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Stress-sensing in flexible epoxy adhesives

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Stress-Sensing In Flexible Epoxy Adhesives

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Abstract

In mechanochemistry, mechanical force causes a chemical change using small molecules, called mechanophores, by covalently connecting them into polymer materials. Stress-sensing mechanophores give a visual signal of mechanical force on the molecular level within a material. To our knowledge, stress-sensing mechanophores have never been incorporated into a commercially available epoxy kit. In this work, the characterization of two 3M^{TM} Scotch-Weld ^{TM} Epoxy Adhesive kits: DP100 Plus Clear and DP190 Translucent have been completed through FT-IR Spectroscopy. The addition of the mechanophore spiropyran to the 3M kits will be discussed; as well as preparation and characterization of three dimerized anthracene derivatives. Our strategy is to synthesize a mechanophore crosslinker and add it into a two-part epoxy adhesive material, taking advantage of the existing cross-linking reaction to covalently incorporate it into the material; with the goal of using it to characterize the relationship between external strain and molecular-level force.

Table of Contents

Glossary

C-C……………………………………………….Carbon-Carbon Bond

DCM…………………………………………………Dichloromethane

ESR……………………………………………….Electron Spin Resonance

FTIR…………………………………………………Fourier-transform infrared spectroscopy

R…………………………………………………..Hydrocarbon Chain

MC……………………………………………………Merocyanine

NMR……………………………………………….Nuclear magnetic resonance

PU………………………………………………….Polyurethane

SP…………………………………………………Spiropyran

SGP……………………………………………….Strep-growth polymerization

THF……………………………………………….Tetrahydrofuran

TCI……………………………………………….Tokyo Chemical Industry

UV………………………………………………. Ultraviolet

Chapter 1

Introduction to Stress-Sensing in Flexible Epoxy Adhesives

Synthetic polymer materials are ubiquitous in the world today. Synthetic polymers can be found in rubber, plastic bags, and high-performance adhesives. When force is applied to these materials, they can become strained and break, which is typically destructive for the material. On the molecular level, this is because the mechanical force causes the polymer chains to become over-extended, resulting in a chemical reaction when bonds break. In polymer mechanochemistry, the stretching leads to an extension of polymer chains, which can be covalently connected to a molecule called a mechanophore.[1]
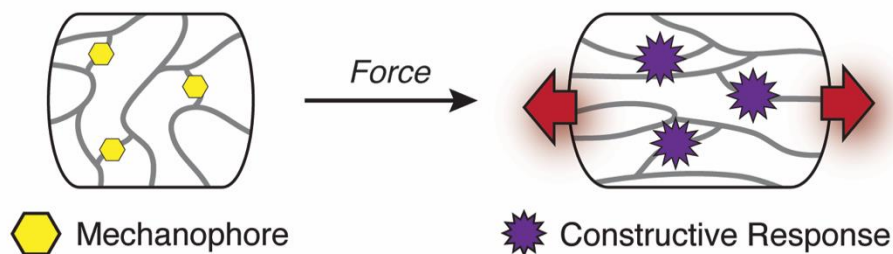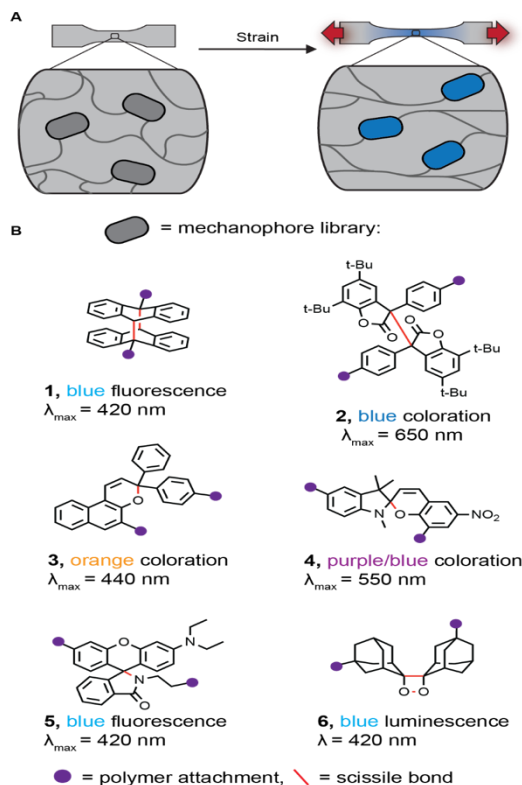

Figure 1: Tension on mechanophores in strained polymer network result in a constructive chemical response, figure adapted from a literature reference [2]

Mechanophores contain a mechanically weak bond that is intended to break, so that it can provide a constructive function to the material. Mechanophores have been developed to produce new, constructive functions in synthetic polymers, including mechanocatalysis, small molecule release, triggered degradation, stress-strengthening, and stress-sensing.[3,4,5]

Stress-sensing mechanophores are an important example because they give a visual signal of mechanical force on the molecular level within a material. Visual and spectroscopic signals are important in polymer materials because they are indicators that a chemical reaction

has occurred. This can be observed by color-change of the material, unveiled florescence, or luminescence (Figure 2).[6]

*Figure 2: A. Tension on stress-sensing mechanophores in highly strained polymer chains results in constructive chemical reactions with spectroscopic output. B. Library of mechanophores that are capable of detecting stress: anthracene dimers **1**, diarylbibenzofuanone **2**, naphthopyrone **3**, spiropyran **4**, rhodamine **5**, and dioxetane **6**. The purple circles represent polymer attachment points, the red bonds are broken mechanically to unveil the color, fluorescence, or luminescence*

Cross-links connect polymer chains into a 3D network, giving the materials their structure and properties. A polymer network is one giant insoluble molecule. Because of the insolubility, when a chemical reaction occurs in the network, the material cannot be characterized through NMR. In contrast, a visual signal can be observed and qualified even in a cross-linked material as long as it is transparent or light colored. Mechanophores have been incorporated into polymer materials using functional group "handles" that are attached to the molecule such that applied mechanical force is transduced to a bond that breaks under tension.

The previously prepared polymer materials with mechanophores have been useful for studies on stress distributions, mechanophore structure-property relationships, and warning of mechanical failure.[7] These materials do not typically have the robust mechanical possessions of materials that are used in practical and industrial applications. The recent exploration of mechanochromism in commercially available silicone elastomers has led to an expansion in both fundamental knowledge of mechanochemical reactions and development of soft devices, such as color changing soft robots,[8] stretchable electronics,[9] and 3D printed materials.[10] These advances are largely due to the toughness, elasticity, and wide range of existing applications of silicones, as well as the synthetic ease of using the existing chemistry for cross-linking these elastomers. The success in this platform motivates work towards developing methodology for incorporating mechanophores into a larger range of elastomeric materials.[11] The purpose of this work is to explore the use of stress-sensing mechanophores in other commercially available materials that already have these ideal mechanical properties to determine whether stress-sensing can be added to their capabilities without sacrificing their other functions.

Adhesives are one of the most used applications where polymeric materials are under stress and distribute tension when force is applied. Stress-sensing mechanophores offer the ability to explore stress distribution at the molecular level.[12] Mechanochemistry provides an opportunity to better understand stress distribution in adhesives. Epoxies, an important and widely used type of adhesive, use a ring-opening reaction of an epoxide with a strong nucleophile to create cross-links (Figure 3). The nucleophile is often an amine group, but alcohols and other nucleophilic functional groups can also react in an epoxy ring-opening.
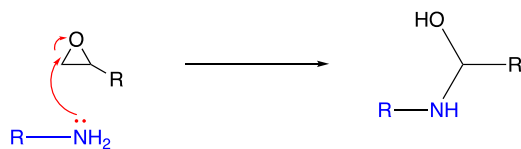
Figure 3: Epoxy ring-opening reaction by an amine nucleophile

Currently, there is only one example of the incorporation of a mechanophore into an epoxy material. Direct covalent grafting of photoactive mechanophore units into an epoxy material was completed for the study of self-sensing thermoset network nanocomposites.[13] To our knowledge, stress-sensing mechanophores have never been incorporated into a commercially available epoxy kit.

Our strategy is to synthesize a mechanophore crosslinker and add it into a two-part epoxy adhesive material, taking advantage of the existing cross-linking reaction to covalently incorporate it into the material; with the goal of using it to characterize the relationship between external strain and molecular-level force. The mechanophore will have nucleophile substituents that will become the polymer attachment points so that it can be incorporated into the polymer matrix, and the polymer will distribute stress to the mechanophore when it is placed under tension.
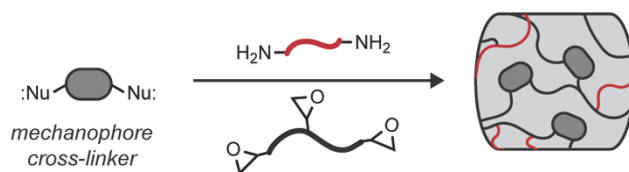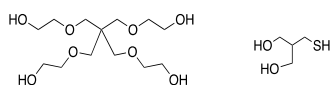

Figure 4: Synthetic scheme for incorporating a mechanophore cross-linkers into the two-part epoxy adhesive kit to form a cross-linked polymer matrix.
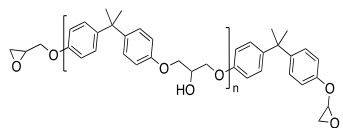
9

Two commercially available flexible epoxy adhesives were selected for this purpose, 3M™ Scotch-Weld ™ Epoxy Adhesive DP100 Plus Clear and 3M™ Scotch-Weld ™ DP190 Translucent (Figure 5.a). These two kits were selected because they are both flexible and transparent. Flexible materials are known to distribute stress well and have been historically used in polymer mechanochemistry. Transparent materials are ideal for visual signals to be observed.
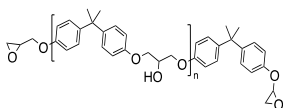
Figure 5.a: Components of Part A and B of DP100 and DP190

Figure 5.b: DP100 being used on a plastic, glass, and metal substrate

Figure 5.c: *DP190 Cartridge, Photos from in figures 5.b and 5.c are from the 3M website.[14]*

We first approached this challenge using a spiropyran mechanophore with terminal alcohol groups to take advantage of the existing cross-linking reaction in the epoxy adhesive. Spiropyran is an example of an isomerization- based mechanochromophore. This means that it undergoes ring-opening under external stimuli, either force or UV light, resulting in a new structure merocyanine (MC) and a change of color.[7] MC shows an absorption peak around 500-600 nm, which corresponds to a purple color.[7] SP and MC are in dynamic equilibrium, with spiropyran the more stable structure. The activation energy for the ring-closing reaction is low enough that SP will convert back to MC over several minutes.
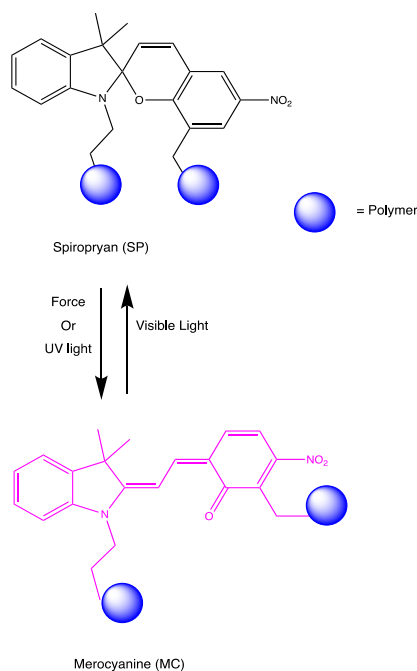
Figure 6: Dynamic equilibrium of SP to MC

We also synthesized an anthracene dimer as a stress-sensing mechanophore. Anthracene dimers contain hydrocarbon and C-C bonds, making them not as susceptible to partake in side reactions as spiropyran might be. Anthracene has been widely used as a fluorophore because of its aromatic properties and its great fluorescent signal.[14] Anthracene dimers, which are not fluorescent, undergo a retro-cycloaddition reaction under mechanical tension to revert to the fluorescent anthracene (Figure 7).[6] We prepared three anthracene dimers for this work (Figure 8). At the time of this report, synthesis of dimer **3** is still in progress.
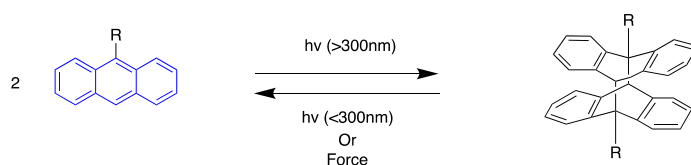
Figure 7: Reversible dimerization of anthracene through UV irradiation or force

dimerized anthracenecarboxylic acid

dimerized anthracenemethanol

dimerized 12- (anthracene-9-yloxy) dodecan-1-ol

Figure 8: The three anthracene derivatives prepared in this work

12

Chapter 2

History of Polymer Mechanochemistry and Today's Applications

2.1 Development of covalent mechanochemistry

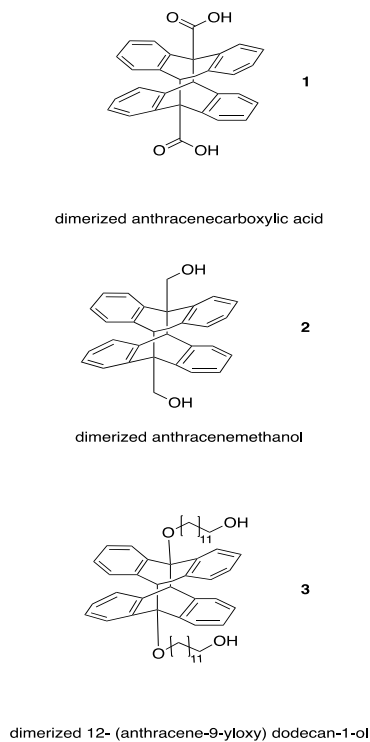Early research on polymer mechanochemistry mainly focused on mechanical degradation of polymers. Molecular responses of synthetic polymers to applied mechanical force was first observed by Staudinger and co-workers in the 1930s.[15] Staudinger observed a decrease in molecular weight of polymers in response to mechanical force. It was suggested that the molecular weight decreased due to homolytic C-C bond cleavage in response to mechanical force.[16] Also in the 1930s, Kauzmann and Eyring proposed that bond dissociation energy became smaller under force and lead to chain scission.[17] In the 1950s, scientists Melville and Murray introduced the "molecular-level understanding of stress induced polymer degradation". This was by their studies in ultrasonic polymer break-down in solution. They subjected a poly(methacrylate) solution that had styrene to ultrasonication which led to the idea of homolytic bond breakage in polymers experiencing forces[15]. Homolytic scission of C-C bonds along a polymer backbone was later (1960s) demonstrated by Sohma and co-workers by electron spin resonance (ESR).[18]

Instead of associating mechanically induced chemical changes to mechanical failure, there has been a shift to constructive uses of force. In modern-day polymer mechanochemistry, there has been a shift towards productive mechanically induced chemical changes centered around mechanophores. Mechanophores change chemically and emit signal under mechanical force. They have been used for damage detection by their ability to act as stress sensors.[14] Mechanophore design has progressed over recent years to provide a range of transformations like color and fluorescence change within a polymer material.[15]

Hard and structural materials are vulnerable to degradation. Long-term degradation leads to microcracks within the material; and can significantly reduce the mechanical properties and

load-carrying abilities of the material.[6] Mechanophores are weak links that are intended to break upon application of a load to the polymer chain.

2.2 Stress-sensing mechanophores: spiropyran and anthracene dimer

When mechanical force is used to activate a mechanophore and the result is an optical change in absorption (visible light) or emission (fluorescence and luminescence), this is called a mechanochromophore.[7] An example of this is the anthracene dimer. Anthracene derivatives can be dimerized by UV irradiation (>300nm) and reversibly dimerized (<300nm).[19] Anthracene derivatives partake in a $4\pi + 4\pi$ photocycloaddition resulting in cyclooctane dimers (Figure 1).[1] Anthracene dimers have the capability to generate emissive anthracene upon bond cleavage with mechanical force.[7] The cyclooctane dimers can be used as cross-link in polymer materials. When this occurs and the material undergoes mechanical tension, the cyclooctane is mechanochemically cleaved to give the original anthracene structure that produces strong fluorescent emission (Figure 1).[1] Anthracene displays a blue (λ_{max}=420nm) fluorescence under ultraviolet (UV) light.
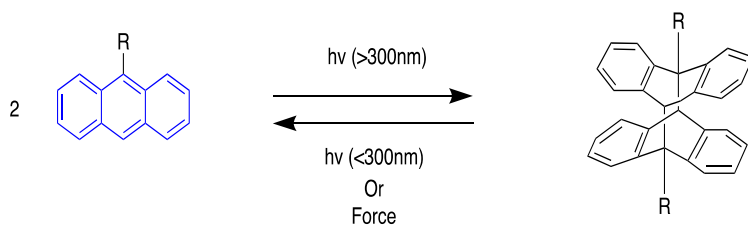

Figure 1: Reversible dimerization of anthracene through UV irradiation or force

Spiropyran (SP) is a widely studied mechanochromophore, which has been incorporated into polymer materials and used as a tool for stress-sensing. SP molecules have an indoline ring and a benzopyran moiety that are connected perpendicularly by a weak C-O bond.[7] Upon activation with mechanical force or UV light, the weak C-O bond cleaves and colorless SP converts into purple-colored merocyanine (MC). Photo switching is dependent on the substituent at the meta position to the weak C-O bond. The mechanochemical activation of many spiropyran derivatives has been studied, including those with meta-substituents consisting of H, Br, and NO_2. The most stable MC formed is substituted with a nitro group at the meta position to the sp^3 C-O bond because the electron withdrawing nitro group stabilizes increasing negative charge on the O atom. SP and MC are in dynamic equilibrium and MC will convert back to SP with a half-life of ~ 3 minutes (with a nitro substituent).
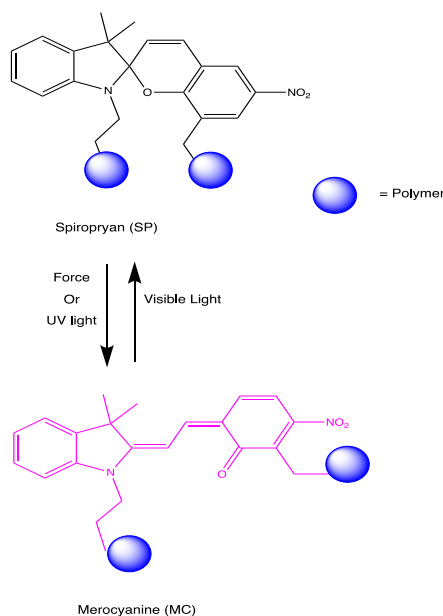

Figure 2: Dynamic equilibrium of SP and MC

2.3 Epoxide chemistry and epoxy materials

An epoxide is a functional group characterized by the presence of an oxirane or epoxy ring (Figure 3).[20] It is a three-member ring containing an oxygen atom that is bound to two sp^3 carbons. Epoxides have similar reactivity as ethers (R-O-R), but are even more reactive due to the release of ring strain.[21] The sp^3 carbons are sites for nucleophilic attack, which can occur with an acid catalyst or under basic/neutral conditions. Under acidic conditions, the oxygen atom is protonated by acid before nucleophilic attack, which readily occurs at room temperature. Attack at the more substitutes sp^3 carbon gives the major product because of developing carbocation character in the transition state.[21]
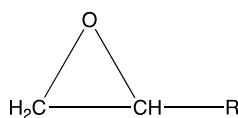
Figure 3: Chemical structure of an epoxy ring

This reaction is widely used in polymer material to create cross-links. Epoxy resins can react with different active compounds called curing agents, or with themselves via an initiator to form cross-linked materials.[20] This is called curing. Cross-linked epoxy polymers are obtained by an epoxide ring-opening reaction with a nucleophile, for example, an amine.[10] Epoxy resins are widely used as high-performance adhesives.[22] Epoxy-based adhesives are traditionally thermally cured. Epoxy resins are commonly referred to as thermosets. Thermosetting polymers (a thermoset) are polymers that are gained by irreversibly hardening a soft solid or viscous liquid pre-polymer. Curing is induced by heat, which is frequently generated by the reaction of the resin with a curing agent.[20]

Chapter 3

Experimental

General Information

All supplies and solvents were purchased from TCI, Acros, and Fisher Chemical and used as received. All reactions ran under open atmosphere unless otherwise stated. ^{1}H NMR spectra were obtained on a JEOL ECX 400 MHz spectrometer and referenced against tetramethylsilane using residual proton signals (^{1}H NMR) resonances of the deuterated solvent. FT-IR spectra were taken with a JASCO FT/IR 6300 and an ATR Pro diamond ATR. Dimerization reactions were completed in a Raymonet Mini Reactor 600.

Curing and pH Tests

The two-part epoxy adhesive kits that were selected for this project, 3M[TM] Scotch-Weld[TM] Epoxy Adhesive DP100 Plus Clear and 3M[TM] Scotch-Weld[TM] Epoxy Adhesive DP190 Translucent were mixed and cured according to the package instructions. The two-part cartridge was loaded into the applicator. A small amount of adhesive was dispensed to give a 50/50 mixture of the two parts.[23] The initial curing test was done by mixing both Part A and Part B of each kit and leaving them overnight at room temperature. The pH of DP100 kit was slightly acidic with a value of 6, and the DP190 kit was slightly basic with a value of 8. The kits are proprietary, which means the exact components that make up each kit is unknown. However, the safety data sheets provide a CAS number for primary components of each kit. To further characterize these materials, a Fourier Transform Infrared Spectroscopy (FTIR) spectrum was taken of the individual parts of both kits.

Addition of solvents to 3M epoxy adhesives kits

To add the mechanophores, which are solid powders, into the viscous components of the 3M kits, it was necessary to dissolve them in small amounts of solvent. To test which solvents were miscible with the kit and whether the addition of solvent influenced the curing process, four solvents (acetone, ethyl acetate, dichloromethane, and tetrahydrofuran) were individually added to the DP100 two-part mixture and the DP190 two-part mixture. The weight percent of the solvents to the kit mixtures were 10%. The DP100 and DP190 cured with all solvents.

Spiropyran addition to 3M[TM] Scotch Weld[TM] Epoxy Adhesive Kit

Spiropyran (Figure 1) was previously synthesized by another UTC student, Kelly Hooper, according to a published literature procedure.[25] A solution of spiropyran (0.0090 g) in THF (3mL) was prepared. The 3M[TM] Scotch-Weld[TM] Epoxy Adhesive DP190 Translucent mixture (2.0281g) was combined with the spiropyran solution with 10% (0.2 mL) and 20% (0.1 mL) by weight of the solution to the DP190. The weight percent of spiropyran relative to the kit was 0.030%. The kit was then mixed according to the package directions and left at room temperature overnight. Spiropyran was added to the 3M[TM] Scotch-Weld[TM] Epoxy Adhesive DP100 Plus Clear mixture following the same procedure.

Photo-conversion of spiropyran to merocyanine on thin-layer chromatography (TLC)

To confirm that the spiropyran used in these experiments was functional as a photo-switch - two TLC plates of the spiropyran solution were ran, one in 100% ethyl acetate, and another with a 50/50 mixture of hexane and ethyl acetate. The spot corresponding to spiropyran

(rf = 1) was not visible under room light initially. After the TLC plates were held under UV light, a pink color change was observed.

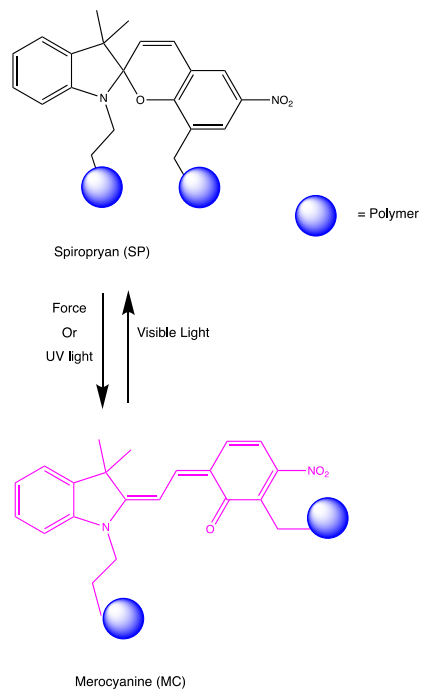*Figure 1: Reaction of Spiropyran to Merocyanine*

Addition of acid or base to the spiropyran solution

An excess amount of HCl was added to the spiropyran solution, and a yellow color change was observed. This was repeated with an excess amount of NaOH, and a reddish color change was also observed. Two TLC plates were taken of the acid and base mixtures, and both photo-switched under UV light.

Synthesis of dimerized 9- anthracenecarboxylic acid
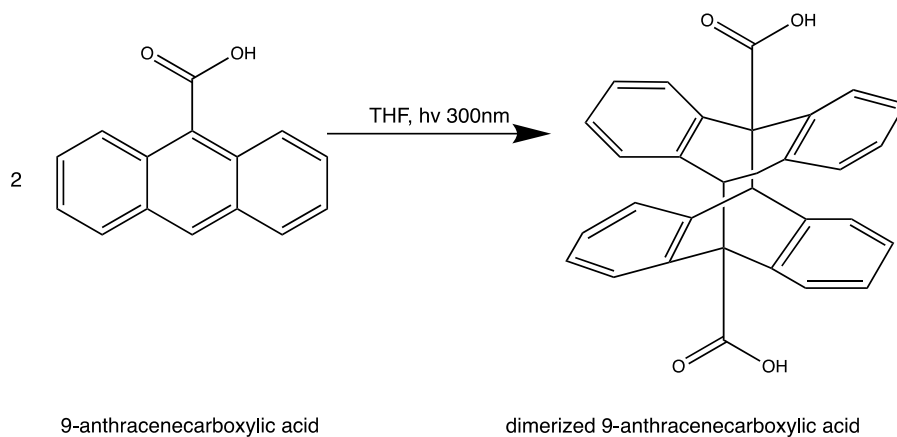
Figure 2: Dimerization of 9-anthracenecarboxylic acid

A solution of 9-anththracenecarboxylic acid (0.5002 g, 2.25 mmol) in THF (10 mL) was prepared. The solution was then pipetted into a 10 mL quartz NMR tube, sealed with Teflon tape, and purged with argon (20 minutes) before placing it into the photoreactor (300 nm) for 48 hours. The reaction produced clear crystals (0.0956g, 19%). ^{1}H NMR (400 MHz, DMSO-d6) δ 6.88 (m, 16H), 5.58 (s, 2H).

Synthesis of dimerized 9-anthracenemethanol

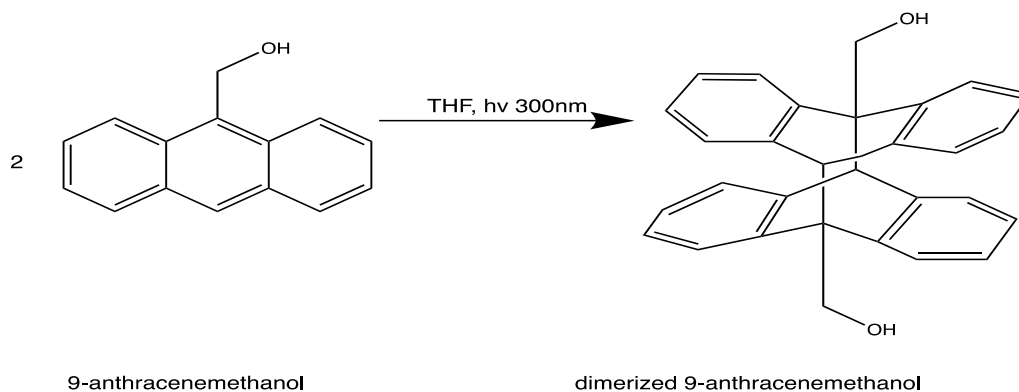*Figure 3: Dimerization of anthracenemethanol*

A solution of 9-anthracenemethanol (0.328g, 1.58mmol) in THF (7mL) was prepared.

The solution was then pipetted into a 10mL quartz NMR tube, sealed with Teflon tape, and

purged with argon (20 minutes), before placing it into the photoreactor (300 nm) for 48 hours.

Crystals were obtained (0.0058g, 26%). An NMR was taken, but the 9-anthracenemethanol

dimer was not soluble in deuterated acetone or deuterated dimethyl sulfoxide. A series of

solubility tests were done to the methanol dimer. 9-anthracenemethanol was tested for solubility

in: methanol, DCM, acetone, hexanes, hot methanol, mixture of methanol and toluene,

chloroform, ethyl acetate, THF, ethanol, acetonitrile. The dimer did not completely dissolve in

any of the solvents.

23

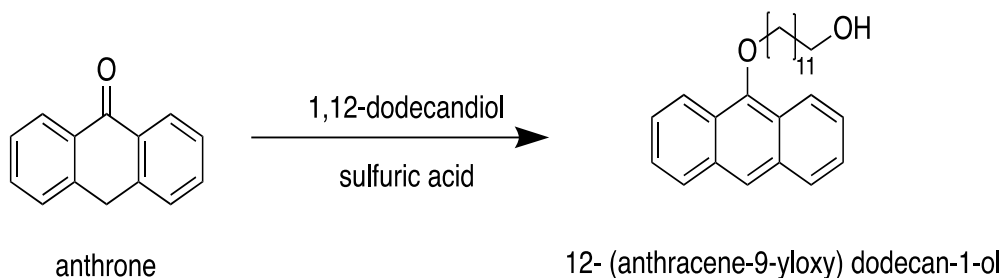## Synthesis of 12-(Anthracene-9-yloxy) dodecan-1-ol

Figure 4: Synthesis of 12-(Anthracene-9-yloxy) dodecan-1-ol

Anthrone (3.0321g, 15.6mmol) was dissolved in toluene (250mL). 1,12- dodecanediol (31.3264g, 155 mmol) and sulfuric acid (2.5 mL) were added, and the yellow-colored solution was heated to reflux in a Dean-Stark apparatus for 24 hours. The 1,12-dodecanediol remained insoluble until around 80°C. There was no water collected, so the apparatus was insulated and refluxed for an additional 24 hours. Water was collected to fill the Dean-Stark apparatus (approximately 25 mL). After cooling, the precipitated excess of 1,12- dodecanol was removed by vacuum filtration. The filtrate was washed with a saturated aqueous sodium bicarbonate solution (300 mL) and water (300 mL). The combined aqueous phases were extracted with diethyl ether. The combined organic phases were dried with magnesium sulfate, concentrated through rotary evaporation, and stored. [26] Purification and characterization of this product is still ongoing.

Chapter 4

Results and Discussion

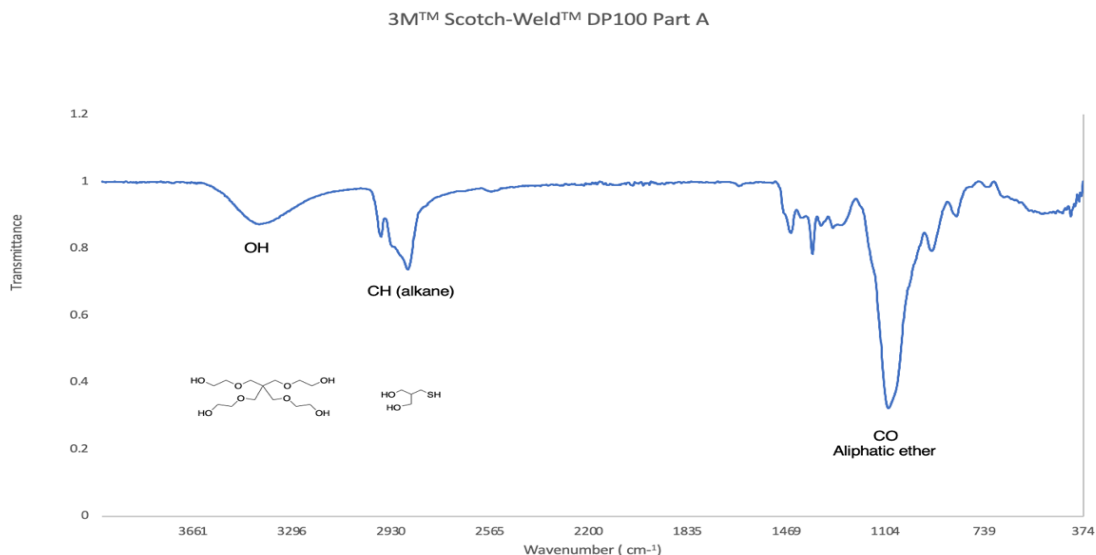## 4.1 Characterization of 3M epoxy adhesive kits

Figure 1: IR of DP100 Part A

[FT-IR Spectroscopy] was used to determine which functional groups were present in each of the individual parts of the DP100 and DP190 adhesive kits. Figure 1 shows the IR of Part A of 3M[TM] Scotch-Weld[TM] DP100 Plus Clear. According to the SDS, 90-99% of the part A is "mercaptan polymer" (Table 1), with the exact structure and composition a trade secret.[10]

Table 1: Composition of DP100 Plus Clear

DP100 Plus Clear		
Composition of Ingredients Part A	**C.A.S. No.**	**% by Weight**
Mercaptan Polymer	72244-98-5	90-99
Other components below reportable level	Mixture	<2
1,8-diazabicyclo[5.4.0]undec-7-ene	6674-22-2	<1.5
bis(dimethylaminoethyl) ether	3033-62-3	<1.5
Triethylenetetramine	112-24-3	<1
Composition of Ingredients Part B	C.A.S. No.	% by Weight
Epoxy Resin	25068-38-6	>98
Organosilane	2530-83-6	<2

26

A broad peak is present around 3200 cm^{-1}. This represents the intramolecular bonded alcohol (O-H) stretching. A medium peak around 2900 cm^{-1} shows alkane stretching. This correlates to the sp^3 hybridized carbons in the mercaptan polymer. A strong peak is present around 1100 cm^{-1} corresponding to the carbon-oxygen aliphatic ether stretching. The other components of Part A each make up less than 2%. Peaks corresponding to these functional groups are not likely to be observed in the IR because of their small relative quantities, but we can predict their likely roles. 1,8-diazabicyclo[5.4.0]undec-7-ene likely plays a role as a catalyst because it is a non-nucleophilic base. Bis(dimethylaminoethyl) ether likely acts as a nucleophilic tertiary amine cross-linker. We expect that triethylenetetramine acts as nucleophilic cross-linker as well.
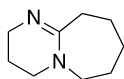

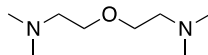*Figure 2.a: 1,8-diazabicyclo[5.4.0]undec-7-ene*
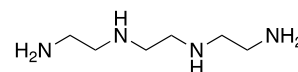
Figure 2.b: bis(dimethylaminoethyl) ether

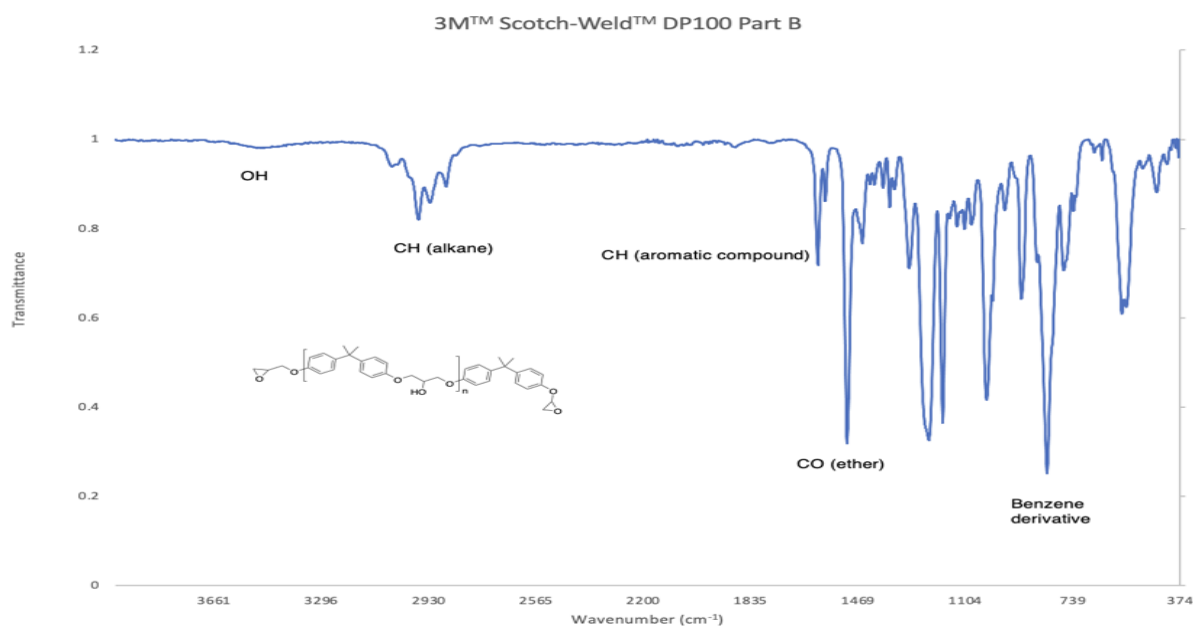*Figure 2.c: Triethylenetetramine*

Figure 3: IR of DP100 Part B

Part B of DP100 has two components listed. "Epoxy resin" is the major component at >98% of the mixture (Table I). As with Part A, the exact composition is unknown. This polymer contains an ether which is present around 1460 cm^{-1}. A medium peak around 2900 cm^{-1} represents the sp^3 hybridized carbons. It is reported that C-H bending for aromatic compounds is shown in the range from 2000-1650 cm^{-1} as a weak peak.[27] The C-H bending is present in Figure 3 around 1170 cm^{-1}. O-H bending can be seen around 1300 cm^{-1}. It is also reported that benzene derivatives are present at 700 ± 20 cm^{-1}. This peak is present at around 740 cm^{-1} in Figure 3. Organosilane makes up less than 2% of Part B. It is such a small quantity that we would not expect its functional groups to be visible in the IR. However, its likely role is to react into the network. The silane likely binds to silica in the substrate.
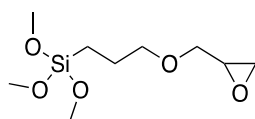
Figure 4: Organosilane

When the two-components of DP100 combine, an epoxide ring opening reaction occurs between some or all the nucleophiles in Part A (amines, thiols, and alcohols) and the epoxides in Part B. This reaction forms cross-links between the "mercaptan polymer" and the "epoxy resin" polymer, creating a polymer network. Alcohols that form because of the epoxide ring-opening help to make the material adhesive, forming hydrogen bonds to the substrate.
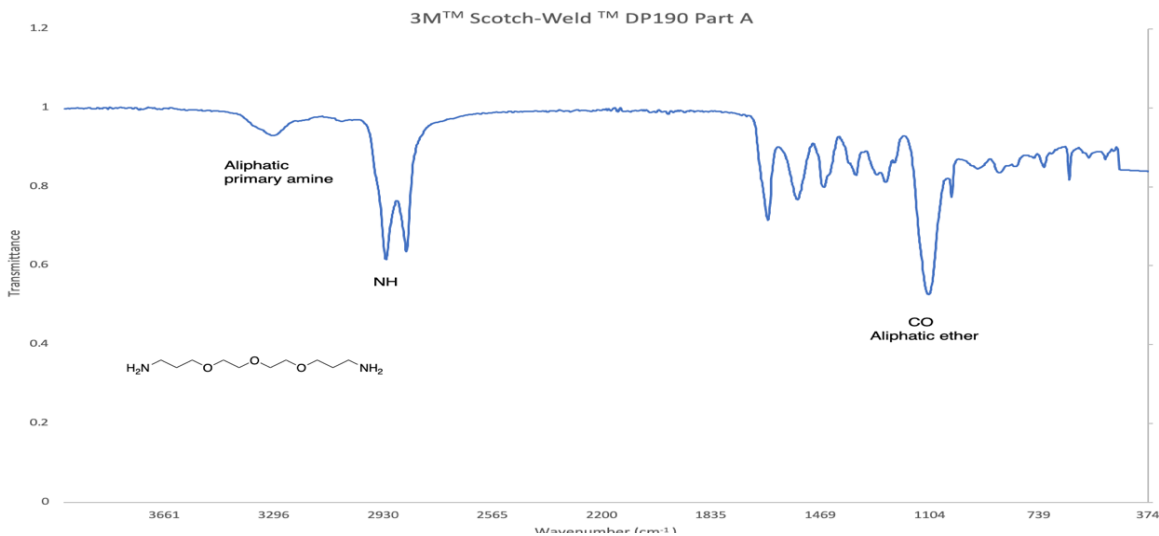
Figure 5: IR of DP190 Part A

Part A of DP190 consists of 94-99% aliphatic polymer diamine (Table II, Figure 5). The N-H stretching is present in Figure 5 around 2900 cm^{-1}. The aliphatic ether C-O stretching is present around 1150 cm^{-1}. There are three other small components of Part A, making up less than 5%. Peaks corresponding to these functional groups are not likely to be observed in the IR because of their small relative quantities, but we can predict their likely roles. 4,7,10-Trioxatridecane-1,13-Diamine likely acts as a nucleophilic cross-linker.

Figure 6.a 4,7,10-Trioxatridecane-1,13-Diamine

Figure 6.b: Toluene

Part B of DP190 consists of 60-70% of the same Epoxy Resin as in Part B of DP100 (Table 2). The IR spectra of Part B of DP190 is very similar to that of DP100. "Epoxy Resin 2" is likely another polymer that makes up the network. The epoxides react with the nucleophiles from Part A.

Table 2: Composition of DP190 Translucent

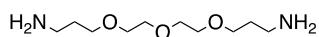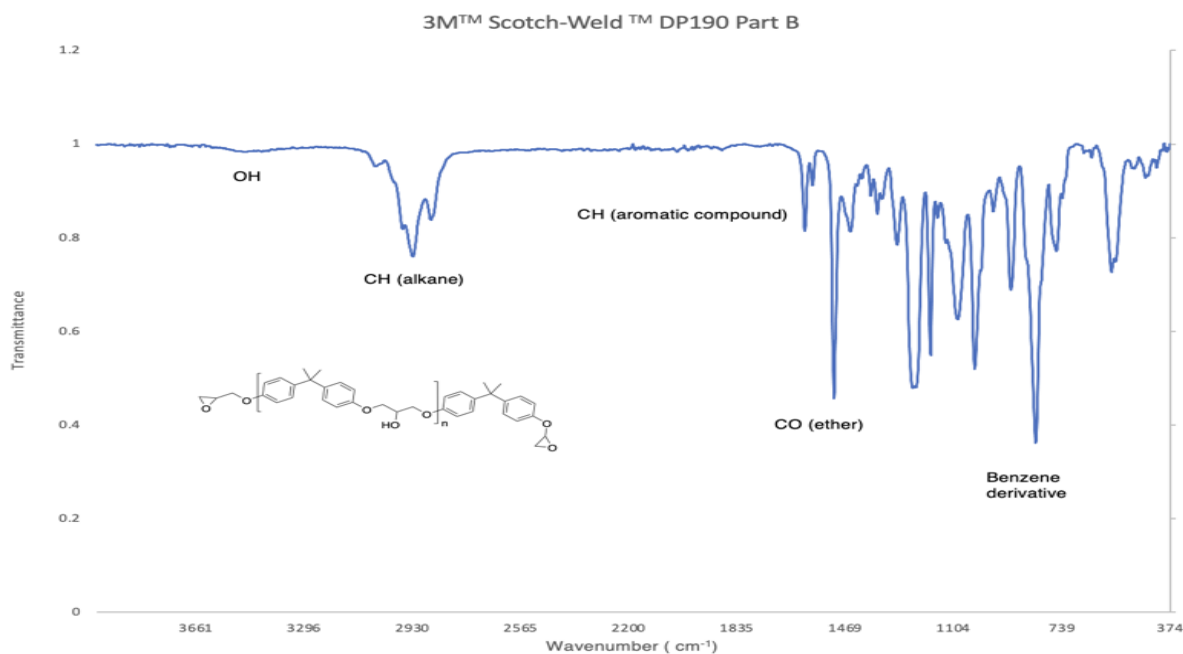| DP190 Translucent		
Composition of Ingredients Part A	**C.A.S. No.**	**% by Weight**
Aliphatic Polymer Diamine	68911-25-1	94-99
4,7,10-Trioxatridecane-1,13-Diamine	4246-51-9	<5
Calcium Salt	55120-75-7	1 to 5
Toluene	108-88-3	<0.8
Composition of Ingredients Part B	**C.A.S. No.**	**% by Weight**
Epoxy Resin 1	25068-38-6	60-70
Epoxy Resin 2	30583-72-3	30-40

Figure 7: IR of DP190 Part B

The DP100 and DP190 mixtures cured at room temperature as expected and were no longer tacky or sticky when touched with nitrile gloves. Both adhesive kits were able to be peeled from a weigh boat using a spatula with moderate force. This indicated that the 3M kits were functional. The main difference between the two kits are the nucleophiles present in Part A

of both kits. In DP190 Part A, the nucleophiles present that participate in cross-linking are amine groups. In DP100 Part A, the nucleophiles that participate in cross-linking are alcohol and thiol groups. Our hypothesis was that an added nucleophile will react in the cross-linking reaction along with the nucleophiles already present, so we chose to focus on synthesizing amine and alcohol functionalized mechanophore cross-linkers.

4.2 Addition of solvents to 3M epoxy adhesive kits

The addition of solvents to the viscous 3M kits were completed to determine possible solvents that could be used to incorporate the mechanophore into the kit. The mechanophores are all solids and need to be dissolved in something that is miscible with the kit. This was done by combining the DP100 mixture and the DP190 mixture with acetone, ethyl acetate, dichloromethane, and tetrahydrofuran. The weight percent of the solvents to the material was 10%. All solvents cured with the 3M adhesives at room temperature in the fume hood. The resulting materials looked and behaved in a way that was indistinguishable from the materials made without the solvents. This indicated that these solvents would not interfere substantially with the cross-linking process within the two-component kits. In the future, we will characterize the materials with lap shear and tensile tests to quantitatively compare the properties of adhesives made with solvents and mechanophores to adhesives prepared according to the package instructions.

4.3 Spiropyran addition to 3M epoxy adhesive kits

Spiropyran (SP) is known to photo-switch to merocyanine (MC) with UV irradiation. The addition of SP into the 3M epoxy adhesive kits was completed to determine if the 3M kits could be cured with the spiropyran added. First, we wanted to determine if the spiropyran was still

functional and capable of photo-switching within the material, and that it was unaffected by the curing process. Then, our goal was to determine whether mechanical stress placed on the material would cause the ring-opening reaction. Spiropyran was combined with the DP190 and DP100 materials while dissolved in THF. The resulting epoxy material felt sticky when touching with nitrile gloves, indicating that it likely did not fully cure. Under UV light, the DP190 and DP100 materials did not photo-switch as expected. Instead of turning purple, the materials remained bright yellow. To confirm that the spiropyran we used was still functional, we ran TLC and observed that the SP was functional and able to photo-switch to MC. This indicated that something about the curing reaction or the environment of the epoxy material altered the structure or reactivity of the spiropyran, preventing the typical ring-opening reaction from occurring. This indicated that the mechanophore spiropyran would not be efficient in stress-sensing studies with the 3M^{TM} Scotch-Weld^{TM} Epoxy Adhesive kits. Because SP was not able to photo switch, it could also no longer act as a mechanophore. To overcome this challenge, we hypothesize that dimerized 9-anthracene derivatives might be less reactive and better suited for use in an epoxy material.

4.4 Synthesis of dimerized anthracene derivatives

The goal for this study is to incorporate a substituted mechanophore to take advantage of the epoxide ring-opening reaction occurring in the 3M kits, and to cross link into the material. Anthracene dimers give a fluorescence signal under mechanical force. Anthracene dimers are not fluorescent, but they undergo a retro-cycloaddition reaction under mechanical tension to revert to the blue, fluorescent anthracene. By including them as a crosslink in the material, there is potential that fluorescence would give a warning sign before the material breaks. Three

anthracene dimers were synthesized in this work. The first anthracene derivative synthesized was dimerized 9-anthracenecarboxylic acid **1**. An ^{1}H NMR of this dimer is shown in Figure 9. This is compared to the starting material, 9-anthracenecarboxylic acid, shown in figure 8. The anthracenecarboxylic acid dimer was synthesized with the goal for using it as a starting material for a previously published procedure to create an amine with four-armed cross-linking capabilities (Figure 10).[3] Before continuing in the synthesis we realized that methyl chloroformate, needed in this synthetic scheme, is fatal if inhaled and that the reaction posed a level of risk that was beyond out comfort level. This scheme was not attempted, and different approaches with other substituted anthracene dimers were pursued.
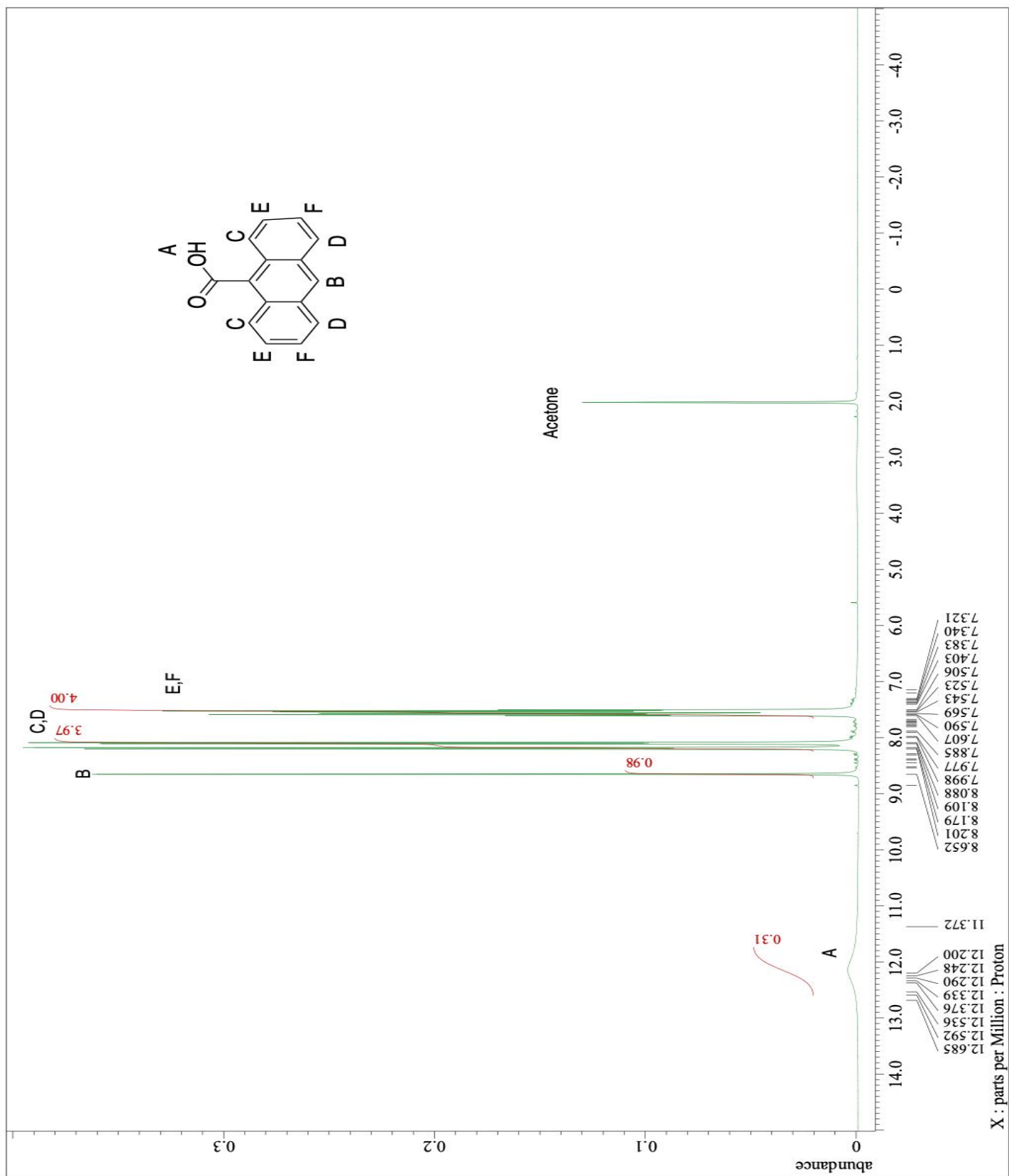
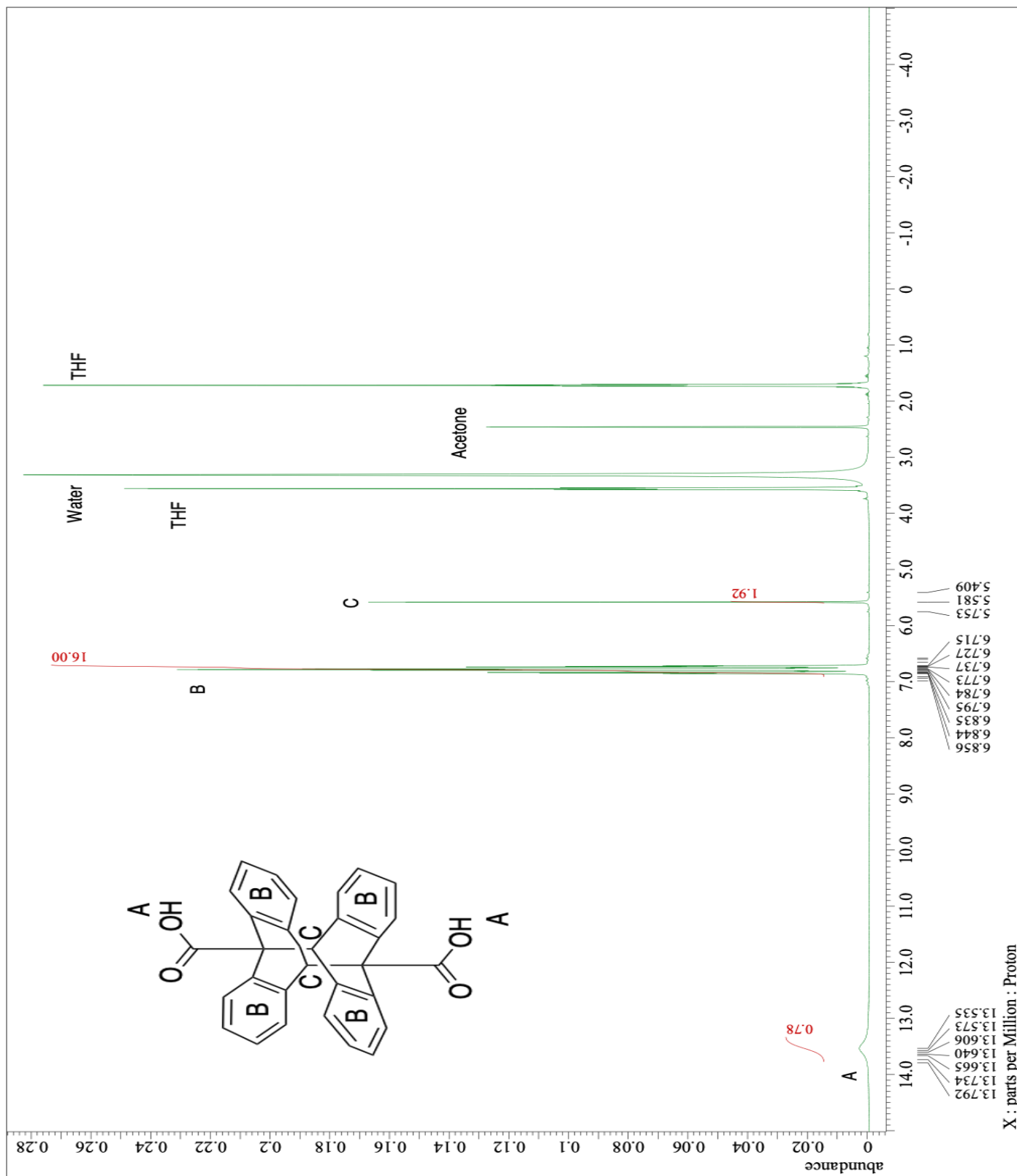*Figure 8: ¹H NMR of 9-anthracenecarboxlyic acid*

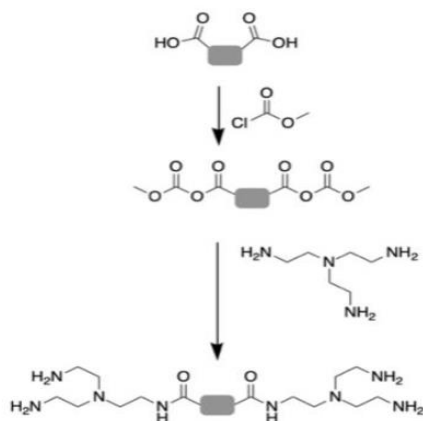*Figure 9: ¹H NMR of dimerized 9-anthracenecarboxylic acid*

Figure 10: Proposed synthetic scheme for four-armed amine cross-linker

An amine can act as a nucleophile and potentially take advantage of the epoxide ring-opening reaction occurring in the 3M epoxy adhesive kits. An alcohol can also act as a nucleophile in an epoxide ring-opening reaction. After deciding not to attempt to synthesize the amine substituted dimer, an alcohol substituted dimer was the next approach. In Part A of DP190, there are alcohol groups present. This creates the possibility for an alcohol substituted mechanophore to be incorporated into the kit, if an alcohol is a strong enough nucleophile to complete with the other cross-linkers that may be present in the kits in reacting with the available epoxies. Anthracene **2** was the second anthracene derivative synthesized in this work. To our knowledge, the 9-anthracenemethanol dimer has not been previously reported in the literature. Following the dimerization photoreaction, a yellow solid precipitated and was collected; however, it was not soluble in the NMR solvent or any solvent we tested in the laboratory (methanol, DCM, acetone, hexanes, hot methanol, 50/50 mixture of methanol and toluene, chloroform, ethyl acetate, THF, ethanol, acetonitrile, and dimethyl sulfoxide). A literature search for a more soluble alcohol substituted derivative was completed.

The third anthracene derivative in this work is 12- (anthracene-9-yloxy) dodecan-1-ol. This anthracene dimer is reported in the literature and is expected to be soluble in the solvent dichloromethane, which we have shown to be compatible with the 3M kits.[4] The capability of this anthracene derivative to dissolve in solvent could be used to characterize it and incorporate it into the 3M kits. This will provide an understanding of whether an alcohol is a strong enough nucleophile to participate in the reaction and cross-link into the material. The synthesis and characterization of this compound are still ongoing. When it is obtained, we plan to conduct the dimerization reaction and incorporate it into the 3M kits.
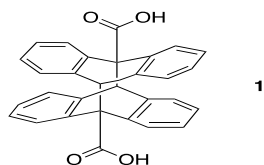
dimerized anthracenecarboxylic acid
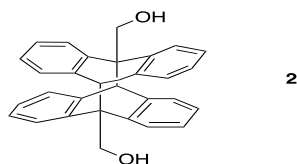
dimerized anthracenemethanol
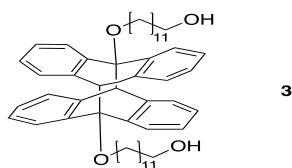
dimerized 12- (anthracene-9-yloxy) dodecan-1-ol

Figure 11: The three anthracene dimers prepared in this work

Chapter 5

Conclusions and Future Directions

5.1 Conclusions

The capability to engineer stress-sensing behavior across molecular, material, and composite scales offer potential for practical and industrial use. Molecular mechanochromism within polymer materials provide a new opportunity to add stress-sensing to the robust mechanical properties of materials that are widely used. Molecular mechanochromism provides indication to help prevent damage to the material, giving the material new functional properties.

Thus far in this work, characterization of two 3M^{TM} Scotch-Weld ^{TM} Epoxy Adhesive kits: DP100 Plus Clear and DP190 Translucent have been completed through FT-IR Spectroscopy. Spiropyran was added as an alcohol cross-linker to the 3M kits but was found to be incapable of photo switching after the epoxy material cured. Dimerized 9-anthracene derivatives were synthesized and characterized to use as potential mechanophore crosslinkers in each kit, toward our goal of utilizing the epoxide ring-opening reaction occurring within the adhesive kits to develop stress-sensing capabilities.

5.2 Future Directions

Additional experiments are needed to understand whether alcohols will be reactive enough to successfully crosslink into the 3M kits, as part of the polymer network and display a change in fluorescence under mechanical force. It is unknown whether an alcohol substituted anthracene dimer will be able to compete with the cross-linkers in the kit. Future work will be to continue the synthesis and characterization of alcohol substituted anthracene dimers that are known to be soluble like, 12-(anthracene-9-yloxy) dodecan-1-ol. After this is obtained, we plan to conduct the dimerization reaction and incorporate it into the 3M kits. Figure 1 shows the proposed scheme for the dimerization reaction, using the same procedure as with anthracene dimers **1** and **2.**

12- (anthracene-9-yloxy) dodecan-1-ol   dimerized 12- (anthracene-9-yloxy) dodecan-1-ol
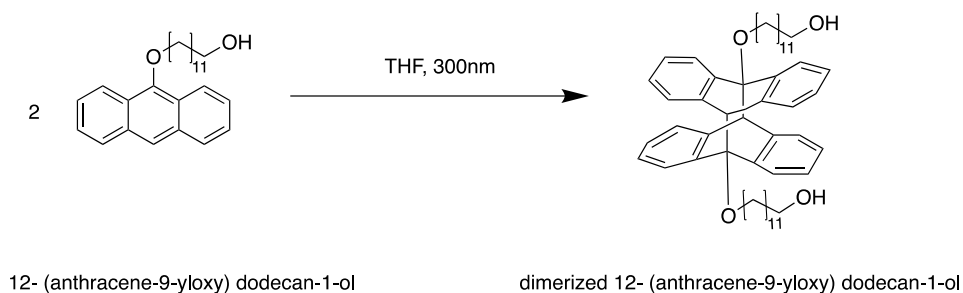
Figure 1: Proposed scheme for the dimerization of 12-(anthracene-9-yloxy) dodecan-1-ol

Future work will also expand on possible synthetic schemes for making anthracene dimers with epoxy substituents. We hypothesize that an epoxy substituted dimer could react in the epoxy ring-opening reaction occurring in the 3M kits, and crosslink within material. A proposed scheme is shown in Figure 2.
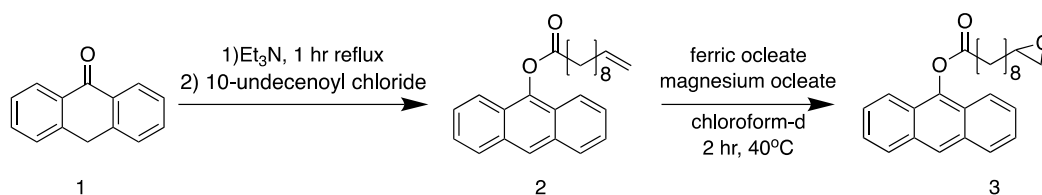
Figure 2: Proposed synthetic scheme for the epoxidation of an anthracene derivative

In Figure 2, the first reaction from molecule 1 going to molecule 2 is from a published procedure.[26] The second reaction from molecule 2 to 3 are similar steps to the published procedure of the epoxidation of vinyl acetate shown in Figure 3.[28]

Figure 3: Epoxidation of vinyl acetate

Figure 3 shown how vinyl acetate can be epoxidized. This could be a reaction that is used in the future to attempt the epoxidation of anthracene derivatives that have ester groups.

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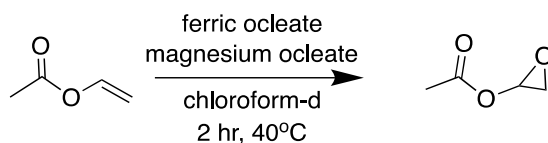
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