Warren J. Baker Endowment
for Excellence in Project-Based Learning
Robert D. Koob Endowment *for Student Success*

CAL POLY

Proposal Cover Page

Title of Project:
Synthesis and Characterization of Conductively-Varying Elastomers for Biomedical Applications

Proposal Author: David Bilger **Cal Poly Email:** dbilger@calpoly.edu

Student ID: 010122862 **Signature (Optional):** ______

Signature provides permission to check financial aid eligibility.

Previous Baker/Koob Endowment funding? (circle one): **Yes** **No** (circled: No)

Team Member(s)	Signature	Cal Poly Email	Department
Kyle Aidukas		kaidukas@calpoly.edu	Chemistry/Bmed

Faculty Advisor: Dr. Shanju Zhang **Department:** Chemistry

Faculty Advisor email: szhang05@calpoly.edu **Telephone:** (805) 756-2591

Anticipated Start Date: January 1st, 2017

Anticipated End Date: December 15th, 2017

Total Funds Requested ($): 5000.00

Signature of Faculty Advisor: ______ **Date:** ______

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PROPOSAL NARRATIVE

(Max. of 3 pages including figures/tables but excluding budget page, 1" margins, 12-point font. See Sec.XII of RFP for more details.)

Proposals not complying with format guidelines will not be considered.

I. Project Title

Synthesis and Characterization of Conductively-Varying Elastomers for Biomedical Applications

II. Abstract

This proposal for EXCELLENCE IN PROJECT-BASED LEARNING and STUDENT SUCCESS outlines a one-year interdisciplinary plan concerning the mechanical properties of elastomers with variable conductivity (CVE's) for biomedical applications. We seek to discover the structure-property relationships necessary for the production of biomedical sensors through collaboration of undergraduate and graduate (MS) students within the Cal Poly Departments of Science and Engineering. *Our key innovation is to simultaneously adhere conductive nanoparticles to elastomers while altering their backbone microstructures. This backbone alteration will significantly effect the elastomer's macroscopic properties, allowing for the optimization of biomedical sensor applications.* This research will be accompanied by equipment and resources available through state-of-the-art laboratories in the Western Coatings Technology Center and Biomedical Engineering Department. *The long-term goal of the proposed work is to introduce a CVE into a functioning circuit for the construction of flexible skins, electrical sensors, or stretchable displays.* Additionally, we hope this work will foster further interdisciplinary research projects between the Cal Poly Departments of Science and Engineering.

III. Introduction

Stretchable electronics have garnered much attention recently due to their wide variety of potential applications. These include, but are not limited to, artificial skins, electrical sensors, stretchable displays, and photovoltaics[1]. With these applications in mind, the desire for elastomeric materials with varying conductivities as a function of tensile stress cannot be understated. Multiple materials have been employed previously to achieve these ends, including carbon black, carbon nanotubes, and semi-conducting polymers. Unfortunately, the above-mentioned materials are plagued by poor characteristics such as insufficient mechanical properties[2], difficult processing[3], and complex synthesis[4]. With this being said, more practical methods are necessary for the easy production of CVE's.

More recently, silver nanowires dispersed on a poly(dimethylsiloxane) (PDMS) substrate showed increased electrical resistance as a function of increasing strain[5]. However, the adherence of nanoparticles through siloxanes can introduce defects, such as cracking, onto the attached surface[6]. An alternative has been proposed by Supriya et al., in which gold nanoparticles are assembled onto elastomers through a solution-based approach[7]. Since the conductivity of gold is dependent on particle distance, the resulting material is conductive at rest, but upon stretching yields an insulator. In the study by Supriya et al., the simple adhesion of gold nano-particles was attributed to the presence of specific functional groups within the elastomer backbone[7]. That being said, gold nanoparticles are strongly attracted to multiple functional groups, including thiols and disulfides[8-10].

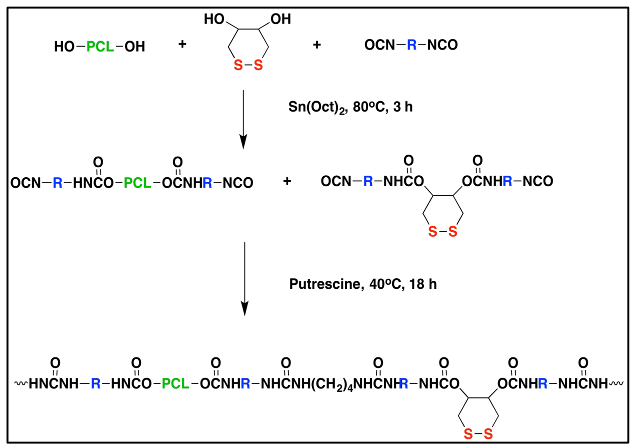
While efficient solution-based processing methods of CVE's have been explored, the tailoring of their mechanical properties remains ambiguous. To our knowledge, a sufficient material for this purpose has yet to be discovered concerning biomedical implants. Here, we propose the incorporation of gold nano-particles onto a flexible disulfide-containing poly(urethane urea) (PEUU-SS) elastomer. By altering the PEUU-SS backbone microstructure, macroscopic properties may be tailored for specific implant applications based on their determined mechanical characteristics. For instance, these characteristics could prove useful in orthopedics, allowing for less invasive procedures. Due to the multi-faceted approach of the proposed work, which includes synthesis, property characterization, and applications, a collaboration between the Cal Poly Chemistry (David Bilger) and Engineering (Kyle Aidukas) Departments will be implemented.

IV. Objectives

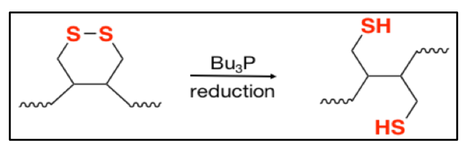
While CVE's have been assembled through solution-based techniques, the synthetic alteration of their microstructure and subsequent implementation in biomedical applications remains uninvestigated. Therefore, our objectives are thus: (1) Synthesize PEUU-SS elastomers with variable microstructures and adhere gold nanoparticles to their surface; (2) Investigate the structure-property relationship between synthesized CVE's; (3) Determine the sensitivity of synthesized CVE's for biomedical applications.

V. Methodology

<u>(1) Synthesis:</u> Gold nanoparticles will be synthesized using the Turkevich method[11]. This technique is extremely robust and is frequently performed in introductory chemistry classes. The synthesis of PEUU-SS is outlined in Fang et. al and follows Scheme 1 at right[12]. This first involves the synthesis of two diisocyanate compounds containing either a flexible (PCL) or disulfide containing diol (O-DTT). Our unique modification to this synthesis includes the incorporation of varying diisocyanate chain lengths (R = 4, 6, or 8 methylene's) providing more control over the final product's microstructure. In order to better adhere gold nanoparticles to the elastomer surface, disulfides may be reduced to thiols by tributylphosphine as shown in Scheme 2[13]. This will produce stronger interactions via thiol-gold dative bonding. Following synthesis of the elastomer and gold nanoparticles, the dried PEUU-SS will be dispersed in colloidal gold solutions for a standard time. This technique has been used by Supriya et al., and should facilitate the self-adhesion of nanoparticles to the elastomeric surface, producing a CVE.



Scheme 1: *Generalized Synthesis of PEUU-SS*



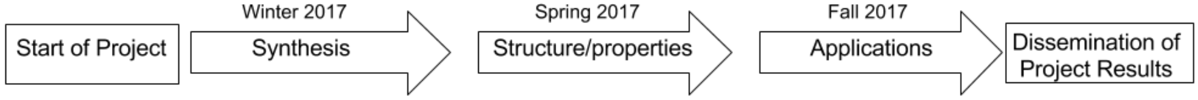
Scheme 2: *Reduction of disulfides to thiols*

<u>(2) Structure-Property Relationship</u>: The macroscopic properties of polymer molecules are known to be heavily influenced through backbone microstructure. As such, our synthesized PEUU-SS CVE's should exhibit different macroscopic properties dependent on alterations of their diisocyanate R groups. Relevant bulk properties can be assessed through dynamic mechanical analysis, differential scanning calorimetry, thermal gravimetric analysis, and four-point probe electrical analysis. Surface characterization can be accomplished with atomic force microscopy. These methods provide a thorough survey of material properties based on microstructure.

<u>(3) Applications:</u> In order to assess the sensitivity of our CVE's for biomedical applications, the synthesized samples will be incorporated into circuits in the Cal Poly Department of Biomedical

Engineering. Each CVE will be implemented as a pressure sensor and utilized to monitor the blood pulses of individuals in real-time. This type of testing is common with flexible sensors, and will therefore provide a substantial basis on which to gauge the sensitivity of our samples[14]. A simplified illustration of this process may be seen in Figure 1.

VI. Timeline



VII. Final Product and Dissemination

If the results of this project prove promising, the authors would seek to publish their data in a peer-reviewed academic journal, such as ACS: Macromolecules. Additionally, in order to make connections for further educational opportunities and gain feedback on research progress, both authors will attend the American Chemical Society (ACS) National Conference in San Francisco from April 2-7, 2017. Concerning the future impact of this work at Cal Poly, there is significant potential to deliver multiple opportunities for interdisciplinary work between the departments of Science and Engineering well after the proposal authors have graduated. Moreover, one of the authors is currently applying to doctoral programs in chemistry-related fields. That being said, beginning this work at Cal Poly would contribute to the university's prestige, and provide a substantial foundation through which to carry this project on to other academic institutions. While the specific long-term application of this project is difficult to deduce, we envision our CVE as an implantable resistor for use in orthopedics to determine implant fit, or in cardiology to confirm stent opening as a supplement to current methods.

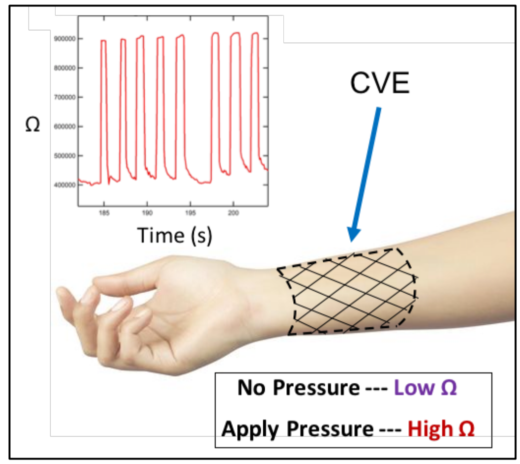


Figure 1: *CVE utilized as a pressure sensor*

VIII. Budget Justification:

The cost of all synthesis and characterization materials were placed under "non-computer supplies and materials." The synthesis reagents and characterization materials were estimated via price quotes from Sigma Aldrich and TA Instruments' websites, respectively. Based on scientific literature[11-13], the required synthetic reagents to meet objective (1) are thus: isopropyl alcohol ($166), DMSO ($304), polycaprolactone diol ($131), trans-4,5-dihydroxy-1,2-dithiane ($641) R-methylene diisocyanate with R = 4, 6, and 8 ($584), stannous octotate ($26), tetramethylene diamine ($32), DMF ($114), tributylphosphine ($35), chloroauric acid ($122), and sodium citrate ($68). Therefore, the total estimated minimum cost for 10 synthetic samples is **$2,710**.

The characterization costs necessary to meet objective (2) include hermetic aluminium DSC sample pans and lids ($200), 7, 15, and 22 mL glass vials for sample storage ($160), medium and large laboratory nitrile gloves for safety ($80), glass slides for microscope imaging ($30), and substrates for AFM imaging ($100). The estimated cost for characterization materials is **$570**.

Two students will be attending the 2017 ACS conference in San Francisco for five days. The total cost includes the price of registration *($210 per student*), estimated lodging *($423 per student*), food *($100 per student*), and transportation mileage *($250*). The total estimated cost for travel is **$1,720**. All expenses considered, we would like to request a total of **$5,000** for the proposed work.

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PROPOSAL BUDGET

Student Applicant(s) David Bilger Kyle Aidukas	
Faculty Advisor: Shanju Zhang	
Project Title: Synthesis and Characterization of Conductively-Varying Elastomers for Biomedical Applications	**Requested Endowment Funding**
Travel *subtotal*	$1,720
Travel: In-state	$1,720
Travel: Out-of-state	$
Travel: International	$
Operating Expenses *subtotal*	$ 3,280
Non-computer Supplies & Materials	$ 3,280
Computer Supplies & Materials	$
Software/Software Licenses	$
Printing/Duplication	$
Postage/Shipping	$
Registration	$
Membership Dues & Subscriptions	$
Multimedia Services	$
Advertising	$
Journal Publication Costs	$
Contractual Services *subtotal*	$ N/A
Contracted Services	$
Equipment Rental/Lease Agreements	$
Service/Maintenance Agreements	$
TOTAL	$ 5,000

A1. Appendix

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November 11, 2016

Dear Selection Committee,

I am writing to strongly support Mr. David Bilger and Mr. Kyle Aidukas's application for the Baker and Koob Endowments. I have read the proposal entitled "Synthesis and Characterization of Conductively-Varying Elastomers for Biomedical Applications" and endorse it with enthusiasm. David and Kyle have proposed a comprehensive research and education plan that is very well aligned with Cal Poly's Learn-by-Doing mission and will contribute Cal Poly's initiative to support the excellence in project-based learning and to maximize student success.

The proposed research provides students with unique opportunities for multi-disciplinary, cross-college collaborative learning activities, from chemical synthesis and property studies to biomedical applications. This research exposure could stimulate students' desire to pursue careers in science and engineering. Both David and Kyle are working with me on the different research projects. They are trained as scientists and are committed to the excellence of project-based learning. They have learned to manage time to work independently, to make research plans, and to discuss about research results with me regularly. With great success in the past research projects and their excellent research skills, I am very confident that they could complete the proposed tasks on time and get success in the project-based learning.

As the faculty advisor, I am fully committed to providing David and Kyle with the support they need to complete proposed research. I will provide David and Kyle with designated research space in the Western Coatings Technology Center. All facilities and equipment in the center will be available and free for them to use. I will provide assistance and advices for them during the course of the project. I am committed to all responsibilities of the faculty advisor that are listed on the program.

Sincerely,

Shanju Zhang