 – $^{13}$C NMR spectrum of 7-allyloxycoumarin
3.5.2 Infrared Spectra

Figure 3.25 – FTIR Spectra of syn HH and syn HT MGOC dimers

Figure 3.26 – FTIR Spectra of syn HH and syn HT MGOC cured with Jeffamine D-2000
### 3.5.3 Lamp Emission Spectra

**Figure 3.27** – Emission spectra of CureZone2 metal halide lamp enlarged in the UV region. Spectra are normalized with respect to the area of the 579 nm peak to allow comparison of relative intensities of the filtered light.

**Figure 3.28** – Emission spectrum of Rayonet photochemical reactor equipped with RPR-3500A lamps, used for solution state irradiation of 4-methyl-7-glycidyloxycoumarin
Figure 3.29 – Emission spectrum of UVGL-25 4-watt UV lamp used for photocleavage experiments
3.5.4 UV-Vis Spectra

**Figure 3.30** – Molar absorptivity of 4-methyl-7-glycidyloxycoumarin, taken in chloroform

![UV-Vis Spectra](image)

**Figure 3.31** – Molar absorptivity of syn head-to-head 4-methyl-7-glycidyloxycoumarin dimer, taken in acetonitrile

![UV-Vis Spectra](image)
3.5.5 X-Ray Diffraction Data for 4-methyl-7-glycidyloxycoumarin

Empirical formula \(-\text{C}_{13}\text{H}_{12}\text{O}_{4}\)
Formula weight \(232.23\)
Temperature/K \(100\)
Crystal system \(-\text{orthorhombic}\)
Space group \(-\text{P2}_1\text{2}_1\text{2}_1\)
\(a/\text{Å}\) \(4.1263(13)\)
\(b/\text{Å}\) \(12.331(3)\)
\(c/\text{Å}\) \(21.066(6)\)
\(\alpha/^{\circ}\) \(90\)
\(\beta/^{\circ}\) \(90\)
\(\gamma/^{\circ}\) \(90\)
Volume/Å\(^3\) \(1071.9(5)\)
\(Z\) \(4\)
\(\rho_{\text{calc}}\text{g/cm}^3\) \(1.439\)
\(\mu/\text{mm}^{-1}\) \(0.107\)
\(F(000)\) \(488.0\)
Crystal size/mm\(^3\) \(0.4 \times 0.07 \times 0.03\)
Radiation \(-\text{MoK}\alpha (\lambda = 0.71073)\)
2\(\Theta\) range for data collection/\(^{\circ}\) \(3.828\) to \(52.272\)
Index ranges \(-5 \leq h \leq 5, -9 \leq k \leq 15, -26 \leq l \leq 25\)
Reflections collected \(6765\)
Independent reflections \(2112 [R_{\text{int}} = 0.0716, R_{\text{sigma}} = 0.0751]\)
Data/restraints/parameters \(2112/0/155\)
Goodness-of-fit on \(F^2\) \(1.068\)
Final R indexes [\(I\geq2\sigma(I)\)] \(R_I = 0.0603, wR_2 = 0.1608\)
Final R indexes [all data] \(R_I = 0.0851, wR_2 = 0.1761\)
Largest diff. peak/hole / e Å\(^{-3}\) \(0.58/-0.26\)
Flack parameter \(0.3(10)\)
Figure 3.32 – Structure of 4-methyl-7-glycidyloxycoumarin. Displacement ellipsoids are at 50% probability level

Figure 3.33 – Unit cell of 4-methyl-7-glycidyloxycoumarin
**Figure 3.34** – Unit cell of 4-methyl-7-glycidyloxy coumarin, view along b-axis
CHAPTER 4: THERMAL CLEAVAGE OF COUMARIN DIMERS

4.1 Introduction

The reversible photodimerization of coumarin has been widely used in polymer systems to make and break bonds in response to UV light. The [2+2] photocycloadduct which forms in response to irradiation with wavelengths of 300-370 nm can be cleaved symmetrically upon exposure to wavelengths < 300 nm, making it an appealing functionality for light-responsive materials. It is also known that coumarin dimers, like other cyclobutane-linked photocycloadducts, cleave into their respective monomers upon heating. However, the thermal dissociation of coumarin dimers has never been studied in detail, and it is not precisely known at what temperatures these molecules can be used before splitting. Coumarin has been used for photocrosslinking high temperature materials such as aromatic polyamides and polybenzoxazines, but the possibility of coumarin dimer cycloreversion at temperatures where such polymers might be applied has been largely overlooked.

The thermal cleavage of coumarin dimers was first observed in the early days of the study of these compounds. Schönberg found that a dimer of parent coumarin (determined in later studies to be the syn head-to-head isomer) decomposed into monomer after measuring the melting point at 260°C. The dimer of 3-phenylcoumarin was likewise found to dissociate after heating in a bath of boiling ethyl phthalate (b.p. = 295°C) for one hour. Since then this behavior has been noted by a few authors, but there has been no detailed investigation of this cycloreversion.

In contrast, the thermal cleavage of anthracene dimers has been well studied. Similarly to coumarin, anthracene undergoes a reversible [4+4] photocycloaddition and has been
utilized to create light-responsive polymers. The thermal cleavage of these dimers has also been used in the context of polymer materials to cleave anthracene dimer crosslinks.\textsuperscript{195}

In the previous chapter, syn head-to-head and syn head-to-tail dimers of 4-methyl-7-glycidyloxycoumarin were synthesized, isolated, and cured with diamines to produce photoreversible epoxy resins. During the course of that work there was a concern that the elevated temperatures required for curing could cleave the coumarin dimers, reducing the expected crosslink density of the polymer, thus motivating the present study. In this work, the thermal dissociation of the syn dimers of 4-methyl-7-glycidyloxycoumarin (MGOC) was studied, allowing kinetic parameters of this reaction to be determined. This data allows for crosslink degradation in a coumarin dimer diepoxide-containing epoxy resin to be predicted at elevated temperatures. This demonstrated that, besides photocleavage, heat can be used as a secondary stimulus to cleave the coumarin dimer crosslinks in a controlled fashion (Figure 4.1). Heat was shown to revert the cured epoxy resin into a viscous liquid, and the debonding of an adhesive joint bonded with the epoxy was demonstrated.

![Diagram](image_url)

**Figure 4.1** – Reversal of an epoxy resin by thermal cleavage of coumarin dimer crosslinks
The purpose of this study is twofold. Firstly, understanding the thermal dissociation kinetics will allow for clear and unambiguous prediction of the useful temperature range of materials containing coumarin dimer crosslinks. Secondly, it offers a new and potentially useful mechanism for reversing bonds in a dynamic stimuli-responsive material. Thermal cleavage offers the same functionality as photocleavage by an orthogonal mechanism and may prove to be a useful new trigger for breaking bonds in reversibly crosslinked materials.

4.2 Results

4.2.1 Coumarin Dimer Thermal Cleavage Kinetics

Syn head-to-head (syn HH) and syn head-to-tail (syn HT) dimers of 4-methyl-7-glycidyloxy coumarin were prepared and isolated as described in Chapter 3. Small samples of the isolated coumarin dimers were heated neat, above their melting points, and the resulting products analyzed with $^1$H NMR. The dimers were found to cleanly dissociate into monomeric coumarin without significant quantities of degradation byproducts detectible within the sensitivity of the NMR spectrometer, as illustrated in Scheme 4.1. This allowed the dimer to monomer conversion to be determined directly from the ratio of monomer to dimer peak integrations without the use of an internal standard. Preliminary measurements immediately showed that syn head-to-tail dimer was significantly more robust than the syn head-to-head, requiring longer times at higher temperatures to generate a measurable amount of monomer. Figure 4.2 shows the fraction of remaining dimer after 30 minutes for syn head-to-head and after 2 hours for syn head-to-tail dimers.
Scheme 4.1 – Thermal cleavage of syn HH and syn HT MGOC dimers

Figure 4.2 – Results of thermal cleavage experiment, showing relative dimer concentrations after 30 minutes (syn HH) and 2 hours (syn HT) at temperature.

From this data, the kinetic parameters for the thermal dissociation rate constant based on the Arrhenius relationship could be calculated. A dimer splitting into two monomers is expected to be a simple first order process, meaning that the rate of change of dimer concentration is directly proportional to the concentration of the dimer $[D]$ and a rate constant $k$.

\[ \frac{d[D]}{dt} = -k[D] \]

Integration of the rate equation using an initial dimer concentration $[D_0]$ as the initial condition gives the expression for dimer concentration as a function of time, and the expression to determine the rate constant at each data point:

\[ \ln[D] - \ln[D_0] = -kt \]
\[
\ln \left( \frac{[D]}{[D_0]} \right) = -kt
\]

\[
[D] = [D_0] e^{-kt}
\]

\[
k = \frac{-\ln \left( \frac{D}{D_0} \right)}{t}
\]

The rate constant \( k \) is a function of temperature and is expected to follow the Arrhenius equation:

\[
k = A e^{\frac{E_A}{RT}}
\]

Rearranging the Arrhenius equation shows that a plot of \( \ln k \) vs \( 1/T \) can be used to determine the activation energy \( E_A \) and preexponential term \( A \).

\[
\ln k = \ln A - \left( \frac{E_A}{RT} \right)
\]

**Figure 4.3** – Arrhenius plot of \( \ln k \) vs \( 1/T \) for syn HT and syn HH MGOC dimers

Figure 4.3 shows plots of \( \ln k \) vs \( 1/T \) for the two dimers. The data shows a linear relationship, indicating a good fit to the Arrhenius relationship and the first order model of the
reaction. From this plot, the slope and y-intercept represent $E_A/R$ and $\ln A$, respectively. The activation energy $E_A$ and preexponential term $A$ were determined and are given in Table 4.1.

**Table 4.1** – Kinetic parameters and predicted half-lives for the thermal cleavage of syn head-to-head and syn head-to-tail 4-methyl-7-glycidyloxycoumarin dimers

<table>
<thead>
<tr>
<th></th>
<th>Syn head-to-head</th>
<th>Syn head-to-tail</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A$ (J/mol)</td>
<td>$1.43 \times 10^5$</td>
<td>$1.21 \times 10^5$</td>
</tr>
<tr>
<td>$A$ (s$^{-1}$)</td>
<td>$2.10 \times 10^{12}$</td>
<td>$3.12 \times 10^7$</td>
</tr>
<tr>
<td>$t_{1/2}$ at 25 °C (yr)</td>
<td>$1.08 \times 10^8$</td>
<td>$9.46 \times 10^5$</td>
</tr>
<tr>
<td>$t_{1/2}$ at 100 °C (yr)</td>
<td>1.01</td>
<td>53.6</td>
</tr>
<tr>
<td>$t_{1/2}$ at 200 °C (hr)</td>
<td>0.53</td>
<td>127</td>
</tr>
</tbody>
</table>

Using this information, the rate constant $k$ can be determined at any temperature and used to predict the dimer concentration after any time $t$ as follows:

$$k = \frac{A}{e^{E_A \frac{k_B}{R T}}}$$

$$[D] = [D_0] e^{-kt}$$

Figure 4.4 shows a plot of the predicted dimer concentrations for both dimers after one hour at the temperature given on the x-axis. Figure 4.5 presents the results in a different form, with dimer concentration as a function of time for different temperatures.
Figure 4.4 – Predicted MGOC dimer concentration after 1 hour at a given temperature.

Figure 4.5 – Predicted dimer concentration as a function of time at different temperatures.

4.2.2 Thermal Reversal of Coumarin Dimer-Crosslinked Epoxy Resins

Epoxy resins were prepared from the MGOC dimers and the diamine Jeffamine D-2000. The results from Chapter 3 demonstrated that photocleavage of the coumarin dimers in this epoxy caused the material to revert to a liquid at a surface exposed to 254 nm light, allowing
adhered glass slides to be debonded. It was therefore hypothesized that thermal cleavage would have the same effect and cause the debonding of adhered substrates.

Thermogravimetric analysis (TGA) was first performed on the cured resins to determine the window in which the polymer can be heated before irreversible degradation occurs. In principle, using coumarin dimers as thermo-reversible groups would allow the material to be re-crosslinked by photodimerization, but only if irreversible degradation of the PPG backbone of Jeffamine D-2000 were minimal. The thermograms are shown in Figure 4.6, and onset temperatures are given in Table 4.2.

![TGA thermograms for uncured Jeffamine D-2000 and cured epoxy resins](image)

**Figure 4.6** – TGA thermograms for uncured Jeffamine D-2000 and cured epoxy resins

<table>
<thead>
<tr>
<th></th>
<th>Onset point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jeffamine D-2000 (unreacted)</td>
<td>305</td>
</tr>
<tr>
<td>DGEBA D-2000</td>
<td>340</td>
</tr>
<tr>
<td>SynHH MGOC D-2000</td>
<td>327</td>
</tr>
<tr>
<td>SynHT MGOC D-2000</td>
<td>326</td>
</tr>
</tbody>
</table>

**Table 4.2** – TGA degradation onset temperatures for Jeffamine D-2000 and epoxy resins
Both syn HH and syn HT-based epoxy resins exhibited very similar thermal degradation behavior, with onset temperatures at about 326 °C. The mass loss onset temperature is about 15 °C lower for the coumarin dimer resins cured with Jeffamine D-2000 than it is for bisphenol-a diglycidyl ether cured with D-2000. This is consistent with the expectation that thermal cleavage of the coumarin dimer would reduce crosslink density and increase the rate of thermal degradation. These results indicate that the coumarin dimer resin could be debonded by thermal cleavage of the coumarin dimers without significant irreversible degradation if the materials are heated to temperatures below 250 °C.

Thermal reversal of the cured epoxies was tested by adhesion of aluminum coupons adhered in a lap-shear configuration. Specimens of the syn HH dimer containing epoxy were heated to 200 °C, and were found to debond after 40 minutes. The residual syn HH-based epoxy was strongly yellowed by this time and had liquified. Specimens adhered with the syn HT dimer-based epoxy were heated to 250 °C and debonded after 4.5 hours. The syn HT material was dark brown, and not fully liquid, suggesting that thermooxidative degradation was largely responsible for the loss of adhesion. Specimens made with DGEBA remained adhered after 24 hours at 250 °C.

4.3 Discussion

The thermal cleavage experiment shows that syn head-to-head dimers readily dissociate upon heating, while syn head-to-tail are considerably more stable. This pattern in stability is reminiscent of the same trend seen for photocleavage quantum yields. Jiang et al. measured the photocleavage quantum yields for anti head-to-head, syn head-to-head, and syn head-to-tail dimers of parent coumarin, determining them to be 0.20, 0.171, and 0.151 respectively. Here,
the authors rationalized the differences in photocleavage efficiency on the basis of radical stabilization. In head-to-head dimers, if the cyclobutane C-C bond at the 3-position cleaves by homolysis, the carbonyl would permit resonance stabilization of the radicals. It is likely that this same reasoning is applicable to the case of thermal cleavage.

Comparing these results to those published on the thermal cleavage of anthracene dimers, we see that these coumarin dimers are considerably more stable. The thermal dissociation behavior of the parent anthracene dimer is comparable to that of the syn head-to-head coumarin dimer, but substituted anthracenes are nearly always less stable. Head-to-head dimers of 9-substituted anthracences are particularly unstable, degrading at room temperature on the scale of hours.\textsuperscript{86} For comparison, Figure 4.7 shows predicted dimer concentrations after one hour at the temperature on the $x$-axis, calculated using published Arrhenius-form kinetic parameters for anthracene ($E_a = 1.54 \times 10^5$ J/mol, $A = 6.31 \times 10^{13}$ s$^{-1}$),\textsuperscript{197} head-to-tail 9-methylanthracene ($E_a = 1.60 \times 10^5$ J/mol, $A = 1 \times 10^{16}$ s$^{-1}$),\textsuperscript{198} and head-to-head 9-methylanthracene ($E_a = 1.1 \times 10^5$ J/mol, $A = 6.31 \times 10^{14}$ s$^{-1}$).\textsuperscript{198}
Figure 4.7 – Comparison of the thermal stability of MGOC dimers and anthracene dimers.\textsuperscript{197,198} Predicted dimer concentrations after 1 hour at a given temperature.

In the epoxy system, the kinetic data offers a means of predicting its decrosslinking. If the functionality of the components and initial conversion of the thermoset are known, we can predict the time and temperature required to reach its gel point.

If we assume the epoxy has been mixed with perfect stoichiometry and cured to 100% conversion of its functional groups, we can predict the dimer concentration at which the network “un-gels.” The network is broken at the coumarin dimer, which means that the system can be understood in the same way as the gelation of a tetrafunctional monomer with four equivalent reactive groups. Using the equation given by Flory\textsuperscript{168}

\[ \alpha_c = \frac{1}{f - 1} \]

where \( \alpha_c \) is the critical gel point conversion and \( f \) is the functionality of the monomer, we predict the gel point for this system is 0.33. This means that once 66% of coumarin dimers are cleaved in this ideal epoxy resin, liquification of the polymer should result. One way of predicting the
time at which this conversion will occur is to construct a time-temperature-transformation plot as shown in Figure 4.8.

![Figure 4.8](image.png)

**Figure 4.8** – Predicted time-temperature-transformation (TTT) curves for predicting the thermal cleavage induced “un-gellation” point of an ideal epoxy network comprised of a coumarin dimer diepoxide and a diamine

For example, for the syn HH MGOC containing epoxy at a temperature of 200° we can predict that the gel point is crossed at $10^{3.48}$ seconds, or 50 minutes. Experimentally, the adhesive bond made by the syn HH-based epoxy resin debonded after 40 minutes at 200 °C, a result quite close to the predicted time. The difference suggests a lower than ideal degree of crosslinking for the system, which is not unexpected in a real epoxy resin and could be a result of imperfect stoichiometry or intramolecular cyclization during curing.
4.4 Conclusions

For the first time, the kinetic parameters of the thermal dissociation of two coumarin dimers were determined. It is hoped that this data will be useful for the engineering of coumarin-based light-responsive materials by giving a clear picture of the temperatures at which thermal cycloreversion occurs. The syn HT dimer of 4-methyl-7-glycidyloxy coumarin was found to be considerably more stable than the syn HH dimer at temperatures over 150 °C. Both dimers are expected to remain stable indefinitely at room temperature over practical time scales. Comparison with literature data shows that these dimers are significantly more stable than substituted anthracene dimers, suggesting that coumarin would be the preferable molecule for use in light responsive materials which may encounter temperatures over 100 °C for any extended period of time.

Thermal cleavage was utilized in a coumarin dimer-based epoxy resin and found to effectively debond a joint adhered with the material. An adhesive bond made using a similar epoxy prepared with DGEBA was left unchanged by heating alone.

This behavior may prove to be a useful function for reversibly crosslinked materials. While the photocleavage of coumarin dimers has already been shown to be an effective way of modifying polymer materials, this work demonstrates that heat can be used as an orthogonal stimulus to accomplish the same function. Unlike photocleavage, which can only be achieved in thin layers due to the dimers’ strong absorption of short wavelength (λ < 300 nm) UV light, thermal cleavage can also break dimer crosslinks in specimens of any thickness or dimer concentration. Unlike a phase change caused by the melting of a thermoplastic or the cycloreversion of a Diels-Alder adduct, the bond broken by thermal cleavage will not re-form upon cooling, and thus heat serves as an irreversible trigger. Because thermal dissociation causes
symmetric cleavage of the cyclobutane rings, the materials could in principle be re-crosslinked by photodimerization.

Future experiments will measure the thermal dissociation kinetics of other dimers, including dimers of parent coumarin, 7-methoxycoumarin, and 4-methyl-7-methoxycoumarin, and both the syn and anti dimers of each. It is hoped that this data will provide a more general picture of the thermal properties of coumarin dimers. This pursuit could potentially provide a new library of molecules able to serve as thermal weak links in materials that could be selected for specific applications based on their unique thermal behavior, thus opening doors to new tailorable photo- and thermoresponsive materials.

4.5 Experimental

4.5.1 Materials and Instrumentation

Syn HH MGOC and syn HT MGOC were synthesized and isolated according to the procedures described in Chapter 3. Jeffamine D-2000 was donated by Huntsman Corporation and used as received. Diglycidyl ether of bisphenol-a (DGEBA) equivalent to D.E.R. 332 was purchased from Sigma Aldrich.

NMR spectra were taken with a Bruker AVIII 400 NMR spectrometer, using CDCl$_3$ as a solvent with chemical shifts relative to TMS as an internal standard. Thermogravimetric analysis (TGA) was performed with a TA Instruments Discovery DSC 25 using a platinum pan under a nitrogen atmosphere. A ramp rate of 10 °C/min was used for all samples, and analyses were performed with approximately 10 mg of material.
4.5.2 Thermal Cleavage Procedure

For syn head-to-head MGOC, 8-9 mg samples of the material were measured in ½ dram vials and capped with PTFE-lined phenolic caps. A bath of silicone oil was heated with a thermostat controlled hot plate while stirring with a magnetic stir bar. The temperature set by the thermostat was verified with a secondary partial immersion thermometer, and remained within ±0.2 °C of the target temperature. Each sample was held in the oil bath for 30 minutes, then removed and quickly cooled to room temperature in water.

Syn head-to-tail MGOC was found to be much more thermally stable than syn head-to-head, requiring higher temperatures than could be supported by the silicone oil. For these samples a thermostat-controlled oven (Ney Vulcan 3-550) was used. 10 mg specimens were measured in glass ampoules and flame sealed under vacuum to prevent loss of monomeric coumarin by sublimation. Ampoules were placed in a heavy aluminum block within the oven, where a thermocouple was used to verify the local temperature. Using this method, the temperature was kept to within ±2 °C of the desired temperature. Each sample was kept in the oven at temperature for 2 hours.

After heating, the samples were dissolved in deuterochloroform, and ¹H NMR spectra were taken using a Bruker AVIII 400 NMR spectrometer. The relative concentrations of dimer and monomer were determined from integrations of the 4-methyl peaks. Any sample with less than 0.5% conversion was excluded from the kinetic calculations due to the limited sensitivity of the NMR data.

4.5.3 Preparation and Thermal Reversal of Epoxy Resins

Epoxy resins were prepared according to the procedures detailed in Chapter 3. A stoichiometric ratio of epoxy and amine was used for all resins. The amine hydrogen equivalent
weight of Jeffamine D-2000 was taken to be 495 g/eq, based on analysis provided by the manufacturer. The epoxide equivalent weights of both coumarin dimers were taken to be 232.24 g/eq.

Lap-shear specimens were prepared on aluminum coupons according to the procedures in Chapter 3. The mixture of the diamine and epoxide was dissolved in dichloromethane, applied to aluminum coupons as a solution, and the solvent allowed to evaporate, leaving the coumarin dimer component uniformly dispersed as a precipitate in the liquid diamine. The aluminum coupons were held together with binder clips and cured in an oven at 120 °C for 12 hours.

The cured specimens were thermally debonded by heating in a thermostat-controlled oven, where a thermocouple was used to verify the local temperature of the samples.
CHAPTER 5: CONCLUSIONS

5.1 Summary and Conclusions

In this research, a series of new reversibly crosslinked thermoset materials were created that harnessed three functions provided by the coumarin molecule: photodimerization, dimer photocleavage, and dimer thermal cleavage.

In Chapter 2, a liquid coumarin functionalized precursor was successfully synthesized, allowing the material to be used as a photocured adhesive. This represents one of very few reported examples of liquid coumarin-containing polymers to be synthesized, a task made difficult by strong intramolecular forces between coumarin groups. This material was demonstrated to be a viable UV-curable adhesive; although the photocured material is soft and flexible, it forms strong bonds between glass after 20 minutes exposure in a conventional UV-curing apparatus. This work is among the first demonstrations of the ability of photodimerization to create an adhesive bond. Although photocuring by photodimerization is slow compared to photoinitiated free radical polymerizations, and limited to fairly thin films of material, it is achievable within practical time scales. A study of possible sources of inefficiency in thermoset network formation, which has largely been overlooked in previous studies, revealed that photooxidative chain scission in the material’s backbone can compete with crosslinking by dimerization when the film is exposed under open air.

Chapter 3 highlighted the capability of coumarin dimer photocleavage to break bonds in an epoxy resin. A method of synthesizing and, most importantly, isolating coumarin dimers was successfully developed, allowing the use of dimers as building blocks in an epoxy resin. When used as an adhesive on a UV transparent substrate, the adhesive joint could be debonded by...
exposure to 254 nm within minutes. Coumarin dimer photocleavage was found to revert the solid epoxy to a liquid in a thin layer at the surface incident to the UV lamp. This represents the first demonstration of coumarin dimer photocleavage used to release an adhesive bond, a bond that could later be rejoined by re-dimerization with exposure to longer wavelength UV. This work also revealed the unexpected insight that the coumarin dimer isomer used has a significant influence on the properties of the cured epoxy, with syn head-to-head dimers creating a stiffer, stronger epoxy than syn head-to-tail.

In Chapter 4, new insights into the capabilities of coumarin dimers as polymer building blocks were gained. Here, the thermal dissociation of coumarin dimers was studied, providing an orthogonal mechanism to photocleavage by which coumarin dimer crosslinked materials can be reversed. For the first time, kinetic parameters of the thermal dissociation of coumarin dimers were measured, showing that the syn head-to-tail dimer is significantly more robust than the syn head-to-head dimer. This also revealed that coumarin dimers are more robust than anthracene dimers, making coumarin an ideal choice for photoresponsive materials which may experience high temperatures. Kinetic parameters allowed the progress of dimer cleavage to be predicted at various temperatures, and this was shown to allow reversal of an adhesive bond made with the coumarin dimer-based epoxy in a controlled and predictable way. The chief limitation of photocleavage is that it is only effective in thin layers due to strong absorption of 254 nm light by the material, and thermal cleavage offers one means of circumventing this limitation.

Together, this work represents an advancement in understanding of the capabilities coumarin photochemistry can bring to polymer materials.
5.2 Future Work and Outlook

This research has raised several questions that remain unanswered and may warrant further study. In Chapter 2, reasons for the inefficiency of the photocurable resin were studied. Photooxidative chain scission in the PPG backbone of the polymer was found as a primary culprit, but it is believed that intramolecular dimerization may play a contributing role, as evidenced by the low gel fractions afforded by resins photocured under inert gas. The contribution of intramolecular dimerization might be studied by kinetic analysis of photodimerization in various concentrations. Such a study might pinpoint how architectures can be altered to minimize this obstacle to network formation.

In Chapter 3 it was discovered that the coumarin dimer isomer used in an epoxy had a substantial impact on the final properties of the cured polymer. Syn head-to-head dimer resulted in stronger and stiffer epoxy than syn head-to-tail. This does not appear to be a result of a difference in reactivity; curing resulted in high conversions for both polymers. This may arise from a difference in miscibility with the diamine curing agent, or perhaps from intramolecular interactions of the more polar head-to-head dimer in the material, but at present such hypotheses are only speculative.

From a materials design perspective, there remain a number of areas where this work can be developed to produce improved and more practical materials by this same approach.

Perhaps the most immediate area for development is the selection of new curing agents. Jeffamine D-2000 was used throughout this work, and while the polyether diamine proved to be highly useful for creating liquid coumarin functionalized polymers with excellent UV transparency, it had drawbacks. Notably, it provided limited solubility for the coumarin dimer diepoxides used in Chapter 3, making it difficult to mix and apply the epoxy-amine mixture. It
also displayed a tendency to degrade with photooxidative chain scissioning, which hampered the photocuring ability of the resin studied in Chapter 2. The selection of a replacement is not a trivial task. PDMS-based polyamines with greater molecular weights than those explored in Chapter 2 might be attractive candidates, as these would be expected to possess both the low T$_g$, noncrystalline structure and high UV transparency required for this application.

In the future, this work could also be expanded to explore other photodimerizing groups. Coumarin is perhaps the most popular molecule capable of reversible photocycloaddition used in light-responsive polymers, but it is by no means the only one capable of this function, nor is it necessarily the best. As the work in Chapter 2 showed, the relatively bulky molecule tends to form solids, making it difficult to synthesize liquid precursors without very dilute systems. The resulting photocrosslinked materials have limited crosslink density and are by necessity soft and elastomeric. Chapter 3 revealed that the coumarin dimer diepoxide had limited solubility in diamine curing agents, making the epoxy amine mixture difficult to mix and apply. Other researchers have noted these same drawbacks, using coumarin analogs with greater solubility such as 1,1-dimethylnaphthalenon dimers as photocleavable linkages.\textsuperscript{199} However, designing photoresponsive materials with less conventional photocycloaddition-capable groups like this one is difficult due to a lack of data in the literature guiding their use.

In the long term, opportunities for progress in the field of photoresponsive materials might depend on the gathering of more fundamental data. Throughout the course of this research, it was found that many design decisions were made difficult by a lack of fundamental data available in the literature. For example, UV absorption spectra are not readily accessible for many coumarin derivatives or other photocycloaddition-capable molecules and their dimers,
data which could allow wavelength sensitivity of a material to be tailored. It is not well understood how common substituents on coumarin affect the quantum yield of dimerization, the regiochemistry of the products, or their solubility in polymers or solvents. It is not known how the concentration of coumarin groups in a polymer affect the quantum yield of dimerization, and in fact, quantum yields have never been measured in polymer films. Such data would allow parameters such as target chromophore concentrations and the exposure dose required to impart a given photoresponse to be predicted, decreasing our reliance on design by trial and error. Instead of narrowly application-oriented research so commonly seen today, it is believed that answering some of these more fundamental questions would better serve to advance the field and enable the development of more efficient, responsive, and useful materials.
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