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Photo-Crosslinking, Bio-Inspired Terpolymer Adhesives Intended for Medical Applications

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THE GRADUATE SCHOOL

PHOTO-CROSSLINKING, BIO-INSPIRED TERPOLYMER ADHESIVES INTENDED FOR MEDICAL APPLICATIONS

By

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Tristan Harper defended this thesis on November 5, 2015.
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To my parents, Gilbert and Valarie Harper, who have always believed in me no matter what

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ABSTRACT

A bio-inspired, modular terpolymer adhesive has been synthesized containing three different functionalities: a photocrosslinking segment, wet adhesion segment, and a water soluble segment. Wet adhesion is brought on by an amino acid from mussel byssal plaques called3,4-dihydroxyphenyl –L-alanine, which has been known to generate strong bonding under wet conditions. . The photocrosslinking segment consists of an anthracene based monomer used for mechanical fortification of polymer chains. The water soluble segment consists of poly(acrylic acid), which has been known to increase water solubility of polymers and increase adhesion strength of adhesives. The terpolymer was designed to easily applicable using biologically friendly solvents including water and ethanol. Structural design was confirmed by NMR and UV-Vis spectroscopy. Reversible cycloaddition reactions were executed using a handheld UV lamp along with a photoreactor. Molecular weight increases were seen from 4.120×10^4 Da to 7.429×10^4 Da. Lap shear strength testing showed effects of UV exposure through increases in adhesion energy above 450%. Multiple application variables were tested to determine optimal conditions, such as solvent, concentration, and substrate. Currently, optimal conditions show a 1:1 weight ratio of polymer:solvent in water for all surfaces.

CHAPTER 1

INTRODUCTION

1.1 Adhesives

An adhesive is defined as a non-metal substance that binds two surfaces together and resist separation via adhesion and cohesion.[1] Adhesives have evolved to accommodate for the wide array of applications by changing characteristics from altering the chemical structure. Depending on the intended timescale of the application, the chemical structures will vary greatly. Structural adhesives are designed to have strong adhesion force, leading to a permanent attachment of adherents. These adhesives will also tend to have a glass transition temperature, the temperature at which a polymer will soften into a more molten rubber-like state, that is much higher than the application temperature. Higher glass transition temperatures will lead to a higher adhesion strength. One reinforcement method that is typically seen is the ability of a polymer to crosslink, creating bridges between multiple polymer chains. Examples of structural adhesives used today include epoxide and acrylics, which are used in applications that require the adhesive to go through high stress-strain changes, such as automobile and aircraft manufacturing.

On the other end of the spectrum, there are the pressure sensitive adhesives that are usually much weaker in terms of mechanical characteristics when compared to the structural adhesives. Where as structural adhesives required the direct covalent bonding to a surface, pressure sensitive adhesives mainly rely on secondary bonds such as van der Waals or hydrogen bonding. PSAs also work at temperatures much closer to their own glass transition temperatures as they are closer to thermoplastics, showing softening and wetting effects when heated. Here, wetting effects are referring to where a polymer is melted into a liquid like state that flows across the binding surfaces to later cool and solidify again.[2] Common adhesives used in everyday applications are PSAs, including tapes and pastes. This category has become a hot topic of research due to their versatility in application methods and ease of manufacturing. Maximization of mechanical characteristics without losing that versatility is of the utmost importance.

Medical adhesives also fall into the category of structural adhesives, leading to some side reactions that may appear due to the high mechanical strength and the structures that are

associated with it. Biocompatibility is the largest concern, requiring that the adhesive does not damage or kill the cells around a wound site, but ideally encourage the healing rate. Not only do the adhesives have to be mechanically strong, they need to be ductile due our constant movements required to maintain our mobile lifestyles. Lastly, if the application is intended to be used inside of the body, it needs to be able to withstand a wide range of different environments with fluctuations in values such as pH, salinity, or hydration along with elevated temperatures when compared to standard laboratory conditions. The ideal medicinal adhesive should be able to be used anywhere from the acidic solution found in the stomach to the more neutral levels found in the blood stream.

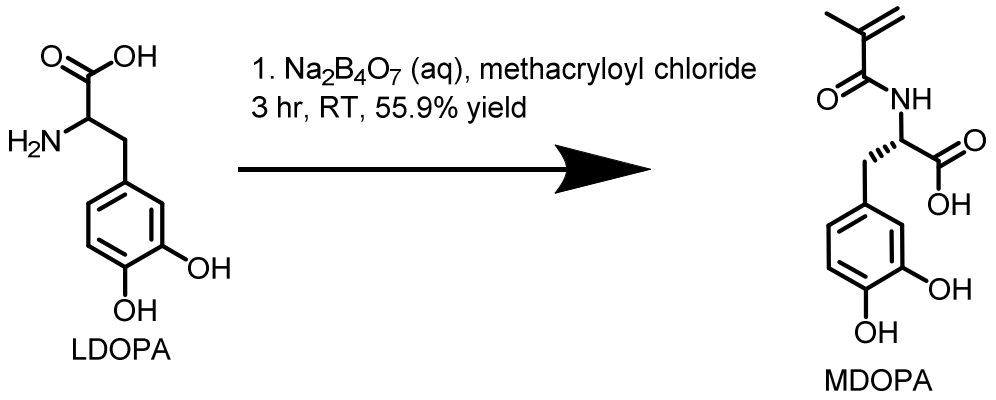
1.2 Wet Adhesion

One of the biggest limitations that is seen in adhesives currently is the inability to create a strong bond to a substrate under an aqueous environment. Additional moisture in a system will have a multitude of effects on both the polymer adhesive itself and its surroundings. Water can cause hydrolisis of the polymer molecules if there are functional groups such as amides or esters. Polymer adhesives are also prone to swelling or even dissolving completely depending on the solubility characteristics. Even if all of these problems are accounted for, polymer-surface interactions can be affected by the formation of a hydration layer on the adhering surface. A thin layer of water can get in between the polymer and substrate surface, either modifying or completely blocking the adherance completely.

For inspiration on finding ways to get around these problems, one tends to look at nature first and see how systems in the real world handle these problems. The best example that has been seen so far is by the marine mussell families, particularly *Mytilus californianus*. Mussels will release a large bundle of threads ending with an adhesive plaque that will adhere to multiple kinds of surfaces, including rocks, coral reefs, and even ship hulls, all while constantly being submerged underwater. The natural adhesive used to attach the plaque of the mussel to whatever surface it is binding to must be quite strong because of the it must withstand the constant barrage of waves and different current patterns that are associated with being out in the open ocean. These organisms have been studied fairly thoroughly and have been shown to secrete a solution that contains many different types of protein structures.

While many of these proteins vary with their marcrostructure, one common component that is seen in the all of the plaque specific proteins is a compound called 3,4-dihydroxyphenyl-L-alanine (Dopa). The concentrations of Dopa in each protein varies depending on the intended function and location at which the protein will be reacting. The primary adhesive mussel foot proteins, labelled mfp-3 and mfp-5, contain the highest concentration of Dopa at around 20-30% respectively. When compared with different mussel foot proteins that contained less Dopa, the energy of adhesion was much lower, and would drop even more drastically when compared to mussel foot protein analogs that contained no Dopa at all.

Dopa facilitates the high bonding strength by one of two methods. Firstly, the catechol groups act as anchors by bonding to the surface molecules of a substrate, typically through means of bidentate coordination for inorganic surfaces or hydrogen bonding and Michael addition for organic surfaces.[3–7] While this primary reaction is occuring, other Dopa groups not bonded to the surface can also be oxidized into the Dopa-quinone form and lead to possible crosslinking to other Dopa molecules. This can either be caused by the environmentally or enzymatically from the mussel itselfto enhance the final adhesion properties. Crosslinking in seawater type aquatic environments are highly favorable as the pH is typically slightly basic and is highly saturated with dissolved O_2 gas. [8]



Scheme 1.1 *Synthesis of methacryloyl-3,4-dihydroxyl-L-phenylalanine (MDOPA)*

With these characteristics, Dopa was considered to become a key component in a polymeric adhesive system. A form of the DOPA molecule could be added as a monomer unit, allowing for the polymer chain to have increased surface adhesion and crosslinking capabilities without sacrificing other characteristics.. A few simple modifications using the procedure listed

later can change it into methacryloyl-3,4-dihydroxyl-L-phenylalanine, or MDOPA as seen in Scheme 1.1. MDOPA has been studied previously and has been used as a monomeric component in terpolymer systems before.[9] MDOPA contains the necessary catechol groups while having the end vinyl groups in the form of methacrylate to allow for for radical polymerization.

1.3 Crosslinking

1.3.1 Crosslinking in Polymer Chemistry

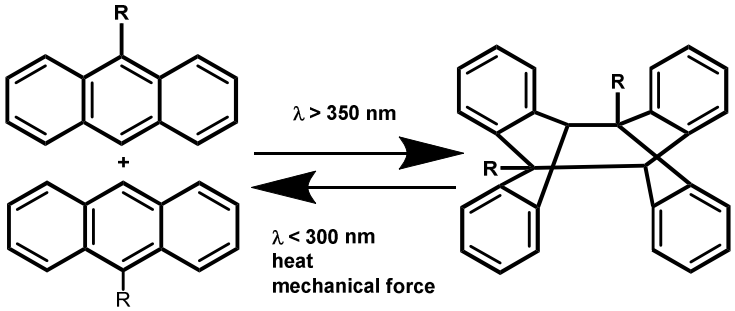
Crosslinking of occurs by interlinking polymer chains through the means of covalent bonds, ionic bonds, or phsycal interactions such as physical crosslinking. From these, the most commonly used crosslinking methods are covalent bonding and physical crosslinking. Covalent bonding is the most stable of the two because of the strength and permanence of the bond. High degrees of crosslinking leads to a high molecular weight, continuous polymer chain. With this increase in molecular weight, the physical characteristics of the polymer will change as well. Flexiblity of the overall structure will decrease, causing limited creep, mobility, and viscous flow due to the reinforcing effects seen by the three-dimesional fortification. An increase in the density of the polymer is seen due to an increase in the molecular packing, leading to a decreased free volume. High crosslinking values correlate to an increased mechanical performance, thermal properties, and chemical resistance generally.

Physical changes in polymer characteristics correspond with the current degree of crosslinking. This is to say that a polymer with a relatively low amount of crosslinking, such as a low modulus thermoplastic, will behave very differently when compared to a polymer with a completely crosslinked polymer, such as a hard, brittle thermoset. Polymer properties can be tuned this way to fit any desired application. Light crosslinking can induce a moderate increase in the viscoelastic properties of an entangled polymer network in both the surface and bulk. Crosslinking will mainly affect the adhesion properties and glass transition temperature (T_g) of soft polymers. The new bonds that are formed during the crosslinking process need to be strong enough to resist bond breakage through physical separation. Bond breakage can be resisted by crosslinking the polymer chains together, leading to a limitation of internal motion with the adhesive network and causing the internal energy to dissipate through the bonds. Crack

propagation is limited by this network as well due to the increased amount of energy needed to break the new bonds that are formed. The current report demonstrates covalent crosslinkiing of polymers via photo-activated anthracene dimerizations between polymer chains.

1.3.2 Photo-Crosslinking

Photo-reactive compounds are chemically inert compounds that will not become active until exposed to a UV light source. They are also going to be aromatic or conjugated, and are fluorescent under noraml conditions. Many different fluorescent aromatic compounds, such as methacrylated sebacic anhydrides[10], coumarin[11], and methacrylated end groups[12], have been used for different systems, but one of the most widely used and understood is the anthracene moeity. It has a wide array of uses including the base for light emitting diodes, photo-mechanical actuators, and stress-strain sensors. One of the most desirable applications is the ability of two anthracene moieties to undergo photocycloaddition reactions, creating new covalent bonds with only a simple UV light treatment. Anthracene is known to undergo a [4+4] photocycloaddition reaction, creating new covalent bonds at the 9- and 10- positions between the two molecules.[13] These new bonds are formed by exposing the anthracene molecules to light that is above 350 nm. While these bonds are easily formed, they are reversible and can broken down just as quickly. When exposed to light below 300 nm or heated to levels of 111-160 kJ/mol, the inter-anthracene bonds are broken, seperating the molecules and renewing aromaticity to both.[13] A visual example of this process can be seen in Scheme 1.2. While simple light based treatments are the easiest mechanism, this dimerization reaction can also be reversed through mechanical means. Physical



Scheme 1.2 *Dimerization of anthracene pendant groups*

grinding of a powderized polymer has shown to have a similar effect to the reversing light treatment.[14,15]

1.4 Water Solubility

As this project does have a potential goal of being used as a medical grade adhesive, solubility of of the polymer in water is important. If the polymer is completely soluble in water, it would be less useful as the adhesive would just dissolve into the into the media without performing its main function. Deciding on a third monomer for the overall polymer system was crucial in that the polymer needed to be able to withstand an aquatic environment without having any adverse reactions to it as well. If the polymer were to lose mechanical strength due to hydration effects such as swelling or hydrolysis, it would not be a viable candidate.

Acrylic acid is a well known polymeric component that has been shown to increase solubility of polymers when in water.[16] Carboxylic acid functional groups become deprotonated at higher pH values, leaving a COO^- group. Ionic interactions with water will increase because of this, leading to increased hydrophilicity of the polymeric system.[17] When the concentration of hydroxyl or carboxylic acid groups reaches a high enough point, the hydrophilicity will result in solubility of the polymer in water. Conversion of the ketone group into an additional hydroxyl group maintains aqueous solubility of the adhesive while under acidic pH conditions as well

Increases in carboxylic acid content also promotes hydrogen bonding between the polymer and aqueous media, leading to an increase in the adhesion strength of the adhesive without reducing the molecular weight by surface erosion.[18] The elastic modulus of the adhesive increases with acrylic acid content at low temperatures, and increases the crack propagation resistance at high temperatures.[19] Given the correct modifications, acrylic acid could even be used as a coating on biological surfaces to either immobilize or encourage cell adhesion and proliferation, yet also lead to decreased stability in water.[20]

1.5 Terpolymer Design Flexibility

Statistical terpolymer architecture has many advantages when used for soft polymer adhesive synthesis. First, a terpolymer system can be created easily using free radical

polymerization methods. Generally, a free radical polymerization reaction will polymerize a diverse range of vinyl monomers by the activation of initiators that react to specific stimuli such as heat, light, pH changes, or even mechanical forces such as pressure or vibrations. After modifying a desired base molecule with vinyl end groups, monomeric starting materials can be combined with initiator coupled with its specific activating stimulus to begin the reaction.[21] Vinyl group containing monomer synthesis has been thoroughly researched, allowing for either quick reference material to create an existing monomer or comparison to create a brand new one. Coupling the previous point with the wide array of starting materials that are available to be modified, a tailor made monomer can be created to suit any possible application

Secondly, the free radical polymerization is a very passive type of reaction, allowing for additional steps in a process to be completed ahead of it. Typical polymerization reaction solutions can be put together very quickly due to the lack of any intricate or time consume processess. The solution then needs to react for anywhere between 3-12 hours, depending on the starting materials, chosen initiator, and polymerization conditions such as temperature. This allows for multitasking opportunities, such as running side by side comparative reactions or just simply preparing fore the next step of the initial reaction. Because the efficiency of the reaction can be seen by a quick check of the viscosity of the solution, free radical polymerizations are a very convinient method to follow.

This process is not as selective as other polymerization techniques, meaning it is impossible to control which monomers will react or be able to create a block polymer architecture. This is still acceptable though due to the end polymers having an amalgam of the characteristics of all of the individual monomer components. For this project, the overall characteristics of the desired terpolymer are that it is swellable in water, adheres to different surfaces, especially under wet and biological conditions, and be able to be mechanically strengthened through exposure to UV light. These characteristics should be able to be tuned easily by simply changing the starting compositions of the monomer components and have a significant effect on the qualities of the final product after polymerization.

CHAPTER 2

MATERIALS AND METHODS

2.1 Starting Materials and Chemical Modifications

9-anthracene carboxylic acid (9AC), 3-(3,4-dihydroxyphenyl)-L-alanine (LDOPA), 2,2'-azobis(2-methyl-propionitrile) (AIBN), oxalyl chloride, and triethylamine were all purchased from TCI America and were used without purification. 4-hydroxybutyl acrylate (4HBA), acrylic acid, and tert-butyl acrylate were also purchased from TCI America, but had stabilizers removed by pushing the liquid through a packed alumina column. Methacryloyl chloride, Na_2CO_3, and Na_2BO_7 were all purchased from Sigma Aldrich and used without further purification.

2.2 Synthesis of Monomers

2.2.1 Synthesis of Methyldihydroxyphenylalanine (MDOPA)

19.5052 g (51.1 mmol) of $Na_2B_4O_7$ was dissolved into 500 ml of ultra-pure filtered water in a 1 L round bottom flask and let to stir and degas for 30 mins. Once thoroughly degassed, the top is removed and further reagents are added while still bubbling with N_2 to help minimize O_2 content in solution. 9.958 g (50.5 mmol) of LDOPA are added to the solution. Once dissolved, the pH of the clear solution is checked. If pH is above 9, a few scoops of Na_2CO_3 are added, allowed to dissolve into solution, and the pH is tested again. If still below 9, repeat process until pH reads above 9. Once this has be achieved, the solution was recapped, degassed for 5 mins, and then cooled to 0^oC in a ice water bath for about 10 mins. 10.815 g (7.5 ml, 103.5 mmol) of methacryloyl chloride was added dropwise to ensure thorough mixing. Fumes would form upon addition, so the use of a mini bubbler was employed to prevent the septum cap from building up pressure and popping. White globules formed in the solution, and would not dissolve upon stirring. The reaction vessel would need to be shaken vigorously to break up the globules and allow them to be mixed into the solution . Once dissolved, the solution is removed from the ice bath, opened, and the pH is tested again. As before, if the pH is below 9, a couple of scoops of Na_2CO_3 is added to bring up the pH. Repeat this process as necessary until it a pH of 9 or higher is achieved. Allow the solution to stir for 3 hours at room temperature before testing pH once more. This time, if the pH is above 2, then the addition of 5 ml of concentrated HCl is used,

repeating until desired levels are reached. Color of the solution will turn from clear or slightly pink to dark brown or almost black, and then lighten to a yellowish brown solution. Transfer the solution to a seperatory funnel where the desired products will be extracted descending amounts of ethyl acetate: first 250 ml, then 150 ml, and then ending with 100 ml. The organic layer is then removed and washed with 100 ml of a 0.1 M HCl solution twice. The organic layer is separated again, and washed once with 100 ml of a NaCl saturated solution. $MgSO_4$ is added to the organic layer to completely remove any water remaining, and excess solvent is removed using a rotary evaporator. The remaining product is a brown, sticky, viscous liquid.

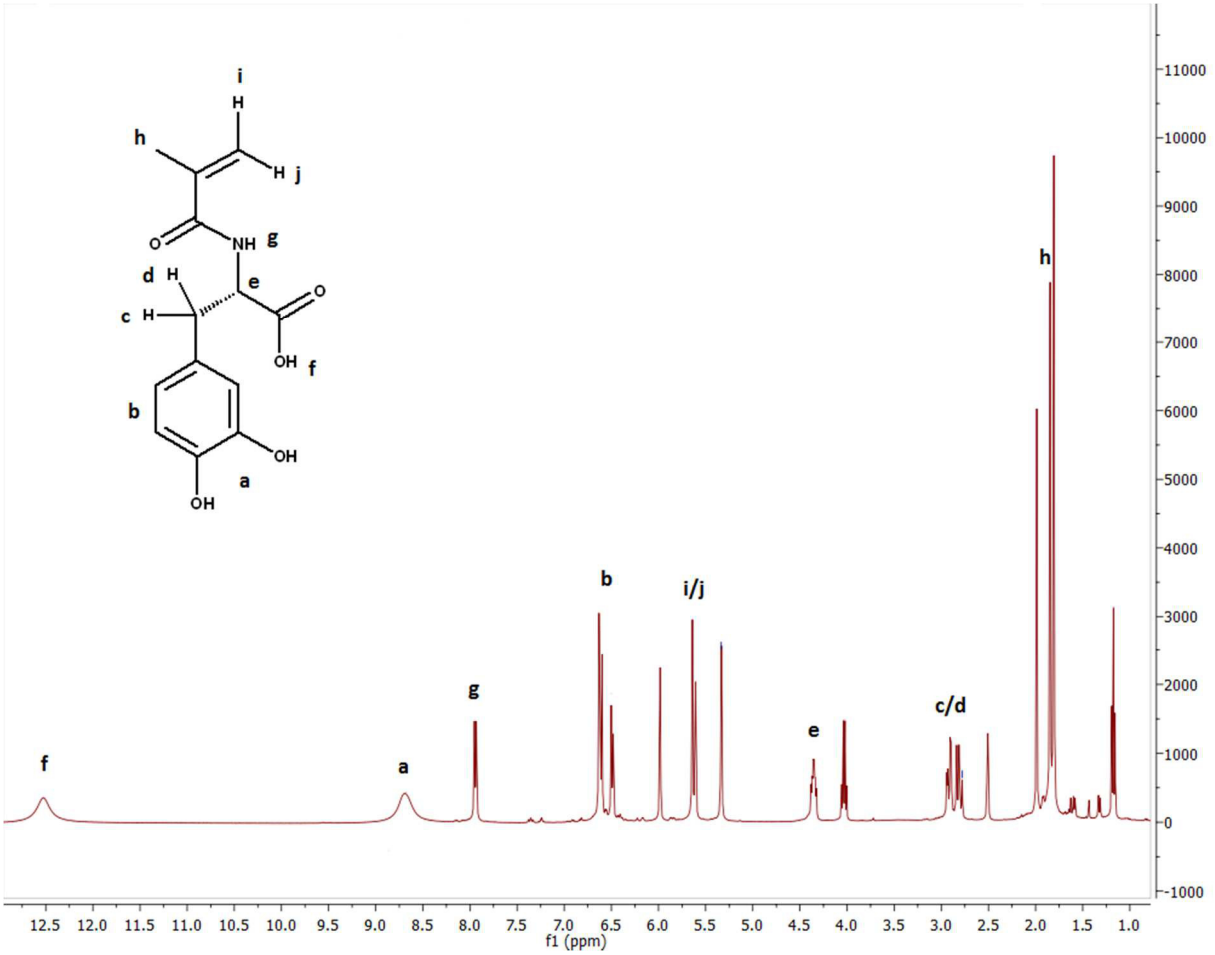


Figure 2.1 *^{1}H NMR spectra of Methyldihydroxyphenylalanine (MDOPA)*

2.2.2 Synthesis of 4-(acryloyloxy)Butyl anthracene-9-carboxylate (AOBA9C)

5.5005 g (24.8 mmol) of 9-anthracene carboxylate acid is dissolved in 25 ml of dichloromethane. Oxalyl chloride (2.335 ml, 3.4558 g, 27.2 mmol) is added dropwise to solution, along with 350 mg (.370 ml, 4.8 mmol) of dimethylformamide (DMF) to act as a catalyst. Solution is capped and sealed with electrical tape, attached to a mini bubbler, covered with aluminum foil to prevent light from entering flask, and then left to stir for 4 hours at room temperature. Unreacted oxalyl chloride is removed using a rotary evaporator, but unfortunately also removes all of the reaction solvent as well. The reaction vessel is capped and sealed. Another 25 ml of dichloromethane is added to replace missing solvent, along with 7.383 ml (7.6857 g, 53.3 mmol) of 4-hydroxybutyl acrylate (4HBA). 17.248 ml (12.522 g, 123.7 mmol) of triethylamine (TEA) is added dropwise due to it being an exothermic reaction. A mini bubbler is

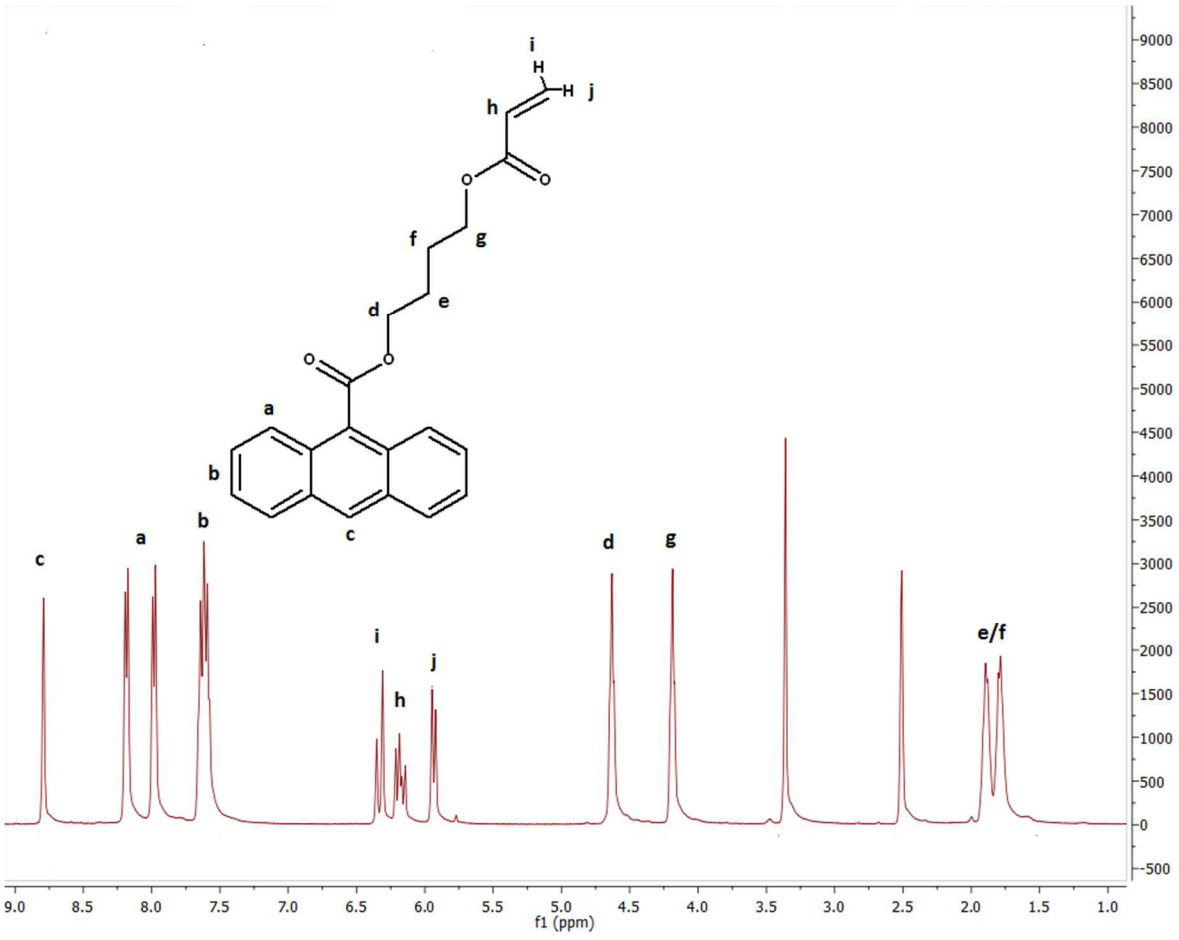


Figure 2.2 *^{1}H NMR spectra of 4-(acryloyloxy)Butyl anthracene-9-carboxylate*

connected to prevent the fumes produced from the reaction from popping the septum cap off and flask is covered again with aluminum foil. A white, wispy side product is also formed, but was easily reintroduced into solution by hand swirling contents. Reaction became a brownish/orange color, and was left to stir for 1 hour at room temperature while degassing for the first 20 minutes. The product is transferred into a seperatory funnel, and is treated with the following wash regimen: twice with 100 ml of 2 M HCl solution, four times with 100 ml of 2 M NaOH solution, once with 100 ml of supersaturated NaCl solution, and twice with 100 ml of DI water. Remove the organic layer and dry using $MgSO_4$, and then rotovap excess solvent away using a rotary evaporator. Additional drying overnight covered with foil in vacuum oven is used if product NMR shows solvent or water peaks. Product is 1.6124 g (41% yield) of a solid, yellow powder.

2.3 Polymerization Reactions

2.3.1 Terpolymerization of Poly(AOBA9C-co-MDOPA-co-AA)

Weigh out .4772 g (1.37 mmol) of 4-(acryloyloxy) butyl anthracene-9-carboxylate and 1.0000 g (3.77 mmol) of MDOPA into two separate vials and dissolve in .5 ml of DMF. Mix secondary solutions into 25 ml roundbottom flask, along with 2.1238 g (2.0207 ml, 29.47 mmol) of acrylic acid. Use remaining .5 ml of DMF to rinse any residual monomer out of vials, and raising total reaction solvent volume to 1.5 ml. Cover roundbottom flask with aluminum to prevent light from entering reaction and degas solution for 20 mins while stirring. Place flask in 70 ^{o}C hot oil bath and cover entire apparatus with aluminum foil. Let reaction stir overnight while venting to mini bubbler to prevent gas formation from building pressure. After ~10.5 hours, solution would show an increase in viscosity. Flask should be removed and cap removed to terminate active sites and reaction. Once cooled, production should be diluted with another 5-10 ml of DMF, or until easily pipetted. Solution is added dropwise to 300 ml of diethyl ether at 0 ^{o}C in a ice bath. Polymer should separate in bad solvent and form a light yellow/off white sticky solid. Excess solvent was removed by simply decanting thanks to solid sticking to side of glassware. The beaker holding the product was placed into a vacuum oven and left to dry overnight at 50^{o}C. A small portion of polymer was removed to analyze in ^{1}H NMRto measure purity. Due to difficulty of removal of DMF, another crashing sequence is necessary. Dried solid

polymer is redissolved in methanol and added dropwise again to another 300 ml of diethyl ether at 0°C. White, solid strings should appear this time and a light yellow powder will form after a drying overnight at 50°C. To ensure complete solvent removal, the solid white powder was ground into a very fine powder using a mortar and pestle, and then placed back into the vacuum oven, covered, at 50°C again overnight. Final product is a faint yellow powder.

2.3.2 Polymerization of Poly(AOBA9C-co-AA)

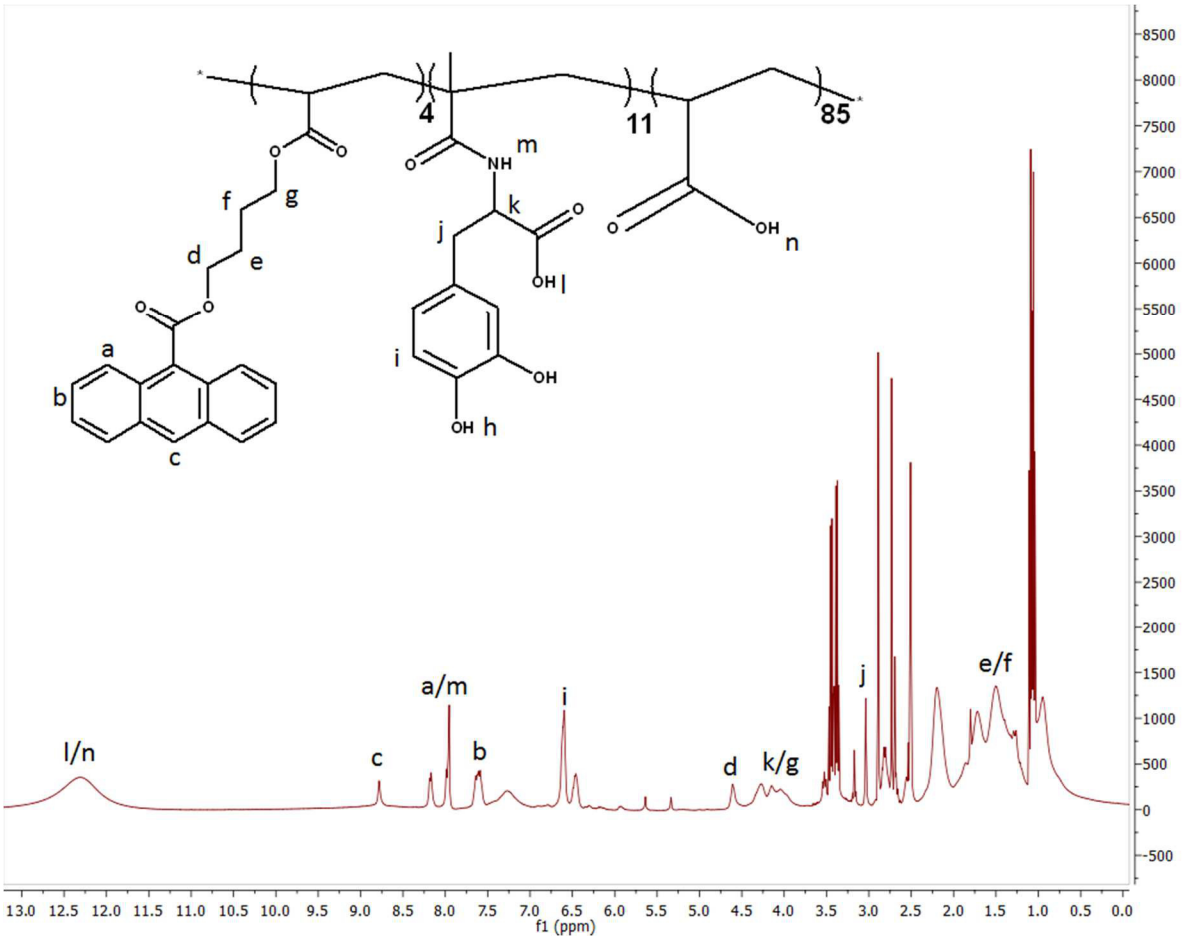


Figure 2.3 *[1]H NMR of Poly (AOBA9C-co-MDOPA-co-acrylic acid)*

.750 g (2.15 mmol) of 9-(acryloyloxy)butyl anthracene -9-carboxylate was dissolved in 2 ml of DMF in 25 ml roundbottom flask. 3.1757 ml (3.3376 g, 46.32 mmol) of acrylic acid was added, followed by 3 wt% (.1226 g) of AIBN as initiator. The solution was sealed with a septum cap and electrical tape, and then degassed for 30 mins while stirring. Polymer solution would be

a bright yellow color with relatively low viscosity. Once thoroughly degassed, the flask was lowered into a hot oil bath at 70ºC and held there for 10.5 hours or until viscosity had increased significantly. Once either condition was fulfilled, the cap was removed and the reaction was allowed to terminate by exposure to oxygen. Solution was diluted with additional DMF (5-15 ml) until easily pipetted, and then added dropwise to 300 ml of cold diethyl ether at 0ºC, forming an off-white sticky solid mass once allowed to condense on bottom and sides of beaker. Excess ether was removed by decanting and vacuum filtration and polymer product was dried overnight in a vacuum oven at 50ºC to remove as much solvent as possible. Dried polymer would be slightly yellow and would return to the original yellow color upon addition of solvent. A small sample was removed from dried polymer to test for purity and solvent removal through NMR analysis. The solid polymer was ground into a fine powder using a mortar and redissolved in methanol and diluted again until easily pipetted. The purification cycle of dissolving in

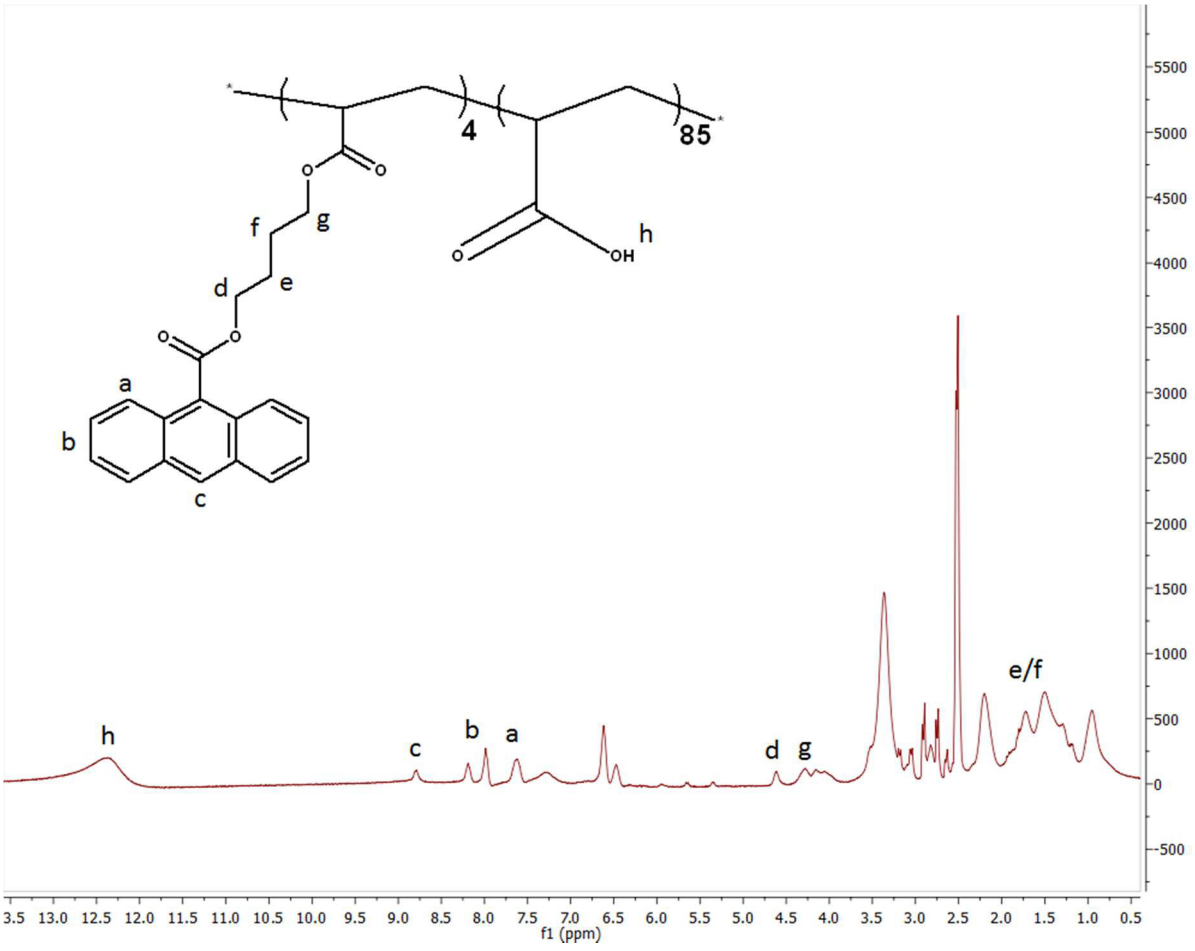


Figure 2.4 *^{1}H NMR spectra of Poly(AOBA9C-co-AA)*

methanol, adding dropwise to cold diethyl ether, and drying in vacuum oven was repeated twice more to remove all of DMF solvent from NMR spectra. Final product is a very light yellow powder.

2.3.3 Terpolymerization of Poly(AOBA9C-co-MDOPA-co-TBA)

Measure out .6334 g (1.82 mmol) of 9-(acryloxy)butyl-anthracene-9-carboxylate and place into a 25 ml roundbottom flask. Weigh out 1.3273 g (5.00 mmol) of MDOPA and dissolve into 2.5 ml of DMF in a small vial. Add MDOPA solution and 5.73 ml (5.0134 g, 39.1 mmol) of tert-butyl acrylate to the roundbottom flask. Rinse out the MDOPA vial with the additional 2.5 ml of DMF and pour into reaction vessel. Lastly, add 3 w% (.2105 g) of AIBN and stir bar to flask, followed by sealing with septum cap and electrical tape. Solution will be yellow with low viscosity. Degas solution for 20 mins while stirring and connected to mini bubbler. Lower flask into a hot oil bath at 70^{o}C and cover apparatus with aluminum foil to avoid exposure to light. Leave reaction for 12 hours or until viscosity increases significantly. After either condition is met, remove flask from oil bath and remove cap to expose solution to air, terminating reaction and catalyst. Once cooled, dilute solution with an additional 5-10 ml of DMF until it is easily pipetted using a standard glass pipette. Add diluted solution dropwise to a mixture of 150 ml of ultrapure DI water and 150 ml of ethanol at 0^{o}C. Off-white strings should appear once the drops are added to the cold solution and collect on the bottom as more drops are added. Once all of the solution has been added, allow the polymer some time to settle and it should stick to the sides or bottom of the beaker. Excess solvent can then be easily removed by decanting directly into a waste container. Transfer the beaker to a vacuum oven and allow to dry overnight at 50^{o}C. Separate a small amount (~10 mg) to be used for a ^{1}H NMR analysis. Redissolve the rest of the polymer into methanol (~ 10-20 ml or until easily pipettable) and add to another mixture of 150 ml of ultrapure DI water and 150 ml to receive a white, sticky solid. Once all of the methanol based solution has been added, decant off excess solution again and place beaker to dry in vacuum oven overnight at 50^{o}C. Dried solid polymer will need to be removed, ground into a very fine powder in a mortar and pestle, and then placed back into the vacuum oven to dry overnight again at 50^{o}C to completely remove any reaction or crashing solvent from the polymer sample.

The final product is a very light yellow powder (2.5781 g) that will turn to a much deeper yellow once dissolved in most solvents.

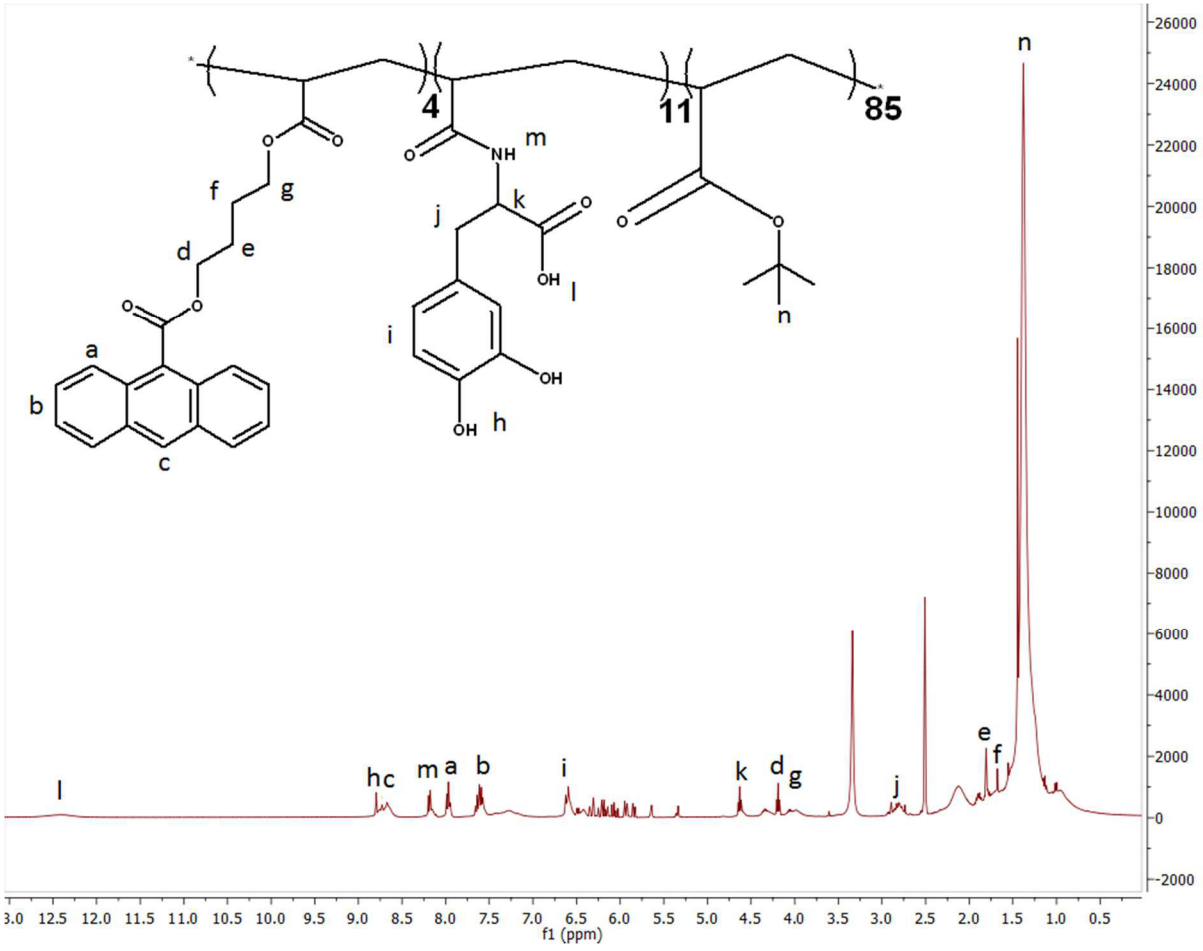


Figure 2.5 *^{1}H NMR spectra of Poly(AOBA9C -co-MDOPA-co-TBA)*

2.4 Preparation of Characterization Samples

2.4.1 Tensile Testing Samples and UV Treatments

Sample solutions are prepared with either a 1:1 or 1:2 weight ratio of polymer:solvent. Polymer and solvent is added together into a vial and vortex mixed for one minute and left for at least 30 mins to ensure homogeneous solution preparation. Substrates were prepared by either cutting mylar sheets (0.01 in) or glass slides into pieces with dimensions of 12.5mm x 75mm. A

adhesion contact area of 8mm x 12.5 mm was used to create a 1cm^2 surface for easy calculations. An average of 30 mg of polymer solution is added to adhesion area surface of one strip and another strip is attached to distribute adhesive evenly across surface. An aluminum block (~130

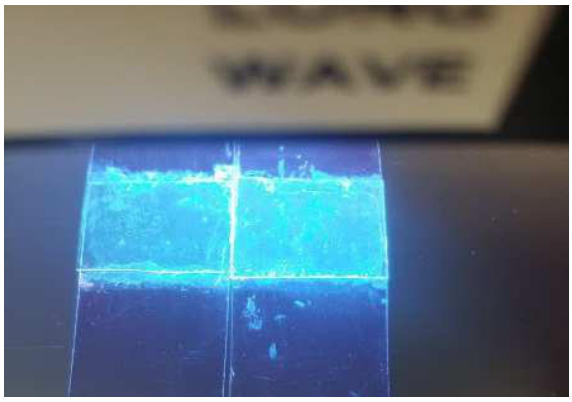


Figure 2.6 *UV reactivity of terpolymer under UV light treatment. Left is ethanol based dissolved polymer, resulting in clearer solution and even distribution. Right is water based swollen polymer, resulting in cloudy distribution*

g) is used as a standard weight for 10 minutes to promote a uniform pressure and weight distribution across adhesion surface. Once this time has been achieved, samples are then placed under a UVP UVGL-15 4-watt UV lamp at the 365 nm setting for either 1, 2, 4, or 8 hour time intervals at a 3 cm distance from the samples. Aluminum foil was placed on the base that the samples were resting on to maximize the amount of UV exposure. Foil was also wrapped around the enitre setup to minimize ambient light exposure and avoid any type of unquantifiable contribution to the crosslinking. Each set of strips were made at the same time and then placed into UV treatment at corresponding times for all samples to be completed at the same time and can be immediately transported to the tensile tester to prevent any differences occuring for solvent evaportation. When strips are being transported or not being irradiated, they are stored in a folded aluminum foil envelope to prevent additional light exposure.

Tensile testing was performed on a Shimadzu EZ-LX system equipped with a 200 N load cell. All samples were tested at a 0 N pre-load and at a 1 mm/min strain rate. Glass strips required a layer of nitrile to be wrapped around sample to ensure both grip of sample and to cushion glass from potentially breaking during sample loading. Mylar strips did not require any specific modifications and were loaded directly into the testing jigs. Ambient light exposure was

minimized by leaving lights off during mounting and testing times. All experiments were ran in triplicate to receive an averaged value and allow for error ranges.

2.4.2 Preparation of NMR Samples and UV Treatment

All samples are prepared at a 5 w% dissolved in dimethylsulfoxide (DMSO). For dimerization tests, polymer samples were dissolved in DMSO in a small vial, and then were placed into the center of a photoreactor chamber. Vials were irradiated for 2 hour with 14 8-watt light bulbs centered around 350 nm to show maximum potential crosslinking. NMR spectra were collected on a Bruker Avance III 400 MHz NMR.

2.4.3 Preparation of UV-Vis Samples

20 mg of polymer sample is dissolved into 20 ml of DMF. A 3 ml aliquot is measured out and placed in a foil covered vial for each of the following radiation times: untreated, 30 sec, 90 sec, 150 sec, and 3600 sec. Each sample was transferred to a quartz cuvette and then placed in photoreactor for corresponding time. After the radiation treatments, the solution was placed back into the original vial and the cuvette is cleaned twice with acetone before the next radiation treatment.

3 ml of samples are loaded into a quartz cuvette and placed into a (UV VIS SPECS). Samples were measured from 200-400 nm at .5 nm/sec. Between measurments, the quartz cuvette was washed 3 times with acetone to prevent any cary over or dilution of consequent samples.

2.4.4 Preparation of GPC Samples

A stock solution of undimerized polymer was created by dissolving 30 mg of sample into 3 ml of THF to reach a concentration value of 10 mg/ml. Dimerized polymer samples were created by first dissolving ~100 mg of the powdered polymer into a 1:1 polymer:solvent weight ratio solution in THF in a small glass vial. Vials were then placed in the center of a photoreactor and were treated with for either 1 or 2 hours using 14 light bulbs of 8-watts and centered around

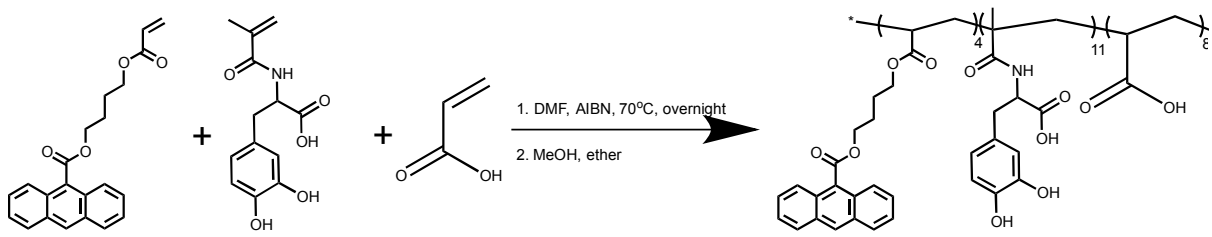
350 nm. Once treated, the solutions were diluted to 10 ml total to have a finished product solution at a 10 mg/ml concentration. Starting solutions were a bright yellow color and became more clear upon dilution after treatment. Spectra were taken using an Agilent 1260 Infinity model equipped with three HPLC columns containging a polystyrene stationary phase of 0.1 μm pore size. The HPLC portion is connected to 3 different Wyatt Technologies detectors: a Mini Dawn TREOS light scattering detector, a Viscostar-II viscometer, and an Optilab T-rEX refractive index detector.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis of Terpolymers

Poly(AOBA9C-co-MDOPA-co-AA) was synthesized using thermally initiated free radical polymerization at 70°C, as shown in Scheme 3.1. The polymer was characterized using ^{1}H NMR to verify monomer ratios in feed versus final polymerized product. The integral ratios of the product reflect the initial feed ratios, leading to a polymerization reaction that conserves monomeric input feeds.



Scheme 3.1 *Synthesis of Poly(AOBA9C-co-MDOPA-co-AA); DMF=dimethylformamide, AIBN= 2,2'-azobis(2-methylpropionitrile), MeOH=methanol*

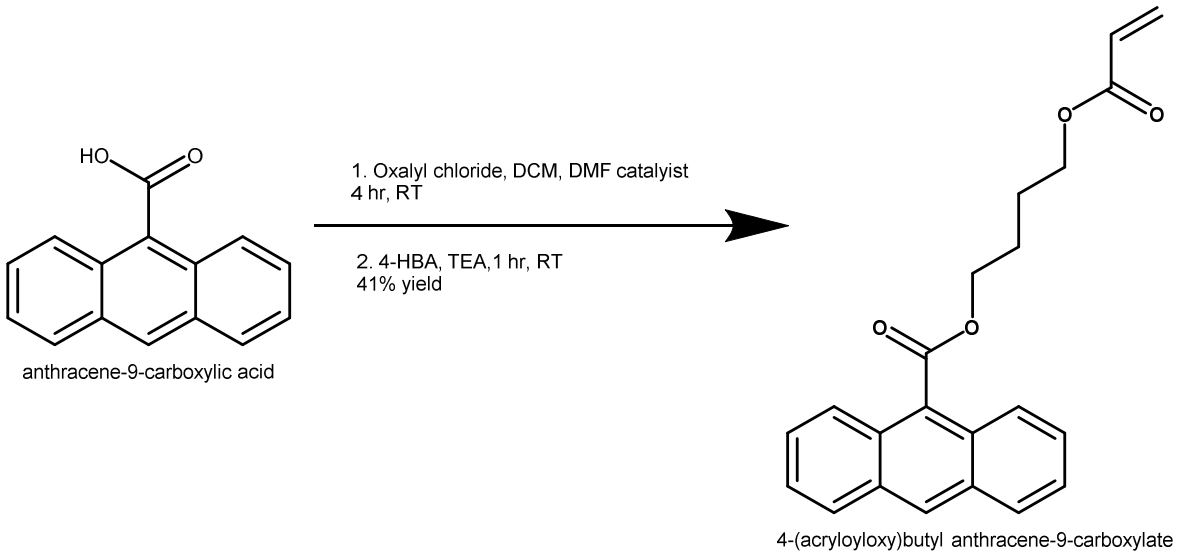
4-(acryloyloxy)butyl anthracene-9-carboxylate was synthesized for many specific reasons. The anthracene moiety located at the end of the chain allows for simple, yet strong crosslinking of polymer chains to allow for mechanical fortification. Crosslinking is attained through reversible cycloaddition reactions that are induced by exposure of UV light above 350 nm, meaning it is an easy procedure that does not run the risk of damaging the substrates with extreme conditions. The long carbon spacer chain allows for the incorporation of higher concentrations of the monomer unit without impeding the movement of the other monomers due to steric hindrance. Methacrylate groups located close to the backbone increase solubility in the overall polymer. MDOPA has been used numerous times before due to high wet adhesion strength values correlated with it.[3–5,9,22–32] It functions as a biomimetic for a strong interfacial adhesive. Acrylic acid has also been shown to increase solubility in multi-component polymer systems, as well as increase adhesion energy when incorporated into a soft polymer adhesives as explained before.[16–20,33–36]

3.1.1 Structure Characterization

Materials characterization of the polymer adhesives were used to confirm a few different aspects of the created terpolymer systems. Nuclear magnetic resonance (NMR) first confirmed that the structure and composition of the polymer chain were indeed what was theoretically designed and to ensure that either all monomeric reagents were either reacted into the system or completely removed through a purification process. Ultraviolet-Visible (UV-Vis) spectra were also taken at indicatve regions to ensure that the anthracene moieties were incorporated into the terpolymer structure to later be used for dimerization studies. Lastly, gel permeation chromatography (GPC) traces were used to determine a baseline for size and trace positions before continuing forward in testing any supra-molecular structure creation.

3.1.2 Monomer Synthesis

One major aspect that requires consideration is steric hindrance of the anthracene pendant group. Due to the bulkiness of the anthracene molecule, a large spacer group is required in order to allow enough room for the anthracene pendant groups to not become sterically hindered. A 2-



Scheme 3.2 *Synthesis of Anthracene based monomer 4-(acryloyloxy)butyl anthracene-9-carboxylate (AOBA9C). DCM = dichloromethane, DMF = dimethylformamide, 4-HBA = 4-hydroxybutyl acrylate, TEA = triethylamine*

carbon spacer chain was first used, but did not show promising results. A 4-carbon spacer chain was tested afterward, and created a viable monomeric compound as can be seen in Scheme 1.2.

Along with requiring a spacer chain, the compound would require an easily polymerizable functionable group on the chain end. As with the MDOPA synthesis, a vinyl group creates an easily polymerizable backbone structure. Free radical polymerizations allows for a selective polymerization method that ensures no side reactions will occur during the reaction.

3.1.3 Composition Optimization

Differing compositions of the individual monomeric components can lead to a drastic change in the characteristics of the final product that is received. Crosslinking of the polymer chains only requires a small amount, around 4 mol%, of 4-(acryloyloxy)butyl anthracene-9-carboxylate per chain, meaning it will have the lowest concentration. Acrylic acid must be the majority of the polymer molar ratios in order for the overall polymer chain to be hydrophilic. Last, MDOPA content must be high enough to allow for sufficient bonding to occur using the catechol groups. The first potential composition that seemed to fit these requirements were to be a feed ratio of 5:15:80 of 4-(acryloyloxy)butyl anthracene-9-carboxylate:MDOPA:acrylic acid, respectively. This composition did not work due to a lack of solubility along with too much MDOPA being used for each terpolymerization reaction. It was then altered to a 4:11:85 ratio, which showed much better solubility in ethanol and swellability in water. As stated before, this feed ratio was reflected in the composition of the final polymer product.

3.1.4 NMR Structure Confirmation

As seen in Figures 2.1-2.5, a few different key peaks are seen that confirm the presence of the individual monomers in the terpolymer. Anthracene has distinct aromatic peaks in between 7.5-9.0 ppm, seen most clearly in Figure 2.3. MDOPA has characteristic catechol peaks at 8.5-9 ppm, such as in Figure 2.2. Lastly, acrylic acid has a proton peak at 12.4 ppm from a pendant carboxylic acid group. Additional peaks that are seen in the lower end of specturm are associated with the carbon backbone of the polymer. In this case, the backbone shows values ranging

between 1-2.6 ppm. These tend to fluctuate due to the statistical polymer structure and can not be accurately assigned.

Other peaks will appear in the spectra that are not corresponding to the chemical structure, such as the peak correlating to dimethylsulfoxide at 2.5 ppm, which is the deuterated solvent used during NMR analysis. Some solvent molecules from the synthesis also could not be completely removed during the purification prcoesses. Because these are completely new polymers that have been created using a relatively new method, an ideal purification method was not always available. An example of this would the presence of leftover ethanol in the polymer sample seen in Figure 2.3, with peaks appearing at 1.06, 3.44, and 4.63 ppm. Because these samples were to be used in tensile testing experiments where large amounts of solvent were to be applied, these levels were deemed acceptable and did not require any additional drying. Another example is seen in Figure 2.4, where a peak at 3.33 is associated with water still incorporated into polymer. Again, because it was to be used in an aquatic environment and because water levels were still below deuterated solvent levels, it fell within an acceptable level.

Designations of all of these peaks insures incorporation of all monomeric components, but not the exact ratios. Post polymerization compositions must be known in order to fully understand the contributions each has in the final product. Incorporation of all monomer groups must be carried out in order to receive desired combination of characteristics. From the integrals shown in the terpolymer spectra, the ratios are held to roughly the same values.

3.2 Dimerization Studies

Photo-dimerization of the anthracene pendant groups in the polymer adhesive is the key point of the presented study. The dimerization acts as a post-bonding treatment that enhances the overall adhesion property of the adhesive after the initial interfacial bonds are formed between the adherents. The adhesion enhancement is caused by inter-chain covalent bond formation brought on by UV exposure, which is also known as photo-crosslinking. The efficiency and rate of photo-dimerization of anthracene groups are characterized by structural changes seen by NMR, UV-vis, and GPC as discussed below. Photoreactivity of the polymer samples can be seen in Figure 2.6. Dimerization of a polymer solution will show many different changes in its characteristics. First, the color of the solution will shift due to the alteration of the aromatic

portions that are responsible for fluorescence and color. When dimerization occurs, the anthraene groups will lose aromaticity to form covalent bonds with adjacent anthracene molecules as seen in Scheme 1.2 previously. The change in aromaticity yields the absorption and emission intensity shifts seen in UV-vis spectra. Color change is the visual indicator of this, and can be seen in these polymer solutions by the yellow color darkening upon prolonged exposure. Quantifiable changes can be measured using UV-vis spectroscopy and NMR, along with measuring molecular weight changes using GPC.

3.2.1 NMR Confirmation

Because dimerization involves the creation of new covalent bonds where there previously was not any, one could expect to see a change in the NMR spectra of a fresh polymer sample when compared to a UV exposed dimerized sample. As the anthracene pendant group is the area where the changes are occuring, the iconic regions of this molecule are going to be the main focus, namely the aromatic regions between 7.5 and 9 ppm. Theoretically, the anthracene aromatic peaks would disappear as the amount of dimerization is increased. This trend can be seen in Figure 3.3, where an untreated and thoroughly UV saturated solution are compared. Because the spectra was taken from the same sample solution before and after a 2 hour, 112 W photoreactor treatment, there is no reason any other outside sources should have altered the structure other than the light treatments.

As the dimerization of the anthracene moieties reaches a maximum, the peaks for b-e almost completely disappear. While the other peaks do not completely disappear, they certainly decrease in size, leading it to be believed that their signals are simply shifted instead of removed. This can be seen from the new peaks that are formed between 6.8-7.0 ppm. This is shown to be the shifted positions of the anthracene alkene protons after the aromaticity has been broken from the new covalent bonds. The peaks are clear and able to be discerned even in the terpolymer spectra for two reasons. First, because there are still aromatic rings on either side of the bonding ring, the protons on each aromatic ring are going to show two distinct peaks per ring. This leads to a total of eight protons per dimer showing two individual signals, with the difference between the two being enough that they are not compiled together due to signal resolution limitations. Secondly, these peaks are appearing in a portion of the spectra where there previously was no

signal at all. The moment dimerization of the polymer chains begins to occur, the reaction could easily be measured and quantified in real time the technical setup could allow it.

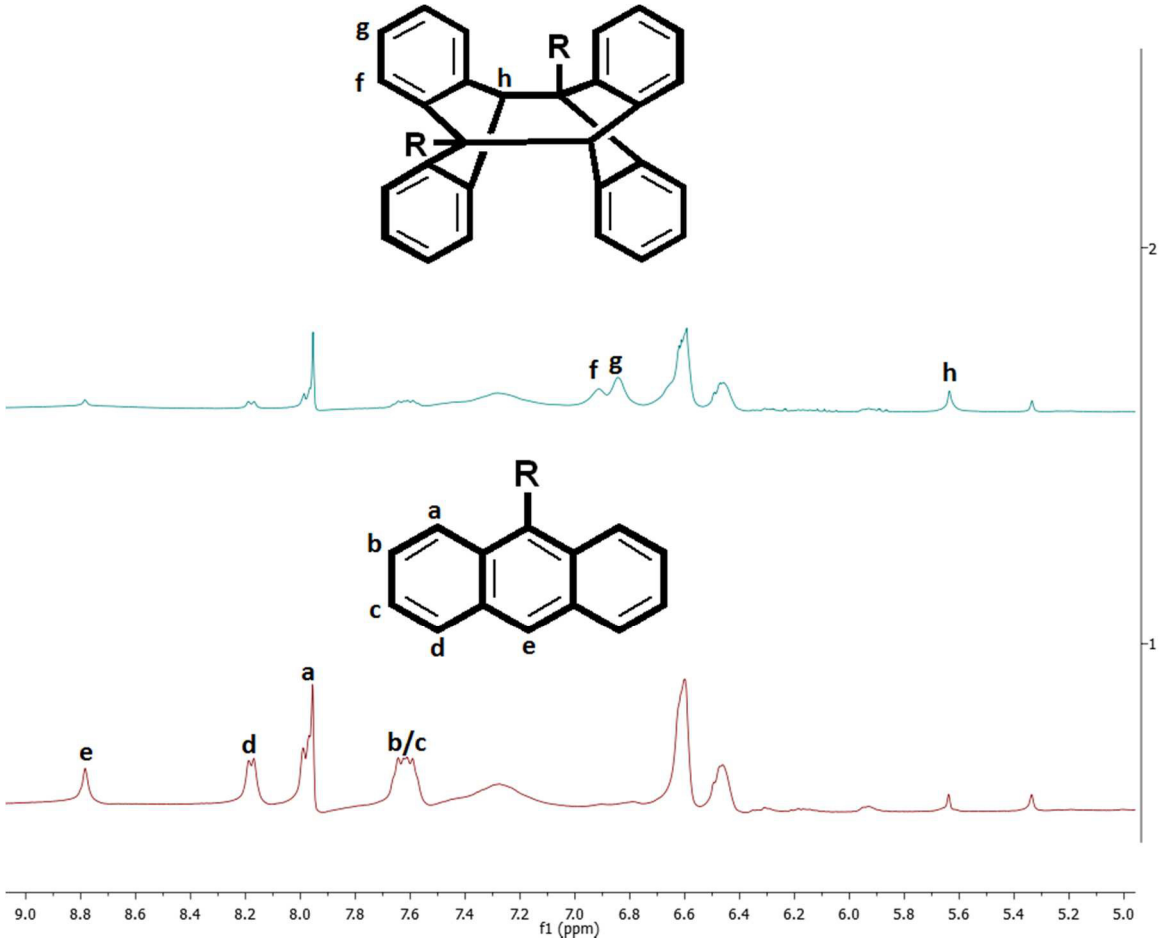


Figure 3.3 *^{1}H NMR spectra showing dimerization of anthracene pendant groups*

3.2.2 UV-Vis Spectroscopy

Similar to the NMR confirmation, the anthracene portion on the spectra are centered around 330-400 nm. This region contains three distinct peaks again relating to the aromatic portions of the anthracene pendant groups. These peaks are used as a reference point for measuring the overall amount of conversion from undimerized to dimerized versions of the polymer chains. Using this as a reference, a small UV treatmentof 112 W for 30 secs was applied in order to measure the responsiveness of the absorption peaks. As seen in Figure 3.4, the absorption levels show a significant decrease after the short amount of time. This shows that the

polymers are very responsive in their dimerization abilities, meaning the adhesion and mechanical properties can be strengthened on a very short basis. Additional UV treatments were done at larger time time scales, increasing with intervals of 60 secs, to increase the total conversion of the polymer chains. The signal continued to decrease, suggesting that more of the anthracene pendant groups were bonding between the chains, creating much longer branched polymers. UV treatments were stopped after 150 secs because the trend of decreasing absorption had been established and there was limited supply of terpolymer sample left that needed to be characterized in other fashions described later. One more sample was created to be used to create a fully dimerized sample by doing an extended UV exposure time of 3600 seconds.. Despite the long exposure time, the peaks do not completely disappear, but are drastically smaller in size when compared to the starting material. It has been shown in other examples as well that the

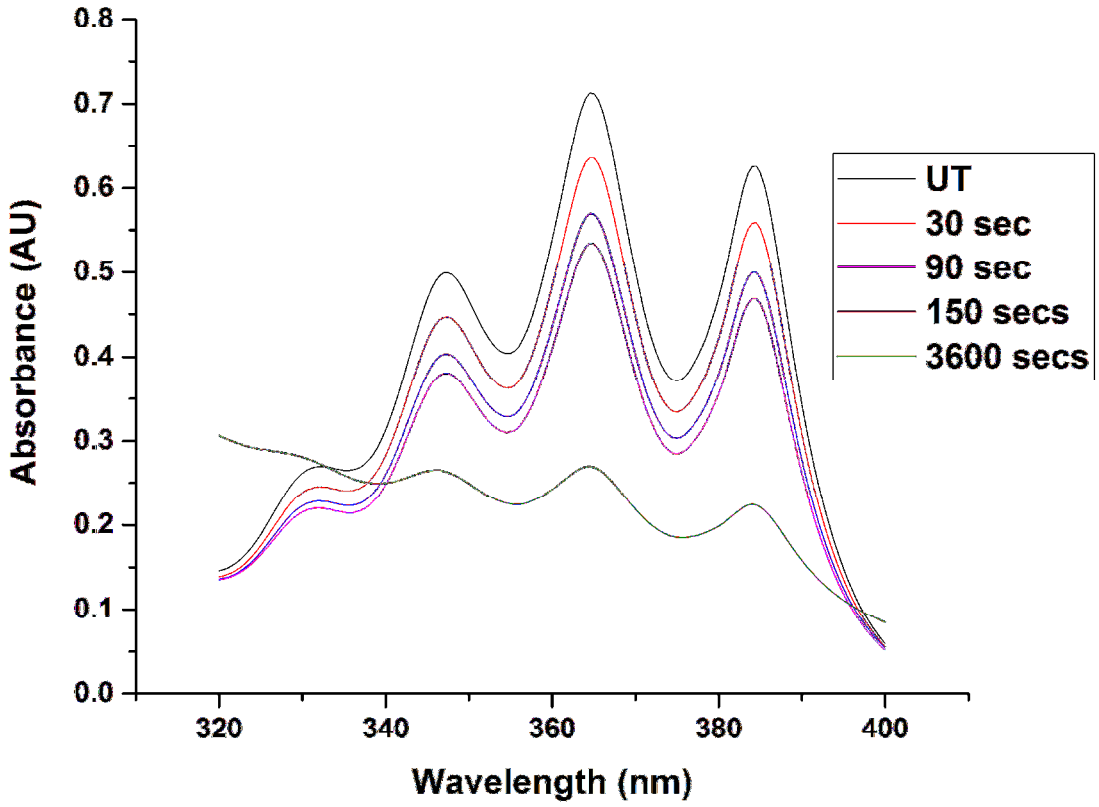


Figure 3.4 *UV-Vis spectra of anthracene aromatic group. Signal decreases with increasing exposure time*

peaks do not completely disappear, but will drop to significantly lower levels of absorption. [37] Tailing on the lower wavelength side does appear due to the formation of some new peaks during the dimerization process, but are unable to be distinguished due to the signal maxing out to undetectable levels.

3.2.3 Gel permeation Chromatography

As the rest of these experiments are using Poly(AOBA9C-co-MDOPA-co-AA), this can not be used in GPC columns as they will damage the packing material inside them due to highly acidic nature of acrylic acid. To counter this problem, a new terpolymer was created, replacing acrylic acid with tert-butyl acrylate (TBA). This was done because TBA does not have an

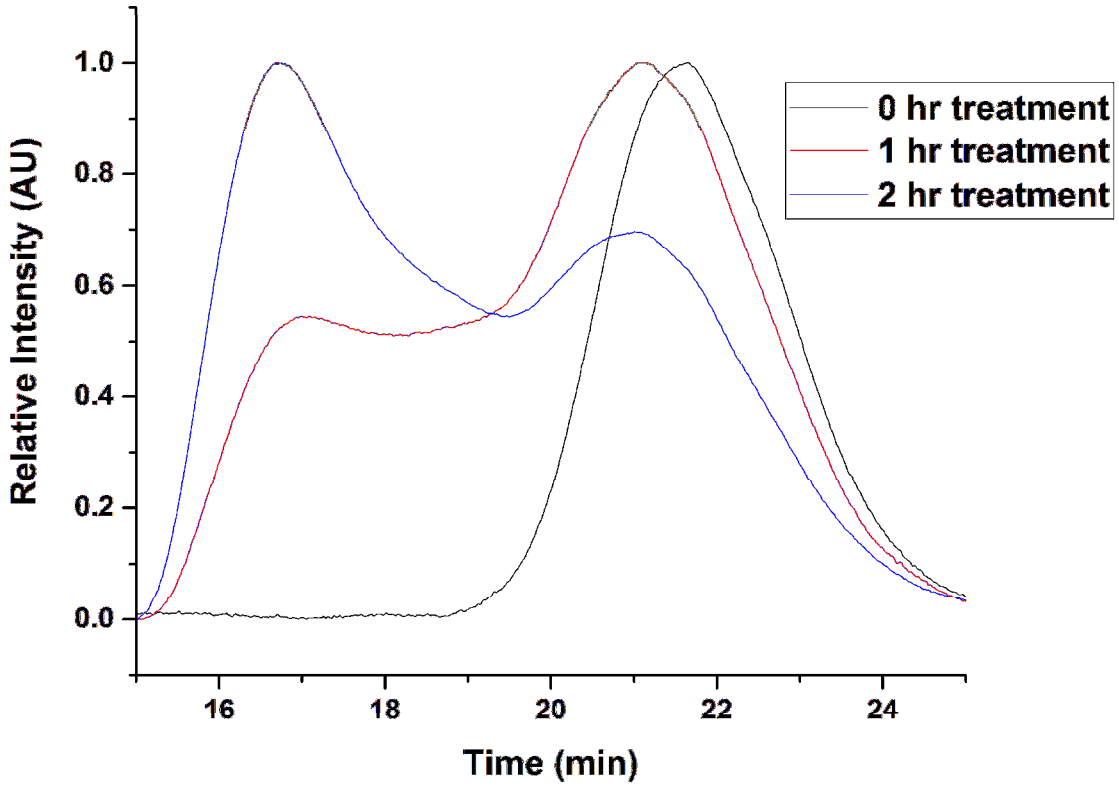


Figure 3.5 *Normalized GPC trace comparison showing shift to earlier retention time with increasing molecular weight*

affinity to the packing material found inside the columns while still having a very similar chemical structure to the original acrylic acid monomer.

GPC trace shifts are the first indicator than an increase in molecular weight has occurred, due to the fact that larger molecules will elute out of the columns quicker than smaller molecules. Distinct shifts can be seen in the polymer distribution curve portion of the spectra, specifically centered around 21.5 mins, as seen by the black trace line in Figure 3.5. After a fresh synthesis where the anthracene groups exhibit no dimerization, the M_n distribution is centered at 20,670 Da with a polydispersity index (PDI) value of 2.375. After an hour of UV exposure in the photoreactor, the main peak shifts to a smaller retention time along a new peak forming . This corresponds with an increase of the M_n values to an average of 40,710 Da with a PDI value of 2.880. To test if the solution had reached a completely dimerized state, a solutions with a 2 hour exposure was created to see if any more shifting occurred during the trace process. The amount of trace shift seen was significantly less than than the initial UV exposure. This explains that the one hour UV treatment under 112 W was enough time to dimerize the majority of the anthracene molecules in the polymer adhesive. During a two hour exposure session, the average M_n value increased to 43,510 Da with a PDI value of 3.47. An increase of the PDI is expected with as different sized polymer chains will be dimerizing with other random polymer chains based on proximity. Widening of the distribution will occur with the shift, leading to a larger PDI value as UV exposure increases.

3.3 Tensile Testing Results

The most crucial result of the presented report is the alteration of the adhesion properties that is seen by photo-crosslinking of the anthracene monomer groups in the polymer adhesive. In order to measure the adhesion property change, lap shear strength tests were perfomed with various adherents including Mylar® (poly[ethylene terephthalate]) and glass (slide glass bought from VWR). To optimize the adhesion energy of the polymer adhesive, five variables were altered during the shear tensile strength testing process: substrate, solvent, concentration of polymer adhesive in solvent, UV treatment times, and MDOPA content of adhesive. All samples were prepared within the same batch using an identical preparation method while changing only one variable at a time while holding all the others the same. Additional details regarding

production of tensile testing samples are described in the experimental section of this report. All reported adhesion values are an averaged value from where sample size is 4.

3.3.1 Solvent Comparison

Two different solvents were used, ultrapure DI water and ethanol, were used to study the effect of solvent on adhesion property. Ethanol is still is not as ideal as DI water in terms of biocompatibility, but is still more acceptable when compared to other organic solvents that are typically used in polymer synthesis and application.

Figure 3.6 *Terpolymer Swollen in 1:1 weight ratio of tertpolymer:H_2O; a turbid solution on the bottom of the vial is a polymer solution*

When exposed to the differing solvents, the solid polymer was completely soluble in the ethanol while only being slightly soluble in water. Water yielded a turbid solution after the polymer was soaked in it overnight and would make a swollen, sticky polymer as seen in Figure 3.6.

The graphs in Figure 3.7 show the general trend of an increase of adhesion energy with increasing UV exposure time. Generally, higher photo-crosslinking occurs through interpolymer chain dimerzation of anthracene with longer UV light exposures. Higher densities of crosslinking between polymer chains prevents debonding from the attached substrates (Mylar® and glass).

While it may be slightly hard to see, this trend holds true for both solvents, although water has a much more drastic change in adhesion strength as compared to the ethanol solution. This trend is also accompanied with the fact that the water based polymer revealed stronger adhesion properties than the ethanol based polymer, over two orders of magnitude as seen from the maximum of each data set. The adhesive shows an induction period for the first 2 hours with a moderate increase in adhesion energy. Assuming the that the changes in the adhesion property reflects the degree of crosslinking between the polymers, it can be assumed that most of the crosslinking is completed before the 4 hour mark. A couple of different factors could be responsible for strong adhesion of water swollen polymer; the first being that the polymer is swollen in the solvent instead of completely dissolved as in the ethanol. Swollen polymer chains are not as dispersed as their dissolved counterparts, meaning the anthracene groups have a much

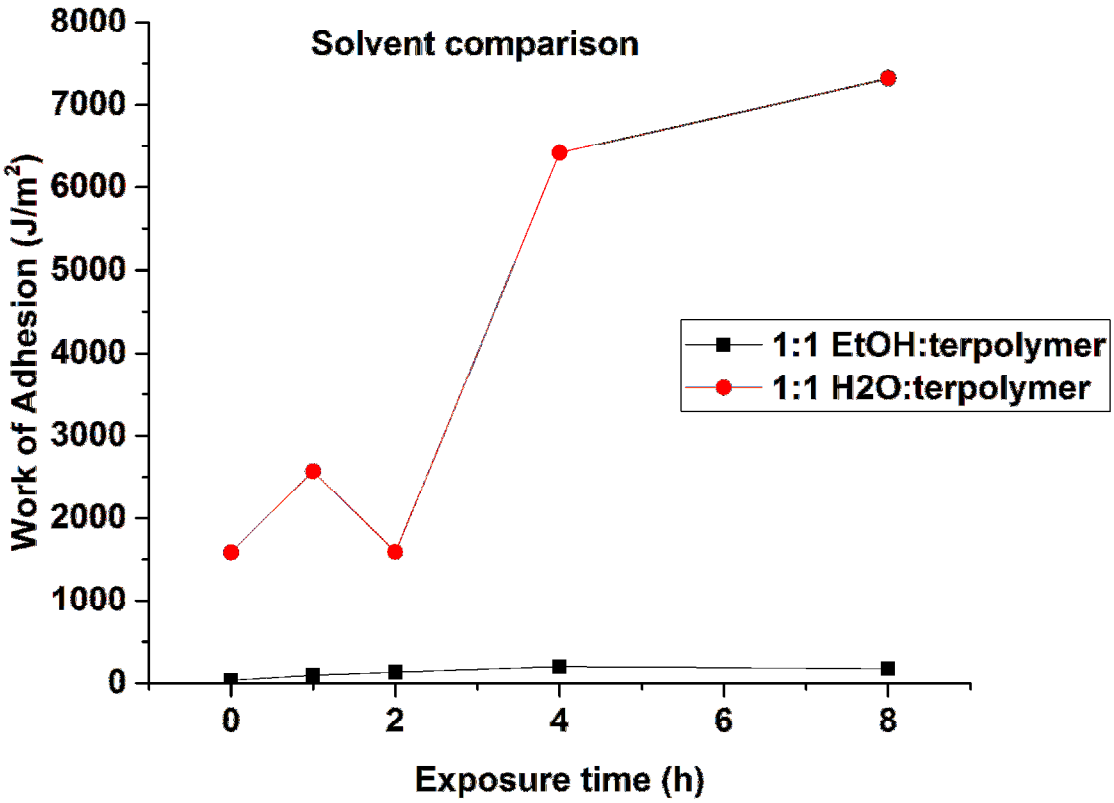


Figure 3.7 *Lap shear tensile testing comparison between ethanol and water*

higher probability of being close to each other, allowing for easier dimerization. Another factor is the fact that water is not a volatile solvent like ethanol. Even though the polymer between the strips may look completely dry, there can still be a small amount that is trapped in between the layers keeping the polymer wet. Thus, the adhesive polymer shows behavior consistent with a hydrogel that contains a constant amount of water distributed within the polymer matrix. The ethanol based polymers tend to dry quickly because a large amount of solution volume is lost while the adhesive is sandwiched between the two substrates. Note that all samples were prepared in a uniform manner, including adhesive being sandwiched with similar sample size, weight, and time. The ethanol based solutions became more brittle and dried when reaching the failure or breaking point during the lap shear strength tests. However, the water based adhesives would show increased ductility and actually stretch during the testing procedure.

3.3.2 Concentration Comparison

Once the optimal solvent has been determined from the solvent comparison test, the next step is to observe how the polymer will interact with different amounts of said solvent. Some polymers will tend to adhere better if they are in a more solvent rich environment if they are more prone to swelling versus dissolution. For this experiment, the solutions are designed to be either at a 1:1 or 1:2 polymer:solvent weight ratio. Doubling the amount of solvent seen in a polymer system shows a general trend of lowering the adhesive energy after UV exposure, but has some differing results at the 2 hour mark. Ethanol solutions show very lttle adhesion property changes in the early exposure treatments, showing that the only real changes seen between the two sets is simply an increase in overall volume. As the exposure times increase, there is only a small increase in the energy gaps until the diluted solution actually ends with a higher energy of adhesion at ~0.025 J/cm^2 at the 8 hour mark. This may be explained by the step size between the last two data points being the largest and the polymer chains being able to move around and form the optimal crosslinked polymer network to maximize adhesion energy.

While diluted solutions worked for the ethanol based solution, we see the opposite effect happening in the water based solution. More concentrated solutions clearly are seen to be the stronger of the two, with the more dilute solution even decreasing in strength as the UV treatments are increasing with time as seen in Figure 3.8. The 1:2 water solution on mylar films

showed an overall decrease from 4689 J/cm^2 at 0 h exposure to 1688 J/cm^2, a drop to almost a third of the original strength. On the other hand, the 1:1 water solution on mylar films started at 1584 J/cm^2 at 0 h and increasing all the way to 7318 J/cm^2 at 8 h of UV exposure, which is roughly a 462% increase.

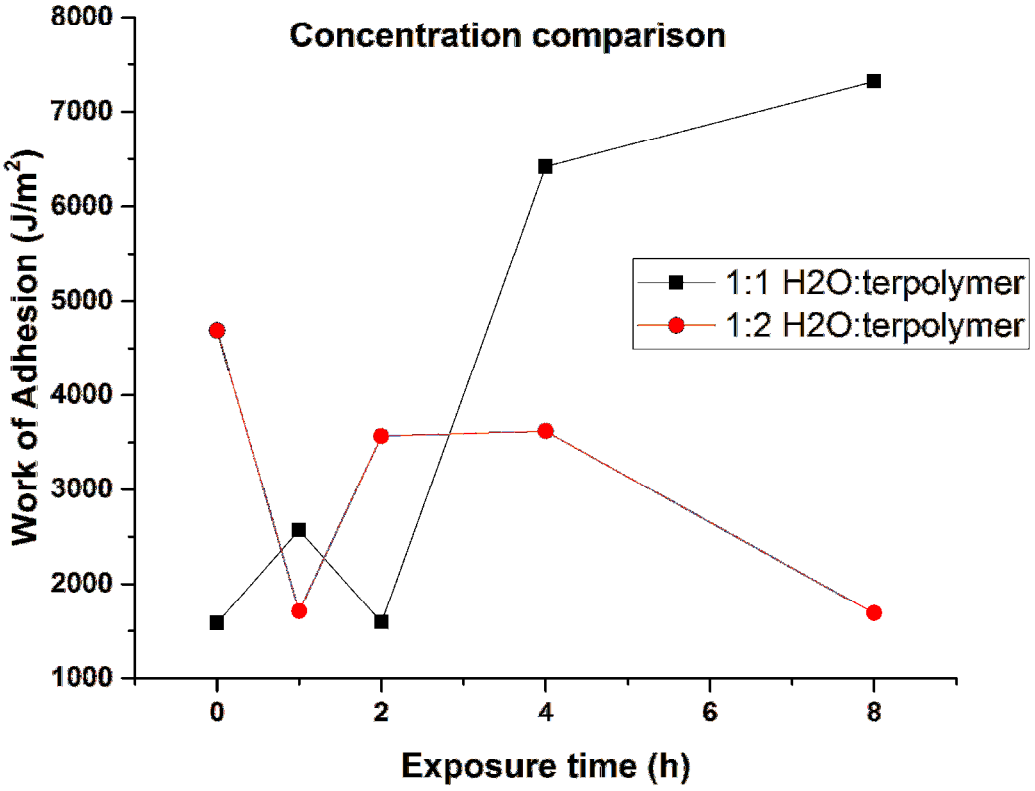


Figure 3.8 *Lap shear tensile testing comparison of concentrations*

It is understandable that the polymer solution will become weaker as more solvent is added to the system for several reasons. First, when the solution between the adhered surface becomes more dilute, there is going to be less polymer in between the strips overall. This is due to the fact that a certain solution mass was being applied to the surface and not a specific mass of polymer. Therefore, if one solution that is being applied is more dilute than another, there will be less adhesive to react with the surfaces, resulting in a lower adhesive energy. Another reason is that when the polymer solution is more dilute, it will have a much harder time of dimerizing as

compared to the more concentrated sample. This is because the polymer chains will have to move much longer distances in order for two activated anthracene pendant groups to be able to find each other and allow for a dimerization reaction to occur. An example of this is shown in the higher exposure time samples. While there may be some fluctuations in the beginning, somewhere after the 2 hour mark there is a drastic increase in the adhesion energy that is due to dimerization. It can be assumed that after this point, a significant portion of the 1:1 ratio samples have become dimerized as there is only minimal increase in adhesion energy with doubling the overall exposure time. While the more concentrated version is able to dimerize easily and created strong bonds on both surfaces, the dilute version is significantly weakened due to being spread out too thinly across the same surface. The dimers formed may not be able to completely reach both ends of the substrates, and also have less total catechol groups to allow for strong surface bonding.

3.3.3 Substrate Comparison

The second factor to be tested is the polymer adhesive's ability to bond to different surfaces. Polymer samples were adhered to both PET films (Mylar) and to glass to simulate a ttaching to organic and inorganic surfaces. Varying the substrates is necessary to prove the versatility of the adhesive.

This system has shown that it is more preferential to towards organic surfaces as seen in Figure 3.9. While all of the mylar based samples stay with the general trend of increasing in strength with increasing exposure times, all of the glass based samples only fluctuate around their starting values, with only small changes in strength in either direction. Glass slide samples were still becoming slightly darker with increase UV exposure, meaning that the polymer solutions were crosslinking just like the mylar samples. Because of this, the problem must lie in the adhesion of the polymer to the substrate and not the dimerization of the polymer chains to each other. The chains would still form a crosslinking polymer network, but without a good source of adhesion to the surface, the strengthening effect of the dimerization had no effect.

Adhesion to the mylar film surface was much better for all of the solution sets when compared to the glass substrate samples. While the ethanol based solutions may have started around the same strength values as on the glass slides, they actually showed a reinforcing effect

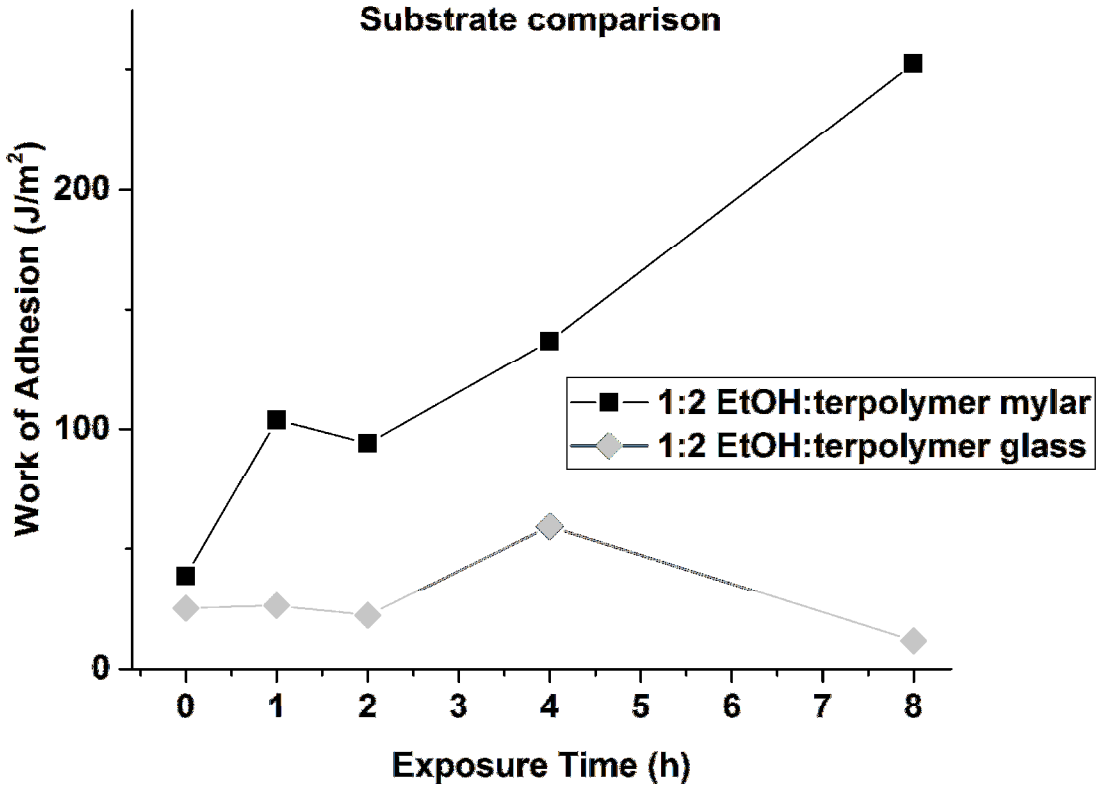


Figure 3.9 *Lap shear tensile testing comparison between glass and Mylar substrates*

when exposed to the UV radiation, as seen in Figure 3.9. There is also an increase by about two orders of magnitude in the DI water solvent sample sets. The best explaination for this is that the glass slide substrates are too stiff and rigid to allow for adequate testing. A good number of attempts would have to be repeated just to get a viable set of data for one sample due to problems occuring at both the adhering and mounting interfaces. First, the glass slides were too slick and would not allow for the tensile tester jigs to grip, causing the sample to simply pull up with the tesnsile tester once the procedure had begun. A few different cushioning materials were tried, but the best was shown to be a strip cut out of a nintrile glove that was wrapped around the base ends of the glass slide samples. This allowed the glass surface to be put under a higher a higher pressure in the mounting jigs without shattering or sliding during the testing procedure. An example of this setup can be seen in Figure 3.10.

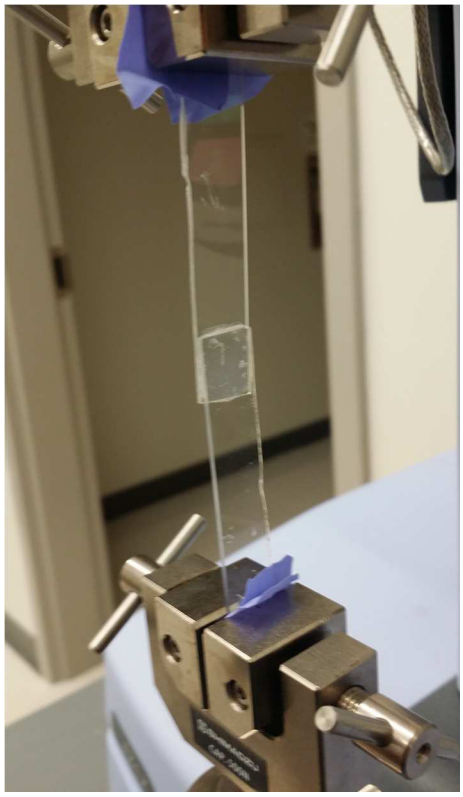


Figure 3.10 *Tensile testing apparatus. Nitrile strips were installed to absorb shock and increase grip.*

3.3.4 MDOPA Control Polymer

A control polymer was created to test two different components of the polymer system. First, that a bipolymer that is missing the wet adhesion component, MDOPA in this case, would have a much lower adhesion energy than the experimental composition. Second, that crosslinking UV treatments would still increase the overall energy of adhesion of the system, meaning that crosslinking was solely dependent on the anthracene based monomer and not the MDOPA. This required a secondary synthesis to be performed as described in 2.2.5

To make a thorough comparison, the application conditions that were seen to show the maximum adhesion from the previous experiments were chosen to show the maximum potential of the two-part polymer system. This was shown to be the 1:1 polymer:solvent mass ratio, with

the solvent being water and adhered substrate being the mylar sheets. While the dried control polymer did look very similar to the experimental terpolymer, after being exposed to water, there were some noticeable differences. The MDOPA containing polymer was a light yellow color and visibly swollen when wet. The control polymer was a an offwhite color that was almost completely dissolved in the water.

The other noticeable characteristic was the difference in adhesion energy when compared to the original terpolymer, as can be seen in Figure 3.11. The control polymer does show a clear increase in adhesion energy corresponding with the increasing UV exposure time, just as before with the experimental polymer. This confirms the theory that the photo-crosslinking anthracene groups are the components responsible for the mechanical strengthening of the polymer system and not the MDOPA molecules. The second theory proposed earlier is also confirmed by comparing the adhesion energies of the control to the experimental terpolymer that was placed

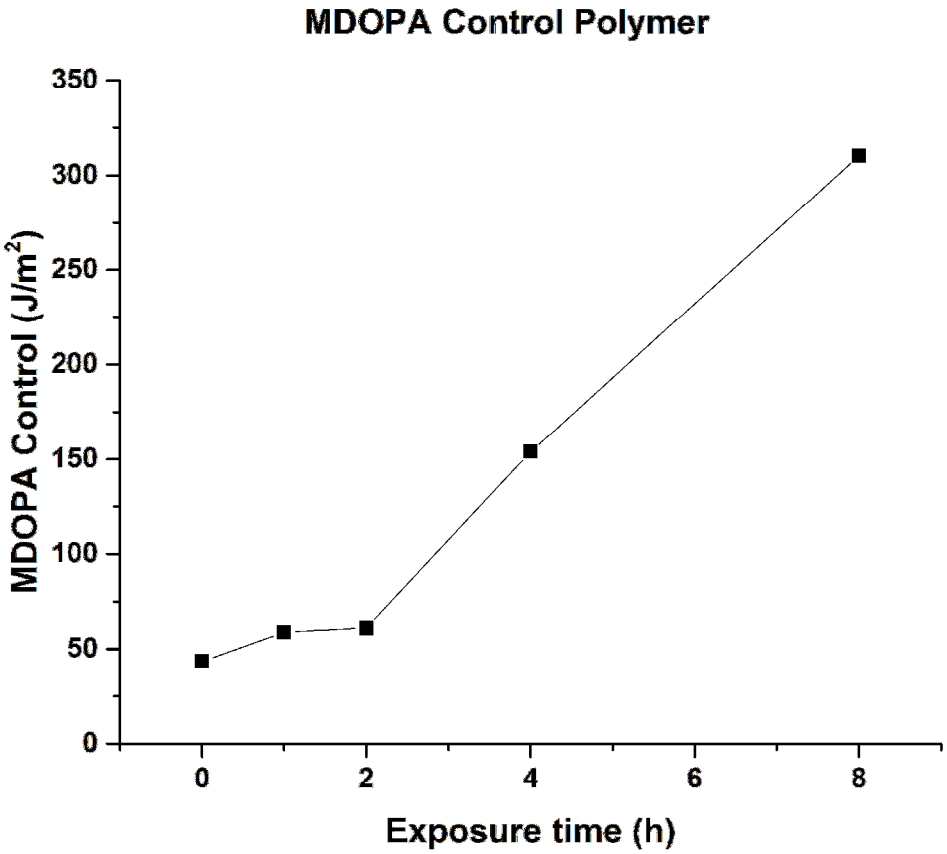


Figure 3.11 *Lap shear tensile testing data of MDOPA control polymer*

under the same conditions. There is a significant difference between the two polymers, up to two degrees of magnitude within the first 4 hours, which can be seen in Figure 3.12. With this data, the control polymer has reinforced that the MDOPA is definitely allowing for the high wet adhesion energy values while the photo-crosslinking is clearly showing a mechanical reinforcement contribution upon dimerization.

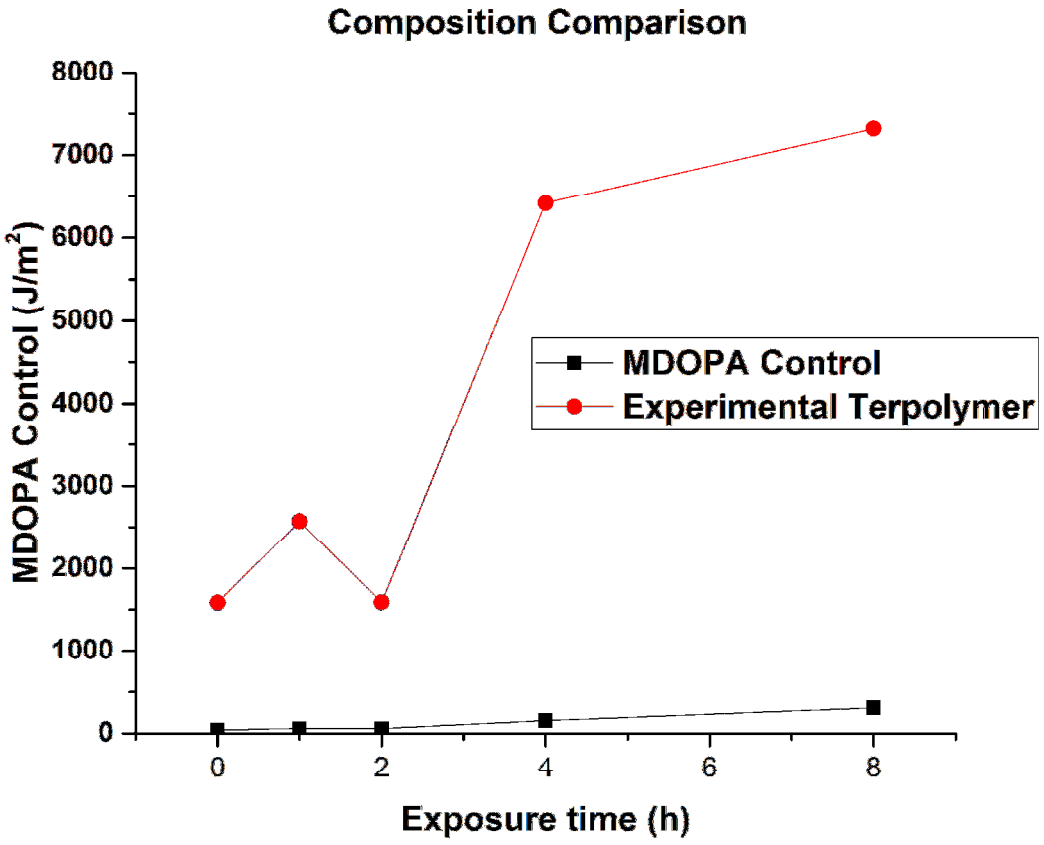


Figure 3.12 *Lap shear tensile testing data of MDOPA control polymer compared to experimental terpolymer of similar conditions. (1:1 polymer:H2O on mylar film)*

CHAPTER 4

CONCLUSIONS

4.1 Summary

A new, biologically inspired terpolymer adhesive system has been created using a free radical polymerization method. MDOPA was incorporated to ensure strong wet adhesion properties. Anthracene based monomer structures were used as photo-reactive crosslinking agents in order to increase mechanical strength of overall polymer. Acrylic acid functioned as a bulk material in order to increase water solubility through ionic interactions as well as increase overall adhesion through increasing ductility.

The terpolymer was characterized in both the undimerized and dimerized states. The structure and composition were confirmed using ^{1}H NMR. Dimerization effects on polymer structure were seen by comparing aromatic peak disappeaerance in both the 7.5-9.0 ppm regions of ^{1}H NMR along with the triple peak seen in the 340-400 nm range in UV-Vis spectras. This was correlated to the breaking of the pi bonds of the middle fused ring of the anthracene moiety that would form new covalent bonds with other anthracene molecules. Dimerization would also increase the molecular weight values of the polymer chains, leading to an increase of the Mn from 41,200 Da to 74,290 Da. The PDI value of the same polymer increased from 1.016 to 1.759, showing a broadening effect in the distribution of the polymer chain sizes. Physical changes were also seen in the polymer solutions, from an increase in the viscosity when completely dissolved in ethanol to a darkening of color when swollen in water.

Variables of application such as concentration, solvent, and substrate choice were tested to optimize the conditions needed for maximum adhesion energy of adhesive. Diluted solutions showed a lower performance due to a general lower amount of adhesive MDOPA segments being incorporated into adhering surface overall. Polymer showed a much higher adhesion when swollen in water rather than dissolved in ethanol, with adhesion energies being over two orders of magnitude higher in the former. Mylar PET films also showed a much larger affinity towards adherance to the polymer when compared to glass surfaces, also showing a decrease in adhesion energy by around two orders of magnitude. A control polymer without MDOPA was created in order to test the wet adhesion contribution to overall adhesive ability of the terpolymer. The

control polymer showed a much lower value of adhesion energy when compared to terpolymer of same conditions,

4.2 Future Work

Future work on this project would include biological cell testing, as the intended purpose of this polymer adhesive was for medical purposes. Intended future testing included cytotoxicity measurements using 3T3 cells with variations in application methods, including differing concentrations and solvents. Similar to what was already done, they would be used in relatively high concentrations with water and ethanol being accepted transfer solvents. Other planned experiments include measuring effects of reversing the dimerization process of the anthracene moiety and seeing relationship of mechanical properties with varying numbers of repeated dimerization and reversing cycles.

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BIOGRAPHICAL SKETCH

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