Incorporation of Polydiacetylene Sensors into Commercial Polymers

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INTEGRITY OF POLYDIACETYLENE SENSORS INTO COMMERCIAL POLYMERS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
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May 2008

Accepted by:
Dr. William T. Pennington, Committee Chair
Dr. Timothy W. Hanks
Dr. Michael S. Ellison
Dr. Philip J. Brown
Dr. Gary C. Lickfield
ABSTRACT

Polydiacetylenes (PDAs) exhibit a chromatic response to solvents, temperature, strain and other environmental perturbations. When formed in a solid-state polymerization, the backbone of the polymer is planar and continuous $\pi$-overlap is observed. However, when the PDA backbone is distorted by an outside force the extended conjugation is interrupted and an optical shift from blue to red is observed. By exploiting the PDAs properties within polymer systems, smart fibers and films have been created that enhance the original intention of the host.

Under this umbrella, a strain sensitive polydiacetylene-polyurethane blend was created using 3 and 4-butoxycarbonylmethylurethane PDA and a medical grade polyurethane, Tecoflex®. Additionally, a temperature sensitive material has been developed with the renewable resource polymer, polylactic acid (PLA) blended with 10,12-pentacosadiynoic acid (PCDA). Finally, PCDA has been incorporated into sodium alginate to be used as environmentally responsive fibers. To match the aqueous solubility of the alginate, the PCDA was forced into a micellular structure through heating and probe sonication. After crystallization and polymerization, the water-soluble micelles were combined with the sodium alginate and wet-spun into calcium alginate “smart” fibers. The visual colorimetric detection (blue to red) was monitored optically and quantitatively by absorbance and Raman spectroscopy.
DEDICATION

I dedicate my dissertation work to my husband and all of our families. I would especially like to thank my mom, Sue, for letting me vent to her everyday about the frustrations involved with generating this type of document and for her assurance that everything would work out well. The love and understanding of my husband, Andy, was an invaluable support system. I truly could not have done this without him. Thanks to my Dad and brother Dan for the calls of support, support, support. I appreciate all the corrections from Andy’s parents, Patty and Bob, whose scientific background has proved very helpful. Thanks to Scot, Kim, Lee, Kathy and Becky for knowing that I could do it.
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I would like to thank my advisor, Dr. William T. Pennington for his guidance and support. I would also like to thank Dr. Timothy W. Hanks and Dr. Michael S. Ellison for their role as additional advisors over the past five years. I have learned a great deal during this process, and they were always there to point me in the right direction. I also thank them for the financial support they provided during my term at Clemson.

I thank my committee members, Dr. Phil Brown and Dr. Gary Lickfield, the School of Materials Science and Engineering and the Department of Chemistry. I thank the committee for all of their corrections to the manuscript and advice on results.

I would like to acknowledge the help and support from all of my colleagues. First, I would like to thank my husband, Dr. Andrew Neilson, for his help with monomer synthesis and for taking part in an endless scientific discussion on polydiacetylenes. I thank Dr. Kate Stevens, Dr. Phil Brown and Brett Ellerbrock for teaching me the technique of wet spinning, specifically of alginate fibers. I thank Jessica He for her training on both the microscope and portable Raman. I would like to thank Dahlia Haynes, Jeff Harris, Hadi Arman and Tony Neely for all I have learned from them and all the help they have given.

Finally, I would like to thank Dr. Pennington for the opportunity to mentor several undergraduate and high school students. Aside from the management skills I learned from the experience, several of the students provided insightful research data and thoughts. I would like to individually thank Chris Pollock for all of his hard work with
polydiacetylenes and his efforts to further the project. I enjoyed many scientific discussions with Chris and look forward to what he will accomplish in the future.
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CHAPTER 1
INTRODUCTION

1.1 – Diacetylene Polymerization

Polydiacetylenes (PDAs) were first isolated by Wegner in the 1960s through the solid-state polymerization of disubstituted 1,3-butadiynes. Wegner characterized the polymerization as a 1,4 addition: adjacent diacetylene (DA) monomers form a bond between the C1 and C4 carbon atoms to form a fully-conjugated chain (Figure 1.1).

![Polydiacetylene Structure](image)

Figure 1.1: Polydiacetylene Structure

Generally, a topotactic polymerization occurs within DA crystals when a translation distance of ca. 5 angstroms and a stacking angle of 45° is observed (Figure 1.2). Polymerization is initiated when DA monomers receive enough energy to overcome the boundaries present to break a bond. This is often provided by UV or gamma radiation; however, some DAs are polymerized thermally. Much of the energy is used to form the initial biradical dimer while a portion of the remaining energy is
required to overcome lattice constraints encountered during the movement of monomers into the correct position for bond formation.\textsuperscript{1}

As described in the book \textit{Polydiacetylenes},\textsuperscript{1} four reaction intermediates exist between approximately two to eighteen monomeric units in the diacetylene system: diradical, dicarbene, asymmetric carbene and stable oligomer (\textbf{Figure 1.3}). A carbene can be described as a carbon with two free valence electrons, while a radical carbon has only one free valence electron. The transition from diradical to dicarbene can be observed at a critical chain length of six repeat units.\textsuperscript{1} The polymerization is terminated with the quenching of the radicals in the chain. These varying states were identified using polarized optical absorbance, electron spin resonance and theoretical equations.\textsuperscript{1}

\textbf{Figure 1.3}: Scheme of polydiacetylene reaction intermediates: (a) diradical, $2 \leq n \geq 5$ (b) dicarbene, $n \geq 8$ (c) stable oligomer.\textsuperscript{1}

\textbf{1.2 – Polymerization by Gamma Radiation, Thermal and Ultraviolet Light}

To obtain complete polymer conversion from diacetylene crystals, such as n-butoxycarbonylmethylurethane (nBCMU, \textbf{Figure 1.4}), samples must be exposed to gamma radiation.\textsuperscript{1} 4-BCMU can be polymerized by radiating monomer crystals with 50 Mrad of $^{60}$Co $\gamma$ rays in air at room temperature.\textsuperscript{4} The ‘n’ previous to the BCMU refers to the length of the alkyl chain connecting the diacetylene to the urethane functionality and is commonly three or four carbons long.
Irradiating samples with UV light yields a maximum of 40% conversion to polymer and the polymerization rate does not correlate to exposure time. Ultraviolet light is capable of initiating the BCMU polymerization; however, the polydiacetylene backbone has a very high absorption cross section and even a thin polymer shell effectively stops the reaction.

Other DAs, such as dodeca-5,7-diyne-1,12-di-p-toluenesulfonate (TS-12), undergo thermal polymerization rather than the photon-induced mechanism. At higher temperatures, an excited state monomer reacts with a ground state monomer to form the biradical. The significant difference in polymerization initiation can be attributed to the UV absorbance of the molecules. The 4-BCM U side chains have a very small UV absorption cross section while the tosyl functionality in TS-12 has shown significant absorption in the ultraviolet spectrum. Therefore, the tosyl group is absorbing the UV light instead of the diacetylene moiety and polymerization does not occur.

Other methods have been developed to provide diacetylenes with unique morphologies to fit a desired purpose. Additionally, these systems have increased
polymer fractions when photo-initiated with UV. Some of these techniques include the dispersion of particles into water through the formation of liposomes, Langmuir-Blodgett (LB) films and self-assembled monolayers (SAMs).

Liposomes may be formed when heterogeneous diacetylenes ($R_1 \neq R_2$), containing one hydrophilic and one hydrophobic side group, are dispersed into water. Probe sonication is used to isolate the molecules from one another followed by crystallization to allow the molecules to align in double layered micelles. The inner micelle surrounds a water droplet, the outer layer of the inner micelle and the inner layer of the outside micelle are composed of the hydrophobic groups, and the outer most layers are composed of hydrophilic groups (**Figure 1.5**). Liposome dispersions are typically made at 1-2 mM and may be polymerized by ultraviolet light.

**Figure 1.5**: Diagram of a PDA assembled liposome.

LB films are typically one or more monolayers created by dipping a solid into a liquid (usually water) at a regulated rate. As with the liposomes, this technique can only be completed with amphiphilic molecules. LB films are successful because the molecules of interest align themselves at the water/air or water/solvent interface with the hydrophobic tail exposed to the air or solvent and the hydrophilic head submerged in
water. As a wafer thin solid is immersed into the liquid and slowly removed, a small amount of water adheres to the surface carrying with it an organized monolayer of the desired molecule. Specifically, the LB films technique was used with 10,12-tricosadiynoic acid in benzene, as a spreading solvent, over a subphase of deionized water. The monolayer, formed over a hydrophilic SiO surface, was found to polymerize under UV light (Figure 1.6).

![Figure 1.6: Structure of a Langmuir-Blodgett film of 10,12-tricosadiynoic acid on a hydrophilic SiO surface.](image)

Self assembled monolayers (SAMs) are substrates containing a single layer of a desired molecule. These are prepared by spreading a solution over a surface and washing off the excess. A typical example of a SAM can be created using an alkane thiol and gold because of the high affinity of sulfur for the gold surface. The thiol head group remains attached to the gold surface by van der Waals forces. This technique has been used to create PDA monolayers by immersing a gold film into an ethanol/octadecanethiol (1 mM) solution for ten hours, then washing it with ethanol. The surface was next coated with a solution of 10,12-pentacosadiynoic acid in chloroform/methanol (5:1). Upon drying the diacetylene was polymerized by exposure to UV light for ten seconds (Figure 1.7).
1.3 – Color Change Theory

In polymers, a conjugated system can be defined as a macromolecule with a backbone containing carbon or heteroatoms where each has a $\pi$ orbital. While the backbone in such a system is planar, there is continuous $\pi$-orbital overlap over the length of the chain. A specific feature to conjugated compounds is the correlation between electronic and geometric structure.

Unlike most polymer properties, optical properties of polydiacetylenes are not determined by the chain length or molecular weight; instead, the optical properties are determined by the conjugation length. Conjugation length can be defined as the length, in polymer repeat units, over which conjugation, or planarity of the backbone, is maintained without interruption. The color of the PDA is in direct relation to its maximum absorbance wavelength, which corresponds to the amount of conjugation within the molecule. An increase in conjugation decreases the energy difference between
the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As the energy difference between the HOMO and LUMO decreases, the energy needed to promote an electron decreases, thereby increasing the absorbance wavelength (Equation 1.1).

**Equation 1.1:** Relationship between energy and wavelength.

\[
\nu = \frac{c}{\lambda}, \quad \Delta E = h\nu, \quad \lambda = \frac{hc}{\Delta E}
\]

\(\nu = \text{frequency}, \lambda = \text{wavelength}, \Delta E = \text{energy}, c = \text{speed of light}, h = \text{Plank's constant}\)

The planar PDA has an absorbance maximum at 650 nm; therefore, it looks blue to the human eye. On the other hand, the non-planar PDA has a maximum absorbance at 540 nm resulting in a red color. The decrease in maximum absorbance wavelength correlates to a loss in conjugation.

Most diacetylenes do not align for polymerization and for the few that do, most crystals are either blue or red at all temperatures; however, a small percentage of PDA crystals have both a blue and red phase dependent upon a critical temperature.\textsuperscript{11} Cast films, LB films and vesicles are also capable of blue to red transitions, but are mostly irreversible.\textsuperscript{11} An exception to these are recently developed PDAs by Yuan et al.\textsuperscript{12,13} and Kim et al.\textsuperscript{14} that are capable of pH and thermochromic reversibility due to hydrogen bonding within terephthalic acid functionalities on the side chains.

The color transition appears when PDAs are exposed to an applied stress. With respect to 4-BCMU and similar polydiacetylenes, the initial blue color is replaced by yellow in a good solvent. These PDAs appear red with the addition of a poor solvent, exposure to heat, mechanical strain, or the strain imposed by binding with a bioreceptor.
It is theorized that the transition from blue to red represents a disruption in the planar conformation and a reduction in the conjugation length of the PDA backbone (Figure 1.8).

![Figure 1.8](image)

**Figure 1.8:** Structural representation of PDA in (a) blue, planar state and (b) red, non-planar, reduced conjugation state.

The solvatochromatism of nBCMU and similar PDAs has been examined by varying good solvent to poor solvent ratios within a solution. PDAs show high solubility in CHCl₃ because this solvent shows special affinity for large flexible substituent groups and the presence of carbonyl groups.⁴ When dissolved in a favorable solvent PDAs appear yellow; however, they undergo a dramatic color change to red when any nonsolvent miscible with CHCl₃ is added.⁴,¹⁵

Initially, it was argued by Patel *et al.*⁴ that the colorimetric response was due to a conformation change from planar to non-planar within the macromolecule in a dilute solution. In another interpretation, Lim *et al.*¹⁰ explained the change as a result of an intramolecular rod to coil transition. The latter theory was corroborated by light scattering studies in which the hydrodynamic radius of 4-BCMU PDA changed with the optical transition.¹⁰ Quasi-elastic light scattering and field induced birefringence were further used to document the coil to rod transition within 4-BCMU.¹⁶ Dynamic and static light scattering were further employed to characterize the colorimetric transitions as an intermolecular effect caused by aggregation of rod-like PDA chains. Evidence for the aggregation effect was found for 4-BCMU dissolved in toluene at 353K.¹⁷
A debate arose concerning the behavior of PDA’s colorimetric activity in solution. The disagreement stemmed from the fact that the extended conjugation, $\pi$-bond structure could be described by two resonance forms. The mesomeric structures can be described as ‘acetylenic’ and what some believe is a ‘butatrienic’ structure (Figure 1.9). Previous researchers felt it was essential to determine the stability of the backbone structures since this was the central region for the chromatic phase transitions of the polydiacetylenes.

![Figure 1.9: PDA structure in the acetylene (a) and butatriene (b) form.](image)

The structure of 3-BCMU was found to be geometrically more like acetylene than pure butatriene in the relaxed state. The vibration of the $\text{C}=$C stretching mode was observed along with the $\text{C}=$C mode in the geometrically relaxed state via time-resolved Raman spectroscopy. If any butatriene-type structure was present, it would have to be mixed with the acetylene-type structures.

Theoretical studies have agreed that the acetylenic structure is more stable than the butatrienic structure because of the large bandgap. Supporting this fact, butatrienic structures have only been reported in very limited cases; most research has yielded acetylenic structures. Also, results from various researchers, comparing the acetylene structure have been in excellent agreement, while the butatriene results have varied
significantly depending on the research.\textsuperscript{19} The most accepted theory has gone full circle, i.e. interruptions in conjugation length caused by changing from planar to non-planar forms of the backbone are the reason for the color effects; however, a definitive agreement has not been reached.\textsuperscript{18}

Color behavior can vary for PDAs with different side chains, even if the variations are small, such as with 3-BCMU and 4-BCMU. Both polymer chains are identical in solution but films cast from 3-BCMU are blue and 4-BCMU are red indicating that the lowest energy state is blue for the former and red for the latter.\textsuperscript{11} Although the red phase is more stable for 4-BCMU, topotactic polymerization yields a blue color perhaps due to the constraints from the crystal lattice.\textsuperscript{11} The differences between these two polymer systems indicate that side chain geometry does have an effect on the color of the compound.

\textbf{1.4 – Diacetylene Hydrogen Bonding}

In some diacylenes, such as n-BCMU, hydrogen bonding occurs between urethane substituents on adjacent side chains.\textsuperscript{1,21} Intermolecular hydrogen bonds provide stacking support between diacetylene molecules. However, they result in a substantial distortion of the ‘n’ alkyl chains during polymerization as they are converted into an intramolecular secondary bonding network resulting in an increase in total reaction enthalpy.\textsuperscript{1} Post-polymerization, the hydrogen bonding stabilizes the planar, fully conjugated conformation of the polymer (\textbf{Figure 1.10}).\textsuperscript{4}
1.5 – Mechanochromic Copolymers

In mechanochromism, the colorimetric transformations have been attributed to strain imposed on the polymer backbone. Mechanically induced color change has interesting potential for being used as a sensor for contact, friction, and adhesion. The PDA exhibits a blue color when the side chains are in the same plane as the backbone. As the polymer is strained (in tension, torsion, or shear) the conjugation is broken and a blue shift occurs, producing a red colored material.

The first study of deformation in polydiacetylene single crystal fibers via Raman spectroscopy was successfully done by Bloor in 1979. Well-defined resonance Raman spectra were used to quantitatively analyze the strain in PDA single crystals. The strain was tracked by following the shift in the Raman peaks corresponding to the polydiacetylene backbone. Polydiacetylene, in the relaxed, planar state, exhibits a carbon triple bond stretch peak at ca, 2080 cm\(^{-1}\). When one percent strain was applied to the single crystal, the carbon triple bond stretch peak center position occurred at ca. 2100 cm\(^{-1}\), a shift of twenty wavenumbers. Bloor et al. theorized that the shift corresponded to macroscopic deformation of the covalent bonds within the polymer backbone.
Upon recognition of PDA’s mechanochromic properties, a surge was made in research to incorporate DA units into commonly used materials. Hydroxyl capped diacetylene units, such as 5,7-dodecadiyne-1,12-diol\textsuperscript{24} or 2,4-hexadiyne-1,6-diol\textsuperscript{25,26,27,28}, were used as hard segment chain extenders in polyurethane (PU) synthesis. After polymerization of the PU, the DA units were polymerized using UV light or heat, crosslinking the PU chains. Initially, simultaneous UV/Vis spectroscopy and tensile testing yielded a blue shift maximum at 300\% strain.\textsuperscript{24} Improved results were obtained through resonance Raman spectroscopy as a linear relationship between strain percentage and carbon triple bond center position was revealed. The carbon triple bond peak shifted 6.2 cm\textsuperscript{-1} within PU-co-PDA bulk sheets via tensile testing at 1.5\% strain.\textsuperscript{25} A similar copolymer generated a ca. 4 cm\textsuperscript{-1} shift to lower wavenumbers for tensile and higher wavenumbers for compression at 1\% strain.\textsuperscript{26} When this copolymer was used as a coating for glass fibers, a shift of ca. 5 cm\textsuperscript{-1} was found when strained to 1\% during flexural testing.\textsuperscript{27} Variations within strain percentages in the PU-co-PDA studies were due to differences in soft segment chain length of the PU.

Polydiacetylene-co-polyesters, synthesized by Hu et al.\textsuperscript{29}, were made through the reaction of various diacetylene diols with a diacid chloride. Simultaneous tensile testing and Raman spectroscopy yielded a carbon triple bond shift of ca. 3 cm\textsuperscript{-1} with a 3\% applied strain; additionally, the \textsuperscript{-C≡C-} peak returned to initial wavenumbers upon removal of strain and shifted again when strain was reapplied.\textsuperscript{30} In another study, a PDA monolayer, created by the LB technique, of N-(2-hydroxyethyl)-10,12-pentacosadinamide was transferred to a hydrophilic SiO\textsubscript{2} substrate.\textsuperscript{22} An AFM tip was utilized to provide a force against the PDA monolayer causing a mechanochromic
transition. It was determined that the blue shift within the monolayer was caused by shear forces normal to the PDA backbone.\textsuperscript{22}

In this work, a PDA, nBCMU (\textbf{Figure 1.4}) was blended into an industrial polyurethane, Tecoflex\textsuperscript{®}, through intermolecular interactions at a low loading percentage (~1\%) and subjected to simultaneous strain and Raman spectroscopy. Additionally, diacetylene monomers were incorporated into the same polyurethane at various levels and polymerized to develop a blend capable of a colorimetric response to impact strain. Raman spectroscopy was used to track the status of the polydiacetylene additive, nBCMU. The Raman peak center position of the carbon triple bond was tracked in accordance to the strain within the material and their relationship was documented. This topic will be detailed in Chapter 3 of this dissertation.

\textbf{1.6 – DA Polymerization within Polymer Blends}

In addition to mechanochromism, PDAs are sensitive to solvent, pH, and temperature. Preparation of diacetylene blends capable of these transitions has proven less challenging than for strain sensitivity. Diacetylene monomers may be dispersed within a host and polymerized to produce embedded supramolecules capable of colorimetric transition upon environmental stimuli. Typically, DAs will be combined with a host polymer in a common solvent and processed into a functional material. Upon harvesting the sample, the DA will be polymerized in-situ with ultraviolet light.

The same geometrical restrictions that apply to single crystals must apply to DA polymerization within a matrix polymer: a translation distance of ca. 5 angstroms and a stacking angle of 45 degrees must be observed.\textsuperscript{1,2} Most diacetylenes do not align to meet
this criteria within host systems; therefore, the embedded monomers will not polymerize. In order for the diacetylene molecules to remain ordered within the hosts there must be some degree of phase segregation. This investigation has been limited to diacetylene monomers that do segregate to polymerize.

Host polymers including embedded diacetylenes have been processed into a variety of material types. Electrospun PEO and PMMA fibers prepared with embedded, 10,12-pentacosadiynoic acid (PCDA) molecules were capable of polymerization with ultraviolet light.\textsuperscript{31} An amine terminated diacetylene monomer, PCDA-2,2’-(ethylenedioxy)bis(ethylamine), was forced into vesicle formation in aqueous solution and blended with polyvinylalcohol. The PVA/DA blend was solution cast into thin films and polymerization.\textsuperscript{32} Additionally, 4-BCMU dissolved in chloroform was mixed into hot ultra-high molecular weight polyethylene (UHMW PE) and processed into gels. Tensile drawing of the gels allowed for polymerization of the 4-BCMU at ca. 20 wt \%.\textsuperscript{33}

The aforementioned post-polymerized samples all showed the ability to create functional images through ultraviolet photolithography.\textsuperscript{31,32,33} Photo-masking host films, prior to polymerization, results in shapes on a macro and micro level that were capable of the same properties as PDA alone. Electrospun fibers containing DA embedded PMMA produced polydiacetylene stripes when polymerized through a photomask.\textsuperscript{31} Arrays of micro scale squares and dots were produced when glass slides were stamped with 3-aminopropyltriethyloxy-silane and submerged into a PCDA/ PCDA-N-hydroxy-succinimide liposome solution for two hours then exposed to UV-light.\textsuperscript{34} PDA/silica nanocomposite films, prepared by spin casting, were irradiated through a mask to yield a blue bird symbol that changed to red with an increase in temperature.\textsuperscript{35}
It is hypothesized that blending 10,12-pentacosadiynoic acid into polylactic acid at low loading percentages will allow for polymerization of functional, chromatic images within the host material. More information can be found on this topic in Chapter 4 of this dissertation.

1.7 – Bio-chromic PDA Liposomes

Diacetylene monomers with hydrophilic R and hydrophobic R groups form liposomes in aqueous solutions with the aid of increased temperature and sonication. Polymerized liposomes dispersed in water share similar colorimetric transitions to solid state crystalline PDAs. The incorporation of biologically sensitive molecules into liposomes during sonication, and subsequent PDA polymerization, has enabled a blue to red shift to occur if an outside species interacts with this molecule.

Polydiacetylenes containing modified lipids can serve as a source for selective recognition of an analyte of interest; as the analyte binds to the receptor, the vesicle changes color from blue to red. The bio-induced chromatic properties of PDA have been used in sensors developed for the influenza virus, cholera toxin, E. coli, c-myc epitope, and even lipopolysaccharides. Additionally, a PDA sensor has been developed for a toxin that is a major factor in strep throat, streptolysin O (SLO). Here, the polydiacetylene is used as the detector in the sensor and cholesterol is added as bait for the SLO. Previous detection methods for SLO, such as an electrochemical sensor, did not provide the visual signaling of the PDA sensor.

Amino acid-tailed diacetylene monomers have also been incorporated into PCDA liposomes. Specifically, tyrosine and tryptophan PCDA derivatives were capable of a
colorimetric response when exposed to *E. coli*, *Pseudomonas aeruginosa*, *Salmonella minnesota*, and *Shigella flexneri*.\textsuperscript{38} A biotin derivative of PCDA was capable of specific binding with streptavidin causing a colorimetric response when embedded within a PCDA liposome.\textsuperscript{39} However, most bio-chromic liposomes have only had success when used in solution. In an exception, liposomes composed of 10,12-tricosadiynoic acid (TCDA) and TCDA-dimyristoylphosphatidylcholine (DMPC) showed sensitivity to salmonella and several strains of *E. coli* while embedded in an agar matrix.\textsuperscript{40}

In this research, PCDA liposomes have been incorporated into sodium alginate through solution blending and converted into calcium alginate by wet spinning. The embedded polydiacetylenes have shown sensitivity to temperature, solvent and α-cyclodextrin. It is hypothesized that PCDA liposomes with incorporated bacterially sensitive molecules will show a response to bacteria, specifically *E. coli*. Additional information can be found about the sensitivity of PCDA liposomes in calcium alginate fibers in Chapter 5 of this dissertation.

\textbf{1.8 – Raman Spectroscopy}

The colorimetric transition and the state of the polydiacetylene backbone can be extensively monitored with UV/Vis and Raman spectroscopy. Various properties of PDAs such as thermochromism, solvatochromism, mechanochromism and others lead to reversible and irreversible color changes. Color changes caused by changes in absorption therefore may be tracked through UV/Vis spectroscopy. In Raman spectroscopy, the PDA planar state yields carbon double and triple bonds peaks in the 1450 cm\textsuperscript{-1} and 2085
However, when the polymer changes to red, these peaks shift to 1515 cm$^{-1}$ and 2115 cm$^{-1}$, respectively.

During Raman spectroscopy, a laser irradiates a sample causing two types of scattering to occur: Rayleigh and Raman scattering. The Rayleigh line is centered at the incident wavelength and is due to light that has been elastically scattered by the molecules. Raman scattering is due to the inelastic scattering of photons (the Raman effect) caused by the interaction of the laser with the electron cloud of the molecule. With symmetric molecules (or functionalities) the energy from the laser excites an electron from the vibrational state to a virtual energy state. As the molecule relaxes, it will typically fall into the first vibrational energy state, resulting in Stokes Raman scattering. However, if the molecule was already in an excited state, the relaxing electron falls to a level below its initial state, causing anti-Stokes Raman scattering. Raman spectroscopy is based on the more intense Stokes scattering due to the infrequency of molecules that are excited prior to irradiation.

Rayleigh scattering is strong, while Raman scattering is considered very weak; one in every $10^7$ photons will be scattered due to the Raman effect. Therefore, the Rayleigh scattering must be blocked and the Raman scattering amplified for the resulting spectra. In another effort to amplify the Raman scattering, resonance Raman spectroscopy may be employed. In resonance Raman, the laser is deliberately tuned to excite a specific electronic transition within the molecule. When the laser provides the exact energy for one transition over another, that transition becomes more likely to occur. Raman bands can be enhanced by a factor of $10^3$ to $10^5$ by using resonance
Raman techniques.\textsuperscript{44} A wavelength of 632.8 nm has been documented to excite the carbon triple bond stretching peak of the polydiacetylene.\textsuperscript{25,26,27,30}

Raman spectroscopy provides a high intensity signal for multiple bonds between the same elements; therefore, it is an ideal choice for polydiacetylene.\textsuperscript{42,44} Raman and infrared (IR) spectroscopy both measure vibrational energies of a molecule but are considered complementary techniques. For a bond, or molecule, to be IR active there must be a change in the dipole moment of the molecule. Bonds between different elements and asymmetric compounds will typically generate informative IR spectra. However, to obtain intense Raman spectra, the polarizability of a molecule or functionality must change with the addition of energy; therefore, functionalities such as carbon triple and double bonds are ideal for Raman scattering.

1.9 – Colorimetric Response Equation

UV/Vis spectroscopy exposes liquid and solid sample to a specific wavelength range of light and measures the absorbance (A) of the sample over that range. A measure of colorimetric response (CR, \textbf{Equation 1.2}) has been used to monitor PDAs via ultraviolet visible spectroscopy.\textsuperscript{45,46} The percent blue within a PDA system is defined as the absorbance at 550 nm, as calculated by UV/Vis spectroscopy, divided by the sum of the absorbance at 550 nm and 640 nm. Colorimetric response is defined as the original minus the final percent blue divided by the original percent blue.
1.10 – Host Polymer: Tecoflex®

Tecoflex® is categorized as a thermoplastic polyurethane elastomer (TPE). Unlike thermoset polymers, which can be cured into a permanent shape, thermoplastic polymers soften or melt when exposed to heat. This property allows thermoplastics to be melt-processed and also enables recyclability through the heating and cooling process. An elastomer is defined as a material that deforms with applied stress but rapidly returns to initial sample size after removal of stress.

A polyurethane (PU) can chemically be defined as a macromolecule containing carbamate groups (OCONH) within the backbone. Polyurethanes, with the exception of foams, are prepared by step growth polymerization in a dry environment through the reaction of a diol with a diisocyanate in strict 1:1 stoichiometric ratio. Typically, polyurethane elastomers are considered block copolymers, ((A)_n(B)_m)_p, formed from hard and soft telechelic, or terminally functional, prepolymers. Soft segments are usually composed of hydroxyl-terminated polyesters or polyethers. Hard segment prepolymers are synthesized by reacting a diisocyanate with a small hydroxyl-terminated molecule, such as ethylene glycol (Figure 1.11).

**Equation 1.2:** Colorimetric response (CR) as indicated by UV-Vis used to determine a quantitative percent blue (PB) within the PDA molecule.\(^{45}\)

\[
P_{B_o} = \frac{A_{blue}}{A_{blue} + A_{red}} \times 100
\]

\[
CR = \frac{P_{B_o} - P_{B_f}}{P_{B_o}} \times 100
\]
The urethane linkages in hard segments of polyurethanes form hydrogen bonds within the chain and with other chains in the system, adding structural support and crystallinity. The hard segments, macrodiisocyanates, are polymerized with the soft segments, macrodiols, to reach a polyurethane with desired properties. Tecoflex® (Figure 1.12) is synthesized through the reaction of hydrogenated methylene diisocyanate, polytetramethylene glycol and 1,4-butane diol.

Figure 1.12: Structure of Tecoflex® by Lubrizol composed of polytetramethylene glycol soft segments and methylene bis-p-cyclohexyl isocyanate with 1,4-butane diol hard segments.
By varying the stoichiometric ratio during prepolymer synthesis, TPEs can be tailored to a variety of durometers (typically Shore 70A to 75D). Hardness is measured as a resistance of deformation when a ball, blunt point or indentation is applied at a specific force. The measure of hardness includes the Shore (Durometer) and Rockwell scales. Shore A and D scales overlap so that 85A is approximately equal to 40D; however, the scales do not directly correlate to one another. For an example of how materials are distributed on the Shore scale, a rubber band is 25A, a hard skateboard wheel is 98A and a hard hat is 75D. Rockwell Hardness scales R and M are used for polymeric materials where Rockwell 30M is equal to Rockwell 105R and correlates to Shore 85D. A scale of common polymers distributed over Shore and Rockwell hardness scales may be found in Table 1.1. A summary of Tecoflex® properties may be found in Table 1.2.
Table 1.1: Range of Hardness of Selected Polymers.\textsuperscript{51}

<table>
<thead>
<tr>
<th>Hardness Scale</th>
<th>Acetal</th>
<th>Kapron</th>
<th>Burgundy</th>
<th>Polycarbonate</th>
<th>Polyethylene</th>
<th>Polypropylene</th>
<th>Polyvinyl</th>
<th>Polyurethane</th>
<th>Polystyrene</th>
<th>Polyethylene Terephthalate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shore A</td>
<td>90-95</td>
<td>75-80</td>
<td>70-75</td>
<td>60-65</td>
<td>50-55</td>
<td>45-50</td>
<td>40-45</td>
<td>35-40</td>
<td>30-35</td>
<td>25-30</td>
</tr>
<tr>
<td>Shore B</td>
<td>85</td>
<td>80</td>
<td>75</td>
<td>70</td>
<td>65</td>
<td>60</td>
<td>55</td>
<td>50</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>Shore D</td>
<td>80-90</td>
<td>75-85</td>
<td>70-80</td>
<td>65-75</td>
<td>60-70</td>
<td>55-65</td>
<td>50-60</td>
<td>45-55</td>
<td>40-50</td>
<td>35-40</td>
</tr>
<tr>
<td>Rockwell A</td>
<td>85-90</td>
<td>80-90</td>
<td>75-85</td>
<td>70-80</td>
<td>65-75</td>
<td>60-80</td>
<td>55-70</td>
<td>50-60</td>
<td>45-50</td>
<td>40-50</td>
</tr>
<tr>
<td>Rockwell M</td>
<td>90-100</td>
<td>85-95</td>
<td>80-90</td>
<td>75-85</td>
<td>70-90</td>
<td>65-85</td>
<td>60-85</td>
<td>55-70</td>
<td>50-60</td>
<td>45-60</td>
</tr>
</tbody>
</table>

Table 1.2: Tecoflex Physical Properties Reported by the Lubrizol Corporation.\textsuperscript{50}

<table>
<thead>
<tr>
<th>Tecoflex\textsuperscript{®} Brand</th>
<th>ASTM</th>
<th>85A</th>
<th>93A</th>
<th>100A</th>
<th>60D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durometer (Shore Hardness)</td>
<td>D2240</td>
<td>77A</td>
<td>87A</td>
<td>94A</td>
<td>51D</td>
</tr>
<tr>
<td>Flex Modulus (psi)</td>
<td>D790</td>
<td>2,300</td>
<td>3,200</td>
<td>10,000</td>
<td>13,000</td>
</tr>
<tr>
<td>Ultimate Tensile (psi)</td>
<td>D412</td>
<td>6,200</td>
<td>7,700</td>
<td>8,200</td>
<td>8,300</td>
</tr>
<tr>
<td>Ultimate Elongation (%)</td>
<td>D412</td>
<td>550</td>
<td>390</td>
<td>370</td>
<td>360</td>
</tr>
</tbody>
</table>

1.11 – Host Polymer: Polylactic Acid

Polylactic acid (PLA, Figure 1.13), a biodegradable thermoplastic polyester, is derived from the fermentation of corn starch and other starch like products such as maize, sugar or wheat.\textsuperscript{52,47} Lactic acid, harvested from the fermentation by bacteria, is converted
into lactide, a ring-shaped monomer, which forms PLA through a ring-opening polymerization.47

![Figure 1.12: Schematic of Polylactic Acid polymerization: The polymerization of Polylactic Acid begins with the production of lactic acid from corn (or other starch), then dimerization into lactide using dehydration and heat(1) and ring-open polymerized into polymer with heat and catalyst(2).47](image)

Previously, the high-cost of PLA production had focused its uses to highly technical materials. However, advances in the fermentation of glucose (to produce lactic acid) and the increasing cost of fuel have dramatically lowered the cost of production for this renewable resource material. PLA has high tensile strength, good processability and resistance to grease, oil and fat.47 Additionally, PLA decomposes to lactic acid which can be metabolized by the body.47 According to Cargill Dow Polymers LLC, (commonly known as NatureWorks LLC) PLA grades 4041D (donated to Clemson) and 4031D have excellent optical properties and good machinability.53 In this regard, PLA is currently in small-scale production for biomedical sutures and scaffolds, grocery bags, fibers, disposable cups and food packaging.54

1.12 – Host Polymer: Alginate

Alginate, a general term used to describe alginic acid and its related salts, is a natural polymer extracted from the cell walls of brown algae. While alginate can be harvested from any source of brown algae, its chemical structure varies with plant species based on the turbidity of the sea water in which it grows.55 Alginic acid is chemically a
co-polysaccharide containing β-D-mannuronate (M) and α-L-guluronate (G) segments (Figure 1.14). This natural block co-polymer is composed of GG, MM and GM segments.

![Figure 1.14: Alginic acid structure containing β-D-mannuronate (M) and α-L-guluronate (G) segments.](image)

The method behind alginate seaweed extraction is based heavily upon its unique gellation properties with respect to mono- and di-valent cations. Generally, the chopped seaweed is treated with sodium carbonate to convert insoluble alginate salts to water soluble sodium alginate. After filtration, the sodium alginate is precipitated as alginic acid or calcium alginate, reconverted back to sodium alginate in a mixture of alcohol and water and milled into pellets or powders. The wet spinning of alginate fibers directly mimics the processes utilized in the raw product extraction. The fibers are created through extrusion of the spinning dope (degassed sodium alginate dissolved in water) through a spinneret into a calcium chloride coagulation bath.

When alginate chains are exposed to calcium, junction zones appear where G segments are dimerized by the divalent cations, known as the egg-box model (Figure 1.15).
According to this model, associations are made between guluronate chain segments meaning that both the percentage of G segment and the amount of calcium affect the strength of interaction between the chains. This theory has been further proven by Morris’s dialysis experiment (separation of a solution by rate of diffusion through a membrane) which yielded a 4:1 ratio of G segments to calcium ions; the calcium ion interacts with two ‘G’ segment on two chains. Additionally, Sikorski et al. (in agreement with Atkins et al.) used fiber X-ray diffraction to determine that the diffraction intensity of guluronate rich alginate containing calcium was consistent with two polymer chains coordinating one Ca$^{2+}$ ion for every four ‘G’ segments and that the chains may pack on a larger scale in a hexagonal lattice.

Alginate has many uses based on three main properties: the ability to thicken a solution when dissolved in water, the ability to form gels and the ability to form fibers. The addition of alginate to fat free salad dressing has been a successful thickening agent. The useful addition of alginate to chicken nuggets has provided the gel needed to keep the desired shape. However, the main focus within this work will be on the ability of sodium alginate to form fibers in the presence of calcium. These fibers may be turned into nonwoven fabrics through the conventional textile processes of carding and needling. In carding, unordered fibers are organized by removing uneven short fibers and other impurities; needling joins the fibers together into a felt without the use of

![Figure 1.15](image-url): Structure of the alginate egg-box model as proposed by Grant and Morris where calcium ions are surrounded by opposing GG segments within polymer chains.
chemical agents. One of the most critical applications for alginate nonwoven fabric is wound dressings. The use of alginate dressings on exuding wounds is unparalleled. As the dressing absorbs the sodium containing secretions of the wound, it forms a gel and provides moisture to the injured area. In addition, the sodium ions exchange for calcium ion within the dressing providing calcium to the wound which has been suggested to improve some cellular aspects of wound healing. Lastly, in a controlled study, more patients chose alginate over gauze dressing because of their ease of removal (they can be rinsed away with saline).

1.3 – Conclusion

Diacetylenes are capable of topotactic polymerization when the monomers are properly oriented and positioned. The polymerization can be initiated thermally or by gamma or ultraviolet radiation. PDAs exhibit a chromatic transition from blue to red with exposure to external stimuli. This transition is caused by a loss of conjugation within the PDA backbone. Through exploitation of their chromaticity, PDAs provide a sensing platform that can be incorporated into a variety of industrial materials. In this research, a strain sensitive material was achieved by blending 3- and 4-BCMU with Tecoflex®, a temperature sensitive material with photolithography capabilities was prepared by incorporation of PCDA monomers into PLA followed by subsequent PDA polymerization, and an environmentally sensitive material was formed through wet-spinning of PCDA liposomes (with and without incorporated biological sensitive moieties) into calcium alginate fibers.
CHAPTER 2
EXPERIMENTAL DETAILS

2.1 – Materials

Chemicals. The diacetylene, 5,7-dodecadiyne-1,12-diol, was purchased from GFS Chemicals or Sigma Aldrich and was used as received. An acetone extraction was used to remove the polymerized portion of 10,12-pentacosadiynoic (PCDA), purchased from GFS Chemical. A THF extraction was used to remove polymerized diacetylene 4,6-dodecadiyne-1,10-diol as purchased from Oakwood Products. Medium viscosity sodium alginate, butylisocyanatoacetate, dibutyltin dilaurate, 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), calcium chloride and α-cyclodextrin were used as received from Sigma Aldrich. Sodium chloride (Morton Iodized salt) was purchased locally.

Solvents. Deionized water was obtained from a Barnstead NANOpure Diamond B-pure filtration system. All organic solvents were purchased from Aldrich Chemical Co. and, with the exception of THF, were used as received. Tetrahydrofuran was distilled from sodium/benzophenone under inert atmosphere.

Host Polymer Company Donations. Tecoflex® polyurethane chip was donated to Clemson University by Lubrizol Corporation, previously Thermedics Polymer Products, in four Shore® (Durometer) hardness levels: 85A, 93A, 100A, and 60D. Polylactic acid 4041D was donated to Clemson University by NatureWorks LLC.
2.2 – nBCMU Blend with Tecoflex®

Synthesis of 4-butoxymethylcarbonylurethane diacetylene (4-BCMU). 4-BCMU was prepared in a dried, single-neck round bottom flask. A solution of 1,12-dodecadiyndiol (1.00 g, 5.147 mmol), butylisocyanatoacetate (1.78 g, 0.011325 mol), triethylamine (7 drops) and dibutyltindilaurate (7 drops) in 50 mL dry tetrahydrofuran was prepared. After stirring at room temperature for two hours, the solvent was removed by rotary evaporation to yield a yellow oil. Pure product (77% yield) was obtained by silica gel flash column chromatography using 50:50 ethyl acetate:hexanes elution solvent. The 4-BCMU monomer was stored in 15 mL chloroform, sealed and wrapped in tin foil to prevent premature polymerization. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 5.14 (b, 1H), 4.09-4.17 (m, 4H), 3.94 (d, $J$ = 5.5 Hz, 2H), 2.26 (t, $J$ = 6.9 Hz, 2H), 1.59-1.62 (2m, 6H), 1.33 (sextuplet, $J$ = 7.2 Hz, 1H), 0.90 (t, $J$ = 7.2 Hz).

Synthesis of 3-butoxymethylcarbonylurethane diacetylene (3-BCMU). 3-BCMU was prepared in a dried, single-neck round bottom flask. A solution of 1,10-dodecadiyndiol (1.00 g, 6.016 mmol), butylisocyanatoacetate (2.08 g, 13.236 mmol), triethylamine (7 drops) and dibutyltindilaurate (7 drops) in 50 mL dry tetrahydrofuran was prepared. After stirring at room temperature for two hours, the solvent was removed by rotary evaporation to yield a yellow oil. Pure product (71% yield) was obtained by silica gel flash column chromatography using 50:50 ethyl acetate:hexanes elution solvent. The 3-BCMU monomer was stored in a 15 mL of chloroform, sealed and wrapped in tin foil to prevent premature polymerization. $^1$H NMR (300 MHz, CDCl$_3$, $\delta$): 5.17 (b, 1H), 4.12-4.17 (m, 4H), 3.93 (d, $J$ = 5.5 Hz, 2H), 2.32 (t, $J$ = 6.9 Hz, 2H), 1.81 (p, $J$ = 7.2 Hz, 2H), 1.57 (p, $J$ = 7.2 Hz, 2H), 1.33 (sextuplet, $J$ = 7.2 Hz, 2H), 0.90 (t, $J$ = 7.2 Hz).
Polymerization of BCMU. After rotary evaporation, 4-BCMU was polymerized via $^{60}$Co $\gamma$-ray irradiation at a rate of 1 Mrad/h. Crystalline 3-BCMU was polymerized under 254 nm light at a distance of 5 cm; any remaining monomer was removed by acetone extraction. The polymerization 3-BCMU was possible due to its reversible solvatochromism.

Solution Preparation. All solutions were prepared by weight of the compound to volume of the solution and are referred to as percent solution.

Solution Blending of nBCMU PDA with Tecoflex®. 4-BCMU PDA (12.5 mg, gamma radiation polymerized) was dissolved in 10 mL CHCl$_3$ and added to a solution containing 60D Tecoflex® (1.25 g each) dissolved in 25 mL CHCl$_3$ (1% PDA to PU). This procedure was repeated with Tecoflex® durometers 100A, 93A and 85A. The blend solution was mixed by magnetic stir bar for 24 hours at room temperature.

3-BCMU PDA (12.5 mg, UV polymerized) was dissolved in 10 mL CHCl$_3$ and added to a solution of 60D Tecoflex® (1.25 g) dissolved in 25 mL CHCl$_3$ (1% PDA to PU). The blend solution was allowed to mix for 24 hours at room temperature.

Control films of Tecoflex® (85A, 93A, 100A, and 60D) were generated in the same manner; 10 mL CHCl$_3$ was added to a solution of Tecoflex® (1.25 g) in 25 mL CHCl$_3$.

Solution Blending of nBCMU DA with Tecoflex®. To 1.25 g 60D Tecoflex® dissolved in 25 mL CHCl$_3$, 4-BCMU diacetylene, dissolved in 10 mL CHCl$_3$, was added at 1% (12.5 mg, 0.0245 mmol), 5% (62.5 mg, 0.123 mmol), 10% (125 mg, 0.246 mmol), 15% (187.5 mg, 0.369 mmol), 20% (250 mg, 0.492 mmol), 25% (312.5 mg, 0.614 mmol) and 30% (375 mg, 0.737 mmol) by weight to polyurethane. To 1.25 g each 60D, 100A,
93A and 85A Tecoflex® dissolved in 25 mL CHCl₃, 4BCMU (486 mg, 0.956 mmol) monomer, dissolved in 10 mL CHCl₃, was added (38.8% DA to PU).

To 1.25 g 60D Tecoflex® dissolved in 25 mL CHCl₃, 3-BCMU DA (187.5 mg, 0.39 mmol) was added (15% by weight DA to PU).

Solution Cast Thin Film Preparation. The blend solution was poured into a 10 cm casting dish and the solvent was removed by regulated evaporation over 48 hours on a leveled lab table. Regulated evaporation was achieved by covering the dish with a light-resistant lab funnel with a 1mm diameter hole at the apex. If solvent remained after the initial 48 hours, the films were allowed to continue to drying process for an additional 24 hours. When all solvent was gone (confirmed by TGA), the thin films were removed from the casting dish.

Top Cast of 4-BCMU onto 60D. To prepare top cast films, a 60D control film was first created by solution blending and casting. After complete solvent evaporation the control films remained in the casting dish and a layer of 4-BCMU dissolved in chloroform was added. To each of four casting dishes containing control films, 4-BCMU dissolved in 10 mL CHCl₃ was added: 1% (12.5 mg, 0.0245 mmol), 5% (62.5 mg, 0.123 mmol), 10% (125 mg, 0.246 mmol), 15% (187.5 mg, 0.369 mmol). Once the second layer of solvent had evaporated and the two film layers became one unit, the film was removed from the casting dish.

Ultraviolet Polymerization of nBCMU Monomer within Tecoflex® Thin Films. Thin films were polymerized upon extraction from the casting dish by 254 nm UV light for five minutes to produce a blue color. The light was placed 6 cm above the top-
side of the films. A section of each film was washed with water and another with acetone prior to polymerization.

**Thermal Response of nBMCU.** 30x10mm sections of Tecoflex® blend films were placed onto a hot plate regulated to 100°C ± 2°C and time was recorded from the moment the sample was placed on the heat source until the sample had turned completely red, if applicable. A Teflon® film was placed between the sample and the heat source to ensure there was no contamination.

**Simultaneous Tensile Strain and Raman Spectroscopy.** Solution blends of 4-BCMU PDA with Tecoflex® 60D were scaled up to 2x the initial amount: 25 mg 4-BCMU PDA, polymerized by gamma radiation, dissolved in 20 mL CHCl₃ was added to 2.5 g 60D Tecoflex® dissolved in 50 mL CHCl₃ (1% by weight PDA to PU). The blend was cast into 135x60 mm casting dished and evaporated for 96 hours. Tensile specimens, according to ASTM D-82267, were cut to 135 mm in length and 20 mm in width. Specimen thickness was measured at 6.0 mils (0.1524 mm). The samples were marked with a small dot and placed into the Instron tensile tester air pressure fit grips. The portable Raman probe head was placed on a lab-jack at the focus length (2.3 cm) from the specimen and an initial sample scan was taken. The crosshead (1019.716 kgf) pulled at 50 mm/min and was manually paused at various strain levels (typically 50%, 100%, 150%, 200% and 250% strain). At each pause, the lab-jack was raised, the Raman laser was focused next to the marked spot and a Raman scan was taken. Once a maximum strain level was reached, the specimen was removed and the Raman spectra were analyzed for the carbon triple bond center peak of the polydiacetylene. The Raman peak center data were plotted against the strain percentages and a trend line was created.
Impact Test of 20% 4-BCMU DA Polymerized in 60D Tecoflex®. Impact samples were completed using a dart drop tester. The dart was constructed from a screw with a capping nut attached to the end. The screw measured ca. 12 cm in length. Samples were obtained from dropping darts (99.26 g or 36.02 g) from a variety of heights. Five drops were completed at each height with the same weight dart at different areas on the same sample. Raman spectra were collected on each sample at the center of impact after the drop test and a Raman Response was calculated. A complete Raman analysis was obtained by collecting spectra at 0.05 mm intervals to the left and right of the center of impact to a final distance of 0.6 mm. The line of data was collected at the center of impact and 0.1 mm, 0.2 mm and 0.3 mm to above and below of the center of impact. Data was collected at the minimum quantifiable distance in each direction. An area strain map was produced by deconvolution of the carbon triple bond peak heights and Raman Response percentage for each point was calculated.

2.3 – PCDA Blend with PLA

Solution Blending. Solutions of polylactic acid (PLA, 1.25 g) in 25 mL CHCl₃ and 10,12-pentacosadiynoic acid (PCDA, 12.5 mg, 0.0334 mmol) dissolved in 10 mL CHCl₃ were prepared. After both compounds were completed dissolved the PCDA solution was added to the PLA solution (1% PCDA to PLA). Additionally, PCDA, in a 10 mL CHCl₃ solution, was added to a PLA solution (1.25 g in 25 mL CHCl₃) at 0.5% (6.25 mg, 0.0167 mmol), 5% (62.5 mg, 0.167 mmol), 10% (125 mg, 0.334 mmol), 15% (187.5 mg, 0.501 mmol) and 20% (250 mg, 0.668 mmol) by weight. Control PLA films
were prepared by adding 10 mL CHCl₃ to PLA (1.25 g) dissolved in 25 mL CHCl₃. The combined solutions were allowed to mix for a minimum of 12 hours.

**Film Casting.** The blend solution was poured into a casting dish and the solvent was removed by regulated evaporation over 48 hours on a leveled lab table. Samples containing 5% or greater PCDA to PLA were cast into dishes with a Teflon® lining. Regulated evaporation was achieved by covering the dish with a cone-shaped, light-resistant, dome with a 1 mm diameter hole at the apex. If solvent remained after the indicated time, the films were allowed to dry for additional time 24 hours. When all solvent was removed (as confirmed by TGA), the thin films were removed from the casting dish. The one percent and control films were soaked in water to reduce the adhesion of the PLA to the glass and then removed from the dish; in films cast into Teflon®, this step was unnecessary.

**Electrospun Mats.** Electrospinning solutions were prepared by combining a solution of PLA (1.0 g in 9 mL CHCl₃) with a solution of PCDA (10 mg, 0.0267 mmol in 1 mL CHCl₃). Electrospun fibers were created by pumping the blend solution through a 10 mL syringe by a syringe pump at 5 mL per hour with an applied voltage connecting the syringe needle to the collection plate. The metal collection plate (15.2 cm. X 15.2 cm.) was wrapped with non-stick tin foil to ease the release of the nonwoven mat. The power supply was set to 12 kV; the positive clip was connected to the syringe tip, the negative clip was attached to the collection plate and a grounding wire was connected the collection plate to the floor to complete the circuit. The plate was 10 cm. ± 1 cm. away from the syringe pump.
**UV Polymerization.** Thin films and non-woven mats were polymerized upon extraction by 254 nm UV light for five minutes to produce a blue color. The light was placed 6 cm above the top-side of the blends.

**Embedded PDA Thermal Sensitivity.** A thermal regime was imposed on the PDA/PLA blend films and fibers using a hot plate regulated to 70°C ± 2°C and time was recorded from the moment the sample was placed on the heat source until the sample had turned completely red. A Teflon® film was placed between the sample and the heat source to ensure there was no contamination of the sample. The Teflon® was found to be additionally helpful in removing the sample, as heating to 70°C is above the glass transition of PLA.

**Embedded PDA Solvent Sensitivity.** A number of solvents of varying polarities were chosen for treatment of the sensor doped PLA. These solvents include: chloroform, methylene chloride, tetrahydrofuran, hexanes, toluene, water, acetone and ether. The samples were cut into strips (1 mm square) and exposed to the solvents. Samples were visually inspected as immersed into the solvent, after five minutes, thirty minutes, and twenty-four hours.

**UV Photolithography.** Images were patterned within PLA, PCDA blend films by selectively exposing portions to short wave ultraviolet light (254 nm). Patterns were printed and cut into light blocking templates. To obtain a blue image, masked films were exposed to UV light for five minutes. To change the same image to red, the patterns were removed from the partially polymerized films and the sample was treated thermally. To obtain further blue imaging within the same films, additional polymerization was possible.
after 72 hours. To create multiple images within one film, this process was repeated several times with a different mask for each set of desired polymerization sets.

**Timed PCDA Polymerization within PLA.** Timed polymerization studies were completed on 0.5% and 1% PCDA to PLA films. The films were cut into 10x10 mm sections and polymerized under 254 nm UV light (6 cm above) for the appropriate amount of time. Upon removal from UV, the samples were placed into tin foil to preclude further polymerization. After all polymerizations were completed the samples were analyzed using absorbance spectroscopy. The 1% samples were obtained at the following times (in seconds): 30, 50, 100, 120, 140, 180, 200, 240, 260, 280 and 300. The 0.5% samples were obtained at the following times (in seconds): 0, 60, 120, 150, 180, 210, 240, 300, 330, 360, 390, 420, 450, 480, 510, 540, 570, 600, 660, 720, 780, 840, 900, 960, 1020, 1080, 1140, 1200, 1260, 1320, 1380, 1440, 1500, 1620, 1680, 1740 and 1800.

**PCDA Polymerization Depth within PLA.** A 1% PCDA to PLA film was cut into five 30x30 mm sections. A paw shaped mask was cut out from an excess of UV-light resistant material (aluminum foil). The five sections were placed on top of one another, labeled one through five and the excess aluminum foil surrounding the mask was wrapped around the entire stack. The packet was placed under 254 nm UV light for five minutes, mask side up. After polymerization, the sections were placed into individual aluminum foil packets to preclude further polymerization. Absorbance spectroscopy was used to analyzed the degree of polymerization within the films.
2.4 – PCDA Liposome Blend with Alginate

**PCDA Liposome Synthesis.** 1 mM 10,12-pentacosadiynoic acid (PCDA) liposome dispersions were created by dissolving PCDA (3.75 mg, 0.01 mmol) into 5 mL THF in a five dram vial. 2 mM dispersed PCDA liposomes were prepared by dissolving PCDA (7.5 mg, 0.02 mmol) into 5 mL THF in a five dram vial. Liposomes containing bacterially sensitive molecules were prepared as 2 mM dispersions with a 9:1, PCDA:bacterial moiety mole ratio. For example, PCDA (6.7 mg, 0.018 mmol) was combined with 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC, 1.35 mg, 0.002 mmol) in 5 mL THF. THF was removed by rotary evaporation to leave a thin film on the inside of the vial. Deionized water (10 mL) was added and the vial was heated to 75°C in a sand bath for ten minutes. After ten minutes, the Branson Sonifier 450 sonication probe (10 mm diameter tip) was lowered into the vial and the sample was sonicated at 5 output control (35%) for 15 minutes. The sonication dispersed the thin film into the water and the dispersion was aspirated into a syringe. Using the syringe, the sample was filtered through a 0.45 μm Whatman PES w/ GMF disk filter. The filtrate was crystallized at 3°C for 12 hours, then polymerized for five minutes using 254 nm UV light from above (3 cm).

**Wet Spinning of PDA Liposome in Alginate – Small Scale.** Small scale spinning solutions were prepared by dissolving sodium alginate (2 g) in 100 mL deionized water (2% solution). The viscous solution was stirred using a VWR Power Max Elite motorized stir rod at 900 rpm. For the control solution, 2 mL of deionized water was added to 9 mL of the 2% sodium alginate solution. The PCDA-alginate blend was prepared by adding 2 mL of 2 mM PCDA liposome to 9 mL of 2% sodium alginate
solution. The PCDA/assay-alginate blend solution was prepared by adding 2 mL of 2 mM PCDA/assay liposome to 9 mL of 2% sodium alginate solution. The solutions were mixed for one hour with a magnetic stir bar and loaded into a syringe. Fibers were produced by extruding the alginate syringe contents through a 16 gauge needle into a 400 mL, 15% calcium chloride (CaCl₂) coagulation bath at a rate of 1 mL per minute. Once extruded, the calcium alginate fiber was moved into a 400 mL 3% CaCl₂ equilibration bath for twelve hours. The fiber was cut into 12 inch sections and moved to a room temperature drying box for a minimum of 72 hours.

**Wet Spinning of PDA Liposome in Alginate – Large Scale.** A large scale control dope was prepared by dissolving sodium alginate (15 g) in 300 mL deionized water (5% solution). Spinning dope containing polydiacetylene was prepared by dissolving sodium alginate (15 g) in 225 mL deionized water, then 75 mL prepared PCDA liposome solution was added. The viscous solutions were stirred using a VWR Power Max Elite motorized stir rod at 900 rpm. The alginate solutions were allowed to rest for 12 hours to remove all air bubbles.

The control dope was placed in a stainless-steel vat, pressurized with nitrogen gas at 25 psi and allowed to equilibrate for 4 hours to ensure no bubbles had formed during the transfer. The solution was pumped into a 15% CaCl₂ coagulation bath through a 100-hole spinneret, hole diameter ca. 300 μm, at a rate of 1.65 cc/minute. The resulting calcium alginate fibers were wound with a take-up speed of 31.4 cm/minute. Samples were obtained in process by cutting yarn bundles every 30 seconds and placing them into CaCl₂ equilibration baths of varying percentages (below). The procedure was then repeated for the spinning dope containing polydiacetylene liposomes.
Equilibration baths, 1.5 L each, were prepared at CaCl₂ concentrations of 0%, 1%, 3%, 5%, and 10% by weight to deionized water. A minimum of two control and two doped bundles were immersed in the equilibration baths for 24 hours then dried under tension at room temperature to create usable fiber samples. All other experiments use dried fibers obtained from the 0% CaCl₂ equilibration bath unless otherwise specified.

**Embedded PDA Thermal Sensitivity.** To examine the temperature response of the PDA liposome within the alginate fiber, a 30 mm section, five doped with polydiacetylene liposome and five control, was placed onto a Teflon® liner on a 60°C hotplate; time was recorded at the onset and completion of temperature induced color change within the fibers. Treated fibers were visually inspected and Raman spectra were collected.

**Embedded PDA Solvent Sensitivity.** To determine a level of solvent response for the PDA liposome embedded in the calcium alginate fibers, 20 mm sections (control and doped) were immersed into 10mL of the specified solvent for 30 minutes at room temperature. Time was recorded at the first sign of visual color change. Solvents included water, hexane, acetone, methylene chloride, chloroform, tetrahydrofuran and ethanol. Fibers were removed from the solvents, allowed to dry for 24 hours and were subjected to Raman spectroscopy and visual inspection.

**Reverse Ion Exchange.** Calcium alginate fibers were manipulated to various level of induced sodium through a reverse ion exchange. The calcium alginate fibers (20mm) were submerged in a 0.5 M HCl bath for 0, 1, 5, 10, 15 and 20 minutes, then washed twice with distilled water. The resulting fibers were then treated with an excess of NaOH in a 6:4 water/isopropanol solution 30 minutes and rinsed in a clean 6:4
(water/i-P) bath. Additionally, calcium alginate fibers were treated in the 0.5 M HCl bath for 20 minutes followed by submersion in the NaOH (6:4 water/isopropanol) bath for 0, 1, 5, 10, 15, 20 and 25 minutes. The resulting fibers were dried for 24 hours then inspected visually and with Raman spectroscopy.

**Embedded PDA Cyclodextrin Sensitivity.** A sensitivity of the PCDA liposome to α-cyclodextrin (α-CD) in solution has been documented.\(^7\) It is also known that introducing sodium ions to a calcium alginate fiber increases its water solubility.\(^6\) Therefore, 20 mm samples of doped calcium alginate fibers (and controls) were exposed to varying levels of NaCl combined with several different α-cyclodextrin molarities. To separate vials, 0 mg, 24.9 mg (10 mM), 124.5 mg (50 mM), 249 mg (100 mM), 1.25 g (500 mM) or 2.49 g (1 M) α-cyclodextrin was added to 10 mL of deionized water. To the same vials, 0%, 1% (100 mg), 2% (200 mg) or 5% (500 mg) sodium chloride was added, by weight, to the water.

**Bacteria Sensitivity.** *E.Coli* DH5-α (novablue) was provided by the Analytical Chemistry program at Clemson University. A 1:100 dilution of 10\(^9\) cells/mL, as determined by absorbance at 600 nm, resulted in a 80 μg/mL bacteria concentration. Samples were prepared by combining 30 μL of 1 mM PCDA liposome suspension with 30 μL bacteria sample, followed by the addition of 30 μL Tris base (pH 8) and dilution with deionized water to reach a final volume of 1 mL.\(^4\)

**2.5 – Instrumentation Settings**

**Raman Spectroscopy.** Raman spectra were collected on a Renishaw Raman Fiber Optic Probe system using a 745 nm high powered diode laser. Data were collected
by 180° backscattering on a ca. 25 micron sample size. Scans were set to 100% laser power for a minimum of 30 seconds (60 s if better S/N ratio was needed) within the wavenumber range of 700 to 2500 cm\(^{-1}\). Computer analysis was performed using GRAMS/32 software and peak positions were calculated by combined Gaussian/Lorentz statistical methods. Statistical sample analysis revealed deviations of less than 0.5 cm\(^{-1}\) per peak center position.

**UV/Vis.** Absorbance spectroscopy was completed on a Perkin Elmer Lambda 900 UV/VIS/NIR Spectrometer using D2 and Tungsten lamp. Data was analyzed using UV WinLab L800/L900 software where scans were controlled to one cycle of 750 to 350 nm with data intervals every 1.0 nm. The slit width was 3.00 nm and the scan speed was 500 nm/min.

**Fluorescence.** Fluorescence measurements were obtained on a steady-state PTI (Photon Technology International) spectrofluorometer using a Xenon arc lamp for excitation. Analysis of raw data was compiled on Felix 32 software.

**Thermal Analysis.** Thermogravimetric Analysis was run on the TA Instrument 2950 TGA under a nitrogen environment generated by liquid nitrogen boil-off at a rate of 40mL/min. Samples, weighing approximately 6mg were placed in platinum pans. Starting at 25°C, the sample was ramped up to 400°C at a rate of 10°C/min. The resulting decomposition temperature and percent loss from starting material were analyzed using TA Instrument Universal Analysis 2000 program, version 3.9A.

Differential Scanning Calorimetry was conducted on the TA Instrument Q1000. The cell was purged with helium at a rate of 20mL/min. Samples, weighing approximately 6mg, were loaded into aluminum pans. The samples started at 25°C and
were heated at a rate of 10°C/min to 250°C then cooled with liquid nitrogen at 10°C/min to 25°C (some samples cooled to -30°C) and reheated at a rate of 10°C/min to 250°C. Any resulting crystallization, glass transition and melting point were analyzed using TA Instrument Universal Analysis 2000 program, version 4.4A.

**NMR.** ¹H and ¹³C NMR spectra were recorded on a JEOL Eclipse 300 spectrometer in CDCl₃ with TMS standard.

**XRD.** Powder X-ray diffraction was obtained from a Scintag XDS 2000 with copper radiation at 1.54Å; Data was collected over 2θ = 6° to 60°.

**Infrared Spectroscopy.** Fourier transform infrared data was collected via Attenuated Total Reflectance (ATR) on a Thermo Scientific - Nicolet Magna 550 FTIR spectrometer equipped with an endurance foundation series single bounce diamond accessory. Sixteen scans were completed of each sample from 4000 to 525 cm⁻¹.

**Liposome Size Analysis.** Size analysis was completed on PDA liposomes in deionized water by dynamic light scattering using a PCS Submicron Particle Size Analyzer with a polystyrene standard. Particle imaging was completed with a 4800 Scanning Electron Microscope with TEM attachment. Samples were placed on a TEM mesh grid and examined up to 80,000X magnification.

**Photomicrographs.** Photomicrographs were taken using a Leitz Laborlux S microscope with an attached Sony DXC-390 camera. Image analysis was completed on Image Pro Plus software, version 4.5.0.29, through the active image program.

**Tensile Testing.** Specimens were exposed to stress by tensile stretching on the Instron 5582 Tensile Tester. Thin films were tested in accordance with ASTM D-822 test standards and fibers were tested with regards to ASTM D 3822. Data were
accumulated from no less than 10 samples each of the polymers with and without the sensor. The means of the samples data were compared using the Student’s t-Test to prove if the means were equal within a 95% probability.⁷²
CHAPTER 3

BCMU PDA/DA BLENDS WITH POLYURETHANES

3.1 – Introduction to BCMU-Tecoflex® Blends

Polydiacetylenes (PDAs), specifically 3- and 4-butoxymethylcarbonylurethane PDAs (3- and 4-BCMU), are capable of a blue to red transition with exposure to an applied force or stress (Figure 3.1). The external shear stress affects some blue PDAs through a loss of conjugation within the PDA backbone. This loss of conjugation translates into a visual blue to red shift and a shift in peak center position of the carbon triple bond and double bond as detected by Raman spectroscopy.1,23,73 Initially, this was observed in the tensile stretching and compression of PDA single crystals.1,23,74,75 The Raman spectra of these compounds show the carbon triple and double bond peak center positions shift to higher wavenumbers with increasing strain.73 Later, additional support was generated by Burns et al.22 via AFM disruption of an assembled PDA monolayer. Distortion by shear to cause a reduction in conjugation length was also observed in semi-dilute solutions.16,76
Tensile strain affects other PDA systems through a force induced alignment causing an increase in conjugation. The change in conjugation may be tracked via Raman spectroscopy through the carbon triple bond center position. An alkyne shift of 4-6 cm\(^{-1}\) has been previously recorded for polyurethane-co-polydiacetylene\(^{25,26,27}\) and a shift of 4-5 cm\(^{-1}\) for polyester-co-polydiacetylene.\(^{30}\)

In the present work, attempts were made to create polydiacetylene blends with shifts similar to those found within the polydiacetylene co-polyurethane and co-polyester systems. Polymer blending is significantly less synthetically challenging than copolymerization. The addition of small percentages of polydiacetylene (referred to as the additive or dopant) to a bulk polymer system (referred to as the host) can provide an opportunity to retain desired host properties while adding the additional properties of the PDA. Obtaining strain sensitive results with polymer blending will open new doors for the application of polydiacetylene strain sensors. In this chapter, 3- or 4-BCMU monomers and polymers will be added to polyurethanes at low loading percentages to create a strain sensitive blend with retained host properties.
The direct synthesis of 4-BCMU was first completed by Patel et al.\textsuperscript{77} and has since been reproduced numerous times.\textsuperscript{1} The synthetic method used in this chapter, reported in the experimental section, was modified from Kim et al.\textsuperscript{66} The number 3 or 4 previous to BCMU refers to the number of carbons linking the BCMU moiety to the polydiacetylene backbone or 1,3-butadiyne, as appropriate (Figure 3.2).

Two approaches were taken with regards to the preparation of strain sensitive blends. In some cases, diacetylene monomers were blended with a host polymer and then converted to polydiacetylenes. In others, the diacetylene was first polymerized then the resulting PDA macromolecules were incorporated into the host polymer. Diacetylenes that have been polymerized (either by gamma or UV) before incorporation into the host will be referred to as BCMUp. Diacetylene monomers that are incorporated into the host, processed and then polymerized with UV light are referred to as BCMUm. A generalized example of the incorporation process can be found in Figure 3.3.

**Figure 3.2:** Reaction of dodecadiyndiol with butylisocyanatoacetate to form butoxycarbonylmethylurethane (BCMU) polydiacetylene where \( n=3 \) in 3-BCMU and \( n=4 \) in 4-BCMU.
The polyurethane, Tecoflex®, was selected to act as a host for 3- and 4-BCMU polydiacetylenes as a complement to the urethane groups within the side chains of the PDA. It was anticipated that the polymers would interact via hydrogen-bonding between the carbonyl (C=O) and the N-H groups contained within the urethane functionalities (Figure 3.4). Hydrogen-bonding between side chains has been well documented within the nBCMU polymer family (Chapter 1: figure 1.9); therefore, the probability of the PDA side chains bonding with the host molecules urethane sites was thought to be good.

**Figure 3.3**: Schematic of the two paths to BCMU incorporation into a host system: (1) BCMU polymers that were incorporated with the host prior to solution casting are referred to as BCMUp and (2) BCMU monomers that were incorporated and solution cast with the host then polymerized are referred to as BCMUm.

The polyurethane, Tecoflex®, was selected to act as a host for 3- and 4-BCMU polydiacetylenes as a complement to the urethane groups within the side chains of the PDA. It was anticipated that the polymers would interact via hydrogen-bonding between the carbonyl (C=O) and the N-H groups contained within the urethane functionalities (Figure 3.4). Hydrogen-bonding between side chains has been well documented within the nBCMU polymer family (Chapter 1: figure 1.9); therefore, the probability of the PDA side chains bonding with the host molecules urethane sites was thought to be good.
Samples of Tecoflex® (Figure 3.5) were provided by the Lubrizol Corporation in four Shore® (Durometer) hardness levels: 85A, 93A, 100A, and 60D (see Chapter 1: Table 1.2 for properties chart). These polyurethanes are listed from softest to hardest; the more pliable polymers have longer soft segments ($n_{\text{soft}} > n_{\text{hard}}$). The soft segment is composed of poly(tetramethylene glycol) (PTMG, MW ca. 2000) and the hard segment is composed of methylene bis($p$-cyclohexyl isocyanate) ($\text{H}_2\text{MDI}$, hydrogenated MDI) and 1,4 butane diol (1,4-BD).50

![Figure 3.4: Representative structure of a hydrogen bond that could occur between BCMU (top) and the carbamate functionality within the host polyurethane (bottom).](image)

Solution blending in chloroform, a solvent for all provided Tecoflex® durometers, BCMU monomers and BCMU polymers, was used to combine the additive with the host, described in the experimental section. Four types of combinations were used between Tecoflex® 60D and the additive: 4-BCMU polymerized by gamma (4-BCMUp), 4-BCMU monomer (4-BCMUm), 3-BCMU polymerized by UV (3-BCMUp) and 3-BCMU monomer (3-BCMUm). The PDAs or DAs were combined with 60D in

![Figure 3.5: Structure of Tecoflex® by Lubrizol composed of polytetramethylene glycol soft segments and methylene bis-$p$-cyclohexyl isocyanate with 1,4-butane diol hard segments.](image)
various ratios to determine the effect of loading on the host system. Additionally, 4-
BCMUp and 4-BCMUm were blended with all available durometers of Tecoflex® (60D,
100A, 93A & 85A) to determine if the length of host polyurethane soft segment had an
effect on the PDA/DA ordering within the system.

3.2 – BCMU Synthesis Observations

The synthesis of 3-BCMU was more difficult than 4-BCMU because the diol
precursor, 4,6-dodecadiyne-1,10-diol, polymerized in ambient light whereas 5,7-
dodecadiyne-1,12-diol, the precursor for 4-BCMU, did not. An accurate starting weight
was determined for the 4,6-dodecadiyne-1,10-diol by separating the monomer from the
polymer by dissolving in dry THF followed by vacuum filtration, then subtracting the
weight of the polymer from the initial sample weight. The 1,10-diol was not simply
purified and re-isolated before weighing because evaporation of the THF resulted in
crystallization and subsequent polymerization of this compound. Therefore, the
remaining reactants were added to the 1,10-diol filtrate in dry THF. A dry environment
was necessary for both the 3- and 4-BCMU reactions to ensure the butylisocyanatoacetate
did not react with water in the air; therefore, all solvents and glassware were dried and
the reaction was run under a dry nitrogen environment.

During the synthesis of 3- and 4-BCMU, great care was taken to avoid product
exposure to environmental light. Although only a small degree of polymerization occurs
with ambient light, the resulting product looks very blue. A 1-2 % conversion to polymer
can cause the material to take on a uniform blue color. Additionally, polymerization
before or during the column process resulted in loss of product due to entanglement
within the silica gel. After the product was purified by chromatography, crystallization and polymerization were avoided during rotary evaporation by keeping the water bath temperature above 60°C, which retained the BCMU monomer in a liquid state. When this technique was not employed, the product immediately crystallized and turned blue upon removal of the solvent.

After rotary evaporation, the 3- or 4-BCMU melt was immediately weighed and an NMR spectrum was collected to ensure product purity. If solvent remained within the system, the reaction product was placed back into rotary evaporation or in a high vacuum line. After an accurate weight was obtained, the product was dissolved in a minimum amount of chloroform (typically 15 mL for 2.85 g product), the solution transferred to a vial, capped, wrapped in parafilm and completely covered in aluminum foil. Previous methods of storing the monomers in solid state at low temperatures with a light protective coating did not yield pure monomer; a slight blue color indicated that a small degree of polymerization had taken place within these compounds. When a portion of the product was converted to polymer, the 3- or 4-BCMU monomer was extracted with acetone. After acetone extraction, the blue form of the 3-BCMU polymer was completely recovered; however, the portion of 4-BCMU that was polymerized was converted to red.

When BCMU polymerization was the goal, exposure to a gamma source (50 Mrad of 60Co) is known to result in the highest amount of polymer conversion. However, the gamma source was only available for the polymerization of one 4BCMU reaction. As a result, 254 nm UV light was used as a polymerization source for subsequent reactions resulting in a maximum of 40% polymer conversion. UV polymerization of 3-BCMU became a viable secondary option because the unpolymerized monomer could be
removed with acetone extraction, leaving pure 3-BCMU PDA behind. A UV polymerization time of five to seven minutes was required to achieve a deep blue crystal color; polymerizing over seven minutes resulted in crystals that appeared black.

3.3 – Characterization of BCMU Monomers and Polymers

Confirmation of the success of the 3- and 4-BCMU monomer syntheses were obtained via proton nuclear magnetic resonance (\(^1\)H NMR) and Raman spectroscopy. In both NMR spectra (Figure 3.6), the hydrogen attached to the nitrogen is represented by a broad peak furthest downfield, ca. 5.2 ppm. Next, at 4.1 ppm, are the protons that neighbor an oxygen atom, followed by the hydrogen in between the nitrogen and carbonyl. These protons are shifted downfield as compared to the rest of the system due to the electronegativity of their surrounding environment. The remaining peaks were assigned to the –CH\(_2\) groups, with the least shifted of the peaks corresponding to the –CH\(_3\). Coupling constants and sample preparation for NMRs may be found in the experimental section.
After the NMR analysis, the remaining compounds were dissolved in chloroform forming concentrated solutions. The minimum amount of solvent present in the system prevented the BCMU from crystallizing; therefore, premature polymerization was avoided. Raman spectra taken of 3- and 4-BCMU monomers as dissolved in concentrated

**Figure 3.6:** $^1$H NMR spectra for 3-BCMU (top) and 4-BCMU (bottom).
chloroform solutions provided identical spectra. A carbon triple bond peak at 2250 cm$^{-1}$ was evident in both samples. This peak was indicative of diacetylene monomer because it represents an acetylene stretch that is not involved in extended conjugation.

### 3.4 – Chromatic Transitions of 3/4-BCMU

A shift of the carbon triple bond Raman peak occurs between the diacetylene monomer (2250 cm$^{-1}$) and the fully conjugated polydiacetylene (2085 cm$^{-1}$). The difference in wavenumber center positions for the carbon triple bond peak has been reported several times and may be attributed to the difference in vibrational energy level of the conjugated polymer system.$^{23,30,74,79}$

The relative position of the Raman carbon triple bond peak is a valuable tool for tracking the colorimetric transitions of polydiacetylenes. Temperatures above 75°C caused a blue to red transition in the PDA, which correlated to a shift from ca. 2085 cm$^{-1}$ to ca. 2108 cm$^{-1}$. The 4-BCMU PDA is known to be thermochromically irreversible; however, the 3-BCMU PDA is completely reversible.$^{11}$

The phenomenon of solvato-chromism within 4-BCMU in good and poor solvents has been reviewed in the introduction. Chloroform is considered a good solvent for 4-BCMU because it shows special affinity for large flexible substituent groups and carbonyls.$^{4}$ As indicated by the Raman spectra of the 4-BCMU-CHCl$_3$ solution, the carbon triple bond peak is recorded at 2123 cm$^{-1}$, a shift of 38 cm$^{-1}$ from the blue state. The solvato-chromism within 3-BCMU was found to be completely reversible to blue; alternatively, 4-BCMU converts permanently to red. This phenomenon is known; theoretical models suggest that the blue form is was the lowest energy conformation for
3-BCMU but red is the lowest for 4-BCMU.\textsuperscript{11} A summary of the Raman spectra from the aforementioned samples may be found in Table 3.1.

Table 3.1: A summary of colorimetric transitions within 3/4-BCMU and their respective Raman carbon triple bond peak center position.

<table>
<thead>
<tr>
<th>PDA state (External Stimuli)</th>
<th>Compound</th>
<th>Visual Color</th>
<th>Raman C≡C Peak Center Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer (dissolved in CHCl₃)</td>
<td>3/4-BCMU</td>
<td>White</td>
<td>2250 cm⁻¹</td>
</tr>
<tr>
<td>Crystalline Polymer</td>
<td>3/4-BCMU</td>
<td>Blue</td>
<td>2085 cm⁻¹</td>
</tr>
<tr>
<td>Thermal (75°C)</td>
<td>4-BCMU</td>
<td>Red</td>
<td>2108 cm⁻¹</td>
</tr>
<tr>
<td>Solvent (CHCl₃)</td>
<td>3/4-BCMU</td>
<td>Yellow</td>
<td>2123 cm⁻¹</td>
</tr>
<tr>
<td>Evaporated from CHCl₃</td>
<td>3-BCMU</td>
<td>Blue</td>
<td>2085 cm⁻¹</td>
</tr>
<tr>
<td>Evaporated from CHCl₃</td>
<td>4-BCMU</td>
<td>Red</td>
<td>2112 cm⁻¹</td>
</tr>
</tbody>
</table>

The largest of these transitions occurs when comparing the diacetylene monomer to the polydiacetylene, a carbon triple bond shift of 165 cm⁻¹. A spectrum of 4-BCMU in the planar, blue state may be found in Figure 3.7. The inset of Figure 3.7 shows the drastic shift between the monomer and polymer states of the 4-BCMU. All Raman shifts documented within this work occurred between these two maximum points. Although most previous work has been completed under resonance Raman conditions, a variety of laser wavelengths provide sufficient spectra in a non-resonant state.\textsuperscript{80} In this work, a 745 nm laser was used to provide Raman data.
The final colorimetric transition for BCMU PDAs is mechanochromism, defined as a change in color with an applied force. To mimic strain being applied to the PDA backbone, the 4-BCMU polymer system was ground using a mortar and pestle and a Raman spectrum was collected (Figure 3.8). Instantly, a red color became apparent within the system, but the color was not uniform. The polymer only became red in the direct spots where the pestle made contact. Initially, a carbon triple bond peak was observed at 2094 cm\(^{-1}\); however, upon further investigation two peaks were seen. The carbon triple bond peaks corresponded to the initial blue polymer (2085 cm\(^{-1}\)) and to the

Figure 3.7: Normalized Raman spectra of 4-BCMU monomer (black, dash) and polymerized by UV light (blue, solid) representing the largest shift in the carbon triple bond peak.
red polymer (2109 cm⁻¹). The red peak was shifted 24 cm⁻¹ from the blue peak, approximately the same transition that was observed in the thermal experiment.

![Figure 3.8](image.jpg)

**Figure 3.8:** Top: A Raman spectrum of 4-BCMUp after grinding with mortar and pestle. Bottom: Deconvolution of the carbon triple bond peak to yield separate red and blue peaks.

### 3.5 – Raman Response Equation

Typically, the heights of Raman peaks are not uniform when collected from separate scans; however, peak heights may be compared within the same scan. Using this theory, an equation for Raman Response based on the carbon triple bond peak height within a spectrum has been developed. Carbon triple bond peaks that represent red PDAs typically fall between 2108 cm⁻¹ and 2119 cm⁻¹; for simplicity, this peak has been referred to as the 2111 cm⁻¹ shifted carbon triple bond peak in the Raman Response
equation (RR, **Equation 3.1**). Raman Response can be defined as the height of the red carbon triple bond peak divided by the sum of the heights of the red and blue carbon triple bond peaks. The numeric value produced by the equation is a percentage of the red acetylene peak as compared to total acetylene peaks.

**Equation 3.1**: Raman Response equation for PDAs generates a percentage of based on the heights of the C≡C blue and red peaks.

\[
\text{Raman Response} = \frac{\text{Height}_{C≡C2111cm^{-1}}}{\text{Height}_{C≡C2111cm^{-1}} + \text{Height}_{C≡C2085cm^{-1}}} 
\]

The Raman Response calculated for the mechanochromism example (**Figure 3.8**) was 40.8%. This means that on the specific spot measured by Raman (~25 μm) 40.8% of the total acetylene peaks within the spectrum were located in the red position and 59.2% remained in the planar state. It is hypothesized that 0% RR corresponds to 100% blue polymer within the system and at 100% RR the entire polymer was converted to the red form. However, it has not been confirmed that any percentages between 0% and 100% correlate to a direct percentage of red polymer conformation within the system.

### 3.6 – Retention of Host Properties in Tecoflex®-blend-PDA

After determining that our Raman system was capable of generating equivalent polydiacetylene data to previously reported results,\textsuperscript{1,2,4} PDAs were incorporated into the host polyurethanes. The main objective of the blend system is to retain host polyurethane properties while adding the desired colorimetric properties of the PDAs. Initial tests of the blends were completed to determine retention of host polymer (Tecoflex®) properties through tensile testing and thermal analysis. A comparison was made between control
60D Tecoflex® films and blend films by tensile testing samples cut according to ASTM D-822 standards. The means of the properties (stress/strain at max load, percent strain at max load, and load at peak) of ten or more test strips were compared using the Student’s t-Test (Figure 3.9, Table 3.2).

![Sample tensile spectra of 60D Tecoflex® film (Load vs. Displacement)](image)

**Figure 3.9**: Sample tensile spectra of 60D Tecoflex® film (Load vs. Displacement)

**Table 3.2**: Comparison of Properties for Films of 60D Tecoflex® control and blend with 1% 4-BCMUp.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load at Peak (kgf)</th>
<th>Percent Strain at Max Load (%)</th>
<th>Stress at Max Load (kgf/mm²)</th>
<th>Strain at Max Load (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60D Tecoflex® Film</td>
<td>3.2 ± 0.9</td>
<td>251 ± 26</td>
<td>0.39 ± 0.12</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>60D Tecoflex® Film with 1% 4-BCMUp</td>
<td>3.0 ± 1.1</td>
<td>250 ± 49</td>
<td>0.37 ± 0.16</td>
<td>2.3 ± 0.4</td>
</tr>
<tr>
<td>T-calculated</td>
<td>0.4738</td>
<td>0.0437</td>
<td>0.2853</td>
<td>0.4561</td>
</tr>
</tbody>
</table>

The Student’s t-Test is a statistical tool used to determine if the means of two sample sets are equal within a 95% confidence (Equation 3.2). It is calculated using the number of samples in each dataset (N), the mean for the dataset (X), the standard deviation for the mean (s) and a ‘t<sub>table</sub>” based on the number of samples that were used in each dataset. The sample size used below resulted in t<sub>table</sub>=2.101 as determined from the Student’s t-Test table. The null hypothesis was proven true, meaning t<sub>calculated</sub> was less than t<sub>table</sub>; therefore, the means of the sample sets were found to be equal within a 95% probability.
In addition to tensile characterization, the control and blend films were examined for retention of thermal properties via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Detailed information on sample size and heating rates can be found in the experimental section.

Three samples were analyzed for decomposition temperature using TGA: 60D control, 38.8% 60D-blend-4-BCMUm and 4-BCMUp (Figure 3.10). The decomposition for all the samples occurred in a two-step process; therefore, it was impossible to determine one decomposition temperature (Td) for each sample. The complexity of decomposition made it difficult to examine the direct effect of the PDA within the Tecoflex® blend (Table 3.3). Generally, the addition of the PDA additive increased the temperature of the onset of thermal decomposition for the blend as compared to both the Tecoflex® control and PDA samples. Similar percentages of mass loss were incurred in Td1 (ca. 75%) and Td2 (ca. 25%) for the blend respective to the amounts lost in the control components. The TGA result for Tecoflex® 60D-blend-(10%)4-BCMUp (not shown) was very similar to the 4-BCMUm blend.

**Equation 3.2**: Student’s t-Test, a statistical method for determining if the means of two sample sets are equal within a 95% confidence.\(^7\)

\[
s_{pooled} = \sqrt{\frac{(N_A - 1)s_A^2 + (N_B - 1)s_B^2}{N_A + N_B - 2}}
\]

\[
t_{calculated} = \frac{|\bar{X}_A - \bar{X}_B|}{s_{pooled}} \sqrt{\frac{N_A N_B}{N_A + N_B}}
\]
DSC was used to prove the crystallization temperature and melting point of crystalline 4-BCMUp did not change when solution cast into a thin film (Figure 3.11). Upon cooling from the first heating, a crystallization temperature occurred at 32°C for the crystalline 4-BCMUp and 33°C for the solution cast 4-BCMUp film. Reheating the sample revealed a melting temperature of 61°C for both samples. It was concluded that the thermal properties of the 4-BCMUp remained constant through the solution casting process.
Samples of 60D Tecoflex® control and blended with 1%, 5% and 10% 4-BCMUp were analyzed by DSC to determine if the additive affected the host glass transition temperature ($T_g$) (DSC Figure 3.12, results Table 3.4). Initially, a shift of 10°C was observed from the Tecoflex® control $T_g$ at 77°C to a $T_g$ at 67°C for the Tecoflex®-blend-(1%)4-BCMUp. Further investigation of the 5% and 10% blends revealed a melting point corresponding to the PDA at 70°C and 67°C, respectively. The overlap of the Tecoflex® glass transition and the PDA melting point prevented an accurate analysis of both transitions. However, it is clear that the addition of the PDA to the Tecoflex® has affected the host polymer properties. It is speculated that the addition of polydiacetylene to polyurethane at 1% by weight acts as a defect to the host polymer. The presence of a small molecule in a high molecular weight host system can interfere with polymer entanglement, reducing the glass transition temperature. This phenomenon commonly
occurs with plasticizers which work by placing themselves between polymer chains increasing the free volume.\textsuperscript{81,82}

![DSC graph of 4-BCMUp-Tecoflex® 60D blend films at 0% (control), 1%, 5% and 10% by weight (from bottom to top).](image)

**Figure 3.12**: DSC graph of 4-BCMUp-Tecoflex® 60D blend films at 0% (control), 1%, 5% and 10% by weight (from bottom to top).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass Transition Temperature</th>
<th>Crystallization</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline 4-BCMUp</td>
<td>--</td>
<td>32°C</td>
<td>61°C</td>
</tr>
<tr>
<td>Solution Cast 4-BCMUp</td>
<td>--</td>
<td>33°C</td>
<td>61°C</td>
</tr>
<tr>
<td>Solution Cast 60D Tecoflex®</td>
<td>77°C</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1% 4-BCMUp in Tecoflex®</td>
<td>67°C</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>5% 4-BCMUp in Tecoflex®</td>
<td>--</td>
<td>--</td>
<td>70°C (4BCMUp)</td>
</tr>
<tr>
<td>10% 4-BCMU in Tecoflex®</td>
<td>--</td>
<td>33°C</td>
<td>67°C (4BCMUp)</td>
</tr>
</tbody>
</table>

| Table 3.4: DSC Results of 4-BCMUp and Tecoflex® Blend Films |

DSC was also used to compare Tecoflex® 60D control to blends with 10% 4-BCMUp, 10% 4-BCMUm and 10% 4-BCMUm polymerized by UV to determine if the in-situ polymerization affected the PDA melting point (Figure 3.13). Control and 10% 4-
BCMUp data remained the same as stated in Table 3.5. However, the 10% 4-BCMUm polymerized blend did not resemble the 10% 4-BCMUp blend. The melting point of 67°C from the 4-BCMUp blend was not seen in the in-situ polymerized 4-BCMUm blend. The thermal properties of the 4-BCMUm polymerized blend were similar to the 4-BCMUm unpolymerized blend, each showing a glass transition at 60°C and 62°C, respectively. It was concluded from this data that PDAs formed by polymerization within the 60D blend by UV were not the same as PDAs formed through solid state gamma radiation.

![DSC graph of 10% 4-BCMUm unpolymerized and polymerized within 60D Tecoflex® as compared to a Tecoflex® control film and blended with 10% 4BCMUp.](image)

**Figure 3.13:** DSC graph of 10% 4-BCMUm unpolymerized and polymerized within 60D Tecoflex® as compared to a Tecoflex® control film and blended with 10% 4BCMUp.

**Table 3.5:** DSC Data from Tecoflex® 60D-blend-4BCMUm as Monomer and Polymerized.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass Transition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>60D-blend-(10%)4-BCMUm</td>
<td>62°C</td>
</tr>
<tr>
<td>60D-blend-(10%)4-BCMUm polymerized</td>
<td>60°C</td>
</tr>
</tbody>
</table>
3.7 – Analysis of BCMUp Blend Films

It was hypothesized that the 4-BCMU would retain all colorimetric properties within a blend of Tecoflex®. The strong yellow color of the 3- or 4-BCMU polymer solution in chloroform carried over through the addition to the Tecoflex® solution. However, the colorimetric similarities between the 3- and 4-BCMU systems ended there. Briefly, the 4-BCMUp produced a red cast film in all Tecoflex® durometers and 3-BCMUp produced a blue cast film in 60D. These systems are discussed below in detail with a complete technical characterization of their colorimetric properties. Additionally, the strain sensitive properties of 4-BCMUp are discussed with respect to blend casting in 60D Tecoflex® films.

A major factor in picking a suitable host for the PDAs was ensuring there were no Raman matrix peaks around the area of the carbon triple bond indicator peak. As previously stated, the carbon triple bond peak of the PDAs can be used to track the conformation of the polymer as it is influenced by outside forces. The Raman spectrum of 60D Tecoflex® (Figure 3.14) showed that there were no peaks or fluorescence interference in the 2000-2250 cm⁻¹ region.
Raman spectra were collected for 1% 3-BCMUp in 60D and 1% 4-BCMUp in 60D, 100A, 93A and 85A Tecoflex® (Figure 3.15, Table 3.6). The carbon triple bond peak corresponding to embedded 3-BCMUp occurred at 2085.7 cm$^{-1}$, approximately the same position as the crystalline state, 2085.64 cm$^{-1}$. Additionally, the 60D-blend-3-BCMUp was blue, the same color as the PDA outside of Tecoflex®, and was so intense that it completely blocked any Raman signal from the host. However, all samples of 4-BCMUp within Tecoflex® were red and the PDA peaks were not as intense as in the planar form. In the red colored samples, Raman peaks from Tecoflex® were observed.
The carbon triple bond Raman peaks occurred at 2111 cm\(^{-1}\) (60D), 2110 cm\(^{-1}\) (100A), 2109 cm\(^{-1}\) (93A) and 2109 cm\(^{-1}\) (85A). The difference in carbon triple bond peaks between 3- and 4-BCMUp within the Tecoflex\(^\text{®}\) was most likely a solvatochromic response as opposed to a strain imposed by the matrix.

**Table 3.6**: Summary of Raman Spectroscopy Results in Tecoflex\(^\text{®}\) Control and 1% Blend Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>PDA C=C Stretching Peak Center Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>60D Tecoflex(^\text{®}) Control</td>
<td>n/a</td>
</tr>
<tr>
<td>4BCMUp</td>
<td>2085 cm(^{-1})</td>
</tr>
<tr>
<td>60D-blend-3-BCMUp</td>
<td>2085 cm(^{-1})</td>
</tr>
<tr>
<td>60D-blend-4-BCMUp</td>
<td>2111 cm(^{-1})</td>
</tr>
<tr>
<td>100A-blend-4-BCMUp</td>
<td>2110 cm(^{-1})</td>
</tr>
<tr>
<td>93A-blend-4-BCMUp</td>
<td>2109 cm(^{-1})</td>
</tr>
<tr>
<td>85A-blend-4-BCMUp</td>
<td>2109 cm(^{-1})</td>
</tr>
</tbody>
</table>

To determine the detection limit of the Raman with respect to the polymer mixture, 4-BCMUp was added to 60D at 1%, 0.5%, 0.1%, and 0.05% by weight respective to the polyurethane. The carbon triple bond peak was present in the Raman
spectra for 1%, 0.5%, 0.1% samples. Spectral peaks present in the 0.05% sample were identical to peaks corresponding to the host, Tecoflex®, indicating that the detection limit for 4BCMU within the matrix was 0.1%.

Powder X-ray diffraction (XRD) was used to determine if the crystalline fingerprint of polydiacetylene could be detected within the Tecoflex® films. Figure 3.16 shows the spectra of 1% 4-BCMUp blended with Tecoflex® 60D, 100A, 93A and 85A. The large, broad peak at 20° corresponds to the amorphous nature of the host polymer; scans of Tecoflex® alone contained only these peaks. The intensity of the amorphous peak increased with the increasing polyurethane soft segment (85A being the softest).

An additional powder X-ray diffraction experiment was completed to determine what percentage 4-BCMUp was required to see part of the PDA crystalline fingerprint in a Tecoflex® blend. Powder XRD was completed on cast films of 60D blended with 0%,
1%, 5% and 10% 4-BCMUp by weight (Figure 3.17). The amorphous peak at 20° was present in all samples; however, the intensity of the peak decreased as the amount of PDA in the film increased. The largest peak from the 4-BCMU PDA fingerprint, at 7°, was present in the 10% sample. It is hypothesized that 10% may be a critical value for polydiacetylene surface aggregation within a Tecoflex® film.

![Powder X-ray diffraction spectra of 4-BCMUp in 60D Tecoflex® at varying weight percentages: (from top) 0%, 1% 5% and 10%.](image)

**Figure 3.17:** Powder X-ray diffraction spectra of 4-BCMUp in 60D Tecoflex® at varying weight percentages: (from top) 0%, 1% 5% and 10%.

### 3.8 – Homogeneity Analysis of 4-BCMUp Blend Films

The Tecoflex® typically took 6 to 12 hours to dissolve in the chloroform while stirring at room temperature but the BCMU dissolved in chloroform almost instantly. Therefore, the two compounds were dissolved separately before they were combined. Films that were cast from one initial solution were not as uniform as those cast from an initial two solutions.
A qualitative homogeneity analysis of Tecoflex®-blend-4-BCMUp was completed through visual inspection and optical microscopy (Figure 3.18). In photos of the films, small islands of PDA exist within a uniform blanket of pink color. However, higher magnification revealed large sections of PDA had aggregated. The Tecoflex® polymer is clear; therefore, it was reasonable to assume the red spots were due to the 4-BCMUp. The areas between the agglomerations were substantially colored, indicating that some of the 4-BCMU may have evenly dispersed into the matrix. The red spots of PDA became less evident as the soft segment increased within the Tecoflex® host.

Figure 3.18: Photographs (top) and photomicrographs (500X, bottom) of 1% 4-BCMUp Tecoflex® 60D, 100A, 93A and 85A blend films.

To determine the effect of hydrogen bonding as a dispersion agent, 4-BCMUp was blended at 1% with a polymer that contained no urethane groups, polymethylmethacrylate (PMMA). The PMMA-blend-4-BCMUp film showed distinct and extreme phase separation where sections of the film were completely clear and other section contained sharp red stripes (Figure 3.19). The polyurethane films were more homogeneous than the PMMA.
To confirm that the red agglomerates in the 60D Tecoflex® films were due to excess diacetylene, films containing 0.05%, 0.1%, 0.5%, 1%, 5% and 10% 4BCMUp were examined (Figure 3.20). Films that contained lower than 1% embedded 4BCMUp were uniform at 200X and higher magnification (not shown). Blend films containing 1% 4-BCMUp contained red PDA clusters, as before. Blends containing greater than 1% had a greater degree of phase segregation between the PDA and the Tecoflex® but the red spots were more uniformly distributed in the matrix.

Figure 3.19: Photographs of 4-BCMUp blend (a) 60D Tecoflex® and (b) polymethylmethacrylate.
Raman mapping of the substrate was used as a quantitative method for determining the homogeneity of the 60D-Blend-(1%)4-BCMUp. A grid of 1 cm x 1 cm blocks was constructed on the film substrate and a Raman scan was taken at the center of each block. It was hypothesized that the diacetylene peaks would occur at the same center positions, because only one batch of PDA was used to make the films and the processing was consistent. However, the carbon triple bond peaks occurred over a range of 1.37 center positions, 2110.84 cm\(-1\) to 2112.21 cm\(-1\), within the blend film (Figure 3.21, Table 3.7). The average wavenumber center position was calculated to be 2111.5 cm\(-1\) with a standard deviation of 0.335 cm\(-1\). Although the Raman is calibrated from several internal sources and externally by cyclohexane before every use, instrument error is still possible. A general error for the Renishaw Raman portable fiber-optic probe (spot size ~25\(\mu\)m) was reported at 0.5cm\(-1\) in the Renishaw instrument packet. It is possible that the host may be causing localized strain in the PDA but it did not seem to be consistent with film.

Figure 3.20: Photomicrographs (200X) of 0.05%, 0.1%, 0.5%, 1%, 5% and 10% 4-BCMUp Tecoflex® 60D blend films.
position. This is additionally unlikely because the carbon triple bond peak corresponding to a crystalline PDA sample showed position variation of ca. 1 cm⁻¹. With regard to the homogeneity of the PDA within the films, each scan of Tecoflex yielded a PDA peak, indicating that there was an even dispersion but that the carbon triple bond center position was variable within 1.37 cm⁻¹, which may be due to instrumental drift.

![Graph of carbon triple bond center position](image)

**Figure 3.21:** A graph of the carbon triple bond center position of PDA as analyzed from individual scans taken at the center of each numbered box on the 60D-blend-(1%)4-BCMUp.

**Table 3.7:** Statistical Analysis of Raman Data for 60D-blend-(1%)4-BCMUp.

<table>
<thead>
<tr>
<th>Statistics</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>2110.84</td>
</tr>
<tr>
<td>Maximum</td>
<td>2112.21</td>
</tr>
<tr>
<td>Range</td>
<td>1.37</td>
</tr>
<tr>
<td>Average</td>
<td>2111.5</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.335</td>
</tr>
</tbody>
</table>

### 3.9 – Analysis of BCMUₘ Blend Films

The addition of the colorless 3- or 4-BCMU monomer solution to the Tecoflex® solution did not change the properties anymore than the addition of pure solvent. 4-BCMUₘ was clear upon casting and turned blue with exposure to UV light in all
durometers of Tecoflex®. 3-BCMUm blends created a clear cast film of 60D that did not polymerized with UV exposure. These systems are discussed below in detail with a complete technical characterization of their colorimetric properties. Additionally, the strain sensitive properties of 4-BCMUm are discussed with respect to blend casting in 60D Tecoflex® films.

Tecoflex®-blend-4-BCMUm films were created by solution blending diacetylene monomer with the polyurethane, solution casting and polymerizing with UV light. Figure 3.22 represents Raman scans of a 60D-blend-4-BCMUm solution cast film before and after polymerization. The monomer embedded film has a carbon triple bond peak at 2250 cm\(^{-1}\), which corresponds to the value of the monomer in solution prior to casting. The polymerized film spectrum contains a carbon triple bond peak at 2085 cm\(^{-1}\), corresponding to 4-BCMUp in the planar blue state. The polymerized film also contained a portion of DA monomer as can be seen by the small peak at 2250 cm\(^{-1}\).
Tecoflex® 60D films that contained 1% and 5% 4-BCMUm did not polymerize when exposed to UV light. 60D films that contained loading percentages of 10%, 15%, 20%, 25%, 30% and 38.8% 4-BCMUm would polymerize when exposed to UV light. Each of these films contained a secondary film layer on top of the Tecoflex® that is hypothesized to be crystallized diacetylene monomer. The Raman spectra for the polymerized films each contained a carbon triple bond peak at ca. 2085 cm⁻¹. However, the monomer peak at 2250 cm⁻¹ increased in intensity with the increasing concentration of DA loading. Peak values obtained in the 60D-blend-(38.8%)4-BCMUm were consistent for all Tecoflex® durometers.

Cast films of Tecoflex® 60D blended with 3-BCMUm at 15% and 20% did not polymerize when exposed to UV light. Raman scans of the films show a carbon triple bond peak corresponding to the diacetylene monomer at 2250 cm⁻¹ (Figure 3.23). The

---

**Figure 3.22**: Raman spectra of 15% 4-BCMUm in 60D Tecoflex® as monomer (black, dash) and as polymerized using 254 nm light (blue, solid).
spectra taken before and after exposure to UV light looked identical, indicating that none of the embedded monomer had polymerized. The 3-BCMUm cast films did not produce a crystalline diacetylene layer on top of the Tecoflex®. The inability of the 3-BCMUm to aggregate to the surface of the Tecoflex® is believed to be the primary reason that polymerization did not occur within these systems.

Figure 3.23: Raman spectra of 3-BCMUm in 60D Tecoflex® at 20% after exposure to UV light.

3.10 – Image Analysis of 4-BCMUm Blend Films

The as cast 60D-blend-(38.8%)4-BCMUm film was clear with a red hue (Figure 3.24). Additionally, scale-like crystalline structure could be seen on the top side of the film. After exposure to 254 nm UV light the films instantly became blue with darker blue spots. Under polarized light, PDA crystalline domains were observed.
It was hypothesized that a portion of the embedded 4-BCMUm had aggregated to the surface of the film during solution casting creating a pure 4-BCMUm top layer. This top layer was essential to polymerization; the monomers still trapped within the film were unable to polymerize. As stated previously, films that contained 1% and 5% 4-BCMUm were unable to polymerize perhaps because they did not contain enough diacetylene for surface aggregation to occur. Films containing 10% or greater 4-BCMUm blends with 60D Tecoflex® all polymerized when exposed to UV light. Surface aggregation did not occur at any loading percentage with respect to 3-BCMUm. It is hypothesized that 3BCMUm is more soluble in the Tecoflex® host than the 4-BCMUm.

Before polymerization, one section of the 4-BCMUm blend films was washed with water and dried with a paper towel, another was rinsed with acetone. The film washed with water and dried retained the polymerization properties of the untreated film. However, the film that was washed with acetone did not polymerize. Raman spectra of the acetone treated film yielded an acetylene peak center position correlating to the diacetylene monomer, indicating that diacetylene monomer was present within the film.

**Figure 3.24:** Photographs of 38.8% 4-BCMUm-blend-60D Tecoflex® (a) as cast, (b) polymerized with UV light and (c) as polymerized under polarized light to reveal PDA crystalline domains.
but incapable of polymerizing. The polymerized 4-BCM in crystalline layer could also be removed by scraping with a razor blade but a light force would not remove it.

The crystalline domains appeared to be the same size under polarized light regardless of the percentage 4-BCM in the film. Under high magnification, it was revealed that although the crystalline domains were the same relative size, the crystallites within the domains varied with concentration of PDA (Figure 3.25). As the percentage of 4-BCM to 60D increased, the crystallites within the top layer grew smaller. Long, needle shaped crystals were present in the 10% samples and a clear change in direction was seen at the grain boundaries. Smaller crystals were seen in the 25% samples that were more circular. It was more difficult to detect the grain boundaries in the 25% sample because a crystallite direction change could not be seen; however, the boundaries were still apparent. In 15% and higher percentage a crystal was seen at the intersection of several grains.

**Figure 3.25**: Photomicrographs of 4-BCM in 60D Tecoflex® at 10%, 15% & 25%; magnifications 200X & 500X.
The crystalline domains of the 4-BCMUm polymerized top layer did not change with respect to host polymer durometer. Films cast of 38.8% 4BCMUm in 60D, 100A, 93A and 85A Tecoflex® contained the same approximate number and size of crystalline domains. At high magnification (Figure 3.26) the approximate grain size is compared from the hardest durometer host (60D) to the softest (85A).

![Figure 3.26: Photomicrographs of 38.8% 4BCMUm in Tecoflex® 60D and 85A at 100X and 85A at 200X.](image)

### 3.11 – Thermochromic Transition of Tecoflex®-blend-PDAs

It was hypothesized that the 60D-blend-4-BCMUm would mimic the thermochromic transition of the PDA in the crystalline state. The 60D-blend-4BCMUm films turns from white to blue upon exposure to ultraviolet light indicating polymerization has occurred. Heating to temperatures above 75°C caused a transition from blue to red within the blend (Figure 3.27). The full thermochromic transition took two minutes in this system as compared to less than 30 seconds in the crystalline form. The time difference was most likely due to the difference in thermal conductivity of the Tecoflex® as compared to the Teflon® sheet. The transition began at the outside of the film instantly as it was exposed to the heat source (a), after one minute the red color had progressed half way into the center of the film (b) and after two minutes the film was
completely red (c). The transparency of the film also changed with exposure to heat; the blue form was opaque while the red form was clear. The difference in transparency is believed to be due to the melting of the crystalline PDA top layer, facilitating diffusion into the host polymer.

![Photographs of 30% 4-BCMUm in 60D as polymerized by UV (a, blue) and after exposure to 75°C for one minute (b, red with blue center) and two minutes (c, red).](image)

**Figure 3.27:** Photographs of 30% 4-BCMUm in 60D as polymerized by UV (a, blue) and after exposure to 75°C for one minute (b, red with blue center) and two minutes (c, red).

The blue to red thermal transition within the 60D-blend-4-BCMUm was monitored quantitatively by Raman spectroscopy (**Figure 3.28**). In agreement with the crystalline thermochromic data, the blue, as-polymerized form generated a carbon triple bond peak center at 2085.78 cm\(^{-1}\); the red, thermally stressed peak occurred at 2107 cm\(^{-1}\). It was expected that the thermal transitions between crystalline PDA and the PDA top-layer formed on Tecoflex® would be very similar; the hydrogen-bonding interaction between the monolayer and the host was not expected to affect the properties of the PDA.
A blue to red transition could not be seen in 60D-blend-(1%)4-BCMUp system because the film was in the “red form” as solution cast. However, exposure to high temperatures did provide enlightenment on the decomposition of the 4-BCMUp within the Tecoflex® matrix (Figure 3.29). At room temperature, 25°C, the film was red and contained a Raman carbon triple bond peak center of ca. 2111 cm$^{-1}$. When exposed to 150°C for two hours, the film turned bright yellow with red spots. At 200°C for two hours, the entire film transformed to a deep red, then finally turned completely black when exposed to 250°C for two hours. Although several Raman scans were attempted on samples 150°C-250°C, no conclusive data could be collected. The carbon triple bond peak within the 150°C and 200°C sample was most likely obscured by localized fluorescence which occurred from 1400-1800 cm$^{-1}$ and 1900-2300 cm$^{-1}$.

Figure 3.28: Normalized Raman spectra of 30% 4-BCMUm in 60D as polymerized by UV (blue, solid) and after exposure to 75°C for two minutes (red, dash).
3.12 – Tecoflex®-blend-PDA Response to Tensile Strain

Raman spectroscopy has been widely used for the determination of molecular deformation and orientation within natural and synthetic polymers. Essentially, there occurs a change in Raman frequency of specific peaks corresponding to the polymer under a state of stress. It was established for a single aramid fiber that the change in wavenumber was a result of the chain stretching and directly related to the whole stress (or uniform stress) on the system.\(^8^3\) Additionally, wool showed a maximum intensity shift to lower wavenumbers upon external deformation; however, the rate of this shift was found to be inconsistent.\(^8^3\) The theory of Raman shifts applied to polydiacetylene single crystals was first researched by Mitra \textit{et al.}\(^7^4\) The PDA crystal was found to shift \(~20\text{cm}^{-1}\) with applied strain regardless of the side groups attached to the polymer backbone.\(^7^4\) The previous three results had all been theorized by analysis based on force constants of bonds within ideal polymer chains and Badger’s rule.\(^8^3\) Badger’s rule (\textbf{Equation 3.3}), simplified, relates a force constant \((k_c)\) to stretching a bond \(X-Y\) to its equilibrium length \((R_c)\).\(^8^4\) Several years of optimization to the equation provided the addition of the

\[ k_c \propto \frac{1}{R_c^2} \]
universal constant $A$ and parameter $B$ that correspond to the positions of $X$ and $Y$ on the periodic table.\textsuperscript{85}

**Equation 3.3:** Badger’s Rule Relates a Force Constant to a Bond X-Y Equilibrium Length.

$$k_c = A(R_e - B)^{-3}$$

Although Badger’s rule focuses on diatomic species, it provides insight into the direct relationship between an applied force and the atomic distance between atoms in a molecule. The shift of the carbon triple bond peak to lower wavenumbers is caused by an increase in conjugation in the polydiacetylene system. However, the applied force is responsible to bringing the atoms to an optimum distance for the added conjugation to occur. Thus, the shift in wavenumber is consistent with the calculated atomic distance of the polydiacetylene chain as induced by tensile strain.\textsuperscript{86} However, the shift of the Raman peak for all systems, including PDAs, is only proportional to the applied strain for elastic region of the deformation.\textsuperscript{83}

In addition to PDA single crystal strain studies, copolymerized PDA-polyurethane and PDA-polyesters have shown a smaller degree of strain sensitivity.\textsuperscript{26,27,30} Copolydiacetylenes have shown Raman wavenumber shifts ranging from $\Delta 4$ cm$^{-1}$ to $\Delta 6$ cm$^{-1}$. It was hypothesized that 60D-blend-(1%)4-BCMUp films would show strain sensitivity approximately in the same range as the copolymerized samples.

Tecoflex® 60D-blend-(1%)4-BCMUp was analyzed for strain sensitivity using simultaneous Raman spectroscopy and tensile drawing. As opposed to previous studies\textsuperscript{26,27,30}, a portable Renishaw Raman fiber optic laser was brought to an industrial sized Instron tensile tester and conditions according to ASTM D-822\textsuperscript{67} (“Tensile Testing
of Thin Films”) were followed. In order to account for the upward drawing motion of the tensile tester, the Raman laser probe was place on a lab jack and raised along with the extension (Figure 3.30). Ideally, the same spot would be scanned every time to minimize the error cause by the distribution of Raman points over the substrate. To combat this potential error, a small box was drawn in the center of the substrate and each Raman scan was taken from the center of the box.

Ten thin films were subjected to various strain percentages between 0% and 300% as determined by the extension of the Tecoflex® film. A generalized procedure for the generation of one data point began with the movement of the crosshead to generate sample strain. The crosshead was stopped at the desired strain percentage, the Raman laser probe was focused in the sample box and a 30 s Raman scan was collected. The crosshead was then moved to the next desired strain point and the process was repeated.

Figure 3.30: Time lapse photography of simultaneous tensile testing and Raman spectroscopy at (a) 0% strain, (b) 100% strain and (c) 200% strain.

Ten thin films were subjected to various strain percentages between 0% and 300% as determined by the extension of the Tecoflex® film. A generalized procedure for the generation of one data point began with the movement of the crosshead to generate sample strain. The crosshead was stopped at the desired strain percentage, the Raman laser probe was focused in the sample box and a 30 s Raman scan was collected. The crosshead was then moved to the next desired strain point and the process was repeated.
The data collected for ten 60D-blend-4-BCMUp samples can be found in Figure 3.31a, where points are displayed as strain percentage (defined as the change in length divided by the initial length) versus the Raman wavenumber corresponding to the carbon triple bond center position of the PDA. The largest shift was seen in sample two, where an overall wavenumber shift of 3.19 cm⁻¹ was reported. Figure 3.31b is a representation of the same data; however, the minimum and maximum shifts have been used to create error bars and the center line represents the average for all data collected at that strain level. The large error within these results was thought to be caused by the variation of carbon triple bond center position across the surface of the film (demonstrated in the film homogeneity study), the inability to focus on exactly the same PDA grouping within the film for every Raman scan and the relaxation that occurred within the sample during the 30 second Raman scan. Due to the large variability in the measurement of strain percentage versus Raman wavenumber, a trend-line could not be fit to the data; however, each sample does represent a linear trend as the peak shifted to a lower wavenumber.
The wavenumber shifts for the 60D-blend-4-BCMUp samples were not within the range of the 4-6 cm\(^{-1}\) as documented for the copolymer systems. However, a shift toward
a more conjugated state was evident with an applied force. It was hypothesized that an applied force on a hydrogen-bonded blend system could have a smaller effect than a covalently bonded copolymerized system because hydrogen bonding is a weaker interaction than covalent bonding. At a specific force, it would be more likely for the hydrogen bonding interaction between the PDA and the host to fail rather than strain the PDA to high levels. This same theory can be applied to why both the blend and copolymer systems would have less of a Raman shift with applied force than a single crystal of PDA with directly applied force. A force applied to an embedded PDA through a host material, attached by hydrogen or covalent bonding, would be less than the force applied directly to a single crystal of PDA.

The moderate strain sensitivity achieved for the 60D-blend-4-BCMUp system was not observed with any of the other blend systems. The 60D-blend-3-BCMUp film did not show a shift in wavenumber with up to 275% applied strain. It was hypothesized that the difference in Tecoflex® solubility between 3-BCMUp and 4-BCMUp was responsible for the difference in strain sensitivity. The increased polymer/polymer solubility may have allowed the polyurethane molecules to move by the polydiacetylene without imposing any additional strain. Simultaneous tensile drawing and Raman spectroscopy did not yield a shift to lower wavenumbers with 60D-blend-(15%)4-BCMUm as polymerized or after exposure to heat. The lack of tensile strain impact on the PDA top-layer indicated that the interaction between the top-layer and host was not strong enough to withstand a tensile force.
3.13 – Tecoflex-blend-4BCMUm Response to Sudden Impact

Although the 60D-blend-4-BCMUm polymerized film did not show any sensitivity to tensile strain, a blue to red transition was apparent with sudden impact. This specific mechanochromic transition first became apparent within the 4-BCMUm blend films when the samples were hit with a hammer, clamped into a vice or typed on with an old-fashioned type-writer. The idea of shear-induced mechanochromism had previously been proven by Burns et al.\textsuperscript{22} Ordered diacetylene monolayers of N-(2-ethanol)-10,12-pentacosadinamide were constructed on a hydrophilic SiO\textsubscript{2} substrate via a LB trough and polymerized by UV light. The sample was exposed to shear stress using an Atomic Force Microscope (AFM) and conversion from the blue to red form was confirmed by fluorescence microscopy.\textsuperscript{22}

To obtain a reproducible form of sudden impact, or shear stress, a dart drop instrument was constructed from a copper pipe, an end-nut on a long screw (impact area ca. 0.12 inch) and additional nuts for added weight. Holes were drilled at inch intervals along the copper pipe so that drop heights could be reproduced. Initial sample data was collected by dropping a 99.26 g dart from heights ranging from 3.75 inches (9.525 cm) to 20.75 inches (52.705 cm). The end of the pipe was place 0.75 inches above the metal sample stage. Five drops were completed at each height on sections of 20% 4-BCMUm PDA in 60D Tecoflex® film. Darts were dropped from 20.75 in, 18.75 in, 16.75 in, 14.75 in, 12.75 in, 10.75 in, 8.75 in, 6.75 in and 4.75 in.

A Raman Response percentage (RR, \textbf{Equation 3.1}) for the center of each impact area was calculated by dividing the height of the carbon triple bond “red” peak by the sum of the heights of the “blue” and “red” peaks as determined by Gaussian/Lorenz
statistical analysis of Raman spectra (Figure 3.32). The largest overall RR, accounting for standard deviation, was caused by the drop from 20.75 inches. The RR percentage grew smaller as the dart was dropped from lower heights. No Raman Response was present in samples where the dart was dropped from 6.75 inches or less.

Figure 3.32: Comparative graph of Raman Response for a 20% 4-BCMUm 60D blend as a dart, weighting 99.26g, was dropped from heights ranging from 4.75in to 20.75in.

The kinetic energy of the dart and therefore the force with which the dart hits the sample will increase with increased drop distance according to the work-energy principle (Equation 3.4, Table 3.9). As the dart moves from rest its gravitational potential energy was converted to kinetic energy, providing a specific force at the moment of impact.


\[ Work_{net} = KE_{final} - KE_{initial} = \frac{1}{2} mv_{final}^2 - \frac{1}{2} mv_{initial}^2 \]
Table 3.8: Conversion of Dart Drop Distance and Mass to Kinetic Energy.

<table>
<thead>
<tr>
<th>Sample Distance (m)</th>
<th>Kinetic Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.527</td>
<td>0.513</td>
</tr>
<tr>
<td>0.476</td>
<td>0.463</td>
</tr>
<tr>
<td>0.425</td>
<td>0.413</td>
</tr>
<tr>
<td>0.375</td>
<td>0.365</td>
</tr>
<tr>
<td>0.324</td>
<td>0.315</td>
</tr>
<tr>
<td>0.273</td>
<td>0.266</td>
</tr>
<tr>
<td>0.222</td>
<td>0.216</td>
</tr>
<tr>
<td>0.171</td>
<td>0.166</td>
</tr>
<tr>
<td>0.121</td>
<td>0.118</td>
</tr>
</tbody>
</table>

A large deviation in Raman Response for each drop height was caused by the variation in conversion to red polymer over the impact area. With no magnification a small red area, approximately 1mm in diameter was seen where the dart impacted the sample. However, under 100X magnification (Figure 3.33) an amazing display of red and blue could be seen. At this magnification, the sample diameter was determined to be 1.2 mm in the longest dimension but the impact area was not circular. The impact area matched the side of the dart end nut, slightly off center, where a flat circular area connected to the rounded nut edge; therefore, it is hypothesized that this was the actual area on the dart that came in contact with the sample.
Due to the wide variation of Raman Response caused by the impact test, an array of Raman spectra was taken over the affected area. The center of impact was determined by the spectra that yielded the largest colorimetric response. From the impact center, Raman scans were taken every 0.05 mm to the right and left, to a final distance of 0.6 mm in each direction. This line of sample collection was completed at 0.1 mm, 0.2 mm and 0.3 mm above and below the center of impact. An example of Raman spectra taken on one side of the center impact can be seen in Figure 3.34a. An example of the statistical peak deconvolution used to determine Raman Response at the impact center can be seen in Figure 3.34b.

Figure 3.33: Photomicrograph of impact area on a sample from height of 20.75 cm with a weight of 99.26 g on a 20% 4-BCMUm blend with 60D Tecoflex®.
Figure 3.34: (a) Overlay of Raman spectra taken from the impact area at 0mm, 0.15mm, 0.35mm & 0.55mm to yield a Raman Response of 0%, 13%, 29% & 39%, respectively and (b) graph of statistical deconvolution of the Raman carbon triple bond peak at the center of impact to yield a 38.8% RR.

Each Raman spectrum was analyzed, the red and blue peaks deconvoluted and their respective heights were entered into the Raman Response equation to yield a RR% for each spectrum. The RR% was converted into a three dimensional value by assigning the X and Y coordinates to the position away from the impact center where the scan was taken. For example, the impact center coordinates were (0, 0, RR%) where as 0.1 mm above the center and 0.05 mm left would have coordinates of (0.1, -0.05, RR%). By
plotting the Raman Response with respect to the position coordinates, a graphical representation of the impact area was created (Figure 3.35). The impact area directly correlates to the photomicrograph in Figure 3.33. Variations in Raman Response were present as close as 0.05 mm to one another; however, the same general shape as determined by the photo can be seen in the graph.
Figure 3.35: A 3-D graph of Raman Response from a 20% 4-BCMUm PDA Tecoflex® 60D sample after an impact force of 3,709 N caused by a drop of 99.26 g from 20.75 inches.
The Raman Response equation has never been used to analyze the impact area of a PDA before this work. There was no current method to compare the heights of the Raman acetylene peaks corresponding to the red form of the PDA from one sample to another. The heights, or intensities, as reported by Raman spectroscopy are not consistent from one scan to another; however, the ratio of one peak to another within a scan remains constant.

3.14 – Conclusion

Polydiacetylenes, specifically 3- and 4-BCMU, have been blended into a medical grade polyurethane, Tecoflex®. These compound have been incorporated into 60D Tecoflex® as a monomer (3-BCMUm & 4-BCMUm) and polymer (3-BCMUp & 4-BCMUp) at several percentages. The 3-BCMUp was blue upon solution casting in 60D with a corresponding Raman peak at 2085 cm\(^{-1}\) and the thermochromic transition was completely reversible. The 3-BCMUm incorporated with 60D did not polymerize with exposure to UV light; however, the presence of the monomer was confirmed by the 2250 cm\(^{-1}\) carbon triple bond peak in the Raman spectra. Incorporation of 4-BCMUp into all durometers of Tecoflex® resulted in red films with a Raman peak at ca. 2111 cm\(^{-1}\). Thin films of 60D-blend-(1%)4-BCMUp showed a shift of the carbon triple bond Raman peak to lower wavenumbers with induced tensile strain. The as cast 60D-blend-4-BCMUm film was clear with a white crystalline top layer, showing a Raman peak at 2250 cm\(^{-1}\) corresponding to the 4-BCMU monomer. Upon polymerization, the PDA crystalline top layer turned blue generating a Raman peak at 2085 cm\(^{-1}\). A sensitivity of sudden impact was mapped through a newly developed Raman Response equation to generate a three
dimensional graph of sample impact area. The Raman Response equation is the first method proposed for relating the Raman heights of the PDA acetylene peak corresponding to the red form from one Raman scan to another. The Raman Response equation will be of great use to the scientific community with regards to PDA research because there was previously no method for comparing data of this kind.
CHAPTER 4
PCDA BLEND WITH PLA

4.1 – Introduction to DA polymerization within a matrix

A common diacetylene (pentacosadiynoic acid, PCDA), has been combined with polylactic acid (PLA) to create a temperature sensitive material. The system was prepared by blending PCDA into a PLA solution, then processing into cast films and electrospun fibers. Post polymerization of the diacetylene revealed the successful alignment and miscibility of the monomers within the polylactic acid. Ultra-violet photolithography enabled the formation of macro and micro images within the blend. The thermochromic polydiacetylene (PDA) images were characterized by absorbance and Raman spectroscopy.

Molecularly-assembled small molecules that contain polymerizable units allow, in some cases, in-situ reactions creating polymers with chromogenic functions. In this regard, diacetylene monomers may be polymerized within polymer matrices to produce embedded supramolecules capable of a blue to red transition upon environmental stimuli. It is hypothesized that blending 10,12-pentacosadiynoic acid into polylactic acid at low loading percentages will allow for additional functionality of the host material.

Recently, several diacetylene monomers have been successfully incorporated into host polymer systems and polymerized after processing. Electrospun PEO and PMMA fibers have been prepared with embedded PCDA molecules that were polymerized with ultraviolet light, PDA/silica nanoparticles were prepared in solution and organized to allow subsequent polymerization and PCDA-NHS molecules have been dispersed and
polymerized within PVA films. More detailed information on the polymerization of diacetylene within matrices can be found in the introduction of this dissertation.

For solid state polymerization of DA monomers to occur, a translation distance of ca. 5 angstroms and a 45° stacking angle is required. The packing of diacetylene molecules in most crystalline systems does not meet these criteria; therefore, they do not polymerize. In order for the diacetylene molecules to remain ordered within the PLA host, a small level of phase segregation must occur. When polymerized under the aforementioned conditions most PDAs exhibit a brilliant blue color with a maximum absorbance at ca. 640 nm. A color shift from blue to red (ca. 550 nm) is observed when the PDA is exposed a specific set of environmental perturbations.

Embedded PDAs have the ability to create functional images through ultra-violet photolithography. Photo-masking host films and polymerizing embedded DAs has created the ability to draw shapes on a macro and micro level that are capable of the chromatic transitions observed in crystalline PDAs. Electrospun fibers containing PMMA embedded with diacetylenes produced polydiacetylene stripes when polymerized through a photomask. DA/silica nanocomposite films yielded a bird shape by polymerizing through a mask using 254 nm light.

4.2 – Polylactic Acid as a Host Matrix

Polylactic acid is an ideal matrix because it is derived from the fermentation of corn starch and other starch like products such as maize, sugar or wheat. The increasing cost of fuel has created urgency for the implementation of renewable resource materials. In this regard, PLA is currently in small-scale production for biomedical sutures and
scaffolds, grocery bags, disposable cups and food packaging. The use of a PLA/PDA blend in these applications could provide an instant color change at a critical temperature.

Polymerization of properly aligned diacetylene monomers with polylactide films has generated brilliant blue polydiacetylene within the clear host matrix. Furthermore, the PDA shifts from blue to red with increased temperature over 60°C. The colorimetric transition and resulting state of the polydiacetylene backbone was extensively monitored with Raman and UV/Vis spectroscopy. In Raman, the carbon triple bond was tracked as it shifted from the planar state (2085 cm\(^{-1}\)) to a non-planar state (2115 cm\(^{-1}\)). Colorimetric response as detected by UV/Vis (CR, Equation 1.2) was used to quantitatively monitor the percentage of blue PDA in the film. As stated in the introduction, percent blue is defined as the absorbance at 550 nm divided by the sum of the absorbance at 550 nm and 640 nm; colorimetric response is the original minus the final percent blue divided by the original percent blue.

4.3 – Diacetylene Polymerization within Polylactic Acid

The carboxylic acid terminated 10,12-pentacosadiynoic acid (Figure 4.1) was combined with polylactic acid in solution (chloroform) at varying weight percentages. The blend solutions were processed into solution cast films by regulated evaporation or electrospun into fibers. Organized diacetylene regions within the thin films and nonwoven mats were polymerized using short wave ultra-violet radiation (254nm) to create embedded polydiacetylene molecules.
Thin films (ca. 200 μm thick) were successfully created using solution casting and slow evaporation. Films containing 0%, 0.5% and 1% by weight diacetylene to PLA were consistent with host polymer properties, with respect to transparency and flexibility, while having the additional chromatic properties of the polydiacetylene. The thin film casting properties of PLA were not retained in blends that contained 5%, 10% 15% and 20% diacetylene.

Electrospinning of PLA control of PLA embedded with 1% and 5% PCDA produced nonwoven mats containing porous fibers. Fibers were spun from viscous chloroform solutions and turned blue upon polymerized with UV light. Both the control and blend fibers contained pores due to the low boiling point of the chloroform. Little difference was observed between control and blend fibers (1% and 5% PCDA to PLA) on images obtained by a scanning electron microscope (2,000X).

Diacetylene polymerization was visually monitored by the blue color and quantitatively tracked through UV/Vis and Raman spectroscopy. The Raman spectrum in Figure 4.2 represents the planar polydiacetylene backbone with the carbon double bond functionality appearing at 1451 cm⁻¹ and the carbon triple bond at 2077 cm⁻¹. The multiplet of peaks that appear between 1000 cm⁻¹ and 1400 cm⁻¹ are attributed to the carboxylic acid (typically ranging from 1000-1300 cm⁻¹), -CH₂ bend (1465 cm⁻¹) and –CH₃ bend (1450 cm⁻¹, 1375 cm⁻¹). The single peak at approximately 875 cm⁻¹ has been
attributed to the C-H out-of-plane bend (650-1000 cm\(^{-1}\)).\(^{42}\) The high intensity of the PDA peaks masked any signal from the PLA matrix.

![Raman spectra of 10,12-pentacosadiynoic acid as polymerized within a polylactic acid.](image)

**Figure 4.2:** Raman spectra of 10,12- pentacosadiynoic acid as polymerized within a polylactic acid.

The extent of polymerization of the PCDA within the PLA matrix was monitored by UV/Vis. The increasing absorbance of the 640 nm peak corresponds to an increase in the degree of polymerization of the PCDA within the film. It was observed that the degree of polymerization (as measured by UV/Vis) was proportional to irradiation time for the first five minutes within 0.5% and 1% blend films. After five minutes, additional sporadic polymerization was achieved at a slower rate. Sample data from 30 seconds to 30 minutes was obtained for the 0.5% blend film (**Figure 4.3**); however, sample data above five minutes for the 1% sample (**Figure 4.4**) was omitted because several data points were above the detection limit of the instrument. An identical trend was observed prior to five minutes for both the 0.5% and 1% blend samples.
Figure 4.3: 0.5% PCDA in PLA; overlay graph of UV/Vis spectra with increasing absorbance at 640nm with respect to time of 254nm exposure of the PCDA-PLA blend film (top) and a plot of time exposed (254 nm) versus absorbance at 640 nm (bottom).
Figure 4.4: 1% PCDA in PLA; overlay graph of UV/Vis spectra with increasing absorbance at 640nm with respect to time of 254nm exposure of the PCDA-PLA blend film (top) and a plot of time exposed (254 nm) versus absorbance at 640 nm (bottom).
Normalization of the 0.5% and 1% film UV/Vis data at 640nm for times up to 300 seconds allowed for the calculation of a linear trend-line. The normalized absorbance value of the polydiacetylene in the film was equal to the 0.0036 times the seconds of UV radiation applied (Figure 4.5, Equation 4.1). The trend-line has the best fit to the 1% data with a correlation value of 96.35%; a correlation factor of 93.94% was determined for the 0.5% data.

![Graph representing the linear trend between exposure time of UV light (x) to normalized absorbance at 640 nm as determined by UV/Vis (y).](image)

**Figure 4.5:** A graph representing the linear trend between exposure time of UV light (x) to normalized absorbance at 640 nm as determined by UV/Vis (y).

**Equation 4.1:** Linear Trend Relating Exposure Time of UV Light (x) to Normalized Absorbance at 640 nm as Determined by UV/Vis (y), graph below.*

\[ y = 0.0036x \]

*assuming a y-intercept of (0,0)

The polymerization of PCDA was monitored by powder X-ray diffraction for PLA-blend-(1%)PCDA as compared to PCDA alone (Figure 4.6). The crystallographic
fingerprint for the PCDA monomer and its conversion to polymer has been studied extensively.\textsuperscript{87,88,89} The samples were exposed to X-rays for a total of 80 minutes by eight successive ten minute scans. As the polymerization proceeded, the intensity of the peaks corresponding to the PCDA polymer grew. Although the peaks corresponding to the PCDA polymer were more intense in the crystalline PCDA sample, there was good agreement in peak location as compared to the PCDA polymerized within PLA.

![Figure 4.6: Powder X-ray diffraction spectra of 20% PCDA embedded with PLA as compared to crystalline PCDA after polymerization by X-ray for 80 minutes from 6° to 30° 2θ.](image)

A polymerization depth between 0.45 mm and 0.60 mm was determined for PCDA within the PLA matrix for five minutes of UV light exposure. Thin films of PLA containing 1% embedded PCDA were stacked on top of each other and encased in a paw-shaped mask. The UV light was able to penetrate into the fourth layer of film, each 0.15 mm thick, but caused no polymerization to occur within the fifth film. Film cross-sections of samples 1-3 revealed uniform polymerization throughout the film depth. An
increase in polymerization depth could be possible in a continuous sample because UV light would not be lost between the film interfaces. Film layers 1-5 as well as their respective absorbance spectra can be seen in Figure 4.7.

Figure 4.7: Polymerization depth for a 1% PCDA PLA blend when exposed to UV light for five minutes: photographs and UV/Vis spectra.

Thermogravimetric analysis of solution cast polylactic acid control and doped with one percent polymerized diacetylene revealed no significant difference in decomposition of volatile products (Figure 4.8). The samples contained 11% retained solvent after drying at room temperature for 72 hours which was removed by annealing
under vacuum at 110°C for four hours. The annealed films exhibited a five degree difference in decomposition temperatures ($T_d$), 323°C for the control and 328°C for the 1% blend.

![TGA graph of PLA control films (black) and blend films with 1% PDA (blue) before (dash) and after (solid) heat treatment.](image)

**Figure 4.8:** TGA graph of PLA control films (black) and blend films with 1% PDA (blue) before (dash) and after (solid) heat treatment.

The glass transition ($T_g$) of PLA (59°C) appeared to shift to 56°C with the addition of 1% PDA to the system, as observed by differential scanning calorimetry (Figure 4.9). However, the 20% PDA/PLA blend revealed that the melting point of the PCDA (61°C) overlapped the glass transition of the PLA. Additionally, a crystallization peak was present at 43°C in the 20%PCDA in PLA sample corresponding to the crystallization of PCDA PDA. The addition of the polydiacetylene had a negligible on the glass transition temperature of the polylactic acid at a 1% loading. The 1% PCDA/PLA blend was found to be the most successful balance between structural integrity and efficient detection of the sensor.
4.4 – Response to Environmental Stimuli

Solution cast PLA films containing 1% PCDA polymerized by UV were heated to 70°C for ten seconds resulting in a colorimetric change from blue to red. The photomicrographs (Figure 4.10) show crystalline regions of the diacetylene polymer within polylactic acid.

Figure 4.9: DSC graph of PLA control and blends of 1, 5 and 20% by weight PDA after heat treatment.
The embedded PDAs were oriented into organized regions that allowed for solid state polymerization. These regions were not disrupted by the thermal transition, indicating that the change occurred within the polydiacetylene and is not a result of a change in interaction with the host. The thermochromic transition was quantitatively monitored by absorbance and Raman spectroscopy (Figure 4.11).

Figure 4.10: Photomicrographs of PLA blend with 1% PDA (a) as polymerized and (b) after exposure to 70°C for ten seconds.
Figure 4.11: Raman (top) and absorbance (bottom) spectra comparison between planar (blue) and thermally stressed (red) polydiacetylene within polylactic acid at 1% by weight.
In both data sets, there was a distinct shift in the resultant spectra as compared to the original state. The Raman peak that corresponds to the carbon triple bond shifted completely from 2087 cm\(^{-1}\) in the planar state to 2120 cm\(^{-1}\) in the stressed (out-of-plane) state, a shift of 33 wavenumbers. Additionally, 84% of the carbon double bond peak was documented at 1515 cm\(^{-1}\) while the remainder appeared at 1451 cm\(^{-1}\). The remaining 16% is believed to correspond to other functionalities within the molecule such as the –CH\(_2\) bend and the –CH\(_3\) bend, reported at approximately 1465 cm\(^{-1}\) and 1450 cm\(^{-1}\), respectively.\(^{42}\) All other peaks within the spectra remained constant before and after the thermal transition. There was a 100% CR (Colorimetric Response, Equation 1.2) within the UV/Vis spectra, as indicated by the appearance of the peak at 550 nm and the disappearance of the 640 nm peak on the absorbance spectra. The temperature induced color change from blue to red was found to be irreversible, as previous literature had indicated for crystalline PCDA.\(^{31,32,35}\)

In addition to UV/Vis and Raman, a shift in the powder X-ray diffraction data was observed after the polymer was exposed to high temperature. Figure 4.12 below shows the difference in crystal fingerprint for 20% PCDA within PLA as polymerized (blue) and after exposure to 70°C for 10 s (red).
The spectral change was composed of three parts, the shifting of existing peaks, the disappearance of PCDA “blue” peaks and the appearance of PCDA “red” peaks. The prominent peak at 23° shifted slightly to 22° and the peaks at 19° and 20° grew larger. The PCDA “blue” peaks at 25° and 10° disappeared but a PCDA “red” peak appeared at 16°. The significant changes apparent in the fingerprint of the PCDA from blue to red indicate a difference in molecular packing between the systems.

The solvato-chromic properties of the PCDA within PLA were limited by the solubility of the polylactic acid. Acetone, methylene chloride, chloroform and tetrahydrofuran dissolved the PLA film doped with 1% polymerized diacetylene and caused an immediate visual change from blue to red. Toluene and ethanol caused the PLA to swell and elicited a gradual PDA transition to purple, then to red in the embedded PDAs. There was no visual change in films that were submerged in water and hexanes.
4.5 – Photolithography through Selective Polymerization

A variety of patterns, both macro- and micro-scale were created in 1%PDA-PLA blend films through selective polymerization. The images were designed by placing light-blocking masks over diacetylene embedded films and exposing them to 254 nm light. A star micro-image was created by illuminating an array mask over a 1% blend films for 5 minutes. Stars with a diameter of ca. 700 μm (Figure 4.13) were successfully polymerized. Clear images with proper dimensions were isolated under magnification.

![Figure 4.13](image)

**Figure 4.13:** A photograph and photomicrograph of micro-scale imaging of 1% PCDA polymerized within PLA through an array mask.

The “Tiger Paw” image (Figure 4.14) was created by exploiting the thermochromic properties of the embedded polydiacetylenes. The 1% blend film was selectively polymerized by UV radiation through a paw-shaped mask for five minutes. The partially polymerized film was then heated to 70°C for ten seconds, turning the image red/orange in color. Immediately exposing the heat-treated film to UV exposure did not yield any additional polymerization. After approximately 72 hours, exposure to UV light for five minutes yielded a blue color surrounding the paw. It is hypothesized that the 72-hour window was necessary for realignment of the diacetylene monomers. The paw color difference between Figure 4.14b (appears red-orange) and 4.14c (appears...
red) is attributed to additional polymerization that occurred within the design region after the thermal transition.

![Figure 4.14: Photographs of macro-scale imaging of 1% PCDA in PLA (a) as polymerized through mask, (b) after exposure to 70°C for 10s and (c) after overall polymerization upon waiting 72 hours.](image)

The painting, “Chromatic Twist” (Herbert Bayer, 1970) was recreated using polymer blend technology and has been titled the “Thermo-Chromatic Twist” (Figure 4.15). The three-color image (including the use of white space) was created by altering the positions of two masks and imposing selective thermal stressing to the film.
10,12-pentacosadiynoic acid was successfully polymerized within a polylactic acid matrix. The diacetylene self-organization was enabled by similarities between the PCDA functionalities, specifically the carboxylic acid, and the PLA repeat unit. The addition of PCDA at one percent did not affect the film forming properties, glass transition or thermal decomposition of the PLA. Through the use of photolithography and exploitation of the polydiacetylene thermochromic properties, micro and macro functional images were prepared in 1% blend films. The polymerization of PCDA within PLA has resulted in a blend system with chromatic properties similar to crystalline PCDA and a specific sensitivity to temperatures over 70°C.

**Figure 4.15:** A photograph of the “Thermo-Chromatic Twist” as prepared by a 3-phase, selective polymerization of 1% PCDA in PLA and was modeled after the painting “Chromatic Twist” by Herbert Bayer from A Series of Eight Screenprints.
5.1 – Introduction to PCDA Liposomes and Alginate Fibers

Diacetylene monomers with hydrophilic R and hydrophobic R’ groups, such as 10,12-Pentacosadiynoic acid (PCDA), form liposomes in aqueous solutions with the aid of increased temperature and sonication (Figure 5.1). Polydiacetylene (PDA) liposomes dispersed in water share similar colorimetric transitions to solid state crystalline PDAs. The incorporation of a biological active moiety into these liposomes during sonication and subsequent DA polymerization has enabled a color shift to occur as an outside species interacts with the assay.

![Figure 5.1: Polymerization schematic of 10,12-pentacosadiynoic acid polydiacetylene liposomes.](image)

Polydiacetylenes containing modified lipids can serve as a source for selective recognition to an analyte of interest; as the analyte binds to the receptor, the vesicle changes color from blue to red. The bio-induced chromatic properties of PDAs have been developed for detection of the influenza virus, cholera toxin, E. coli, c-myc epitope, streptolysin O and even lipopolysaccharides. Tyrosine and tryptophan derivatives of
PCDA were capable of a colorimetric response when exposed to *E. coli, Pseudomonas aeruginosa, Salmonella minnesota*, and *Shigella flexneri*. Sialic acid derivatized PCDA was capable of detecting the influenza virus.

Interestingly, bacterial sensors do not have to contain DA functionality to be incorporated into the liposome. For example, dioctadecyl glyceryl ether-β-glucosides (DDG) has been incorporated into PDA liposomes and provided a colorimetric response after exposure to *E. coli*. Additionally, dimyristoylphosphatidylcholine (DMPC) was incorporated into PDA liposome and showed sensitivity to *Salmonella Bacillus Cereus* and K-12 strains of *E. coli*.

Most bio-chromatic liposomes have had success when used in solution or as monolayers. However, embedded liposomes have also proven effective in a few instances. Embedded PDA liposomes are advantageous over solution or monolayer PDA liposomes because they provide a tangible material that could be taken into a workspace or hazardous environment and provide detection on the spot. The embedded liposome is also more robust than previously mentioned materials, a solution vial could leak or break and an exposed monolayer could be accidentally removed. Liposomes composed of 10,12-tricosadiynoic acid (TCDA) and TCDA-DMPC showed sensitivity to salmonella and several strains of *E. coli* while embedded in an agar matrix. Additionally, PCDA liposomes were shown to be sensitive to α-cyclodextrin while embedded in a polyethylene glycol gel.

In the following work, PCDA liposomes were solution blended with sodium alginate then wet spun into calcium alginate fibers with embedded PDA liposomes. Alginate, a general term used to describe alginic acid and its related salts, is a natural
polymer extracted from the cell walls of brown algae. Alginic acid is chemically a copolysaccharide containing β-D-mannuronate (M) and α-L-guluronate (G), composed of GG, MM and GM segments (Figure 5.2).\(^{56}\)

![Figure 5.2: The chemical structure of alginic acid containing β-D-mannuronate (M) and α-L-guluronate (G) segments, showing the possible GG, GM and MM units within the polymer.](image)

Wet spinning of alginate fibers is based heavily upon the system’s unique gellation properties with respect to mono- and divalent cations. Fibers are created through extrusion of sodium alginate into a calcium chloride coagulation bath.\(^{58,69}\) The water soluble sodium alginate is converted into insoluble calcium alginate as the spinning dope is forced through a spinneret. As the alginate is exposed to calcium, junction zones appear where G segments are associated by the divalent cations, known as the egg-box model (Figure 5.3).\(^{59}\)

![Figure 5.3: Structure of the alginate egg-box model as proposed by Grant and Morris where calcium ions are surrounded by opposing GG segments within polymer chains.](image)

Calcium alginate fibers may be turned into nonwoven fabrics through the conventional textile processes of carding and needling.\(^{69}\) In carding, unordered fibers are
organized; needling joins the fibers together into a felt without the use of chemical agents.

One of the most critical applications for alginate nonwoven fabrics is wound dressings (Figure 5.4). The effectiveness of alginate dressings on exuding wounds is unparalleled. As the dressing absorbs the sodium containing secretions of the wound, it forms a gel and hydrates the wound through retention of exuded biological fluids. In addition, the sodium ions exchange for calcium ion within the dressing providing calcium to the wound which has been suggested to improve some cellular aspects of wound healing.

![Figure 5.4: Photographs of alginate ADAPTIC non-adhering dressing (left) and KALGINATE calcium alginate dressing (right).](image)

**5.2 – Discussion and Characterization of PCDA Liposome**

PCDA is soluble in common organic solvents; however, aqueous dispersions of ordered particles, in the form of liposomes, may be produced through sonication. Sonication is the process of using ultrasonic wave energy to fracture liquids through cavitation. Cavitation occurs when bubbles, formed in the liquid by the ultrasonic wave, become unstable and violently collapse. Sonication is especially useful in breaking
intermolecular bonds and dispersing solids into a liquid. Probe sonication was utilized to disperse PCDA molecules in an aqueous solution. Filtration through a 0.45 μm syringe filter separated dispersed particles from undesired aggregates.

Following a previous literature procedure\textsuperscript{36,37,38,97}, PCDA was evaporated from chloroform or THF to leave a thin film on a vial. The vial was then filled with water, heated to 75°C and probe sonicated for 15 minutes. The initially clear solution became opaque after sonication caused by the light scattering of aggregated particles. Further sonication did not yield a clear solution; however, filtration was successful in removing the larger aggregated particles. The dispersion was crystallized at 3°C for 12 hours and polymerized from above with UV light (Figure 5.5).

\textbf{Figure 5.5:} Time-lapse photographs showing the polymerization of a 2 mM PCDA liposome dispersion with UV light over five minutes (time in seconds).

The polymerized particles were analyzed for size distribution via dynamic light scattering (DLS) using a sub-micron particle analyzer. The 2 mM PCDA liposome dispersion was diluted with DI water (1:20) and scanned over a range of 5 to 1000 nm. The particle size analysis yielded two valid particle sizes within the dispersion (Figure 5.6). The largest particles were 144 ± 22 nm in diameter and represented 69.7% of the sample. It was believed that this size corresponded to the targeted liposome (duel layer
micelle) of the PCDA. The liposome was hypothesized to be the most stable dispersion of PCDA in water. It was thought that a small water droplet would be trapped in the center of the liposome, thereby increasing the stability of a molecular arrangement that contained a hydrophilic inner layer. The secondary particle size diameter was $46 \pm 6$ nm and represented 21% of the sample. These particles were approximately one third the size of the targeted particles and may represent a micelle (single layer) of the PCDA. The 9.3% of the sample that corresponded to a particle diameter of $3 \text{ nm} \pm 0.2 \text{ nm}$ was attributed to dust within the sample. Previously, DLS had been used to characterize PCDA liposomes containing 10-tetradecyloxymethyl-3,6,9,12-tetraoxahexacosyl-2-acetamido-2-deoxy-β-D-glucopyranoside (PB1124) to yield three size dispersions at 55-70 nm, 75-100 nm and 120-180 nm.99
The morphology of a PDA liposome is not necessarily round and the shape tends to vary with respect to composition. TEM analysis of a PCDA/Sialic acid liposome yielded a particle size of 50 nm. Okada et al. reported an ellipsoid of 130 nm in the long direction. Cheng et al. reported viewing “tubes and ribbons” via TEM of ten different amino-acid derivatized PCDA molecules upon heat and agitation. Bolaamphiphilic PDAs (containing a different polar group on either side chain) have been shown to be round or egg shaped between 150-200 nm. Round vesicles were documented by SEM at ca. 60 nm in a PCDA-NH$_2$ system. Round vesicles, diameter 150 nm, were also documented using TEM for molecules containing PCDA and 4,4-difluoro-5-(2-thienyl)-4-bora-3a,4a-diaza-s-indacene-3-dodecanoic acid (BO558).

<table>
<thead>
<tr>
<th>% Total Particles</th>
<th>Size (nm)</th>
<th>St. Dev. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3 %</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>21.0 %</td>
<td>45.6</td>
<td>6.3</td>
</tr>
<tr>
<td>69.7 %</td>
<td>144.1</td>
<td>21.5</td>
</tr>
</tbody>
</table>

Figure 5.6: Dynamic Light Scattering (PCS Submicron Particle Size Analyzer) graph from 2 mM polymerized PCDA liposome aqueous dispersion.
It was essential to determine the shape of the PCDA liposome because the diameters determined by DLS were formed under the assumption that the particles were spherical. The size and shape of the PCDA dispersion was determined by scanning electron microscopy (SEM) using a transmission electron microscope (TEM) attachment. At 70,000X magnification, both particles were found to be spherical in shape (Figure 5.7, 50 nm particles not shown). The particle diameters were confirmed by a computational measuring program as approximately 150 nm and 50 nm, respectively. The spherical shape and size of the 50 nm particles with respect to the larger particles confirmed the hypothesis of micelle formation. Particles of this size would not have been filtered out during the pre-crystallization 0.45 μm syringe filtration; therefore, their presence in the dispersion was possible.

Figure 5.7: Scanning Electron Microscope (4800) photograph showing a spherical PCDA liposome (ca. 150 nm), spherical micelles of PCDA (ca. 50 nm) were also observed (not shown).

The composition of the polymerized PCDA liposome dispersed in water was confirmed by Raman spectroscopy (Figure 5.8). Previous research had indicated the retention of the PCDA structure after exposure to probe sonication.\textsuperscript{105} The resulting Raman spectra confirmed the presence of a highly conjugated carbon triple bond peak at 2087.3 cm\textsuperscript{-1}. Spectral peaks within this region have been correlated to the blue, planar
state of the PDA backbone. The peak at 1450 cm$^{-1}$ corresponds to the carbon double bond stretching peak.

![Figure 5.8: Raman spectra of PCDA-PDA Liposome while dispersed in deionized water.](image)

PDAs are known to retain their thermochromic transitions from the solid state to aqueous dispersion via polymerized liposomes. To confirm that this system was equivalent to systems produced in the past, the liposome dispersion was exposed to heat and absorbance spectra was taken of each form (Figure 5.9). After exposure to 60°C, the dispersion turned bright red showing a maximum absorbance at 540 nm. The absorbance peak corresponding to the blue form of the PDA at 650 nm completely disappeared after thermal exposure indicating a full transition to the red form. Data produced was identical to data documented in previous papers; the blue form ranged from 620-640 nm and the red form between 490-540 nm. Su et al. specifically reported respective absorbance maxima at 640 nm and 540 nm.
5.3 – Solution Blending and Wet Spinning of Alginate

The extrusion of a mono-valent cation alginate solution (such as sodium alginate) into a divalent cation coagulation bath (calcium chloride) results in an ion exchange, thus alginate fiber formation. The calcium acts as a cross-linker between alginate polymer chains creating a fiber that is insoluble in water. Wet spinning is a bulk technique in which the polymer solution, known as “dope” is pushed through a spinneret into a coagulation bath where the polymer is separated from the solvent. Figure 5.10 contains a block diagram for the large scale wet spinning apparatus used in the alginate fiber production.

Figure 5.9: Schematic and respective absorbance spectra of PCDA-PDA liposome, dispersed in deionized water, as polymerized (blue, dash) and after exposure to heat (red, solid).
Small scale wet spinning of sodium alginate did not require the high viscosity needed for large scale wet spinning. To produce fibers on a small scale, the sodium alginate was dissolved at 2% to water. For control fibers, 9 mL of 2% alginate solution was combined with 2 mL of water, blended by magnetic stir bar, extruded through a syringe needle into a 15% calcium chloride bath and the fiber formed was then moved to a 3% CaCl$_2$ equilibration bath for 12 hours (Figure 5.11). The same procedure was followed to create the PCDA liposome embedded fibers except the 2 mL of water was replaced with 2 mL of 2 mM polymerized PCDA liposome dispersion, a loading percentage of 0.83% of PCDA to alginate by weight.

Figure 5.10: Block diagram of wet spinning apparatus.
The most effective fiber extrusion was completed with one continuous, even paced push of the syringe while keeping the tip of the needle moving back and forth under the surface of the calcium coagulation bath. It was also essential to use a clean needle as any debris in the needle prevented suitable fiber formation. The control fibers were white while the fibers that contained embedded liposomes were blue (Figure 5.12). Lower concentrations of PCDA resulted in fibers that appeared faint blue; however, it was difficult to distinguish these fibers from the control.

Figure 5.11: Schematic of the small scale alginate wet spinning apparatus.

Figure 5.12: A photograph of an alginate fiber containing PCDA liposome (left) and control (right) after drying from a small-scale spinning process.
The large scale wet spinning trial required a higher viscosity solution (5%) for proper fiber formation through the spinneret. Control spinning dope was prepared by dissolving 15 g sodium alginate in 300 mL of water. The blend spinning solution was prepared by adding the same amount of alginate used in the control (15 g) to 225 mL of water and then 75 mL of PCDA liposome dispersion was added. The solution was mixed for an additional hour to obtain a uniform dispersion of the liposomes in the alginate (Figure 5.13). It was difficult to remove all the bubbles formed during mixing; therefore, the solution was allowed to rest overnight. Additionally, the solution was allowed to rest for four hours after pouring into the pump chamber to allow bubbles to rise to the top of the solution. Samples were collected from the spin in 10-yarn bundles, bound together and placed into various calcium chloride equilibration baths.

In agreement with the small scale wet spinning experiment, the control alginate fibers were white and the fibers with embedded PCDA liposome were blue (Figure 5.14). Single fibers were not retained from the 10-yarn bundles because additional calcium crosslinking in the equilibration bath adhered the yarns to one another. However,
it is believed that single fibers could have been isolated by placing individual fibers into the equilibration baths.

![Image](image1.png)

**Figure 5.14:** Photograph of an alginate fiber containing PCDA liposome as wound during the large-scale spinning process.

The spinneret used in the large scale alginate wet spin contained 100 holes in a circular pattern (**Figure 5.15**). Under magnification, the diameters of twenty holes were measured, three times each, to determine a mean diameter. The mean diameter of the holes was measured to be 314 μm with a standard deviation of 5 μm (**Table 5.1**).

![Image](image2.png)

**Figure 5.15:** Photographs of the 100-hole round spinneret used in Alginate fiber wet spinning.
Table 5.1: Statistical Summary of Spinneret Hole Diameter.

<table>
<thead>
<tr>
<th>Mean Hole Diameter</th>
<th>314</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Deviation</td>
<td>5</td>
</tr>
<tr>
<td>Maximum</td>
<td>321</td>
</tr>
<tr>
<td>Minimum</td>
<td>307</td>
</tr>
</tbody>
</table>

5.4 – Characterization of Alginate Fibers

Alginate control fibers were compared to fibers with embedded PCDA liposomes to determine any effects that the embedded molecules had on the host. Thermogravimetric analysis (TGA) was used to determine if the alginate decomposition temperature was altered by the addition of small particles. The TGA curve contained the same pattern for the control and the doped fiber (Figure 5.16). An initial weight loss of 20% between 50°C and 200°C was correlated to a loss of water previously trapped in the fiber. The onset of thermal decomposition began at 200°C and tapers off at 315°C; the cessation of decomposition was at 400°C.
An attenuated total reflectance (ATR) infrared experiment was completed on the control and doped fibers to determine if the addition of PCDA had an effect on the basic alginate structure. The ATR spectra of the control and doped fibers were identical after normalization (Figure 5.17). It was not expected that peaks corresponding to the diacetylene backbone would be observed in this scan because carbon double and triple bond peaks are weak in IR. The ATR spectra showed bands at 3400 cm\(^{-1}\) (-OH stretch), 1600 cm\(^{-1}\) (COO\(^-\) asymmetric stretch) and 1425 cm\(^{-1}\) (COO\(^-\) symmetric stretch). The –OH band was most likely caused by the large amount of water retained in the fibers. The COO\(^-\) stretches correspond to the many carboxylic groups in the alginate. Although these groups are also present in the PCDA liposome, the percentage of liposome was too low to
cause a change within the ATR spectra. The ATR data collected for alginate corresponds to spectra previously collected for alginate fibers.\(^{110}\)

![FTIR-ATR spectra of Alginate control fiber (black, dash) and with PCDA Liposome (blue, solid).](image)

The Raman spectrum of alginate microspheres has been previously reported\(^{111}\); however, the Raman spectrum of PCDA liposomes within alginate fibers has never been documented (Figure 5.18). The alginate control fiber Raman spectra contains peaks according to: C=O (1670-1640 cm\(^{-1}\)), ethers (1300-1000 cm\(^{-1}\)), -CH\(_2\) bend (1465 cm\(^{-1}\)) and C-H out-of-plane bend (1000-650 cm\(^{-1}\)).\(^{42}\) However, these peaks were not apparent in the spectra of the alginate containing embedded PCDA because the peaks corresponding to the PDA completely overshadow the peaks of the alginate. The most prominent peaks within the PCDA spectra are the carbon triple bond stretch peak at 2085 cm\(^{-1}\) and the carbon double bond stretch peak at 1450 cm\(^{-1}\). Yuan et al. provided a detailed account of PCDA Raman spectra as solution cast onto a glass slide.\(^{112}\)
As mentioned, after sodium alginate was extruded into the calcium chloride coagulation bath on a small scale, the resulting fibers were stored in a 3% CaCl₂ equilibration bath for twelve hours. This same process was followed for the first large scale spinning of the control and doped fibers; however, after twelve hours in the 3% equilibration bath, the doped fibers had changed from blue to purple. The fibers had been sealed and submerged in the 3% solution, so it was assumed that the color change was related to the calcium in the bath. As a result, another large scale wet spin was completed and 10-fiber bundles were placed in equilibration baths containing 0%, 1%, 3%, 5% and 10% CaCl₂. The fibers responded with an increased colorimetric transition to red according to the increased calcium present within the bath (Figure 5.19). Fibers obtained

**Figure 5.18:** Normalized Raman spectra of alginate fiber control (black, dash) and with PCDA liposome (blue, solid), inset Raman spectra without normalization, control (red) with PCDA (purple).
from the 0% equilibration bath were deemed the most successful due to the retention of the blue color. Calcium chloride and cadmium chloride had previously been used with regards with PCDA LB-films as a stabilization agent for the carboxylic acid head group during monolayer deposition and it was noticed that the use of metal ion salt complicated the structures through metal ion chelation.\textsuperscript{113} 

\textbf{Figure 5.19}: Photographs of alginate bunches (1 inch long) with embedded PCDA liposome as dried after CaCl\textsubscript{2} baths, from left: 0\%, 1\%, 3\%, 5\% and 10\%.

A Raman spectrum was collected for a fiber from each equilibration bath (\textbf{Figure 5.20} shows the C≡C stretch peak). It was concluded that as the percentage of calcium increased, the height of the carbon triple bond peak corresponding to the blue form (2085 cm\textsuperscript{-1}) decreased and the height of the carbon triple bond peak corresponding to the red form (2111 cm\textsuperscript{-1}) increased.
The color shift to red, as corroborated in the Raman spectra, was measured using the Raman Response equation (RR). The RR is represented as a percentage and is calculated by dividing the height of the shifted carbon triple bond stretch peak (~2111 cm\(^{-1}\)) by the sum of the heights of the shifted (2111 cm\(^{-1}\)) and planar (2085 cm\(^{-1}\)) peaks. Raman data used in these calculations and the resulting RR\% can be found in Table 5.2.

Table 5.2: Raman data results and Raman Response percentage of alginate fibers with PCDA liposome as dried after CaCl\(_2\) equilibration baths of 0\%, 1\%, 3\%, 5\% and 10\%.

<table>
<thead>
<tr>
<th>CaCl(_2) Bath</th>
<th>Color</th>
<th>C≡C (cm(^{-1}))</th>
<th>Height</th>
<th>C≡C Shifted (cm(^{-1}))</th>
<th>Shifted Height</th>
<th>RR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Blue</td>
<td>2087</td>
<td>91516.6</td>
<td>--</td>
<td></td>
<td>0</td>
<td>0.0%</td>
</tr>
<tr>
<td>1% Purple</td>
<td>2087</td>
<td>24511.8</td>
<td>2120</td>
<td>2050.54</td>
<td>7.7%</td>
<td></td>
</tr>
<tr>
<td>3% Purple</td>
<td>2087</td>
<td>14099.1</td>
<td>2120</td>
<td>2293.13</td>
<td>14.0%</td>
<td></td>
</tr>
<tr>
<td>5% Red</td>
<td>2087</td>
<td>10770.6</td>
<td>2119</td>
<td>1955.79</td>
<td>15.4%</td>
<td></td>
</tr>
<tr>
<td>10% Red</td>
<td>2087</td>
<td>8662.74</td>
<td>2120</td>
<td>2280.18</td>
<td>20.8%</td>
<td></td>
</tr>
</tbody>
</table>
The collection of Raman spectra on linear polydiacetylenes is common practice; however, very few of the literature papers on PDA liposomes contain this valuable information. Raman data was presented by Geiger et al.\textsuperscript{105}; however, the signal to noise ratio within the spectra was low. From the data retrieved and citing previous references for linear PDAs, Geiger speculated that the double signal from the carbon triple and double stretch peaks could be attributed to the blue and red forms of PDA present within the film.\textsuperscript{105} However, a direct relationship between the peak heights as a comparison of the percentage of red within the substrate was never discussed. The presence of dual peaks, or double signals, seen in previous literature without the generation of a Raman Response equation confirms that this equation and the percentages generated by the calculations are novel.

Previously, a measure of percentage color intensity had been calculated in a PCDA liposome-PEG gel by counting the number of blue and red matrices on captured images (photographs) of the gels.\textsuperscript{95} This process was optimized in 2007 and referred to as Digital Colorimetric Analysis (DCA) where images of TCDA/DMPC lipids on glass slide (after exposure to bacteria) were scanned into a computer, sample images were cropped and pixels of red were counted by MATLAB software.\textsuperscript{68}

It was clear that the calcium was having an effect on the PCDA liposomes within the alginate fiber. However, it was undetermined if the calcium was binding the alginate chains closer together and this was causing strain on the PCDA liposome. Another alternative is that the calcium was directly reacting with the liposome causing a chemical response. To answer this question, 1mL of a polymerized 2 mM PCDA liposome dispersion was added to 4 mL of 3% CaCl\textsubscript{2} in deionized water. After one hour, the
solution became pink and the dispersion had grouped together into large aggregates (Figure 5.21). A control of 1mL PCDA dispersion was placed into 4 mL of deionized water and no response was seen, other than a lighter blue color caused by the dilution.

![Figure 5.21: Photographs of 2 mM PCDA liposome aqueous dispersion as polymerized (left) and 24 hours after the addition to 3% CaCl$_2$ (right).](image)

Visually, the PCDA liposome dispersion seemed to clump together and it was hypothesized that the calcium ions were interacting with the carboxylic acid groups on the hydrophilic tails of the liposomes. This idea was emphasized by SEM analysis of the dispersion after 24 hours of calcium chloride exposure. The particles perfect spherical shape had been altered and noticeable surface deformations were apparent (Figure 5.22). The diameter of the particles increased from ca. 150 nm to over 500 nm, indicating that particle agglomeration around calcium ions could be possible.
In addition to affecting the PCDA liposomes within the fiber, the calcium equilibration bath percentage caused a change in the water retention of the control and doped alginate fibers. The percentage of water retained by the control fibers was measured by TGA (Figure 5.23). The control fiber from the 0% bath contained 20% water, the lowest recorded amount. The percentage of retained water increased as the calcium concentration increased: 23% water for 1% CaCl₂, 28% water for 3% CaCl₂, 27% water for 5% CaCl₂ and 37% water for 10% CaCl₂. The addition of the PCDA liposomes had no affect on water retention of the fibers.

Figure 5.22: SEM photographs of PCDA liposome aqueous dispersion after the addition to 3% CaCl₂ to the solution measuring ca. 567nm.
5.6 – Reverse Ion Exchange

Alginate fibers containing embedded PCDA liposomes were subjected to a reverse ion exchange to mimic the environment encountered when applied as a wound dressing. Although the conditions set forth in the laboratory ion exchange are more severe than those present on the human body, the test provided an idea of the sustainability of the blue liposome color through various alginate salts. The calcium alginate fibers were submerged in a 0.5 M HCl bath for times of zero to twenty minutes and washed twice with distilled water, according to literature. The resulting fibers were then treated with an excess of NaOH in a 6:4 water/isopropanol solution for zero to thirty minutes and rinsed in a clean 6:4 (w/i-P) bath. Conversion from calcium alginate to
sodium alginate was achieved through exposure to 0.5 M HCl for 20 minutes followed by exposure to excess NaOH for 30 minutes (Figure 5.24).

The embedded PCDA liposomes retained their blue color from the calcium alginate through alginic acid to sodium alginate (Figure 5.25). As expected, the water solubility of the fiber increased upon conversion to sodium alginate. The sodium alginate fiber immediately began to swell after being rinsed with water.
5.7 – Embedded PDA Response to Environmental Stimuli

Alginate fibers containing embedded PCDA liposomes shift in color from blue to red with external perturbations. Environmental stimuli that cause the transition include temperature, solvent and chemical. These properties have been seen in PCDA liposome solutions\(^7\), PDA LB films\(^{105}\) and gels of PCDA in agar\(^4\) and PEG\(^9\). The generation of a fiber with embedded PDA sensors would enable colorimetric detection of temperatures above 60°C, a variety of solvents and specific chemicals that would not be limited to a laboratory environment. The following sets of experiments were performed to confirm that the colorimetric properties of PDA were retained while embedded in the alginate fibers.

The doped fibers were immediately responsive to temperatures greater than or equal to 60°C. The fibers were laid on a glass slide which was set on top of a controlled hot plate to 60°C ± 2°C. After 15 seconds, the ends of the fiber had turned to red. The color change propagated towards the center of the fiber from both ends until the visual color change was complete at 45 seconds (Figure 5.26). The control alginate fiber did not change after being exposed to heat.

Figure 5.25: Photographs of the three stages of the reverse ion exchange calcium alginate (left), alginic acid (middle) and sodium alginate after rinsing with water (right).
Photomicrographs were taken of an alginate fiber with embedded PCDA liposome at room temperature and 75°C (using microscope with attached hot stage). At 60°C the fiber began to change and by the time the hot stage reached 75°C the fiber was completely red (Figure 5.27). The individual fiber filaments each contained an even amount of PCDA liposome and all seemed to change to red with exposure to heat. The blue to red response to heat appeared uniform at this magnification.

Figure 5.26: From left: Photographs of as spun control Alginate fiber, as spun alginate fiber with PCDA liposome and alginate fiber with PCDA liposome after exposure to 60°C for 45 seconds.

Raman spectra were taken of alginate fibers with embedded PCDA liposomes after thermal exposure and compared to the spectra obtained from the as spun fibers (Figure 5.28). The as spun fiber contained a carbon triple bond peak at 2087 cm\(^{-1}\) with each PCDA peak having a strong enough intensity to completely mask the alginate peaks.

Figure 5.27: Photomicrographs (100X) of Alginate fiber with PCDA Liposome at 0°C and 75°C using hot stage.

Figure 5.28: From left: Photographs of as spun control Alginate fiber, as spun alginate fiber with PCDA liposome and alginate fiber with PCDA liposome after exposure to 60°C for 45 seconds.
The thermally treated fiber contained a dual carbon triple bond stretch peak, 2119 cm\(^{-1}\) corresponding to the red portion of PCDA and 2086 cm\(^{-1}\) corresponding to the blue portion of PCDA. The wavenumber difference between the centers of the red alkyne peak and the blue was calculated to be 32 cm\(^{-1}\). The intensity of the PCDA peaks within the red form did not block the alginate peaks. The Raman Response calculated for the thermally treated fibers was 78.9%, meaning that 78.9% of the acetylene peaks in the Raman spectra were in the shifted position. Although the fiber visually looked completely red, part of the liposomes within the 25 \(\mu\)m spot size corresponded to the planar, blue form.

![Graph showing Raman spectra](image-url)

**Figure 5.28**: Raman spectra of alginate fibers with PCDA liposome as spun (blue, solid) and after exposure to 60°C for 45s (red, dash).

Fibers were submerged into a variety of solvents to determine the effect of solvent on the color of the embedded PCDA liposome. Previously, PCDA liposomes assembled on a polyelectrolyte membrane, using layer-by-layer deposition, have shown a 100%
colorimetric response to ethanol, as detected by UV/Vis.\textsuperscript{107} It must be noted that the ability for the solvent to penetrate the alginate fiber ultimately determined its ability to cause a transition within the PCDA liposome. Control fibers and those exposed to water and hexane retained the initial blue color. However, a colorimetric response was observed in fibers submerged into acetone, methylene chloride, chloroform, tetrahydrofuran and ethanol (\textbf{Table 5.3}).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{Solvent} & \textbf{Fiber Color} \\
\hline
Control & Blue \\
Water & Blue \\
Hexane & Blue \\
Acetone & Purple \\
Methylene Chloride & Purple/Red \\
Chloroform & Red \\
Tetrahydrofuran & Red \\
Ethanol & Bright Red \\
\hline
\end{tabular}
\caption{Photographs of alginate fibers with PCDA liposome after exposure to various solvents.}
\end{table}

After fibers were subjected to a 30 minute solvent submersion and allowed to air dry, a Raman spectrum was collected (\textbf{Figure 5.29}). A Raman Response (RR) was calculated based on the height of the alkyne red peak as compared to the sum of the heights of the alkyne red and blue peaks (\textbf{Table 5.4}). The visual perception of red was accompanied by an increasing RR\%, where the onset of visual purple color corresponded to 7.07\% and the appearance of a true red was shown to be 53.28\%.
The ability of α-cyclodextrin (α-CD) to penetrate into a film or fiber and interact with the PDA molecule has proven to be a good preliminary indication of possible bacteria detection. An extensive study of the effects of α-, β- and γ-cyclodextrins on

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**Table 5.4:** Raman data used to obtain a solvent Raman Response (RR%) for PDA-Alginate Fibers

<table>
<thead>
<tr>
<th>Solvent</th>
<th>C≡C Peak (cm⁻¹)</th>
<th>Height</th>
<th>C≡C Shifted Peak (cm⁻¹)</th>
<th>Shifted Height</th>
<th>RR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2090</td>
<td>73441.1</td>
<td>--</td>
<td>0</td>
<td>0.0%</td>
</tr>
<tr>
<td>Water</td>
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<td>62726.1</td>
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<td>Hexane</td>
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<td>MeCl₂</td>
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<tr>
<td>CHCl₃</td>
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<td>2118</td>
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<tr>
<td>THF</td>
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<td>5755.07</td>
<td>2119</td>
<td>2826.62</td>
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<tr>
<td>Ethanol</td>
<td>2087</td>
<td>3786.05</td>
<td>2119</td>
<td>4317.59</td>
<td>53.3%</td>
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</tbody>
</table>

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**Figure 5.29:** Raman spectra collected after the solvent test of alginate fibers with embedded PCDA liposomes. The inset is an enlarged image of the Raman spectra of fibers that have been exposed to CHCl₃, THF and ethanol.
PCDA liposomes revealed that the diameter of the cyclic sugar caused a variation of the colorimetric response within a PDA liposome dispersion.\textsuperscript{70} The inter-chain distance within the PCDA supramolecules, which is approximately 0.5 nm, is the primary reason why α-cyclodextrin exposure results in a higher colorimetric response than the β or γ forms.\textsuperscript{114,115} A schematic cartoon of the reaction between α-CD and a polymerized PCDA is presented in Figure 5.30.

![Cartoon exhibiting α-cyclodextrin reacting with a PCDA PDA.](image)

Figure 5.30: Cartoon exhibiting α-cyclodextrin reacting with a PCDA PDA.

The calcium alginate fibers showed no sensitivity to α-CD when the two were combined in deionized water due to the inability of the water to penetrate into the fiber and reach the PCDA liposomes. However, the addition of 1\% by weight of sodium chloride to the solution enabled enough conversion to sodium alginate, thus water solubility, for the solution to penetrate the fiber. In solutions containing 1\% sodium chloride, a 2 cm sample of a 10-fiber bundle of alginate containing PCDA liposomes, submerged for 30 minutes, showed a visual color change to red and Raman Response up to 75\%. The various combinations of α-CD molarities, salt percentages and the respective
Raman Response is presented in Table 5.5. The increased weight percentage of salt did not increase the RR% except for the 10mM sample changing from 1% to 2%.

**Table 5.5**: Raman Response Percentages of Alginate Fibers with PCDA liposomes as exposed to α-cyclodextrin (α-CD) and NaCl.

<table>
<thead>
<tr>
<th>α-CD</th>
<th>0% NaCl</th>
<th>1% NaCl</th>
<th>2% NaCl</th>
<th>5% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 mM</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>10 mM</td>
<td>0%</td>
<td>0%</td>
<td>10.1%</td>
<td>11.8%</td>
</tr>
<tr>
<td>50 mM</td>
<td>0%</td>
<td>24.6%</td>
<td>12.9%</td>
<td>11.3%</td>
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<tr>
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<td>0%</td>
<td>54.7%</td>
<td>50.1%</td>
<td>52.6%</td>
</tr>
<tr>
<td>500 mM</td>
<td>0%</td>
<td>72.0%</td>
<td>71.5%</td>
<td>82.8%</td>
</tr>
<tr>
<td>1 M</td>
<td>0%</td>
<td>75.6%</td>
<td>76.0%</td>
<td>76.6%</td>
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</table>

The increase in concentration of the α-CD within the 1% NaCl solutions correlated to an increase in the height of the 2111 cm⁻¹ carbon triple bond stretch peak in the Raman (Figure 5.31). Increasing the concentration of the α-CD in a solution at a constant submersion time and salt percentage resulted in an increase of red color within the fiber caused by the embedded PCDA liposomes.
Figure 5.31: Raman spectra collected for Alginate fibers with PCDA liposomes after exposure to 10 mM to 1 M α-cyclodextrin (α-CD) and 1% NaCl.

5.6 – Embedded PDA Sensitivity to Bacteria

Human blood contains approximately 0.9% sodium chloride\textsuperscript{116}; therefore, the salt provided by an active wound would provide enough sodium to enable water penetration into the alginate fibers. At percentages of only 1% NaCl, the solubility of the alginate fiber was high enough to absorb α-CD molecules, cause up to a 75% Raman Response and a visual color change to red.

The addition of a bacteria sensitive molecule into PDA liposomes has proven to be a successful technique for colorimetric bacteria detection. The incorporation of DMPC into PCDA and TCDA liposomes has been successful for the detection of various strains of \textit{E.coli}.\textsuperscript{63} DMPC (\textbf{Figure 5.32}) was incorporated into PCDA liposomes at a ratio of 1:9 with an overall molarity of 2 mM.
The PCDA/DMPC liposome dispersion turned blue upon exposure to UV light; however, the liposomes became red after small scale spinning into alginate fibers. Additionally, the PCDA/DMPC liposome changed from blue to red within the sodium alginate blend solution after approximately an hour. It was hypothesized that the charged groups within the DMPC interacted with the alginate to cause the colorimetric transition from blue to red. A Raman spectrum was collected of the alginate fibers with embedded PCDA/DMPC liposomes to reveal dual peaks in the carbon triple and double bond regions (Figure 5.33). A Raman Response of 39.7% was calculated for the as spun alginate fibers with PCDA/DMPC liposome.
Although the red transition of the liposomes caused by the alginate fibers was not the desired product of their combination, it provided evidence that the liposomes were capable of a color change. The embedded PCDA/DMPC liposome changed from blue to red as the DMPC interacted with a compound, in this case the alginate. PCDA liposomes without a bacterial sensitive moiety remained blue while in the sodium alginate solution and calcium alginate fiber, confirming the incorporation of DMPC into the liposome.

A realistic future direction for this project revolves around the creation of a bacterial sensitive assay that is not sensitive to the alginate host material. It is speculated that the incorporation of amino acid tailed PCDAs would be a more appropriate bacterial assay. Additionally, a glucose derived assay such as dioctadecyl glyceryl ether-β-glucosides (DDG, Figure 5.34) would be appropriate because the tail would be of similar composition to the host polymer.

Figure 5.33: Raman spectra of alginate fiber with embedded PCDA/DMPC liposome as spun.
PCDA liposomes with incorporated bacterial assays have proven to be successful colorimetric bacterial sensors in aqueous dispersions, LB films and encased in gels.\textsuperscript{40,91,95} PCDA liposome dispersions have been successfully reproduced and polymerized using UV light. The liposomes were solution blended with sodium alginate and wet spun into calcium alginate fibers. Using D.I. water as an equilibration bath instead of the common 3% CaCl$_2$, embedded PCDA liposome retain their blue color within the alginate fiber. A color response was observed in fibers that were exposed to heat, solvent and $\alpha$-cyclodextrin (with 1% NaCl). The addition of sodium chloride during the $\alpha$-cyclodextrin test mimicked the environment of a wound dressing on the human body. The salt increased the water solubility of the fibers (through partial conversion to sodium alginate) and allowed the solution to contact the embedded sensor. Incorporation of the bacterial assay, DMPC, into PCDA liposome resulted in a colorimetric change to red upon incorporation into the alginate fibers. It is believed that the charged groups on the DMPC interacted with the surrounding alginate host and initiated the change to red. Although this was not the desired response, it was proof of concept that the embedded

\textbf{5.7 - Conclusion}

Figure 5.34: Chemical structure of bacterial sensitive molecule dioctadecyl glyceryl ether-$\beta$-glucosides (DDG), a next approach for bacteria response in an alginate fiber.\textsuperscript{93}
PCDA/DMPC liposomes exhibited a colorimetric response. All experiments were monitored by Raman spectroscopy and a Raman Response was calculated. Raman Response provides a quantitative value for the percentage of acetylene stretch peaks in the shifted position as determined by Raman spectroscopy.
CHAPTER 6
CONCLUSION

Polydiacetylenes (PDA) were first isolated through the solid-state polymerization of disubstituted 1,3-butadiynes. Generally, this topotactic polymerization occurs within DA crystals when a translation distance of ca. 5 angstroms and a 45° stacking angle is observed. The polymerization may be initiated thermally or photochemically.

PDAs are of great interest due to their chromatic transitions from blue to red with exposure to external stimuli. The color of the PDA is in direct relation to its maximum absorbance wavelength, which corresponds to the degree of conjugation within the polymer. An increase in conjugation decreases the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), leading to absorption of longer wavelength light and a deep blue color. As the energy difference between the HOMO and LUMO decreases, the energy needed to promote an electron decreases, thereby increasing the absorbance wavelength and altering the observed color. As the PDA remains in the as polymerized, fully planar state, a deep blue color is maintained. However, as the polymer is exposed to specific external stimuli (heat, pH, solvent or strain), the backbone is forced from its planar state, extended conjugation is lost and the molecule appears red.

Within this work, PDAs have provided a sensing platform that was incorporated into a variety of industrial materials. Attempts were made to create a strain sensitive material by blending 3- and 4-BCMU monomers and polymers with Tecoflex®. A temperature sensitive material with photolithography capabilities was created by
incorporation of PCDA monomers into PLA followed by subsequent PDA polymerization. Finally, an environmentally sensitive material (temperature, solvent and chemical) was developed through wet-spinning of PCDA liposomes (with and without incorporated assays) into calcium alginate fibers.

Strain sensitive materials were developed through the incorporation of 3- and 4-BCMU into a medical grade polyurethane, Tecoflex®. These compound have been incorporated into 60D Tecoflex® as a monomer (3-BCMUm & 4-BCMUm) and polymer (3-BCMUp & 4-BCMUp) at several percentages. The 3-BCMUp was blue upon solution casting in 60D with a corresponding Raman peak at 2085 cm⁻¹ and the thermochromic transition was completely reversible. The 3-BCMUm incorporated with 60D did not polymerize with exposure to UV light; however, the presence of the monomer was confirmed by the 2250 cm⁻¹ carbon triple bond peak in the Raman spectra.

Incorporation of 4-BCMUp into all durometers of Tecoflex® resulted in red films with a Raman peak at ca. 2111 cm⁻¹. A shift of the carbon triple bond Raman peak to lower wavenumbers with induced tensile strain was observed in thin films of 60D-blend-(1%)4-BCMUp. The as cast 60D-blend-4-BCMUm film was clear with a white crystalline top layer, showing a Raman peak at 2250 cm⁻¹ corresponding to the 4-BCMU monomer. Upon polymerization, the PDA crystalline top layer turned blue generating a Raman peak at 2085 cm⁻¹. The PDA top layer turned from blue to red after exposure to shear strain through a dart drop test. A three dimensional map of the impact area was generated through a newly developed Raman Response equation.

The Raman Response equation is the first method proposed for relating the Raman heights of the acetylene peak corresponding to the red form of PDA from one
Raman scan to another. Typically, the heights of Raman peaks are not uniform when collected from separate scans; however, peak heights may be compared within the same scan. Raman Response is defined as the height of the acetylene peak corresponding to the red form of PDA divided by the sum of the heights of the acetylene peaks corresponding to the red and blue forms of the PDA. The numeric value produced by the equation is a percentage of the red acetylene peak as compared to total acetylene peaks.

It is presumed that 0% RR corresponds to 100% blue polymer within the system and that at 100% RR the entire polymer has been converted to the red form. However, it has not been confirmed that any percentages between 0% and 100% correlate to a direct percentage of red polymer conformation within the system. The Raman Response equation will be of great use to the scientific community with regards to PDA research because there was previously no method for comparing data of this kind.

Temperature sensitive materials were developed by blending 10,12-pentacosadiynoic acid with polylactic acid. The diacetylene was able to self-organize while embedded in the PLA because of the similarities between the PCDA functionalities, specifically the carboxylic acid, and the PLA repeat unit. The addition of PCDA at one percent did not affect the film forming properties, glass transition or thermal decomposition of the PLA. Through the use of photolithography and exploitation of the polydiacetylene thermochromic properties, micro and macro functional images were prepared in 1% blend films. The polymerization of PCDA within PLA has allowed for a blend system with increased chromatic properties as compared to PLA alone and a specific sensitivity to temperatures over 70°C.
Environmentally sensitive materials were created through the addition of PCDA liposomes to alginate fibers. The liposomes were solution blended with sodium alginate and wet spun into calcium alginate fibers. Replacing the typical 3% CaCl₂ equilibration bath with deionized water allowed the embedded PCDA liposomes to retain their blue color within an alginate fiber. All experiments were monitored by Raman spectroscopy yielding a Raman Response for each colorimetric transition. Raman Response provides a quantitative value for the percentage of acetylene stretch peaks in the shifted position as determined by Raman spectroscopy. A visual color change and Raman Response was observed in PDA doped fibers that were exposed to heat, solvent and α-cyclodextrin (with 1% NaCl). The addition of sodium chloride during the α-cyclodextrin test mimicked the environment of a wound dressing on the human body. The salt increased the water solubility of the fibers (through partial conversion to sodium alginate) and allowed the solution to contact the embedded sensor.

PCDA liposomes with incorporated bacterial assays have proven to be successful colorimetric bacterial sensors in aqueous dispersions, LB films and encased in gels. Incorporation of the bacterial assay, DMPC, into PCDA liposome caused a color change to red with exposure to sodium or calcium alginate. It is believed that the charged groups on the DMPC interacted with the surrounding alginate host and initiated the change to red; however, the alginate was not sterilized indicating that bacteria may have been present. The concept that the PCDA/DMPC liposomes embedded in the alginate fibers could exhibit a colorimetric response was proved to be true.
REFERENCES


