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Final Report: Exploring Mechanaphore and Polymer Design Rules for Mechanochemical Transduction

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15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Andrew Boydston
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RPPR Final Report
as of 22-Oct-2018

Agency Code:

Proposal Number: 62317CH **Agreement Number: W911NF-15-1-0139**

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Begin Performance Period: 01-May-2015 **End Performance Period:** 30-Apr-2018
Report Term: 0-Other
Submitted By: Ph.D Andrew Boydston Email: boydston@chem.washington.edu
Phone: (206) 616-8195
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 3 **STEM Participants:** 6

Major Goals: At the outset of our proposed work, we had established the following goals:
1) Computational Modeling and Identification of Target Flex Activated Mechanophores.
For each model mechanophore, relaxed potential energy surface scans will be conducted in a method consistent with the envisioned effects of mechanical force upon the molecule. We will use the computational results in combination with experimental reactivities to establish guidelines for predicting mechanochemical transformations via flex activation.
2) Synthesis of Flex Activated Mechanophores and Incorporation into Polymers and Crosslinked Networks.
We will synthesize flex activated mechanophores designed to release small molecules without degradation of the polymer main chain. These will be incorporated into linear polymers and crosslinked networks for solid state and solution-based studies. Particular focus will be placed on incorporating mechanophores into elastomeric materials capable of multiple cycles of mechanical activation with shape recovery following each cycle.
3) Evaluation of Flex Activated Mechanophores in Solution and Solid State.
We will use a combination of solution techniques and solid state methods to evaluate the mechanochemical reactivity of the mechanophores. Quantitative assessment of percent activation as a function of applied load will be determined, and correlations between material type, method of applying stress, mechanophore structure, and calculated activation energies (from Aim 1) will be investigated.

During the course of the project, we added the following goals:
A1) Evaluation of mechanophores as tools in additive manufacturing.
A2) Fundamental investigations of metal-free ring-opening metathesis polymerization

Accomplishments: Please see attached document.

Training Opportunities: Participants in the research program had multiple opportunities for professional training, including participation in group meetings, attendance at conferences, enrollment in advanced chemistry courses, and contributions to scientific writing. Notably, students were directly involved in drafting patents as co-inventors on technologies that were borne out during the funding period. As the projects matured, students and postdocs took part in collaborative research, which exposed them to joint group meetings with experts in mechanical engineering and materials science. During the joint group meetings, researchers were responsible for presenting and discussing their recent results, strategizing to address challenges, and corresponding with collaborators to advance the project goals. Students also took classes outside of chemistry to enhance their training, including courses in materials science, mechanical engineering, and bioengineering.

Results Dissemination: Several talks were presented on the funded research topic. These were largely at conferences of professional societies (e.g., ACS National Meetings, Gordon Research Conferences, Fusion Conference). Additionally, researchers in the program participated in several outreach activities. These included assisting in hands-on lab activities at Sammamish High School (Problem-Based Learning Curriculum), Yakima Valley Science Fair, Bellevue School District Science Fair, the University of Washington Math Science Upward Bound program, and the University of Washington "Research Exposed" seminar series.

Formal presentations at departmental seminars, conferences, and symposia are listed below:

The Ohio State University, departmental seminar, March 2018
Virginia Tech, departmental seminar, February 2018
University of Wisconsin–Madison, departmental seminar, February 2018
University of Massachusetts–Amherst, departmental seminar, February 2018
ExxonMobil, invited seminar, December 2017
University of Chicago, Institute for Molecular Engineering seminar, November 2017
University of Michigan, student-invited seminar, November 2017
University of Minnesota, departmental seminar, November 2017
Virginia Tech, departmental seminar, October 2017
Florida State University, College of Engineering Seminar, October 2017
Florida State University, departmental seminar (Chemistry), October 2017
University of Southern Mississippi, departmental seminar, October 2017
Tulane University, departmental seminar, October 2017
Case Western Reserve University, departmental seminar (student invite), September 2017
254th National Meeting of the American Chemical Society, Washington, D.C., August 2017. Seminar Title: Expanded Materials Space for Digital Light Processing Additive Manufactring.
Polymers Gordon Research Conference, South Hadley, MA, June 2017. Invited talk: Integration of Mechanoresponsive Materials and Additive Manufacturing.
International Conference of Photopolymer Science and Technology, Chiba, Japan, June 2017
Lawrence Livermore National Labs, Livermore, CA, May 2017.
Society of Polymer Science, Japan, 66th Annual Meeting of SPSJ, Chiba, Japan, May 2017
253rd National Meeting of the American Chemical Society, San Francisco, CA, April 2017. Seminar Titles: Polymers for Thermal and Mechanochemical Release of Nitroxyl (HNO) and Other Small Molecule Payloads; Redox-Mediated Metal-Free Ring-Opening Metathesis Polymerization
Boston College, departmental seminar, March 2017
Air Force Research Labs, Dayton, OH, December 2016
Materials Research Symposium, Boston, MA, December 2016
12th International Symposium on Organic Reactions, Kyoto, Japan, April 2016
Stanford University, departmental seminar, March 2016
IBM Almaden Research Center, invited seminar, February 2016
University of Akron, departmental seminar, February 2016
University of Colorado, departmental seminar, January 2016
Colorado State University, departmental seminar, January 2016
Air Force Academy, invited seminar, January 2016
14th Pacific Polymer Conference, Kauai, HI, December 2015. Seminar Titles: 1) Metal-Free Ring-Opening Metathesis Polymerization. 2) Integration of Mechanochemistry and Additive Manufacturing.
University of Massachusetts–Amherst, departmental seminar, November 2015
2015 International Symposium on Stimuli-Responsive Materials, Santa Rosa, CA, October 2015. Seminar Title: Integration of Polymer Mechanochemistry and Additive Manufacturing.
University of California, Santa Barbara, departmental seminar, September 2015
Washington University in St. Louis, departmental seminar, September 2015
Aberdeen Proving Ground, Army Research Labs, August 2015
2015 Polymers for Advanced Technologies, Hangzhou, China, June 2015. Seminar Title: Metal-Free Ring-Opening Metathesis Polymerization.

Honors and Awards: Boydston:
Camille Dreyfus Teacher-Scholar Award
Thieme Chemistry Journal Award
Distinguished Teaching Award for Innovation with Technology, University of Washington

Dr. Laura Pascual:
NDSEG Fellowship

Miss Johanna Schwartz:
Eastman Chemical Graduate Student Award (finalist)

Protocol Activity Status:

Technology Transfer: Five US patent applications and one European patent application were filed (each currently pending). We have also launched a startup company based upon our metal-free ROMP technology. That same project also transitioned into a cooperative research agreement with the ARL APG (main point-of-contact: Dr. Dan Knorr, Jr.). Additional interactions have included visits and material transfer with New Balance, Henkel Corporation, ExxonMobil, and 3-D Systems.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Andrew Jackson Boydston
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Laura Pascual
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Victoria Kensy
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Bo Cao
Person Months Worked: 10.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Adam Goetz
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Pengtao Lu
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Ashlynn Vander Meer
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Damian Dunford
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Thomas Bearrood
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

PATENTS:

Intellectual Property Type: Patent Date Received: **26-Sep-2018**
Patent Title: METATHESIS POLYMERIZATION METHODS
Patent Abstract: The present disclosure is directed to methods of making a polymer, including exposing a reactio
Patent Number: 20170240695
Patent Country: USA
Application Date: 24-Aug-2017 Application Status: 2
Date Issued:

Intellectual Property Type: Patent Date Received: **26-Sep-2018**
Patent Title: THREE-DIMENSIONAL PRINTED MECHANORESPONSIVE MATERIALS AND RELATED METHODS
Patent Abstract: The present disclosure provides additive manufacturing methods that include depositing onto a
Patent Number: 20170225395
Patent Country: USA
Application Date: 10-Aug-2017 Application Status: 2
Date Issued:

Intellectual Property Type: Patent Date Received: **26-Sep-2018**
Patent Title: POLYMERS FOR THERMALLY-REGULATED RELEASE OF HNO AND OTHER MOLECULES
Patent Abstract: Multivalent scaffolds configured to facilitate drug release upon exposure to a stimulus, such as h
Patent Number: 20170202874
Patent Country: USA
Application Date: 20-Jun-2017 Application Status: 2
Date Issued:

Intellectual Property Type: Patent Date Received: **26-Sep-2018**
Patent Title: CONTROLLED RELEASE OF CARBON DIOXIDE FROM SELF-IMMOLATIVE POLYMERS
Patent Abstract: The present disclosure is directed to a carbon dioxide-releasing device, including a chamber ha
Patent Number: 20160066553
Patent Country: USA
Application Date: 10-Mar-2016 Application Status: 2
Date Issued:

Intellectual Property Type: Patent Date Received: **26-Sep-2018**
Patent Title: THERMALLY-ACTIVATED SELF-IMMOLATIVE MATERIALS
Patent Abstract: A polymer including a self-immolative polymer segment and a thermally-activated trigger moiety
Patent Number: 20150368403
Patent Country: USA
Application Date: 24-Dec-2015 Application Status: 2
Date Issued:

ACCOMPLISHMENTS

1. FLEX-ACTIVATED MECHANOPHORES:

1.1. NHC-CDI adducts as flex-activated mechanophores

Our recent efforts have centered on mechanochemical activation of adducts occurring between N-heterocyclic carbenes (NHCs) and carbodiimides (CDIs). The NHC-CDI mechanophore structures and envisioned reactivity are depicted in Figure 1. Following CoGEF modeling, we next confirmed the mechanochemical activation and release of NHC species from bulk polyurethane materials (each described in our previous IPR). As depicted in Figure 2, the chain extenders and NHC structure are expected to be modular in nature. We have prepared samples with PEG, PPG, and alkyl linkages that display a range of mechanical properties and swelling behaviors.

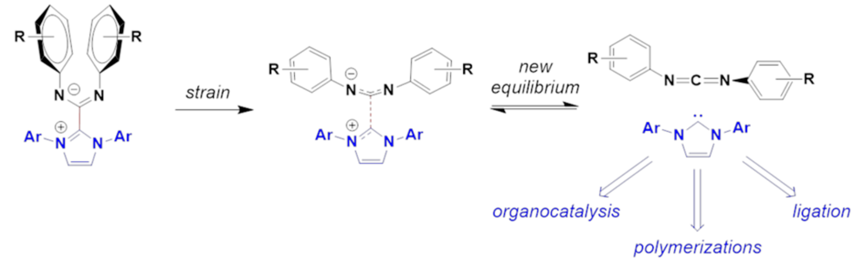

Figure 1. Generalized depiction of force-induced redistribution of NHC-CDI adduct equilibrium, leading to NHC release. R = site of polymer attachment.

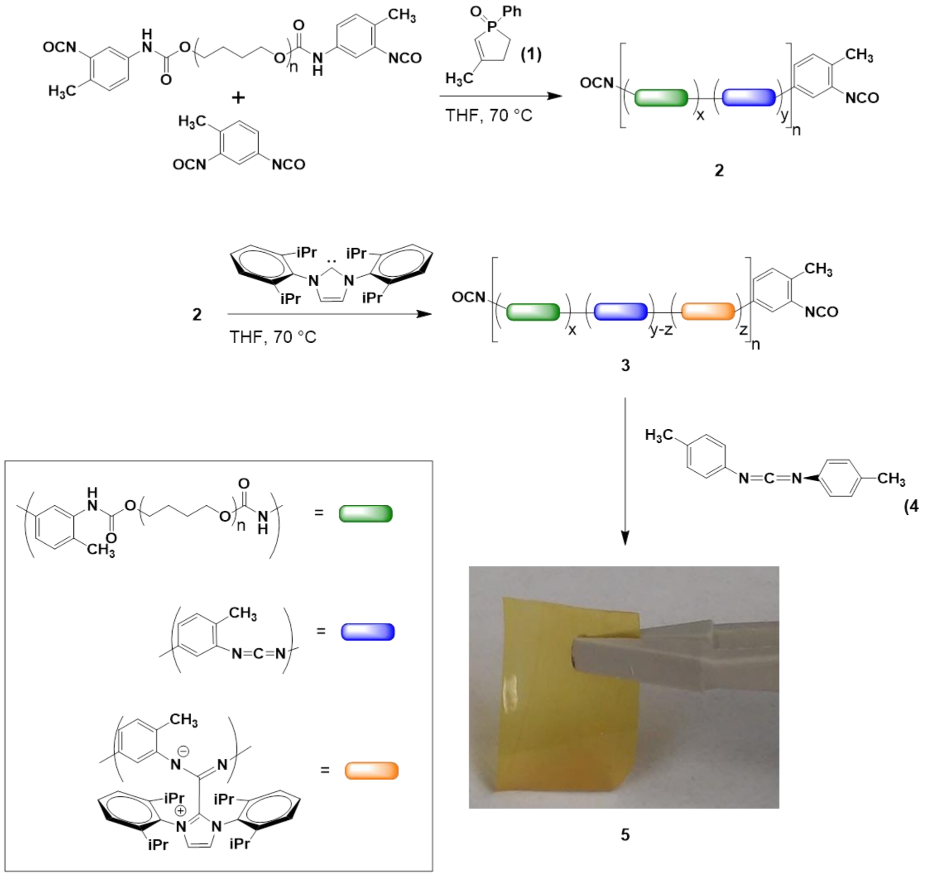

Figure 2. Synthesis of polymers containing NHC-CDI mechanophores.

Variations in the NHC reactivity have also been the focus of our current funding period. Toward this end, we have prepared a series of small molecule NHC-CDI adducts (Figure 3). These small molecules adducts serve multiple purposes for our studies: 1) we are determining the thermal equilibrium parameters for each adduct, 2) the adducts are used as internal standards for LS-MS analysis of activated NHC species from polymeric networks, and 3) they confirm the product species spectroscopic signatures for crossover experiments. Moreover, the NHCs in this series represent a broad range of nucleophilicity and basicity. Therefore, we expect to find correlations between fundamental physical organic parameters and the efficiency of mechanochemical reactivity.

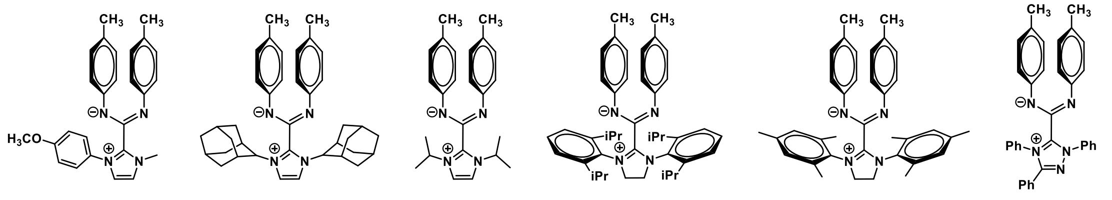

Figure 3. NHC-CDI adducts currently on hand.

2. FLEX ACTIVATED MECHANOPHORES IN ADDITIVE MANUFACTURING

2.1. Chemical control over each voxel in 3D printed objects.

Our desire to integrate mechano-responsive materials with additive manufacturing (AM) began inspired us to consider the interplay between object geometry and chemical composition. For example, the unit cell for an octet truss lattice (Figure 4) compensates for uniaxial compression through a combination of non-uniform local stress and strain fields. This prompted questions about the potential to modulate mechanical responses as a function of crosslink density (chemistry to enhance engineering designs) and the use of localized strain to activate mechanophores (engineering designs that enhance chemical responses). We first explored modifications to digital light processing (DLP) AM. The research goal was to assess the feasibility of using grayscale input to control crosslink density in prescribed regions of the test specimen, and therefore achieve heterogeneous or graded material properties. Digital image stacks were created based upon implicit sign-distance field representations of the octet truss crossbars. This enabled an overlay of geometric and materials functions (Figure 4) such that each voxel within the digital object was assigned a grayscale light intensity based upon location within the object (visually depicted as yellow and blue for 200 to 80 klux intensities). The results were exciting in that different stress-strain profiles were obtained, which included increased mechanical toughness and strain to break for graded and heterogeneous specimens in comparison with the homogeneous counterparts.

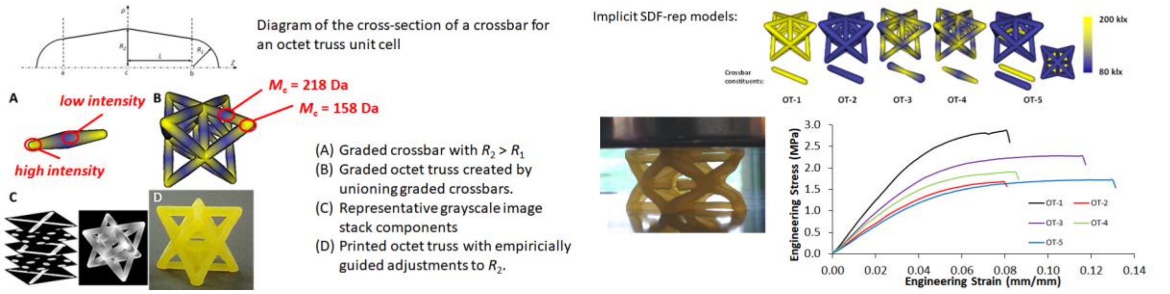

Figure 4. (left) Schematic for graded octet truss unit cells. (right) Results of compression tests for specimens having homogeneous, graded, and heterogeneous crosslink densities.

Before integrating mechanophores into lattice structures via DLP-AM we wanted to address two challenges: 1) thermoplastics are not ideal for evaluating mechanochemistry since permanent plastic deformation is required before mechanophores are activated, and 2) quantifying of mechano*chromic* changes would be difficult in a complex, small feature size lattice. The first challenge was addressed by developing new elastomer photoresin formulations, which were recently accepted for publication. This work required a combination of custom synthesis and formulations science to establish low viscosity photoresins with good "printability." Ultimately, we found the mechanical properties and swelling behavior of printed parts to be easily tuned. These materials also enabled rapid access to a multi-material pneumatic gripper (an air-driven soft robot) as depicted in Figure 5 (bottom).

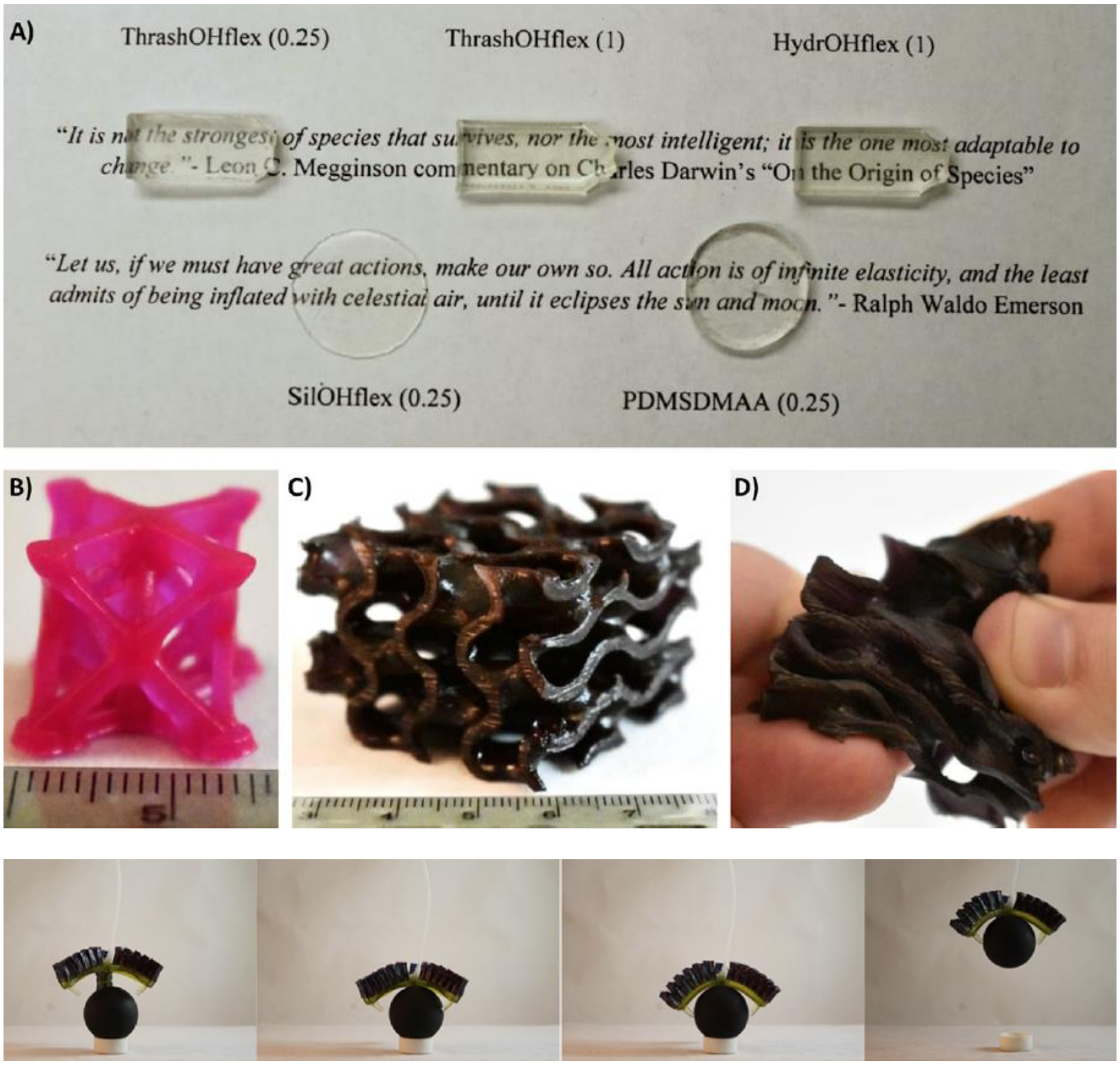

Figure 5. (top) A) Photos of printed objects of different resin compositions overlaid on printed text (font = Times New Roman 11 pt). Numbers in parentheses indicate wt % of Irgacure 819 in the feed. B) Octet truss unit cell printed from SilOHflex, ruler units = cm, cell dimensions = 1.5 × 1.5 × 1.5 cm^3, print time = 31 min. C) Gyroid lattice printed from HydrOHflex, ruler units = cm, lattice dimensions = 4 × 4 × 3 cm^3, print time = 49 min. D) Gyroid lattice being twisted. (bottom) A 3D printed multi-material pneumatic gripper descending, pneumatically actuating, and lifting a plastic ball.

The second challenge, quantifying mechanophore activation in lattice structures, was addressed by using our flex activated mechanophore design. This enables us to extract and quantify the amount of small molecule that is release upon mechanophore activation in a way that is nondestructive to the printed object. The results of these studies thus far are currently being prepared for publication.

2.2. DLP-AM and mechanical loading of flex activated mechanophores in truss structures.

We have printed a number of geometries using a combination of the mechanophore, HEA, EEEA, Irgacure 819 photoinitiator, and Nile Red as a dye to enhance resolution (representative structures shown in Figure 6). Examples of a cube and an octet truss unit cell are shown in Figure 6.

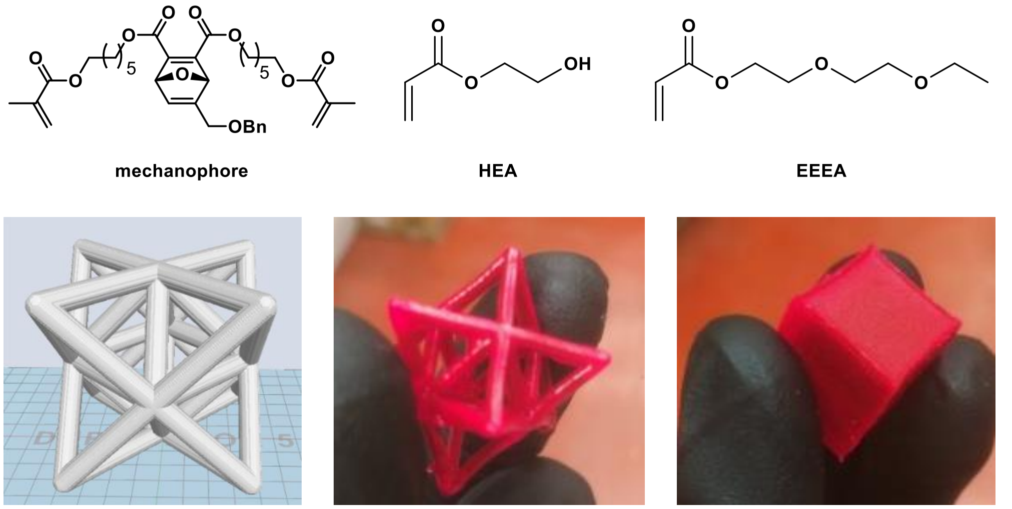

Figure 6. Representative photoresin components, CAD design for an octet truss unit cell, and representative printed objects.

Our goal was to obtain preliminary results on how an object’s geometry could translate into different mechanochemical activation efficiencies at the molecular level. Upon compression of the printed test specimens, we found that the octet truss unit cell gave equal or greater percent activation of mechanophores in comparison with the cube. This is consistent with the greater local strains experienced in the truss structure at the same global strain as the cube. Figure 7 shows the results of loading each specimen type in a hydraulic press to the same global strain. As can be seen, the truss consistently gives roughly 2-3 times the percent activation of the cube.

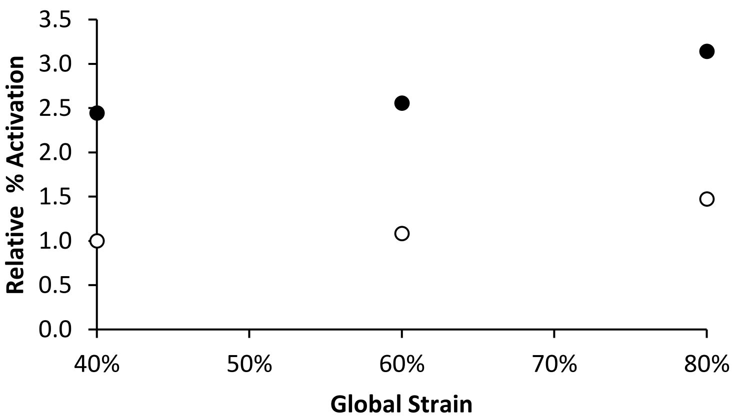

Figure 7. Results of mechanical loading of 3D printed octet truss unit cell (black circles) and cube (white circles) from mechanoresponsive photoresin materials.

3. METAL-FREE RING-OPENING METATHESIS POLYMERIZATION.

Building from our initial success with organocatalyzed anodic oxidations, we recently discovered a method for “metal-free” ROMP (MF-ROMP). Our first major advance came when we applied visible light photoredox catalysis. The general polymerization scheme (Figure 8) involves use of a photo-oxidant to reversibly oxidize an electron rich vinyl ether initiator. The resulting radical cation reacts with strained cycloalkene monomers to facilitate ring opening metathesis and generation of a new radical cation chain end. Since our initial discovery in 2015, we have worked to increase our depth of understanding for the mechanism and broaden the potential fields of use for MF-ROMP.

The reversibility of the oxidation and dynamic interplay between the chain end and photo-oxidant enable temporal control over the polymerization. The results presented in Figure 9 demonstrate the ability to switch the polymerization on and off using the photoredox-mediated method. Notably, no significant changes in conversion and molecular weight were observed during the dark periods, and each re-exposure to light resulted in increased conversion and molecular weight while maintaining monomodal molecular weight distributions. In this regard, the MF-ROMP shows characteristics of a living polymerization. This level of temporal control is distinct from many of the metal-based externally-controlled initiators.

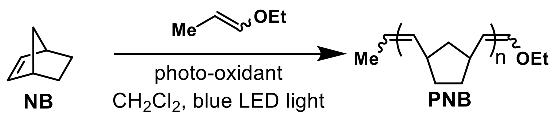

Figure 8. Generalized MF-ROMP using a photoredox catalyst and visible light.

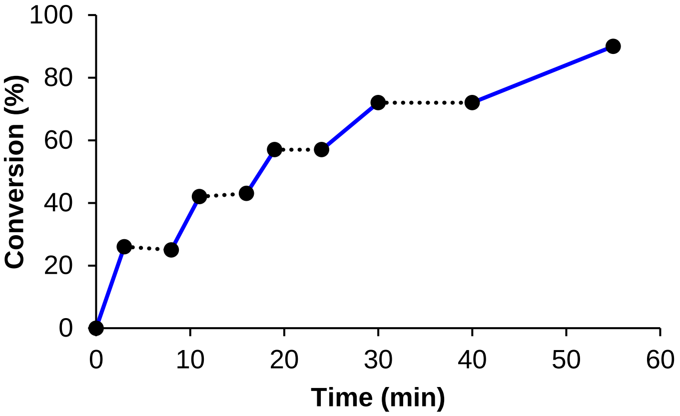

Figure 9. Plot of % conversion of NB over time. Solid blue line = time under blue LED light. Dashed black line = time in the dark.

Efforts parallel to our mechanistic studies have focused on expanding functional group compatibility (in collaboration with Dr. Dan Knorr, Jr. at ARL APG), synthesis of complex polymer architectures (e.g., cyclic, block, and graft copolymers), production of thermally processable linear polydicyclopentadiene for commercial applications, and collaborative work with the ARL APG (Cooperative Research Agreement via Dr. John La Scala and Dr. Dan Knorr, Jr.). For example, initial studies identified esters, ethers, carbonates, silyl ethers, halides, and arenes as compatible functional groups for homo- and copolymerizations via MF-ROMP. Those results enabled us to then target block and random copolymers that can function as surfactants and film formers for glass fiber sizing packages by controlling the hydrophile-lipophile balance. Copolymers were obtained initially by direct copolymerization of two or more monomer species. However, we also capitalized on the ease with which vinyl ether initiator moieties could be installed to produce multitopic macroinitiators. We prepared ditopic (bidirectional) initiators from polyethylene glycol and polypropylene glycol. Subsequent MF-ROMP produced ABA triblock copolymers in good yield. "Grafting from" approaches were also successful, such as grafting via MF-ROMP from vinyl ether functionalized polystyrenes. Separately, we discovered that dicyclopentadiene, the most widely commercial resin feedstock for ROMP, can be polymerized via MF-ROMP to give a linear (non-crosslinked) product. This offers unique processing capabilities and potential for broadened fields-of-use in commercial applications. The production of linear polydicyclopentadiene and composites thereof are currently the centerpiece for our commercialization efforts through our recently formed startup company.