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Peer reviewedlThesis/dissertation

UNIVERSITY OF CALIFORNIA, MERCED

Stimuli-Responsive Polymers with Unique Shape Changing Molecular Design

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics

by

Michael P. Leveille

Committee in charge: Professor Linda S. Hirst, Chair Professor Jennifer Lu Professor Ryan Baxter Professor Sayantani Ghosh Copyright

Michael P. Leveille, 2023

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The dissertation of Michael P. Leveille, titled Stimuli-Responsive Polymers with Unique Shape Changing Molecular Design, is approved and it is acceptable in quality and form for publication in print and electronically:

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University of California, Merced

2023

Dedications I dedicate this work to my loving friends and family.

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Acknowledgements

I would like to express my heartfelt gratitude to the following individuals and organizations for their invaluable support and contributions to my dissertation:

I am deeply appreciative of the financial support provided by the National Science Foundation (NSF) through grants CHE-1900647 and DMR-1309673, as well as the National Aeronautics and Space Administration (NASA) through grant numbers NNX15AQ01A and NNH18ZHA008CMIROG6R to J.L., and NSF grant CHE-1905395 to N.-H.G. This funding has been crucial in enabling me to conduct my research and achieve my academic goals.

I would like to thank Dr. Linda Hirst, Dr. Ryan Baxter, Dr. Daniel Beller, Dr. Jennifer Lu, and Dr. Sayantani Ghosh for their valuable feedback and suggestions as committee members. Their insights and expertise have greatly enriched my work. Additionally, I'm grateful to Prof. Sayantani Gosh and Prof. Jennifer Lu for their unwavering guidance, mentorship, and support as my graduate advisors. Sai always pushed me when I needed it and gave me a realistic vision. Jennifer helped me believe in myself and taught me many skills. I'm grateful to have had two advisors that helped me grow so much, allowed me to pursue my own research interests and were extremely patient. Their expertise and encouragement have been instrumental in shaping my research and academic journey.

I extend my appreciation to my lab mates, especially Dr. Wenxin Fu, for their support, camaraderie, and willingness to help throughout my research. Their contributions and friendship have created an unforgettable graduate experience.

I am deeply grateful to my family and friends, including my mom, siblings, and grandpa, for their unwavering love, support, and encouragement. Their belief in me has been a driving force behind my success. My friends here, especially Cole and Nick, have made Merced home during these years. I'm working towards a better future and hope to be able to help and inspire my friends and family as they have me.

I would like to acknowledge Dr. Kathryn Bourke for her valuable insight and support throughout my PhD.

I would like to express my appreciation to my kitties, Simba and Charlie, for their companionship and all the naps on my lap when I was writing my dissertation.

Last but not least, I would like to thank my wife, Fereshteh, for her unconditional support, love, and understanding throughout my graduate studies. Her encouragement and presence have been a constant source of motivation and inspiration. Her love, support, patience, and understanding cannot be overstated and has carried me to new heights.

I am sincerely thankful to all the individuals and organizations mentioned above for their contributions and support, which have been instrumental in the completion of my dissertation.

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Education

PhD, Physics, University of California Merced, Anticipated Spring 2023	2018 - 2023
• GPA 3.8	
BS, Biophysics, Loyola University Chicago IL, USA	2015 - 2017
o GPA 4.0	
AS, Joliet Junior College IL, USA	2013 - 2015
o GPA 4.0	

Professional Experience

Graduate Researcher – University of California Merced 2018 - 2023

Advisors: Prof. Sayantani Ghosh and Prof. Jennifer Lu

- Stimuli-Responsive Thermoset Composites
 - Collaborated with 3 groups internationally to develop new low-energy driven stimuli-responsive polymer composite
 - Molecular design and synthesis of negative thermal expansion alternating multiblock copolymers
 - o Developed soft-actuating prototype for low-grade thermal energy harvesting
 - Characterized morphology, chemical, mechanical, and thermal properties of polymers to understand structure-property relationships
 - \circ Utilized polymer science and engineering principles to solve material challenges
- Lab Management
 - o Negotiated 50% off cost of \$120,000 instrument
 - Maintained, repaired, cleaned, calibrated, wrote SOPs, and trained users on CVD, TGA, DSC, TMA, AFM, GPC, UV-ozone, vacuum pumps, and glovebox.
 - Lab safety coordinator conducting annual lab inspection and ensuring continued compliance with EH&S regulations

• Mentored and/or trained post-docs, graduate and undergraduate students *Advisor: Dr. Sarah Kurtz*

• Performance of photovoltaic technologies for automotive integrated PV

• Set up outdoor simulated vehicle environment, monitored data, and performed quantitative analysis for comparing solar panel performance on vehicles

Teaching Assistant	2016 - 2023
University of California, Merced	
Intro Physics 1 Discussion	Fall 2022 – Spring 2023
 Intro Physics 2 Discussion and Lab 	Spring 2019
• Calculus 1	Fall 2018
Loyola University Chicago	
Intro Physics 2 lab	Spring 2017
Intro Physics 1 lab	Fall 2016

Electrochemical Research,

Technology, and Engineering Intern - NASA JPL

Summer 2022

Supervisors: Dr. Ruoqian Lin and Dr. William West

- 0-volt tolerance of Li-ion batteries for increased safety and elimination of spacecraft failure mode
 - o Analyzed and correlated cell performance with material properties
 - \circ Developed anode to mitigate corrosion during deep discharge
 - \circ Co-optimized electrolyte and anode materials for deep discharge
 - o Sputter coated current collectors for material evaluation of novel electrode designs
 - Designed charge-discharge experiments for assessment of deep discharge performance
 - o Guided future research efforts through analysis of cycle data
 - o Assembled coin cells, including electrolyte and electrode fabrication
 - Prepared regular progress reports, communicating results and direction with technical team and supervisors

Research Assistant – *Loyola University Chicago* 2016 - 2018

Advisor: Dr. Brian Cannon

- Biophysical characterization of the effects of repetitive sequences on stability and structure of DNA anomalies
- Measurement of conformational dynamics for DNA three-way junctions with changes in sequence
- Developed curriculum for interdisciplinary physics labs for non-physics majors

Technical Skills Optics

- Custom optical setups and alignment
- Photoluminescence
- Lifetime measurements
- Quantum Yield
- Single molecule total internal reflectance microscopy

Processing

- Polymer synthesis, purification
- Polymer-carbon nanotube composites
- Thin films
- Annealing
- Slurry mixing
- Sputter, spin and blade coating
- Surface treatment: UV-ozone, piranha and hydrofluoric acid etching
- Chemical vapor deposition (CVD)
- Glovebox, Dry room, and Schlenk line experience
- Electrolyte and anode fabrication
- Battery assembly (coin cell, 3 electrode cylindrical)

Electrochemistry

- Charge-discharge
- Cycle life
- Rate capability testing
- Deep discharge
- Experience with Biologic, Arbin, and Maccor

Characterization

- Size exclusion (SEC), Gel permeation chromatography (GPC)
- Nuclear magnetic resonance spectroscopy (NMR)
- Infrared spectroscopy (FTIR)

- UV-vis spectroscopy
- Scanning and transmission electron microscopy (SEM) and (TEM)
- X-ray photoelectron spectroscopy (XPS)
- Atomic force microscopy (AFM)
- Profilometry

Materials Testing

- Thermogravimetric analysis (TGA)
- Differential scanning calorimetry (DSC)
- Thermomechanical analysis (TMA)
- Bending measurements
- Strain cycling
- Solvent exposure testing
- Piezoelectric testing

<u>Software</u>

OriginLab, Fusion 360 CAD, ImageJ, Microsoft Office, Adobe Cloud

Publications

- Brisbin, R., Bartolo, M., Leveille, M., Rajan, A. K., Jahan, B., McCloskey, K. E., Gopinathan, A., Ghosh, S., Baxter, R. (2022) "Tuning three-dimensional nano-assembly in the mesoscale via bis(imino)pyridine molecular functionalization" *Sci. Rep.* 12, 844. https://doi.org/10.1038/s41598-022-04851-6
- Leveille, M., Shen, X., Fu, W., Jin, K., Acerce, M., Wang, C., Bustamante, J., Casas, A. M., Feng, Y., Ge, N.-H., Hirst, L. S., Ghosh, S., Lu, J. Q. (2021) "Directional, Low-Energy Driven Thermal Actuating Bilayer Enabled by Coordinated Submolecular Switching" *Adv. Sci*, 2102077. <u>https://doi.org/10.1002/advs.202102077</u>
- Wheeler, A., Leveille, M., Anton, I., Leilaeioun, A., and Kurtz, S. (2019) "Determining the Operating Temperature of Solar Panels on Vehicles" 2019 IEEE 46th Photovoltaic Specialists Conference (PVSC), 3592-3597. doi: 10.1109/PVSC40753.2019.9311292
- Wheeler, A., Leveille, M., Kurtz, S., Anton, I., and Limpinsel, M. (2019) "Outdoor Performance of PV Technologies in Simulated Automotive Environments" 2019 IEEE 46th Photovoltaic Specialists Conference (PVSC), 3103-3110. doi: 10.1109/PVSC40753.2019.8981352
- Leveille, M., Tran, T., Dingillo, G., and Cannon, B. (2019) "Detection of Mg2+dependent, coaxial stacking rearrangements in a bulged three-way DNA junction by single-molecule FRET" *Biophysical Chemistry*, 245, 25-33. <u>https://doi.org/10.1016/j.bpc.2018.12.001</u>

• Mitchell, M. L., Leveille, M. P., Solecki, R. S., Tran, T., and Cannon, B. (2018) "Sequence-Dependent Effects of Monovalent Cations on the Structural Dynamics of Trinucleotide-Repeat DNA Hairpins" *The Journal of Physical Chemistry B*, 122 (50), 11841-11851. <u>https://doi.org/10.1021/acs.jpcb.8b07994</u>

Presentations

- 2022 Materials Research Society Spring Meeting, May 2022, Honolulu, HI
 - Oral: Sensitive Multi-Stimuli Responsive Actuating Films Driven by Submolecular Switching
- 2021 Materials Research Society Spring Meeting, April 2021, Virtual
 Oral: Harnessing a Molecular Switch in an Energy-Efficient Thermal Actuating Bilayer
- IEEE Photovoltaic Specialists Conference, June 2019, Chicago, IL
 Oral: Determining the Operating Temperature of Solar Panels on Vehicles
- UC Solar Symposium, Oct. 2018, San Francisco, CA
 O Poster : Testing Solar Modules for use in BIPV/AIPV Applications

Fellowships/Awards

• Best presentation for energy harvesting or storage, MRS Spring Meeting	May 2022
• MACES GRADSLAM (lightning talk) winner 1 st place, UC Merced	2022
• NSF funded National Research Training: Innovations in Graduate Educati	on 2020
Program in Interdisciplinary Computational Graduate Education (NRT-IC	GE)
Dan David Solar Fellow, UC Merced	2019 - 2020
• MACES GRADSLAM (lightning talk) winner 1 st place, UC Merced	2019
• MACES Fellow: Merced Nanomaterials Center for Energy and Sensing	2019
• Southern California Recruitment Fellow, UC Merced	2018
• Fr. Gerst, S.J. Memorial Award, Loyola University Chicago	2017
• Laudatory Honor: Summa cum laude, Loyola University Chicago	2017

Associations

• UC Merced Graduate Pedagogy Association – Vice President, Treasurer 2020 - 2022

List of Figures

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Changes of Dibenzocycloocta-1,5-dienes. Journal of the American Chemical Society,
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Figure 5.10. Proposed polymer structures to help understand the material-solvent
interactions, including the polyamide DBCOD studied thus far and three additional
proposed structures that can potentially be made under the same polymerization conditions
in order to compare with and without DBCOD as well as polyester (PE) vs. polyamide
(PA)70

List of Abbreviations

AFM	Atomic force microscopy
BCB	Benzocylcobutene
CNT	Carbon nanotube
DBCOD	Dibenzocycloocta-1,5-diene
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
$M_{ m w}$	Molecular weight
NIR	Near Infrared
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance spectroscopy
ODA	Oxydianiline
PA	polyarylamide
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PVDF	Polyvinylidene fluoride
SEM	Scanning electron microscopy
T_{g}	Glass transition temperature
T _m	Melting temperature
TGA	Thermogravimetric analysis
TMA	Thermomechanical analysis
UV	Ultraviolet
XTA	1,2-dihydrocyclobutabenzene-3,6-dicarboxylic acid chloride

Abstract

Stimuli responsive polymers change shape or properties in response to external stimuli such as light, heat, electric or ionic current, or solvents to name a few. These materials have gained a lot of attention in recent years due to their promising application as artificial muscles, smart clothes and wearable devices, drug delivery systems, and more. This dissertation introduces a new class of stimuli responsive polymers, dibenzocyclooctadiene (DBCOD) based materials. DBCODs are molecules capable of negative thermal expansion through a low energy activated conformational change. Similar actuators are compared and a history of DBCOD polymers and their unique properties is provided. Herein, contribution to the field is made by taking advantage of DBCOD as a new mechanism for actuation. A highly sensitive thermal and light actuating bilayer capable of reversible deformation at as low as a few degrees of temperature rise is presented. Coordinated conformational changes of DBCODs result in macroscopic thermal contraction that is inherently fast, repeatable, and low-energy driven. High precision actuation and excellent cycle stability of the bilaver is demonstrated. A platform consisting of poly(vinylidene fluoride) in tandem with the bilayer can harvest low-grade thermal energy and convert it into electricity. Furthermore, the DBCOD active material is shown to be sensitive to moisture and solvents, adding additional stimuli for actuation. The outlook of DBCOD-based materials is promising with actuation adding the potential to be used as energy harvesters, sensors, soft robots, biomedical devices, etc. The main focus of this dissertation is to take advantage of DBCOD's unique properties to offer new stimuli-responsive behavior which expands the application potential of polymeric DBCOD.

Chapter 1: Motivation and Overview

Responsive polymers have led to a multitude of actuating designs and functional materials towards the next generation of advanced devices and technology. A wide range of applications, including soft robotics,¹ microfluidics,² smart clothing,³ and energy harvesters,⁴ draw excitement to the field. Photothermal actuators, in particular, are popular for their simple, available, and tunable remote stimulus.⁵ Additionally, photothermal actuation can be achieved by mechanisms such as expansion, desorption, and most recently, contraction, with the advent of negative thermal expansion polymers.

A new class of materials has been developed over the last 10 years in which contraction upon heating arises from collective switching between conformations of dibenzocyclooctadiene (DBCOD) molecules within a polymer. DBCOD consists of a flexible 8-membered ring fused to two rigid benzene rings. The flexibility allows for both the twist-boat and chair conformers (**Figure 1.1**).



Figure 1.1 The dibenzocyclooctadiene (DBCOD) molecule twist-boat and chair conformers. Thermally driven DBCOD conformational change from boat to chair can result in negative thermal expansion depending on the substitutions. Hydrogen bonding can stabilize the boat.

DBCOD-based polymers show tremendous potential for a large range of applications. Although not all DBCOD-based polymers exhibit the peculiar negative thermal expansion, they still show improved material properties compared to similar materials lacking DBCOD, in particular for high performance polymers with high thermal and mechanical properties as well as properties for interlayer dielectrics. Additionally, the amount of DBCOD in different materials has been adjusted as a way to tune these properties. For example, zero thermal expansion was achieved in this way,⁶ a significant impact in the field of controlled coefficient of thermal expansion materials for coefficient of t

In fact, most DBCOD-based materials do not exhibit negative thermal expansion, making this class of materials of particular interest on a fundamental level. Three rules have been determined for achieving negative thermal expansion in DBCOD-based materials.^{7, 8} 1) The energy difference between the boat and chair states should increase to favor the chair conformation with increasing temperature. 2) The chair conformation should have a smaller volume. This depends on the substituents. 3) The polymer with more chair states should have tighter chain packing. It is difficult to design materials meeting these criteria, and only a few examples exist. Thus, DBCOD-based materials remain

understudied. However, attention has grown in recent years as DBCOD materials that do possess negative thermal expansion offer a new host of advances to the field of stimuli-responsive materials.

In **Chapter 1**, I broadly introduce the group of materials containing DBCOD moieties in the context of responsive materials. The goal of this dissertation is to explore and realize further possibilities of stimuli-responsive DBCOD-containing polymers.

This dissertation summarizes the author's work at the University of California, Merced related to intrinsically negative thermal expansion polymers. The author's group at the University of California, Merced, in collaboration with Fudan University and the University of California, Irvine, have created a low-energy driven thermal actuating bilayer, working off of abnormal polymer thermal contraction.⁹ Chapter 3 and Chapter 4 are adapted from the author's publication in Advanced Science. A chapter will be dedicated to the synthesis and unique properties of the active material of the bilayer actuator. From there, the actuator itself will be discussed, including everything from design and fabrication to performance and potential applications. Finally, an investigation of the interaction between polymeric DBCOD and various chemical solvents will be summarized as the topic of another chapter. The state of the art, the author's contributions, and the implications for application in the context of each chapter will be discussed. Specifically, the organization will be as follows:

Chapter 2 will discuss background on stimuli responsive polymers and DBCOD materials. This prepares the reader for the following chapters in which DBCOD-based polymers realize significant stimuli responsive behavior. Photothermal and molecular switch driven actuation designs and mechanisms will be discussed. These are the closest systems for comparison to DBCOD actuators. The history of DBCOD polymers will then be presented for the reader to understand the state of the art and the following contributions made by the author to this field.

Chapter 3 will focus on creating the active polymer used in chapter 4. It discusses the synthesis, processing, and characterization of DBCOD-based multi-block polyamide material. I show that in a DBCOD-containing polyamide polymer, conformational changes from boat to chair lead to abnormal polymer contraction. This begins with the synthesis steps creating each block of the multi-block polymer followed by purification. Next, the fabrication of polymer films is reviewed in detail, and finally, various characterizations and properties of this material are covered.

Chapter 4 will discuss a directional, low-energy driven thermal actuating bilayer based on the material developed and characterized in chapter 3. This new type of actuator is inherently low-energy driven and reversible. Actuation performance is analyzed, and the unique structure, tunability, and properties of the bilayer are discussed. Finally, an energy harvesting platform based on this bilayer is proposed.

Chapter 5 will discuss another class of stimuli available for DBCOD-based

actuation: solvents. This includes the ability to deform in response to moisture. The material developed in chapter 3 is subjected to various tests involving moisture and solvents, and the actuation behavior and material changes are discussed. Future studies in this direction are suggested as well.

Chapter 6 will conclude with overall conclusions and future directions. The outlook of DBCOD-based materials, as actuators as well as more generally, is promising with many avenues for future investigations and large potential impact.

Chapter 2: Background

2.1 Stimuli-Responsive Polymers

Stimuli-responsive polymers have attracted a lot of attention in recent years due to an expanse of promising applications such as artificial muscles,¹⁰⁻¹² sensors,^{13, 14} soft robotics,^{15, 16} micro biomedical devices,^{17, 18} energy harvesters,^{19, 20} and many more.^{3, 21, 22} Although "smart" materials' response to external stimuli could be a change in color,^{23, 24} stiffness,²⁵ or other material properties, the most common is a mechanoresponse, i.e., an actuator. Actuators can be categorized by stimulus (humidity,^{26, 27} solvents,^{24, 28} pH,²⁹ electric current,³⁰⁻³² light,³³⁻³⁵ temperature, etc.), structure (monolayer, bilayer, multilayer, complex, gradient), application, material (liquid crystal, hydrogel, carbon-based, dielectric elastomer, ionic polymer-metal composite), or by being nature-inspired (fly trap snap, pine cone opening, pea pod twisting, structure change in gecko feet,³⁶ and countless more).³⁷⁻³⁹

The photothermal actuator is popular for its simple, available, and tunable remote stimulus. Light is a relatively cheap source of stimulus that can easily be adjusted with high accuracy in terms of time of exposure, area of exposure, wavelength, intensity, and polarization. One working principle for actuators in general is to pair a responsive layer (active) with a material that has a low (passive) or opposite response, but for photothermal actuation, light must first be converted to heat. For example, Deng et al. reported a photothermal actuator composed of a passive polyimide layer and active polydimethylsiloxane (PDMS) layer. The PDMS layer contained aligned carbon nanotubes (CNTs) which absorbed light and heated the film photothermally. The anisotropic expansion of wax upon heating (due to alignment of CNTs), but not the passive layer, induced bending of the film.⁴⁰ This is just one example of many in which a carbon allotrope is used to photothermally heat an expanding polymer for actuation. Carbon-based actuators make up the majority of photothermal actuators due to their desirable optical absorption and thermal conductivity, and have been reviewed nicely by Han et al.⁵

Even within this narrowed category of actuators, designs and mechanisms vary greatly. For example, photothermal actuation can be achieved by expansion, desorption, magnetic susceptibility change, and various phase transitions (**Figure 2.1**). Aside from their desirable stimulus and excellent performance, this is another reason for their prevalence.



Figure 2.1. Various photothermal actuation mechanisms using carbon-based designs. Reproduced with permission from Carbon-Based Photothermal Actuators.⁵ Photothermal expansion reproduced from Graphene-Based Polymer Bilayers with Superior Light-Driven Properties for Remote Construction of 3D Structures.⁴¹ Photothermal desorption reproduced from Origami-Inspired Active Graphene-Based Paper for Programmable Instant Self-Folding Walking Devices.⁴² Photothermal magnetic susceptibility change: Reprinted (adapted) with permission from Kobayashi, M. and J. Abe, Optical Motion Control of Maglev Graphite. Journal of the American Chemical Society, 2012. 134(51): p. 20593-20596.⁴³ Copyright 2012 American Chemical Society. Soluble-insoluble transition: Reprinted (adapted) with permission from Wang, E., M.S. Desai, and S.-W. Lee, Light-Controlled Graphene-Elastin Composite Hydrogel Actuators. Nano Letters, 2013. 13(6): p. 2826-2830.44 Copyright 2013 American Chemical Society. Shape memory effect reproduced with permission.⁴⁵ Nematic-isotropic transition: Reprinted (adapted) with permission from Yang, Y., et al., Making and Remaking Dynamic 3D Structures by Shining Light on Flat Liquid Crystalline Vitrimer Films without a Mold. Journal of the American Chemical Society, 2016. 138(7): p. 2118-2121.46 Copyright 2016 American Chemical Society. Insulator-metal transition reproduced from Maximizing the Performance of Photothermal Actuators by Combining Smart Materials with Supplementary Advantages.⁴⁷

Another, more complex, type of light driven actuator design is to make use of molecular switches, molecules that can switch between two or more conformations or forms in response to a stimulus. Examples include spiropryans,⁴⁸ anthracites,⁴⁹ fulgides,⁵⁰ overcrowded alkenes,⁵¹ stilbenes,⁵² azobenzene derivatives,^{53, 54} donor-acceptor Stenhouse adducts,⁵⁵ and many more (**Figure 2.2**).^{28, 56, 57} Spiropyrans, anthracites, and fulgides are examples of reversible cyclization. Overcrowded alkenes and azobenzenes (azobenzenes being the most commonly used switch) are examples of *trans-cis* isomerization. Most of these require the breaking and forming of covalent bonds, typically by exposure to UV light. This is a con because it could be damaging to a polymer matrix or to biological systems and also has low penetration depth.



Figure 2.2. Examples of molecular photoswitches and their pros and cons.

There are, however, examples of visible light switches. For example, donoracceptor Stenhouse adducts work with visible light and have negative photochromicity, i.e., after switching the material becomes transparent to the excitation wavelength, allowing for penetration through the bulk material. Francis et al. created a spiropyran-based hydrogel actuator responsive to white light.⁴⁸ Upon exposure, a swollen hydrophilic state would reversibly photoisomerize into more hydrophobic spiropyran causing deswelling and bending. The downside of this example is slow response and solvent dependence as it needs to be in a liquid medium.

Dry photochromic actuation is usually performed by photoswitching induced (typically azobenzene) nematic to isotropic phase change in liquid crystal elastomers. Ryabchun and coworkers developed a significant contribution to this field recently, creating a hyrdazone based liquid crystal elastomer.⁵⁸ It exhibited bistability and only required UV in one bending direction (and visible in the other). The film would passively retain built-in stress at any desired bending position until further stimulated. Additionally, their design did not depend on order to disorder transition of the liquid crystal. Instead, expansion and contraction were due to molecular movement of the polymer matrix, directly caused by photoswitching. The problem for real applications is that their film was only bistable in the dark, or would otherwise relax.

Every actuator has pros and cons. Emerging molecular shape changes enabling new actuation schemes depend on either a chemical or electrochemical reaction in solution⁵⁹ or photoinduced *trans-cis* isomerization or cyclization enabled by bond breaking and reforming.^{60, 61} The former only operates in a specific solution whereas the latter requires a high-energy stimulus (e.g., ultraviolet light) which can be harmful to surrounding environments and the material itself. The performance of many conventional solid-state systems (including both photothermal and photoswitching actuators) rely on thermodynamic transitions, e.g., polymer glass transition, melting, or liquid crystal order to disorder transitions, and suffer from limited cycle stability due to large-scale molecular movement. A significant number of technologies require low-energy driven actuating components that operate under an ambient, solid-state environment, thus highlighting the need for a new system to fulfill such a requirement.

2.2 DBCOD

A series of papers have been published on dibenzocycloocta-1,5-diene and its derivatives, and their use in stimuli responsive materials is demonstrated in this dissertation. DBCOD, consisting of a flexible eight-member ring fused with 2 rigid phenyl rings, is a molecule that undergoes a thermally induced conformational change between twist-boat and chair conformers. The change from boat to chair can be associated with a decrease in volume and is inherently low-energy driven and reversible. Collective submolecular shape changes of DBCODs in polyaromatic amide polymers have led to observed giant polymer thermal contraction. The macroscopic shape change resulting from submolecular conformational change does not require a solution-based chemical reaction, high-energy input to break a covalent bond, and does not involve large-scale molecular motion. Overcoming many of the barriers to increased performance other switches face, DBCOD has great potential for actuating designs, providing a pathway to low-energy driven and reversible solid-state actuators. Since its introduction as a responsive material in 2012,⁶² DBCOD has received increasing interest in this regard. Although a variety of studies have been done since, investigations remain limited. This section reviews all relevant DBCOD works up to the present, focusing on the different materials that were used.

It should be noted that many polymer systems have been prepared through thermal curing of benzocyclobutenes (BCBs),⁶³⁻⁶⁶ and that dimerization of these moieties produce DBCOD. However, many of these studies do not even mention DBCOD and do not report unusual thermal contraction. DBCOD's unique properties went undiscovered despite the existence of many BCB-crosslinked materials due to the strict conditions required for this anomaly. These indirect investigations will not be reviewed here. Furthermore, DBCOD small molecules are naturally found in a variety of plant species within a class of molecules known as lignans, offering antioxidant, anti-inflammatory, and other health benefits.^{67, 68} This body of research also falls outside the scope of shape changing DBCOD molecules for stimuli-responsive polymers.

The following is a comprehensive review of DBCOD-focused publications of polymeric materials.

2.2.1 2010s

DBCOD was first introduced within stimuli-responsive materials as a near infrared (NIR) responsive polymer thin film by Dr. Lu's group at the University of California, Merced in collaboration with the University of California, Berkeley.⁶² However, in this paper it was not referred to as DBCOD, and the negative thermal expansion behavior was not yet known.



Figure 2.3 a) Aramid-*alt*-PEG structure used to make the first negative thermal expansion DBCOD polymer. b) DBCOD-continaing film fabrication. c) Actuation in response to NIR light. Polymer structure and film actuation: Reproduced with permission from *A Near-Infrared Mechano Responsive Polymer System.*⁶² Film fabrication: Reprinted (adapted) with permission from Huang, Y.H., et al., *Zero Thermal Expansion Polyarylamide Film with Reversible Conformational Change Structure*. Macromolecules, 2018. **51**(21): p. 8477-8485.⁶ Copyright 2018 American Chemical Society.

Using 1,2-dihydrocyclobutabenzene-3,6-dicarboxylic acid chloride (XTA), 4,4'oxydianiline (4,4'-ODA), and acid chloride terminated polyethylene glycol (PEG-COCl) monomers, a multi-block aramid-*alt*-PEG polymer containing benzocyclobutenes (BCBs) was synthesized (**Figure 2.3**a). Successful polymerization was supported by Fourier transform IR spectroscopy (FTIR) and thermogravimetric analysis (TGA). Atomic force microscopy (AFM) revealed different polymer film morphologies based on annealing temperature, with formation of nanofibers before annealing as well as after annealing at 350 °C. It was already known that BCB groups would thermally crosslink at this temperature in similar polymers.^{69, 70} Figure 2.3b is a schematic of the fabrication process of DBCOD-containing films. Annealed films were found to be responsive to green, blue, and NIR light, that is, they exhibited a small mechanical deflection (Figure 2.3c). Connected to a piezoelectric polyvinylidene fluoride (PVDF) film, a nanoamp current was measurable in response to light exposure. At the time, the mechanism was not understood, and "further theoretical and experimental investigations...[were] underway."⁶²

Indeed further investigations were underway and published a year later, unveiling negative thermal expansion at play in a triblock polymer-carbon nanotube (CNT) blend.⁷¹ This time, XTA, 4,4'-ODA, and mono-amine terminated PEG were used to form the polymer. Due to the aromaticity of the rigid block and polar nature of PEG, CNTs were well dispersed with polymer in NMP. AFM (**Figure 2.4**a) and scanning electron microscopy (SEM) showed that polymer again formed fibers but tended to align perpendicular to CNTs. The addition of CNTs increased thermal conductivity which resulted in more active material when stimulated, but too many CNTs would both increase stiffness adversely and reduce BCB crosslinking. The reduction of BCB crosslinking came from disrupted packing of polymer fibers as well as BCB cycloaddition with CNTs rather than each other.



Figure 2.4 a) AFM phase image of DBCOD triblock film with different amounts of carbon nanotubes mixed in. b) Tensometer data showing stress of film under NIR irradiation. Thermal expansion is highlighted in blue and thermal contraction in red. c) Stress and temperature during NIR irradiation. Taken with permission from *Greatly Enhanced Thermal Contraction at Room Temperature by Carbon Nanotubes*.⁷¹

Negative thermal expansion was revealed through tensometer testing where a prestrained film was exposed to NIR stimulation (Figure 2.4b,c) A fast drop in baseline stress tracked temperature rise well and was attributed to typical thermal expansion. However, a slower response of increasing stress over more than 60 s after temperature equilibration was attributed to an unknown molecular rearrangement resulting in thermal contraction. The thermal expansion component could be separated out by stimulating with NIR at 1.3 Hz, too fast for the contraction to take place. With increasing temperature rise, this component scaled up whereas the contraction was noted to taper off around 30-35 °C above room temperature. 3 wt% CNT loading was found to give the largest contraction stress, about 24-fold larger compared to pure polymer, but had the largest temperature rise as well (20x pure polymer). For a given temperature rise, however, 1 wt% gave the largest contraction stress at 10 °C above room temp. This indicates a different loading can be used to optimize response to either NIR stimulation or simply temperature rise depending on the application.

Stress from tensometer data was used to calculate a negative thermal expansion coefficient. Thermal stress, σ , measured from a pre-strained state is given as

$$\sigma = -\varepsilon E = -f_{heat} \alpha \Delta T E \tag{2.1}$$

where ε is thermal strain, *E* is Young's modulus, f_{heat} is the fraction of the film heated, α is the linear coefficient of thermal expansion, and ΔT is the change in temperature. Young's modulus was determined by tensometer data and film geometry while thermal stress was directly measured. The fraction heated and change in temperature were measured with an infrared camera. The resulting negative coefficient of thermal expansion calculated was found to be about -1200 to -1300 ppm/K, regardless of CNT loading. This was much larger than any known negative thermal expansion materials at the time.

Later in 2013 the mechanism of large negative thermal expansion was explained.⁷² In this study, triblock polymer was used as described in the previous report. The negative thermal expansion was about the same as initially reported, but contraction levelled off after only 20 °C. The fact that it reached a plateau along with the fact that contraction was not observed in commercial polymers or films that were not annealed suggested DBCOD to be key to this phenomenon. Through a combination of theoretical and experimental analysis, it was discovered that the thermal contraction was caused by a conformational change from the energy global minimum (twist-boat) to the local minimum (chair) state of DBCOD moieties.

Density functional theory (DFT) predicted the change from boat to chair to result in a 40% decrease in volume of a DBCOD molecule. Additionally, twist-boat was found to be the global minimum state with an activation enthalpy of about 21 kcal/mol to convert to chair (Figure 2.5a). The twist-boat conformation was stabilized by intramolecular hydrogen bonding between amide functional groups. However, when modeling 2 molecules, the difference in enthalpy was reduced (from 10 to 2-3 kCal/mol) as intermolecular hydrogen bonds stabilized the chair. This hydrogen bonding scheme implies narrower -NH- stretching peaks to be found associated with chair conformations as they lack the ability to participate in intramolecular hydrogen bonding. Indeed, FTIR revealed a broad -NH- stretching peak at room temperature (attributed to twist-boat conformations having free -NH-, inter- and intramolecular H-bonding) but a narrowed peak with increasing temperature (Figure 2.5b). This plateaued around 45 °C, in agreement with measurements of contraction. Lastly, the original FTIR spectrum was recovered upon cooling, and this narrowing and broadening phenomenon was not observed in films that were not annealed. The combination of evidence provided in this publication solidified DBCOD conformational changes as a new route to achieving inherent negative thermal expansion in polymers.



Figure 2.5 a) DFT calculated enthalpies tetra phenyl amide substituted DBCOD from BCB crosslinking showing the twist-boat as the lowest energy state. b) FTIR of DBCOD film before, during, and after heating to 50°C showing a narrowing of -NH- upon heating as evidence for boat to chair conversion. Taken with permission from *Large Negative Thermal Expansion of a Polymer Driven by a Submolecular Conformational Change.*⁷³

A few years later doubling the negative coefficient of thermal expansion was achieved and shown to be adjustable from -1140 to -2350 ppm/K.74 The same triblock polymerization procedure was used except 3,4'-ODA was used in place of 4,4'-ODA, randomly incorporating meta substituted amides (Figure 2.6a). This reduced polymer crystallinity and facilitated DBCOD conformational changes to occur at lower temperature. AFM, DSC, X-ray diffraction analysis (XRD), polarized optical microscopy (POM), and simulation all pointed to reduced crystallinity. AFM showed different morphologies between 3,4'- and 4,4'-polymer with reduced order in 3,4'-polymer. POM and XRD showed an ordered crystalline phase in 4,4'-polymer that was not present in 3,4'-polymer. Additionally, DSC revealed a glass transition, T_g , of 300 °C for 3,4'-polymer while 4,4'polymer had no T_{g} . Furthermore, all atom molecular dynamics simulations supported these findings, showing 4,4'-polymer packing tighter and more linear (Figure 2.6b). Contraction for a 7 °C temperature rise from a NIR laser was almost double in 3,4'-ODA polymer. However, the contraction levelled off around 34 °C compared to 42 °C for 4,4'-ODA polymer. Although a larger negative coefficient of thermal expansion was found, it was over a smaller temperature range. Perhaps this was because the amount of DBCOD in the material was not controlled, and a similar amount of DBCOD was present in both, simply reaching an equilibrium sooner in the 3,4'-polymer.



Figure 2.6 a) DBCOD polymer structure with meta- and para-substituted amides by using 3,4'-ODA in polymerization. b) All atom molecular dynamics simulations showing the 3,4'-ODA derived DBCOD taking on less linear structures. The shape parameter describes the molecular structure from spherical (S=0) to more elongated ellipses the larger the value. Taken with permission from *Adjusting Local Molecular Environment for Giant Ambient Thermal Contraction*.⁷⁴

In the next DBCOD publication in 2018, a different approach was used which allowed control over DBCOD content and resulted in adjustable coefficient of thermal expansion from positive to negative.⁷⁵ In this study, di-COOH functionalized DBCOD small molecules were synthesized for the first time and subsequently used in a Yamazaki-Higashi phosphorylation polycondensation with 4,4'-oxybisbenzoic acid (4,4'-OBA) and 3,4'-ODA. This was the first linear polymer containing DBCOD. The structure is shown in Figure 2.7a. A PEG block was not needed, but 3.4'-ODA was used to increase flexibility and reduce crystallinity. The polycondensation was performed with just OBA and ODA to make a control. Then, increasing ratios of DBCOD:OBA were also made, including one polymer without OBA, which increased DBCOD content from 0-42 wt%. These polymers were well characterized. Gel permeation chromatography (GPC) was finally available to characterize the molecular weight distribution of DBCOD polymers, reporting number average molecular weights, M_n , from 17,000 g/mol to 34,000 g/mol and dispersities, D, from 1.55 to 2.3. All polymers exhibited a glass transition near 250 °C by DSC measurements. Lastly, thermomechanical analysis (TMA) was performed for the first time which directly measures thermal expansion/contraction during a temperature program. This strain could simply be divided by a temperature range in order to calculate the coefficient of thermal expansion for that temperature range.

The result of increasing DBCOD content was apparent in the TMA data. While the control showed a positive thermal expansion of 92 ppm/K, all films containing DBCOD showed contraction starting around 75 °C (Figure 2.7b). The film consisting of mostly DBCOD but with 1 part OBA showed the greatest negative coefficient of thermal expansion, reaching -700 ppm/K over a wide range from 100-200 °C resulting in -10%

strain. The film with the most DBCOD content (lacking OBA) did not contract the most due to increased crystallinity as evidenced by wide angle x-ray diffraction (WAX) measurements. It should be noted that heating rate had a large effect on contraction. Heating rates decreasing from 10 °C/min to 1 °C/min increased average negative coefficient of thermal expansion by more than double. This new contraction was 94% recoverable, but only after 42 h because the polymer needed to relax to the minimum energy state well below the glass transition temperature. DFT for this polymer predicted a small activation energy and decrease in volume from twist-boat to chair, similar to previous studies (Figure 2.7c). However, it predicted that with increasing temperature, chair eventually becomes the global minimum due to its higher entropy. Finally, NMR at low temp. (-100 °C) was able to distinguish twist-boat and chair conformations of a DBCOD small molecule with 92% in twist-boat.



Figure 2.7 a) Structure of first linear DBCOD polymer. b) Thermomechanical analysis of linear polymers with increasing DBCOD content showing varying amount of thermal contraction. c) DFT calculated free energies showing a transition in preferred state from boat to chair upon heating of a representative small molecule. Reprinted (adapted) with permission from Wang, Z., et al., *Design and Synthesis of Thermal Contracting Polymer with Unique Eight-Membered Carbocycle Unit.* Macromolecules, 2018. **51**(4): p. 1377-1385.⁷⁵ Copyright 2018 American Chemical Society.

The same year, a new study came out achieving finer control of thermal expansion, including zero thermal expansion.⁷⁶ The Yamazaki-Higashi phosphorylation polycondensation method was applied in conjunction with BCB dimerization to form crosslinking DBCOD in a rigid-only block aramid. The synthesis scheme and structure of pre-crosslinked polymer is shown in **Figure 2.8**. 4,4'-OBA and 3,4'-ODA monomers were used to make a control while 1,2-dihydrocyclobutabenzene-3,6-dicarboxylic acid (DDA)

was added in increasing amounts relative to OBA to create a set of 6 polymers with increasing BCB content up to 26.5 wt%. High molecular weight polymers (20,000 to 50,000 g/mol) were obtained with glass transitions around 230 °C. Average coefficient of thermal expansion and strain were measured from 20-150 °C and ranged from -17.7 to 15.7 ppm/K and -0.23 to 0.2% respectively. The threshold for zero thermal expansion is ± 2 ppm/K, and one polymer from the set of 6 fell in this range with a strain of -0.016%. However, it had a much larger state of contraction around 95 °C and then began to expand. Additionally, heating rate largely affects coefficient of thermal expansion and strain measurements. Zero thermal expansion materials for application are difficult to realize but DBCOD-based coefficient of thermal expansion response here was expected to be isotropic, although never confirmed.



Figure 2.8 Synthesis scheme for BCB crosslinked polymer that achieved tunable low thermal expansion including zero thermal expansion. Taken with permission from *Zero Thermal Expansion Polyarylamide Film with Reversible Conformational Change Structure.*⁶

Six reports of DBCOD-based polymers were reported in the 2010's and have been reviewed. Five of these first studies employed BCB crosslinked DBCOD polymers while one made use of DBCOD monomer to make a linear DBCOD polymer. The various polymers exhibited a range of properties, most notably a tunable coefficient of thermal expansion range from positive to zero to negative. The mechanism of negative thermal expansion was revealed through agreement between DFT calculations and experimental observations of contraction and FTIR. Additionally, NMR could directly observe twistboat and chair confirmations. These initial findings revealed DBCOD-based polymers as promising candidates for controlled coefficient of thermal expansion composites and NIR or thermal actuators.

2.2.2 2020s

The results of polymeric DBCOD studies in the 2010's prompted further investigations. The 2020's already have 8 notable publications, 6 of which will be reviewed in this section. A 7th includes the author's publication and will be discussed in Chapter 3 and Chapter 4.

First, a new route to DBCOD small molecules enabled a more detailed study of the effect of substitution on DBCOD conformational changes.⁷⁷ A tetra-methyl substituted DBCOD along with an additional 1,10-di substitution of aldehyde, ester-ethyl, ester-phenyl, amide-ethyl, or amide-phenyl were prepared (**Figure 2.9**a). Additionally, a 2,9-
CHO DBCOD was compared. Using variable temperature ¹H NMR (VT ¹H NMR) twistboat and chair conformers were distinguishable at low enough temperatures. Their ratio was used to calculate the energy difference between boat and chair. Additionally, activation energies, enthalpies, and entropies were analyzed. Finally, experimental results were compared and agreed with DFT calculations and trends (Figure 2.9b,c).



Figure 2.9 a) DBCOD small molecule variations and their experimental and DFT calculated b) activation energy and c) change in Gibbs free energy from boat to chair conformations. Reprinted (adapted) with permission from Fu, W., et al., *Arene Substitution Design for Controlled Conformational Changes of Dibenzocycloocta-1,5-dienes.* Journal of the American Chemical Society, 2020. **142**(39): p. 16651-16660.⁷⁷ Copyright 2020 American Chemical Society.

The results indicated that increased molecular interaction, either attractive or repulsive, would reduce molecular freedom resulting in a negative entropy of activation, i.e., a more ordered activated complex during conformational change. Therefore, the activation energy, or conformational kinetics, could be adjusted by this entropy penalty and tailored through substitutions. The di-phenyl amide DBCOD had the largest intramolecular interaction and the largest activation energy of 68 kJ/mol compared to 40 kJ/mol for the tetra-methyl DBCOD.

On the other hand, conformational energetics were determined by whether interactions were attractive or repulsive. Amide substitutions exhibited intramolecular hydrogen bonding which stabilized the boat conformation as the global minimum energy state, in agreement with previous publications. Conversely, ester substitutions exhibited electrostatic repulsion which favored the chair conformation. For example, 1,10-diethyl ester had 86% C while 1,10-diethyl amide had only 14% C at room temperature.

This paper demonstrated control over the DBCOD conformational change by customizing the energy landscape through various substitutions and provided some guidelines for further molecular engineering. The largest activation energy was only 68 kJ/mol which is in the range of enzyme catalyzed biological reactions and much less than azobenzenes with 150-250 kJ/mol activation energies. Additionally, this substitution is most representative of the environment for which DBCODs exhibited low-energy activation in polymeric materials of previous publications.

A similar study was led by the group at Fudan University in China, specifying the requirements for negative thermal expansion.⁷ Using DFT, relative energies between boat and chair of 6 different small molecules were calculated at room temperature (r.t.) and elevated temperatures. The volume of these conformations was also calculated. Most

exhibited a preference for twist-boat at r.t. but only some showed a change in global minimum from twist-boat to chair with increased temperature up to 200 °C. Furthermore, only 1 of these actually decreased in volume, a 2,9-diphenyl amide DBCOD. Therefore, the requirements for negative thermal expansion were found to be that a change from twistboat to chair occurs with increasing temperature and that the chair conformation is smaller in volume. Preparation of 3 linear DBCOD-containing polymers confirmed their DFT predictions. Their structures and TMA data are shown in **Figure 2.10**.



Figure 2.10 TMA data at 2 °C/min for three linear DBCOD polymers and their structures. Only the 2,9-amide (left) substituted DBCOD showed negative thermal expansion which agreed with DFT prediction. Taken with permission from *Influence of Conformational Change of Chain Unit on the Intrinsic Negative Thermal Expansion of Polymers.*⁷

A number of polymer DBCOD publications all came out in 2021, including the author's. First, a tetra-ethyl substituted DBCOD monomer (TE-DBCOD) was synthesized and incorporated into polyarylamides and aromatic poly(amide-imide)s (PAIs), showing that alkyl substituents can be used to improve both solubility and thermal stability.⁷⁸ The polymer synthesis route is shown in Figure 2.11. Both aramids and PAIs were determined to be amorphous by WAX, and decreased chain packing was shown with increasing amounts of TE-DBCOD. This resulted in enhanced solubility for both types of polymers in less polar solvents. However, mixed results were found with TE-DBCOD's effect on $T_{\rm g}$ for the two types of polymers. The typical trend is that $T_{\rm g}$ decreases with increased solubility. This is what was observed in PAIs but not the aramids. Chain stiffness, chain packing, and interchain interactions all affect polymer mobility and therefore T_{g} . Addition of TE-DBCOD improves stiffness but disrupts packing and reduces interchain interaction. The aramids have more chain mobility compared to PAIs, and the dominant factor with the addition of TE-DBCOD was increased stiffness, resulting in increased T_{g} . The dominant factor in PAIs, on the other hand, was decreased chain packing and interchain interactions, lowering $T_{\rm g}$. Indeed, structure-property relationships in polymers are complex and difficult to predict. Nevertheless, the use of alicyclic rings to increase $T_{\rm g}$ while also using alkyl side chains to simultaneously improve solubility has been achieved. Although this paper does not measure negative thermal expansion as a result of DBCOD incorporation, it has shown that DBCOD moieties can increase T_g and solubility as well as thermal stability, mechanical properties, and optical transmittance. More importantly, it foreshadows a later result that disrupting chain packing can prevent DBOCD negative thermal expansion at a macroscopic level.



Figure 2.11 Synthesis scheme and structure of a) linear DBCOD polyarylamide and b) linear DBCOD poly(amide-imide) using a tetra-ethyl substituted DBCOD monomer (shown in shaded blue box). Reprinted (adapted) with permission from Jin, K., et al., *Significant Influence of Alkyl Substituents in the Alicyclic Rigid Backbone on Solubility and Thermal Stability of Polyarylamide Copolymers*. Acs Applied Polymer Materials, 2021. **3**(4): p. 2120-2130.⁷⁸ Copyright 2021 American Chemical Society

Another publication in 2021, led by researchers at Sandia National Lab, examined DBCOD in an epoxy matrix for the first time.⁷⁹ First, DFT calculations investigating the differences between regioisomers of di-amine substituted DBCODs predicted that for all 6 isomers twist-boat is the global minimum at room temperature and that the chair conformer has a smaller volume. However, only the *cis*-DBCOD had a negative free energy change from twist-boat to chair at elevated temperature (200 °C), satisfying both requirements for negative thermal expansion. The change in energy was found to be mostly dependent on entropy as previously reported.

An epoxy thermoset was prepared with commercial EPON 828 resin with diamine DBCOD crosslinkers. Epoxy/amines are typically easy to cure, and these were simply heated to 150 °C for 1 h. Results agreed with DFT predictions. *cis*-DBCOD had a low coefficient of thermal expansion (20 ppm/K compared to 60 ppm/K for typical epoxies) below its glass transition temperature and contracted above T_g . Maximum contraction was around 0.5% from 20-180 °C. It also had a T_g 10-30 °C lower than all others tested, possibly due to B to C mobility. All other resins expanded.

The next two studies discussed involve di-BCB functionalized precursors as a means to DBCOD crosslinked thermosets. The first study showed that this method, with the properly designed precursors, could allow for melt processing of thermosets.⁸ The T_m for one of the precursors was found to be 200 °C below the cure temperature. In addition to melt processing, solution processing is more accessible due to high solubility. The precursors and cured polymer structures are shown in **Figure 2.12**. Only one of these DBCOD-containing polymers exhibited negative thermal expansion from 20-60 °C. This was in agreement with DFT calculations for 6 DBCOD small molecules (2,9- and 2,8-substituted amide, ester, and imine), predicting only 2,9-amide to meet the requirements for negative thermal expansion. However, DFT alone could not explain why other

polyamides did not exhibit negative thermal expansion. VT-FTIR was used to show the polyamide with negative thermal expansion underwent a loss of free -NH- with increased temperature as B to C caused increased chain packing and intermolecular interactions. This agreed with previous studies. On the other hand, a DBCOD-containing polyamide with positive thermal expansion showed less loss of free -NH-. It was proposed that DBCOD-based polymer contraction requires tighter chain packing, which is facilitated by increased intermolecular hydrogen bonding in polyamide. However, if this is disrupted (in this case by flexible linkages), negative thermal expansion can be precluded.



Figure 2.12 Structures of 6 di-BCB monomers and their crosslinked DBCOD structure. Only polymers made from 3,4'-ODA-BCB showed negative thermal expansion, in agreement with DFT predictions. 4,4'-ODA-BCB monomers could not form films. DODA-BCB polymers prevented tighter chain packing with twist-boat to chair changes due to flexible linkages. Taken with permission from *High-Performance Polymers Adapted to Facile Melt Processing Through Structure Design of Benzocyclobutene-Containing Precursors.*⁸

The second study using di-BCB monomers did not produce negative thermal expansion polymers; however, formation of DBCOD via BCB dimerization offered a route to all-carbocycle thermosets with superior properties for dielectric applications.⁸⁰ The monomers and resulting polymer are shown in **Figure 2.13**. They exhibited extremely high thermal stability and mechanical properties due to the rigid structure. The all hydrocarbon structure also led to high hydrophobicity measured by contact angle and water absorption. It also endowed low dielectric constants (2.66 and 2.52) due to the large amount of C-C and C-H bonds which have low polarizability. This example demonstrates again the complex nature of DBCOD polymer contraction, requiring the right conditions to be met.



Figure 2.13 Di-BCB monomers and resulting all-carbocycle DBCOD thermoset structure, offering ideal properties for dielectric applications. Taken with permission from *All-Carbocycle Hydrocarbon Thermosets with High Thermal Stability and Robust Mechanical Strength for Low-k Interlayer Dielectrics.*⁸⁰

Overall, the 2020's have seen an increase in polymer DBCOD-focused publications with many important findings. Most notably, three rules governing DBCOD negative thermal expansion were proposed. This manifested through the creation of more DBCOD-containing polymers, the first experimental calculations of DBCOD conformational kinetics and energetics, and many more DFT calculations. More BCB crosslinked and linear DBCOD polymers were introduced while DBCOD epoxies also emerged. A wide range in properties were observed including benefits other than negative thermal expansion such as increased solubility, processability, thermal stability, mechanical strength, and dielectric properties arising from the structural nature of DBCOD and its derivatives.

2.3 Summary

In chapter 2, I have provided background on materials and concepts that are relevant to the projects discussed in this dissertation. Specifically, a section discussed stimuli responsive polymers, focusing on light driven actuation and its various mechanisms from photothermal heating of temperature sensitive materials to activation of molecular switches. Following this section, a review of DBCOD-focused work was provided. This included early studies of anomalous behavior, seminal work identifying the mechanism and principles by which such behavior is based on, and the various DBCOD materials created since and their unique properties. The main focus of this dissertation is to build upon the prior work done studying DBCOD, taking advantage of these unique properties, to offer stimuli responsive behavior and broaden the scope of polymeric DBCOD understanding and application.

Chapter 3: Synthesis and Characterization of Aramid-Based Stimuli Responsive Polymers

3.1 Introduction

In this chapter, I describe the synthesis, processing, and characterization of polymers used throughout my studies. These materials can be classified as multi-block copolymers with an AB repeating sequence of dissimilar blocks, specifically aramid and PEG blocks. They exhibited a self-assembled nanostructure that was important in the design of multi-stimuli responsive actuating films. Combined with DBCOD moieties, this structure led to negative thermal expansion, the property driving thermal actuation of cast films. The design and performance of these devices will be discussed in the following chapters.

An aramid-*alt*-PEG material with a slightly different synthesis has already been published, however only its NIR response was studied.⁶² The presence of DBCOD moieties with negative thermal expansion was unknown at the time. Here, negative thermal expansion is directly measured and rationalized in terms of a twist-boat to chair conformational change which is supported by DSC and NMR results.

In my studies, aromatic polyamide was synthesized via polycondensation of di-acid chloride and di-amine monomers, one of which contained a benzocyclobutene group, the DBCOD precursor. Another polycondensation was performed to introduce the PEG block, completing the aramid-*alt*-PEG polymer.

Thin films were fabricated by solution casting and air drying. During subsequent thermal annealing, ring opening BCBs dimerize to form crosslinking DBCOD. This post-annealed, DBCOD-containing polymer will be referred to as PA-DBCOD.

Both aramid-*alt*-PEG and PA-DBCOD were examined with AFM and SEM. Selfassembled nanofibers about 15-20 nm in diameter were found, arranged isotropically. TGA showed that the ratio of aramid to PEG resulting in this morphology was about 7:3. Additionally, this morphology was preserved in PA-DBCOD, assisting in alignment and dimerization of BCBs to form DBCOD.

PA-DBCOD exhibited negative thermal expansion and was measured in both ambient and dry atmospheres using thermomechanical analysis. The amount of contraction quantified as coefficient of thermal expansion reached below -80 ppm/K. This contraction was a result of DBCOD conformational changes which began around 0 °C and persisted up to 65 °C. A larger response in the ambient atmosphere was expected to be a result of plasticization of the polymer by moisture in the air, thus allowing more conformational freedom. This was the first observation of moisture dependence of DBCOD-based polymer contraction despite numerous studies on similar materials.

PA-DBCOD was then studied with DSC. The DBCOD conformational change was observed, as was the affinity for moisture in the atmosphere. A large water desorption peak usually covers the small DBCOD transition peak which had an enthalpy of 2.2 J/g. This

was consistent with an 8-12 kJ/mol enthalpy of DBCOD transition, which was predicted by DFT, as well as a 10-25% yield of BCB dimerization.

Finally, variable temperature NMR was also used to investigate the DBCOD transition. Using a model small molecule, the switch from twist-boat to chair was found around 50 °C, further supporting the idea that DBCOD contraction in PA-DBCOD polymer occurs at elevated temperatures not far from room temperature.

Polymeric materials with intrinsic negative thermal expansion are difficult to realize. The PA-DBCOD described here has achieved this unique property and is the foundation for a new actuation concept revealed in Chapter 4 with application to biomedical, space, and energy harvesting devices.

3.2 Methods

3.2.1 Synthesis

Aramid Block Synthesis

The first polymerization step was to make the aramid block. This was done via condensation polymerization using the monomers 1,2-dihydrocyclobutabenzene-3,6-dicarbonyl dichloride (XTA) and 4,4'-oxydianiline as shown in **Scheme 3.1**. The molar ratio of XTA to 4,4'-ODA was greater than one, typically 1.1-1.2, to ensure polymer chains end with acid chloride groups from XTA monomers. This allowed condensation with the 2nd block which was amine terminated. The presence of moisture could terminate these polymerizations because water reacts readily with acid chlorides to form carboxylic acids (**Scheme 3.2**). Furthermore, because condensation polymerization proceeds in step-wise growth, termination occurring even in a late stage of the polymerization can result in low molecular weight polymer (**Figure 3.1**). Therefore this polymerization was done under an inert atmosphere and using anhydrous solvent. Additionally, glassware was dried in an oven or via blow torch and transferred directly into a glovebox antechamber under vacuum while cooling so as to not absorb moisture.



Scheme 3.1 Synthesis of P(XTA-ODA), the first step of making Polyamide-DBCOD.



Scheme 3.2 Reaction of acid chlorides with water



Figure 3.1 Comparing molecular weight vs. percent conversion for chain growth, living, and step growth polymerization. Step growth polymerizations must reach very high percent conversion in order to yield high molecular weight. In other words, termination before completion can result in small chains. Image taken from <u>https://www.pslc.ws/macrog/synth.htm</u> provided by Prof. Elizabeth S. Sterner at Lebanon Valley College.

The following describes the experimental procedure in detail. 4,4'-ODA, 99%, and Poly(ethylene glycol) bis(3-aminopropyl) terminated (PEG-NH₂) was purchased from Aldrich and used as received. Anhydrous NMP was purchased from Sigma-Aldrich and freshly activated molecular sieves were added. XTA, the terephthaloyl chloride derivative with a benzocyclobutene group, was provided by Gary Spilman.

A round bottom flask equipped with a stir bar with at least two necks was used. Additional materials transferred into the glovebox included a flow control flask adapter with a vacuum greased joint, a septum for each neck of the flask not occupied by the adapter, a keck clip, a vial equipped with a stir bar, and syringes while the box already contained anhydrous NMP, all other reagents including monomers, a balance, a stir plate, and a spatula. Within the box, XTA was added to the flask followed by NMP to make a 0.5 M solution. The adapter and septa were added next and the solution was put on the stir plate to speed up the dissolution of XTA. Then, 4,4'-ODA and NMP (0.5 M) were added to a vial and stirred to dissolve. Next, the fume hood was prepared with an ice bath on a stir plate just below a syringe pump. The pump was programmed for the syringe containing 4,4'-ODA, and set to dispense at 2 mL/h. This hood was equipped with a Schlenk line connected to a nitrogen gas tank. The dissolved 4,4'-ODA solution was then extracted with a syringe and transferred out of the box along with the reaction flask containing the XTA solution, making sure the stopcock was closed and septa were in place. The nitrogen line was purged and then connected to the flask adapter while flowing gas. The reaction flask

was then opened to nitrogen flow, lowered into the ice bath, and stirred. The syringe containing 4,4'-ODA was loaded onto the pump and pierced through the septum on the flask below it. Finally, the pump was started and began adding 4,4'-ODA to XTA, making sure the needle would not be submerged in the reaction solution. This setup is shown in **Figure 3.2**. After two hours, the flask was removed from the ice bath and continued to stir overnight at room temperature. This completed the aramid portion of the target multi-block polymer. The desired polymerization parameters are shown in **Table 3.1**.



Figure 3.2 Photo of polymerization setup for step 1, adding 4,4'-ODA to XTA in an ice bath using a syringe pump and protected with dry nitrogen using a Schlenk line.

0.5 M	XTA
0.5 M	4,4'-oxydianiline
140 mg/mL	PEG-NH ₂
1.2:1	XTA:4,4'-oxydianiline molar ratio
70 wt%	Aramid (XTA + 4,4'-oxydianiline)
30 wt%	PEG-NH ₂

 Table 3.1 Desired Polymerization Conditions

Multi-Block Synthesis

After completion of the aramid block, another polycondensation was performed to create a multiblock polymer with alternating rigid and flexible blocks (**Scheme 3.3**). The aramid reaction had been left overnight protected by nitrogen. Before continuing, a GPC sample was extracted for analysis of the aramid molecular weight. With XTA in excess of 4,4'-ODA, aramid chains were expected to have acid chloride functional groups on their ends. Therefore, a diamine terminated flexible block was used, PEG-NH₂, having an average molecular weight of 1,500 g/mol.

PEG-NH₂ was added to a vial in the glovebox followed by NMP to make a 140 mg/mL solution. The solution was stirred to dissolve and transferred out of the box in a syringe. The aramid reaction flask was lowered into an oil bath equilibrated at 80 °C. While stirring, the PEG-NH₂ solution was added dropwise to the aramid reaction flask by piercing the septum with the syringe needle, keeping the solutions protected by nitrogen. This reaction was left to complete overnight.



Scheme 3.3 Synthesis scheme of multi-segment aramid-alt-PEG

Purification

After completion of the 2-step polymerization, the polymer was crashed out of solution, collected, and purified by Soxhlet extraction. First, a GPC sample was extracted from the reaction flask, and the flask was raised from the oil bath to cool down. The reaction mixture was then fully extracted into a large syringe and loaded onto the syringe pump. The pump was configured to dispense at 20 mL/min and setup over vigorously stirring water. The volume of water to polymer solution was 10x, causing precipitation with each drop. The solid was collected via vacuum filtration or centrifugation and transferred to a thimble for Soxhlet extraction.

The Soxhlet extraction setup is shown in **Figure 3.3**. Greater than 60 mL of THF was refluxed using an oil bath with the polymer-containing thimble in place. Aluminum foil could be used around the glassware to help with refluxing. The polymer was left to wash in hot THF overnight. The solubility of all starting materials in H₂O and THF was tested and the results are shown in **Table 3.2**. Water could remove PEG-NH₂ and HCl, while hot THF could remove all starting materials. Based on this, the Soxhlet extraction was performed using THF. Any solid remaining was polymer product which was dried in a vacuum oven.



Figure 3.3 Soxhlet extractor setup with THF to wash the polymer product

Table 3.2 Solubility of starting materials and side products, confirming adequate quench and purifying solvents. Solubility determined qualitatively at room temperature by observation as + indicating soluble, - insoluble, slightly soluble, or n/a not tested.

	H ₂ 0	THF
XTA	-	+
4,4'-ODA	-	Slightly
PEG-NH ₂	+	Slightly
HCl	+	n/a

3.2.2 Film Fabrication

After purification, polymer thin films were fabricated. This began with substrate treatment, followed by drop casting polymer solution, drying, annealing, and etching.

The substrates for films were polished silicon wafers treated with piranha solution. First, a 100 mm diameter, 0.5 mm thick wafer was scored with a diamond tipped scribe and snapped in half. Only a millimeter or two from the edge needed to be scored. Then, slight pressure would create a clean, straight break. This was repeated until the Si pieces were an appropriate size for our tube furnace (< 1" wide). These substrates were placed in a quartz or Teflon holder.

Piranha solution was prepared in a glass beaker (**Figure 3.4**). Extra caution was taken when handling piranha such as using a full face shield, secondary gloves, and clearly labeling the fume hood with "piranha in use". This solution was only used on clean wafers as it reacts violently with organics, potentially exploding, and should only be used to clean residuals. Additionally, less than half of the container was used to prevent bubbling over. A secondary container was used in case this happened. Also, a lid was used to catch splatter. Concentrated sulfuric acid was first added to the beaker. Then 30% hydrogen peroxide was slowly added to the acid, never in reverse. The solution bubbled, steamed, and became very hot. Finally, substrates were lowered into the piranha and placed on a hot plate at 100 °C for 2 hours. Afterwards, Si substrates were removed and washed with DI water. They were then clean and hydrophilic. Piranha treated substrates were stored in IPA until needed, and the piranha solution was left in the hood overnight to become less reactive before proper waste disposal.



Figure 3.4 Cleaning of Si substrates by piranha treatment

In order to cast polymer films, dry product was re-dissolved in NMP (~40 mg/mL). Piranha treated substrates were removed from IPA and blown dry with nitrogen. A photo was taken, and the area of substrates was analyzed by imageJ. This allowed for the same loading to be cast on different sized substrates, e.g., 50 μ L/cm². The desired volumes of polymer solution were dropcast onto the substrates after filtered using a micro pipette, and the samples were put in a drying chamber at room temperature on a levelled surface with controlled air flow (**Figure 3.5**). They were left to dry for a week before annealing. Drying slowly allowed for polymer chains to rearrange to their preferred configuration.



Figure 3.5 Room temperature drying chamber with levelled platform and controlled airflow for polymer films

Dry films were annealed in a tube furnace in order to remove remaining solvent, remove the PEG-NH₂ block, and crosslink the aramid via 4-member ring opening and dimerizing XTA moieties. Scheme 3.4 shows the dimerization of BCBs resulting in a DBCOD derivative. Within the tube furnace, pressure was kept at 500 torr and with an argon flow rate of 20 SCCM. Films were slowly heated to 310 °C over the course of 3.5 h and then held there for 16 h to remove solvent and PEG-NH₂. The temperature was then increased to 350 °C and held for 10 h to accomplish DBCOD formation. Figure 3.6 shows the tube furnace setup with a batch of films after annealing had completed. Finally, the films were peeled off from the silicon substrate using a hydrofluoric acid bath to etch the SiO₂.



Scheme 3.4 Benzocyclobutene (BCB) dimerization. One of the products is DBCOD.



Figure 3.6 Tube furnace setup with a batch of films after annealing had completed

3.2.3 Characterization

Gel Permeation Chromatography (GPC)

Gel permeation chromatography was performed using a Waters 1515 pump, equipped with a column heater and Waters 2414 refractive index detector. The two-column set consisted of a Waters Styragel HT 3 DMF and Waters Styragel HT 2 DMF column. HPLC grade N-methyl-2-pyrrolidone was utilized as the eluent with a flow rate of 1.0 mL/min at 40 C. The GPC system was calibrated with a series of commercially available polystyrene narrow standards. Samples were dissolved in HPLC grade NMP at a concentration of 1-2 mg/mL and filtered through 0.2 μ m PTFE filters before testing.

Microscopy

AFM (XE-100, Park system) was used to observe the morphology of films before and after annealing. SEM images were performed on a Zeiss Gemini 500 electron microscope. Samples were coated with an approximated 7 nm thick layer of gold using a Cressington HR sputter coater due to issues of charging while attempting to image uncoated films.

Thermogravimetric Analysis (TGA)

TGA (TA instruments SDT Q series) was performed (under N_2 flow of 100 mL/min) on PA-DBCOD to obtain the weight percentage of aramid and PEG. Samples were first heated to 130 °C in order to remove moisture and then cooled back down to 50 °C. This typically resulted in about 1 % weight loss. After equilibrating, the weight was recorded as 100 % and a temperature ramp (at a heating rate of 20 °C min⁻¹) was performed.

Thermomechanical Analysis (TMA)

Thermomechanical analysis was carried out on an TA thermomechanical analysis instrument equipped with a tension measurement system. The applied bidirectional force was adjusted based on sample dimensions so that the cross sectional stress was equivalent for different films. All measurements were done under a dry nitrogen atmosphere with a heating rate of 2 °C min⁻¹. The first measurement of a film was performed after being stored in ambient conditions for an extended period, called "humid." After the sample was naturally cooled back down to room temperature and followed by an additional 24 h purge under dry nitrogen, a second measurement was performed, called "dry." This sequence was carried out at different applied stresses (143 kPa, 214 kPa, and 500 kPa).

In order to determine the coefficient of thermal expansion, length vs temperature was plotted and best fit with a 9th order polynomial curve fit (R-Square > 0.997) using OriginLab. The fit was differentiated and divided by film length at each temperature to plot the linear coefficient of thermal expansion, given by:

$$\alpha_{\rm L} = \frac{1}{L} \frac{\partial L}{\partial T} \tag{3.1}$$

where *L* is the instantaneous length of the film and *T* is temperature. Furthermore, net negative thermal expansion capacity, χ_{α} , originally introduced in terms of isotropic negative thermal expansion materials as a means of comparing their thermal contraction,⁸¹ can be given for linear negative thermal expansion materials as:

$$\chi_{\alpha L} = \int_{T_1}^{T_2} \alpha_L dT = \frac{\Delta L}{L}$$
(3.2)

where T_1 and T_2 bound the domain in which negative thermal expansion is observed. $\chi_{\alpha L}$ is simply the net strain over the negative thermal expansion temperature range. Integrating $\alpha_L(T)$ between its roots, T_1 and T_2 , yielded $\chi_{\alpha L} = -0.14\%$ and -0.25% for "dry" and "ambient". The contraction component alone was estimated by setting a baseline at 33 ppm K⁻¹ and integrating the area below.

Differential Scanning Calorimetry (DSC)

A DSC (Netzsch Polyma 214) was calibrated for temperature and sensitivity using adamantane, bismuth, tin, zinc, and indium standards covering the full range of the instrument. All corrected onset temperatures differed from nominal values by less than 0.1 °C, and all experimental sensitivity values differed from the theoretical calculated values by less than 2% for the 5 calibration standards. PA-DBCOD polymers were tested in pierced aluminum pans under nitrogen with a heating rate of 10 K min⁻¹.

The enthalpy of DBCOD conformational change in a PA-DBCOD polymer, $\Delta H_{PA-DBCOD}$, can be estimated by:

$$\Delta H_{PA-DBCOD} = \frac{x * \Delta H_{DBCOD}}{M_W}$$
(3.3)

where x is the molar fraction of repeat units that formed DBCOD, ΔH_{DBCOD} is the enthalpy associated with the DBCOD conformational change, and M_W is the molecular weight of the repeat unit (717 g mol⁻¹). According to DFT, the enthalpy associated with the DBCOD conformational change is 2 - 3 kcal mol⁻¹ (8.4 - 12.6 kJ mol⁻¹).⁷² The estimated yield for DBCOD during thermal annealing is about 10 - 25%. This DBCOD transition would therefore produce 1.1 - 4.3 J g⁻¹.

Nuclear Magnetic Resonance (NMR) Spectroscopy

DBCOD monomer (2,3,8,9-tetramethyl-1,10-diphenylamide substituted DBCOD; **Figure 3.11**) was synthesized using the published method⁷⁷ and dissolved in $C_2D_2Cl_4/DMSO-d_6 = 1/2 (v/v)$ at a concentration of 3 mg mL⁻¹ in preparation for VT-¹H NMR. The VT-¹H NMR spectra were recorded on a Bruker Avance500 II spectrometer. Tetramethylsilane (TMS) was used as an internal standard with an applied temperature coefficient of -5×10^{-4} ppm K⁻¹ as per the IUPAC's recommendation.⁸² Peak identification was guided by integration and DFT predictions.

3.3 Results

3.3.1 Formation of DBCOD

An aramid-*alt*-PEG multi-block polymer was created as described in the Methods section. Di-acid chloride and di-amine monomers were condensed to form an aromatic polyamide rigid block with BCB substituents. Subsequent polycondensation with PEG-NH₂ completed the aramid-alt-PEG polymer. Polymer molecular weight was analyzed first as samples for GPC were extracted during polymerization. Typical molecular weights remained low, around 13,000 g/mol. The product was collected by precipitation and centrifugation and was purified by Soxhlet extraction.

Polymer thin films were cast on piranha treated Si wafers, thermally annealed, and removed by HF etching. When annealed at 350 °C, BCBs dimerize to form DBCOD in a crosslinking position of the material, referred to as PA-DBCOD compared to aramid-*alt*-PEG for the pre-annealed polymer. Pre- and post-annealed polymers were characterized using a variety of analytical techniques, including TGA, AFM, SEM, TMA, DSC, and NMR.

Morphology

Thermogravimetric analysis was performed on PA-DBCOD powder to determine the weight percent of aramid and PEG-NH₂ blocks. **Figure 3.7**. shows the TGA curve of PA-DBCOD powder under a nitrogen atmosphere, revealing two regions of degradation. The 5% weight loss temp, $T_{d,5\%}$, was about 390 °C. The derivative weight curve was used to determine the inflection point corresponding to thermal degradation of a second species around 460 °C. The first and second part to degrade were determined to be the PEG-NH₂ and aramid, respectively, from TGA experiments on these materials individually. From this set of experiments, the PA-DBCOD was determined to consist of about 33 wt% PEG-NH₂ and 67 wt% aramid.



Figure 3.7 Thermogravimetric analysis of aramid-*alt*-PEG under nitrogen with a heating rate of 20 °C min⁻¹. The derivative weight % is shown in blue to distinguish degradation of aramid and PEG in the multi-segment aramid-*alt*-PEG, indicating about 33 wt% PEG.

The ratio of blocks in a block copolymer is one key factor affecting morphology.^{83, 84} In the case of PA-DBCOD, the PEG-NH₂:aramid ratio of about 3:7 resulted in self-assembly of polymer chains as revealed by AFM and SEM (**Figure 3.8**). The polymer assembled into nanofibers approximately 15-20 nm in diameter as a result of the contrast between PEG-NH₂ and aramid. This morphology was preserved through annealing and was expected to have aided in DBCOD formation.



Figure 3.8 a) AFM phase image and b) SEM image of pre-annealed aramid-alt-PEG

3.3.2 Origin of Low-Energy Driven Shape Change Thermomechanical Analysis (TMA)

Thermomechanical analysis was conducted to understand the thermal response of PA-DBCOD polymers. **Figure 3.9**a shows a comparison of the TMA results of the same sample after storing under ambient conditions ("ambient") versus after 24 h in dry N₂ purge ("dry"). The film displayed a normal, positive thermal expansion below 0 °C due to increased molecular vibrations upon heating. However, from 0 to 50 °C, abnormal thermal

contraction was observed in the "ambient" test. Above 50 °C, this effect disappeared and only thermal expansion was present. Comparing "ambient" versus "dry", a greater extent of thermal contraction was observed for "ambient." We posit Dha(1000iBt) re in "ambient" solvates the crystalline domain of the polymer, facilitating they DBCOD conformational changes. The noticeably higher thermal contraction for "ambient" is a combination of moisture desorption and greater extent of the DBCOD conformational change. It is reasonably assumed that the observed thermal contraction of any DBCOD conformational change.

DBCOD conformational change. In order to rule out a "rubber effect", that is, an entropy driven thermat contraction observed in stretched rubbers above their glass^{0.00} transition temperature, "dry" was characterized with TMA at different applied loads of the stress of the str





mer films. a) PA-DBCOD film strain versus itrogen (dry) revealing thermal contraction. The Polymer linear coefficient of thermal expansion bient conditions cross into the negative thermal ctively, and were found to exhibit linear thermal considering the DBCOD contraction component

bbserved, polymer coefficient of thermal plotted as a function of temperature (Figure nal expansion value became negative and then "ambient." The contraction effect ninished upon further heating until ≈ 65 °C,

measurements from 20–65 °C in Chapter 4 (Figure 4.12a) when discussing actuation of a bilayer. Further quantifying thermal contraction, we found the net linear negative thermal expansion capacities, $\chi_{\alpha L}$, the length change observed over the respective 35 and 50 °C

negative thermal expansion temperature ranges for "dry" and "ambient." The contraction component alone yielded $\chi_{\alpha L} = -0.30\%$ and -0.44% for "dry" and "ambient".

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (**Figure 3.10**) was used to investigate thermodynamic transitions in PA-DBCOD polymer films. Neither glass transition nor melting point was observed from -50 to 200 °C. One large endothermic peak, 208 J g⁻¹, was observed for the sample in a pierced pan stored in ambient conditions for more than 10 h. After the measurement, the sample was cooled down to room temperature and rested under dry N₂ purge for 14 h. There was a small and very broad peak, 2.2 J g⁻¹, repeatedly detected.



Figure 3.10 DSC of PA-DBCOD under nitrogen atmosphere in a pierced aluminum pan and heating rate of 10 $^{\circ}$ C min⁻¹ after resting in air (black), resting in dry nitrogen for 14 h (green), and resting in air for 3 h (red).

The amount of enthalpy associated with the DBCOD conformational change (details found in the Methods section) within the film is $\approx 1.1-4.3$ J g⁻¹ assuming that the DBCOD yield from dimerization is 10–25%. The experimental data falls within the range of the theoretical calculation, using 8–12 kJ mol⁻¹ for the DBCOD conformational change from twist-boat to chair, indicating that the small peak in the absence of water was generated by the DBCOD conformational transition in the polymer. When the sample was left in air for a few hours, the large endothermic peak quickly restored (Figure 3.10), indicating that the observed endothermic absorption was mainly caused by moisture desorption upon heating.

Variable Temperature ¹H NMR

The dynamic nature of amide-substituted DBCOD was studied by variable temperature ¹H NMR (VT-¹H NMR). Di-amide substituted DBCODs were synthesized since this form can be obtained with high purity⁷⁷ and closely models the DBCOD units in PA-DBCOD. The disappearance of a set of peaks associated with protons on the aromatic rings ($\delta = 6.8-7.7$) (**Figure 3.11**) in VT-¹H NMR suggested that a portion of DBCOD units underwent a conformational change from one conformer to another \approx 50 °C. The contention is supported by the similar changes in amide ($\delta = 9.7-10.1$) and methyl ($\delta = 2.0-2.3$) regions. The porous nature of annealed aromatic polyamide film may afford enough free volume and mobility to allow the DBCOD conformational change to occur. Despite medium dependence, this set of VT-¹H NMR analyses indicates that the DBCOD conformational changes occur at a temperature around and above room temperature.



Figure 3.11 Variable temperature ¹H NMR of diphenyl amide substituted DBCOD monomer in $C_2D_2Cl_4/DMSO-d_6 = 1/2$ (v/v). Proton signals a-h were labeled on spectrum. The set of peaks (highlighted with arrows) that disappeared with temperature indicated DBCOD conformational transitions.

3.4 Conclusion

This chapter covered the production and analysis of aramid-*alt*-PEG and PA-DBCOD films used in the author's research. The polymers exhibited a self-assembled nanostructure that is crucial to the development of multi-stimuli responsive actuating films. By adding DBCOD moieties to the structure, the polymers displayed negative thermal expansion, a necessary property for unique thermal actuation.

The polymers were synthesized through a two-step polycondensation and characterized using techniques such as AFM, SEM, TGA, and DSC. The results showed that the ratio of aramid to PEG in the polymer played a role in the self-assembly of nanofibers, and that negative thermal expansion was occurring in PA-DBCOD. The use of DSC and variable temperature NMR support that DBCOD moieties were responsible for the negative thermal expansion observed. Finally, the data suggest that moisture in the atmosphere acts to plasticize the polymer and allow for more conformational changes to occur. Overall, an in-depth study of the relevant properties of the polymers used in the author's research was provided.

This synthesis and detailed study of this material had not been reported prior to our investigation. Such a material sets the stage for a low-energy driven bilayer actuator which will be the topic of chapter 4 and is promising for biomedical and thermal energy harvesting applications, among others.

Chapter 4: Directional, Low-energy Driven Thermal Actuating Bilayer

4.1 Introduction

In this chapter, I describe a new type of bilayer made of approximately 15 µm thick PA-DBCOD that is covalently connected to a thin sheet of aligned multiwalled CNTs, with less than 0.1 µm in thickness. The DBCOD conformational change in response to a low-energy thermal stimulus, such as heating a few degrees above room temperature, can produce an appreciable shape change. Under the same temperature range, the CNTs do not change in shape, thus generating substantial stress. Without any process optimization, \approx 4.7 mm per centimeter deflection was observed by heating the film from 25 to 55 °C. A flat bilayer at room temperature (25 °C) placed onto the palm of a hand (< 37 °C) curled up substantially, further exemplifying the ultrasensitive nature of this new system. Actuator performance has been quantified by bending angle, curvature, and cycle stability. However, since bending performance depends on key factors such as thickness, aspect ratio, modulus, energy input, and energy conversion efficiency,^{85, 86} it is difficult to draw fair comparisons to existing actuators in the literature that often rely on a thermodynamic transition involving large scale molecular motion.

 π - π stacking between aramid and CNTs directs assembly of DBCOD actuating units along the longitudinal direction of CNTs, therefore enabling controlled anisotropic shape changes by the design of a CNT pattern. Further, because of covalent linkages between CNTs and polymer chains as well as the intrinsic reversibility of the DBCOD conformational change, this bilayer acts as one, offering excellent cycle performance without any observed changes after 70,000 cycles.

This type of actuator differs from liquid crystal based thermal actuators, moisturedriven thermal actuators, and other existing thermodynamic-based actuators in a number of ways. First, the shape change is due to a low-energy driven conformational change. Second, shape change produced by a submolecular conformational change does not involve large and unrestrained molecular motions such as those at glass transition temperatures and melting temperatures. It therefore offers intrinsically high reversibility and excellent cycle stability. Third, all the submolecular shape changing units are well aligned with respect to each other and to the underlying CNTs. In a synchronized manner, each submolecular shape-changing event occurs simultaneously, potentiating a macroscopic event. Fourth, the bilayer bending direction is opposite to conventional polymer-carbon allotrope bilayers which rely on the large thermal expansion of a polymer.

Furthermore, compared with other bilayers, CNTs have an additional two functionalities in the PA-DBCOD-CNT bilayer. Covalent linkages between the CNTs and responsive polymer layer contribute to the bilayer's cycle stability, whereas most published bilayer systems do not offer a covalently reinforced interface. The aligned CNT sheet also serves as a structural guiding layer to direct molecular self-assembly. As a result, the concerted submolecular conformational changes can be manifested into a substantial macroscopic change. Compared to published thermal actuating systems driven by heat, humidity, NIR, or electrical stimuli, thermal contraction due to collective submolecular events offers distinct advantages and has never been reported before.

Indeed, thermal contraction can be generated by moisture evaporation with increased temperature. However, this moisture-driven actuation requires precise control of moisture content and thus prohibits its use in many applications. Moreover, a large shape change requires moisture to diffuse into and out of the solid bulk and thus limits the response rate. In comparison, conformational change-based contraction does not require the presence of moisture and is inherently fast and reversible at the molecular level.⁷⁷

To demonstrate the efficacy of this unique system, PA-DBCOD-CNT bilayer was coupled with PVDF to serve as an AC generator which has the potential to harness lowgrade waste heat or for ultra-sensitive thermal sensors. Our environment is replete with waste heat. It can be converted to useful electricity using either thermoelectric or pyroelectric effects.⁸⁷⁻⁸⁹ The former requires a large temperature gradient and a complex material system that offers low thermal conductivity but high electrical conductivity. The latter, which is under-explored, can generate electrical energy from thermal fluctuations without the need of large temperature gradients. The pyroelectric effect is observed in materials with spontaneous polarization. A change in polarization of the material results in a change in potential across the material or current through an external circuit. The pyroelectric effect is this production of electricity as a result of heating which decreases the amount of spontaneous polarization by increased dipole vibrations. This requires a change in temperature over time rather than space. Pyroelectric current depends on the rate of change of the polarization with temperature, the area, and the rate of change of temperature with time. PVDF has certain crystalline phases which exhibit piezoelectric and pyroelectric properties.⁹⁰ The piezoelectric effect is similar to the pyroelectric effect, except that mechanical deformations alter the polarization rather than a change in temperature. Coupling the PA-DBCOD-CNT bilayer with PVDF offers the ability to incorporate the piezoelectric effect in harvesting waste heat, resulting in an 86-fold enhancement in energy conversion compared to PVDF alone. This preliminary demonstration shows the promise of this system for low-grade thermal energy harvesting.

Many technologies operate under conditions of energy scarcity and thus demand low-energy driven actuators. This bilayer actuation system operated under new shapechanging mechanisms offers highly precise, reversible, and low-energy driven actuation. Since submolecular actuating units are aligned along the CNTs, this bilayer can be scaled down to micro- and nano-scale. This system lays the foundation for soft material-based robotics and in vivo micro-implants that can be controlled by near infrared remotely. By exploiting its ultra-sensitivity to ambient temperature variations, fluctuating thermal energy can be harvested.

4.2 Methods

4.2.1 Bilayer Fabrication

The bilayer film was prepared in the same way as a pure film (Ch. 3 - Methods – Film Fabrication), except that the solution was drop cast onto silicon substrates that contained an array of multi-walled CNTs.

Spinnable multi-walled CNT arrays were synthesized by chemical vapor deposition and then were drawn out on the pre-cleaned silicon substrates to prepare the aligned CNT arrays with different layers. The typical dimension of CNT was ≈ 20 nm. Detailed fabrication methods were reported in literature.⁴⁰

The fabrication procedure of the bilayer film is displayed in **Figure 4.1**. First, aramid-*alt*-PEG is drop casted onto an aligned CNT sheet atop a Si wafer and allowed to air dry. Second, the film is thermally annealed, during which PEG is removed, the polymer becomes DBCOD-crosslinked by benzocyclobutene dimerization, and covalent linkages are made between the polymer and CNTs. Third, a free-standing stimuli responsive bilayer (PA-DBCOD-CNT) is obtained by etching the Si substrate.



Figure 4.1 Schematic illustration of the bilayer fabrication in three steps: i) beginning with aligned CNTs on a Si substrate, aramid-*alt*-PEG is drop casted and allowed to dry. The BCB units within the polymer chain are shown (blue); ii) thermal annealing, where both dimerization of BCBs forms DBCOD (green) and covalent linkages form between polymer and CNTs (magenta); and iii) after removing from the substrate, a free-standing stimuli responsive film is obtained. The polymer exhibits negative thermal expansion, inducing thermal stress for reversible actuation. The origin of negative thermal expansion between layers is the origin of bending actuation depicted in the lower box.

Polymer synthesis, DBCOD formation, and formation of covalent linkages between polymer chains and the underlying CNT layer can be found in Ch. 3. TGA used to estimate weight percentage of aramid and PEG as well as AFM analysis showing polymer selfassembled morphology facilitating BCB dimerization can also be found in Ch. 3.

4.2.2 Bilayer Characterization

SEM images were performed on a Zeiss Gemini 500 electron microscope. Polarizing optical microscope (POM) images were obtained with a Leitz POM. An example of an SEM image of pure polymer film can be found in Chapter 3. Figure 4.2 shows an example of POM images of a pure polymer film.



Figure 4.2 Polarized optical images of pure polymer film. Pure film isotropy: transmission at 0° and 45° indicate no preferred alignment of polymer fibers. Arrows indicate crossed polarizer orientation.

Fourier-Transform Infrared Spectroscopy

All FTIR spectra were acquired on a Jasco 4700 FTIR under ambient humidity. The samples were held between two metal plates with a 3 mm hole in the center. The polymer side was facing the IR beam. The incident IR polarization was controlled by a wire grid polarizer. The FTIR data was collected with 8 cm⁻¹ resolution and 325 scan average. The CO₂ and H₂O absorption lines were minimized using the Jasco reduction algorithms. Background removal and difference spectra calculation were performed using an asymmetric least squares algorithm. An example of difference spectra for pure polymer film is shown in **Figure 4.3**.



Figure 4.3 Difference FTIR spectra revealing isotropy of pure polymer film: (gold) the difference between the two spectra taken with the IR polarization set to 90° and 0° with respect to one chosen axis; (purple) the difference between spectra taken with the polarization set to 45° and -45° with respect to the same axis. The peak at around 2300 cm⁻¹ comes from CO₂ vapor.

Uniform Heating

To apply uniform thermal stimulation, a bilayer film was heated in an oven. To cool the film, the oven heater was turned off, and the oven door was gradually opened at various temperatures. **Figure 4.4** shows the temperature during heating and cooling and corresponding heating and cooling rates.



Figure 4.4 Temperature vs. time during a) heating and b) cooling of a PA-DBCOD-CNT bilayer in an oven. Solid lines are guides for the eye with the corresponding heating rates shown. During cooling, the chamber was slightly opened twice before being fully opened around 35 °C.

Near IR Response Measurement of the Bilayer Film

The setup of thermo-response measurement via near infrared light is shown in **Figure 4.5**. The bilayer films were fixed at one end for an effective length of 1.5 cm. The distance between the laser and film was set as 5 cm. The heated area was ≈ 0.4 cm in diameter. An infrared camera was used to obtain thermal images.



Figure 4.5 NIR setup. A 785 nm laser was defocused so that the entire width of the film was exposed. Current could be changed to adjust the laser power.

Estimating Film Temperature Rise

A typical laser beam is usually regarded as a Gaussian beam, so the peak intensity is twice the average intensity.^{91, 92} The peak intensity, I_p , is found at the center of the beam and given by

$$I_p = \frac{2P_0}{\pi w^2}$$
(4.1)

where P_0 is the total power and w is the beam waist, defined as the radial distance from the beam axis where the intensity is I_p/e^2 . Therefore more than 86% of the power is within the beam waist. The average intensity, I_{avg} , can be estimated as

$$I_{avg} = \frac{P_0}{\pi w^2} = \frac{1}{2} I_p \tag{4.2}$$

the total power divided by the area of the beam within the waist, equal to half the peak intensity. Furthermore, power is directly proportional to intensity, and temperature rise is directly proportional to power (**Figure 4.6**). Therefore, the peak temperature rise (measured by an infrared camera) is twice the value of the average temperature rise. For example, when room temperature is measured at 24.3 °C and peak temperature measured as 28.6 °C, then the temperature rise was calculated as (28.6 - 24.3) * 0.5 = 2.2 °C.



Figure 4.6 Temperature rise vs power of the bilayer-PVDF construct when exposed to a 785 nm laser source. Temperature rise is directly proportional to power.

4.2.3 Thermal Energy Harvester

An in-house AC generator consisted of a 28 µm thick, poled, uniaxial, gold-covered PVDF film (Precision Acoustics) \approx 30 mm x 10 mm, a piece of PA-DBCOD-CNT bilayer \approx 21 mm x 7 mm, and wax adhesive in between. The setup is shown in **Figure 4.7**a. The sample was covered with a glass beaker to isolate it from air flow. A 785 nm laser was defocused to fill the width of the film (exposure area \approx 0.44 cm² as estimated by ImageJ, Figure 4.7b). For power series experiments, the laser was attenuated with different neutral density filters and the power was measured at the sample with a power meter (Thorlabs PM100D with a Thorlabs S121C photodiode power sensor). An infrared camera (Fluke TiS10) was used to obtain thermal images (**Figure 4.8**). To generate AC signals, a chopper was placed in between the film and laser source. Open circuit voltage measurements were taken with a BioLogic potentiostat. Data were baseline subtracted, translated, and overlaid.



Figure 4.7 a) Photograph of the energy harvesting setup. The NIR source is located 30 cm from the film. Power was measured at the film. A beaker was placed over the device to insulate it from air flow, b) ImageJ analysis indicating an irradiation area of the bilayer of about 0.44 cm².



Figure 4.8 Thermal images of the bilayer-PVDF construct during 1.25 Hz exposure to 77.3 mW of defocused 785nm laser. The average temperature fluctuation is estimated to be about 3.3 °C. Average temperature rise was estimated according to a gaussian beam (see "Estimating Film Temperature Rise" section above).

The relationship between generated voltage and energy of the reported AC generator can be seen from Eq. 4.3 and Eq. 4.4 for a pure resistive circuit:

$$E = \int p(t)dt = P_{avg}\Delta t \tag{4.3}$$

$$P_{avg} = I_{rms} V_{rms} = \frac{1}{2} I_0 V_0 \tag{4.4}$$

where *E* is energy, p(t) is instantaneous power, P_{avg} is average power, Δt is change in time, I_{rms} is the root mean square current, I_0 is current amplitude, V_{rms} is the root mean square voltage, and V_0 is voltage amplitude. Additionally, in a simple circuit with voltage, V, current, *I*, and resistance, *R*, the current is directly proportional to the voltage as stated by Ohm's law. Thus, a 9.3 fold increase in voltage with the addition of the PA-DBCOD-CNT bilayer to PVDF theoretically leads to a 9.3, 86.5, and 86.5-fold increase in current, P_{avg} , and *E*.

4.3 Results

4.3.1 Actuation

Figure 4.9 is a series of optical images to show the response of a set of bilayers to different thermal stimuli, for example, NIR absorption by CNT induced photothermal effect from 34 to 52 °C (Figure 4.9a), uniform heating in an oven from 25 to 55 °C (Figure 4.9b), heated from 50 °C water vapor (Figure 4.9c), and even curling when placed in the palm of a hand (<37 °C) (Figure 4.9d). The large magnitude responses were rapid with no apparent time delay under low-energy stimuli, for example, in the palm of a hand. Independent of thermal sources, films bent away from the CNT side, indicating that the polymer thermally contracted. This bending direction in response to temperature is opposite to that observed in conventional systems due to fundamentally different bending mechanisms, thermal contraction versus thermal expansion. A new actuation platform that can be driven by a low-energy input is set forth.



Figure 4.9 Optical images of the bilayer film's response to different thermal stimuli, a) before and after exposure to 785 nm light with a total power of 40 mW, b) at 25 and 55 °C heated in an oven, c) before and after placing the film near hot water (50 °C), and d) in air and the same film placed on the palm of a hand. Film thicknesses were approximately 15 μ m.

NIR Response

Mechanoresponse was further examined by exposing the new bilayer film to a defocused 785 nm laser. The setup is shown in Figure 4.5. Film temperature was monitored by an infrared camera while film bending was recorded by a digital camera (**Figure 4.10**). Films bent in the direction toward the polymer side regardless of NIR irradiation on the polymer or CNT side, thus supporting the notion that the polymer undergoes thermal contraction. Despite a low-energy stimulus, these new bilayer films are able to generate a considerable amount of bending (Figure 4.9a). To the best of our knowledge, such a large magnitude photothermal response of a solid film, due to thermal contraction and induced by a low-energy stimulus, has seldom been reported.



Figure 4.10 a) A series of optical images of a bilayer film captured before, during, and after laser illumination which resulted in a 10 °C temperature increase. Bending angle, θ , defined as the angle between the vertical and the tangent to the bilayer midpoint. b) A series of images showing the bending behavior of a bilayer film illuminated at different laser powers giving 2.2, 10.5, and 13.8 °C temperature rises. c) Corresponding infrared thermal images showing the temperature rise of the bilayer film. Average temperature rise was estimated according to a gaussian beam (see Methods section "Estimating Film Temperature Rise").

The bending angle, θ , is plotted as a function of "on" and "off" time (**Figure 4.11**a) for three laser power settings to give an average temperature rise of 2.2, 10.5, and 13.8 °C. Figure 4.11b shows the change in bending angle, $\Delta\theta$, as a function of temperature rise from room temp. For a 10 °C temperature rise, $\Delta\theta$ was $\approx 22^{\circ}$. The response time estimated by

video recording was on the order of milliseconds, comparable if not better than CNTs in paraffin wax on a polyimide substrate.⁴⁰ Furthermore, the bilayer responded to as low as 1.1 °C temperature rises with $\Delta\theta > 5^\circ$, showcasing its sensitivity. The observed excellent cycle stability, no visible change after 1000 cycles (Figure 4.11c), can be attributed to the highly reversible nature of the DBCOD conformational change together with π - π interactions and covalent linkages between the polymer layer and CNT sheet.



Figure 4.11 a) Bending angle versus time at different laser powers giving 2.2, 10.5, and 13.8 °C temperature rises. b) Change in bending angle versus temperature rise. d) Cycle stability test of photothermal actuation, showing bending behavior under 785 nm laser illumination with a temperature rise of 1.1 °C after 1, 500, and 1000 on/off cycles.

Uniform Heating

To quantify thermal response, a bilayer film was subject to a uniform thermal stimulation by heating the entire film in an oven. **Figure 4.12**a shows the film curvature, K, analyzed by ImageJ, as a function of temperature. As can be seen, the increase in film curvature gradually levelled off as temperature increased from room temperature up to 65 °C, in agreement with contraction results measured by TMA in Chapter 3 (Figure 3.9). This set of heating and cooling data indicates the reversible nature of the mechanoresponse of this new bilayer film.



Figure 4.12 a) Curvature, *K*, of a 1.4 cm-long bilayer as a function of temperature when heated in an oven. Curvature measured as the inverse of the radius of the circle that matches the arc of the film. b) Images of the film in an oven when repeatedly heated and cooled to set temperatures, with arrows indicating the sequence. Heating to setpoints more than once revealed that the film's response is precise and reversible. 4.7 mm cm⁻¹ deflection was observed when heated from 25 to 55 °C.

Figure 4.12b is a series of images of the bilayer film taken after repeated heating and cooling, demonstrating that the degree of bending as a function of temperature is precise. A 1.4 cm-long film could generate 6.4 mm deflection at 55 °C (a deflection per length of 4.7 mm cm⁻¹), on par with the best reported systems.^{21, 40, 93} Figure 4.13 is a plot

of curvature versus time of the film at each set point. The slight change in shape at 25 °C suggests that a bilayer film that experienced higher temperature stimulation requires a longer recovery time to compensate for the moisture depleted at high temperatures as images were taken at equal time intervals.



Figure 4.13 Curvature vs. time at various temperature setpoints of a PA-DBCOD-CNT bilayer repeatedly heated and cooled in an oven. Increase in curvature at 25 .C suggests that the film needs more time to recover from moisture depleted when cooling from higher temperatures. Measurements were taken at equal time intervals.

Directional Bending

Scanning electron microscopy (SEM) images (**Figure 4.14**a) revealed the bilayer consisted of a thin aligned CNT sheet (0.1 μ m) and relatively thick polymer film layer (14 μ m). Because of high contrast in properties between rigid aramid and flexible PEG, polymer chains self-assembled into nanofibers. Due to π - π stacking between aromatic rings on the aramid and CNT surface, which consists of nothing but fused aromatic rings, polymer fibers aligned perpendicular to CNTs. According to AFM height and SEM image analyses (Figure 4.14b), polymer fibers had a uniform diameter of less than 10 nm whereas the diameters of CNTs were in the range of 20–40 nm. CNT induced polymer self-assembly has been reported before in which crystallization of polyethylene and nylon 6,6 around CNTs formed a shish-kebab structure,⁹⁴ but to the best of our knowledge, the formation of such uniform nanoscale diameter fibers that are well aligned and evenly distributed with respect to CNTs has never been reported. This finding is in corroboration with optical polarization analysis (**Figure 4.15**a). The difference in the index of refraction between two polarizations based on Fourier-transform infrared spectroscopic analysis (Figure 4.15b), further supports the preferential self-assembly of polymer nanofibers

perpendicular to an aligned CNT sheet. In contrast, a pure polymer film without CNTs does not possess preferential optical and submolecular orientation (Figure 4.2 and Figure 4.3).



Figure 4.14 a) Cross-section and top-down SEM images of the bilayer film. b) SEM image and AFM height image of the bilayer film, showing alignment of polymer fibers and CNTs. c) Illustration of the alignment of DBCOD units with respect to CNTs and corresponding bending direction upon heating. Polymer chains align perpendicular and DBCODs align parallel to CNTs. Polymer contraction thus occurs parallel to CNTs, and bending, away from CNTs as depicted for three cut angles, i) $\alpha = 0^{\circ}$, ii) $\alpha = 90^{\circ}$, and iii) $\alpha = 45^{\circ}$, relative to CNT alignment. Corresponding optical images of a bending film prepared with cuts (i), (ii), and (iii) are shown.

Due to the underlying force imposed by the aligned CNT sheet, DBCOD units are oriented along the CNT backbone. An anisotropic thermal contraction resulting from twistboat to chair conformational change illustrated in Figure 4.1 leads to bending toward the polymer side upon heating. Most of the published methods involve isotropic thermal expansion. To investigate the effect of film anisotropy on performance, films were cut vertically, horizontally, and at $\alpha = 45^{\circ}$, where α is defined as the angle between the length of the cut and CNT direction as illustrated in Figure 4.14c. Figure 4.14c also shows a set of optical images taken under the same NIR irradiation condition. In case 1 ($\alpha = 0^{\circ}$), DBCOD units oriented along the length of the bilayer film. The long ends of the bilayer curled toward the polymer upon heating (Figure 4.14c-i) due to a large thermal contraction of the polymer film along the DBCOD/CNT direction. For case 2 ($\alpha = 90^{\circ}$), DBCOD units oriented along the width of the film. As a result, the long ends did not curl. Rather, force was generated along its width, but did not cause buckling (Figure 4.14c-ii). Finally for case 3 ($\alpha = 45^{\circ}$), twisting was observed (Figure 4.14c-iii), demonstrating facile preprogrammability and further corroborating the contention that thermal contraction takes place along the direction of aligned DBCODs and CNTs. Aligned CNT arrays have been used to induce anisotropic bending of a bilayer film before,^{40, 95-97} but the ability to generate multiple bending shapes resulting from a CNT induced assembly of conformational change moieties has not been reported before.

This new bilayer utilizes a highly directional thermal contracting polymer film, different from all known bilayer actuation mechanisms. Furthermore, this design could be used in conjunction with the conventional bilayer, whose polymer system offers high thermal expansion, to maximize mechanical bending.


Figure 4.15 Bilayer Anisotropy. a) Optical images with crossed polarizers of a bilayer film with arrows to guide the eye. Transmission at 0° and 45° indicate alignment of polymer fibers and CNTs, respectively. b) Difference FTIR spectra revealing birefringence of a bilayer film: (blue) the difference between the two spectra taken with the IR polarization set to 90° and 0° with respect to the CNT axis; (red) the difference between spectra taken with the polarization set to 45° and -45° with respect to the CNT axis. The strong oscillations shown in the blue difference spectrum result from the difference in the index of refraction between the two polarizations. Some oscillations can still be seen in the red difference spectrum due to small misalignment of 0° polarization from the CNT axis, as performed visually. The small peak at around 2300 cm⁻¹ comes from CO₂ vapor.

4.3.2 A Platform for Low-Grade Thermal Energy Harvesters

We designed a thermally driven AC generator by coupling the bilayer film with a PVDF film. The setup is depicted in **Figure 4.16**a in which a NIR source was used to generate heat photothermally. A photo of the device and irradiated area can be found in Figure 4.7. When coupled with PVDF, the mechanical bending force generated by thermally triggered DBCOD conformational changes can be converted into electrical energy via the piezoelectric effect. Figure 4.16b shows the power generation capacity of the PVDF alone in comparison to the bilayer film that is attached to PVDF using a thin layer of wax. For PVDF alone, exposure to NIR led to heating and consequently a voltage gain which was primarily a pyroelectric effect. For the bilayer and PVDF construct, over a nine fold increase in voltage, equivalent to 86 times more electrical energy, was observed under the same NIR irradiation. 20 V could be generated from a temperature rise of the bilayer of ≈ 6 °C from room temperature. Based on results with and without the bilayer, it was estimated that the contribution from piezoelectricity constitutes the majority of the signal for the bilayer-PVDF construct.

Furthermore, a chopper was used to create a fluctuating thermal source, analogous to thermal waste from exhaust pipelines for example. An infrared camera was used to estimate the average temperature fluctuation (Figure 4.8) of \approx 3.3 °C. The generated potential by PVDF, open circuit voltage, is plotted in Figure 4.16c. Not only does this setup effectively convert heat into electrical energy but more significantly, it offers excellent stability at elevated temperature with no obvious degradation after 70,000 cycles using a design to minimize PVDF heating (**Figure 4.17**) or at least 27,000 cycles using a design that can harness both piezoelectric and pyroelectric properties (Figure 4.16). The superior cycle stability is due to a combination of the excellent reversibility of the bilayer along with the inherent reversibility of piezoelectricity.



Figure 4.16 a) Schematic of a NIR light powered AC generator. Open circuit voltage was measured across a bilayer coupled to a piezo- and pyroelectric PVDF film while a 785 nm laser was defocused to cover the width of the bilayer film (21 mm x 7 mm) and cycled with a chopper. The energy conversion pathway is displayed in the box. b) Electrical energy harvesting comparison between PVDF alone and the bilayer/PVDF system when exposed for 45 s to different laser powers and corresponding temperatures measured using an infrared camera on the bilayer film. c) AC generation in response to an estimated average temperature rise of 3.3 °C and stability test before and after 27,000 cycles at 1.25 Hz.



Figure 4.17 a) Alternative setup of AC generator isolating piezoelectric energy conversion. b) Open circuit voltage output offering excellent stability with no obvious degradation after 70,000 cycles at moderate power (1.25 Hz, 77.3 mW)

The pyroelectricity of PVDF has been exploited for low-grade thermal energy harvesting.^{88, 89} However, pyroelectric based energy harvesting offers limited cycle stability. The ability to employ piezoelectricity to harness energy from small thermal fluctuations into electricity has never been reported before to the best of our knowledge.

Figure 4.18a shows the voltage induced by mechanical force generated in the bilayer film with and without moisture. To remove the moisture, a dried molecular sieve was placed in a sealed container containing a bilayer-PVDF device for an extended period of time. The fact that the data taken before and after 19 h drying via molecular sieve is almost identical suggests that moisture absorption and desorption via temperature fluctuation at 1.25 Hz does not contribute to the observed AC signals. The observed AC voltage gains were mainly generated by the DBCOD conformational changes.



Figure 4.18b, shows that the thin adhesive layer between the PVDF and DBCOD films has no effect on performance.

Figure 4.18 a) Open circuit voltage of an AC generator under ambient and dry conditions. b) Electrical energy harvesting comparison between PVDF alone and PVDF with a thin piece of wax (used as the adhesive layer in the bilayer/PVDF system) when exposed for 45 s to different laser powers.

Designing an electronic circuit for low-power generation is a research topic itself.⁹⁸⁻¹⁰¹ Future efforts could evaluate different circuit designs and further examine energy harvesting efficiency using the bilayer with optimized material properties. PVDF-based thermal energy harvesting has previously been explored, but the ability to convert low-grade thermal energy into electricity by employing the piezoelectric (primary) and pyroelectric (secondary) effect sets this system apart from existing systems.

4.4 Conclusion

A new type of low-energy triggered actuator based on submolecular actuating DBCODs, that are self-assembled in parallel to aligned CNTs, has been described. Macroscopic anisotropic thermal contraction, originating from concerted DBCOD submolecular conformational changes, is low-energy driven and reversible. The low-energy driven nature is demonstrated by the considerable deformation achieved when placing the bilayer onto one's palm. Gradual curling on one's palm, exposed to heat and moisture from the body, indicates the occurrence of additional conformational changes, facilitated by moisture absorption. This is corroborated by the increased thermal contraction observed in a sample stored in an ambient condition for over 24 h, in comparison to a completely dried sample (as seen in Ch. 3). Nevertheless, both TMA and PVDF stress analyses support that DBCOD conformational change can take place without moisture.

The polymer shape change induces the bending of the bilayer structure due to a thermal mismatch between the polymer film and underlying aligned CNTs. The anisotropy

of the submolecular changes in this system potentially enables shape-controlled bending at high precision. Further, the bending direction of the new bilayer is opposite, thus complementary, to conventional systems which rely on a material that offers a large positive thermal expansion, therefore adding a new dimension to the existing toolbox.

Compared to PVDF alone, a nearly 86-fold increase in thermal energy harvesting has been observed by coupling the bilayer with PVDF, using an identical energy source. This significant enhancement is due to piezoelectricity resulting from the bending force produced by the DBCOD conformational change upon thermal stimulation. Extended cycle stability has not been reported for pyroelectric-based thermal energy harvesting devices. In contrast, excellent cycle stability of piezoelectricity together with the inherent reversibility of the bilayer actuation, bestows this new type of AC generator with excellent cycle performance, over 70,000 cycles. Coupled with the bilayer's thermal to mechanical energy conversion in response to few-degree thermal fluctuations above room temperature, this platform opens a pathway to harvest low-grade thermal energy.

A low-energy driven actuator, hitherto unavailable, enables facile and controlled mechanical deformation in shape and magnitude with excellent reversibility at the macro, micro-, and nano- scale. This new actuation concept could address key technological challenges in biomedical devices, soft robotics, and other applications where preserving energy is critical, such as in outer space, or those that absolutely require low-energy driven actuators.

Chapter 5: Solvent Effect on DBCOD-Containing Polymer Thin Film Actuators

5.1 Introduction

DBCOD polymer actuation has shown a moisture dependence, prompting further investigation of moisture and solvent interactions with this material. The active material described in detail in Chapter 3, PA-DBCOD, exhibited a greater degree of thermal contraction upon heating in ambient atmosphere compared to a dry atmosphere. We proposed that moisture in the atmosphere plasticized the polymer, enabling additional conformational changes to occur upon heating. Furthermore, based on previous studies, solvent can shift the twist-boat/chair equilibrium of DBCOD small molecules so it can be conceived that moisture or solvent absorption in itself could induce actuation of DBCOD polymer films through a shift in twist-boat/chair equilibrium.⁷⁷ This chapter discusses further studies into DBCOD polymer-solvent interaction, solvent driven actuation, and future routes to understand the interesting observations made herein.

Solvent driven actuators, similar to other stimuli driven actuators, are promising new materials for soft robots, artificial muscles, sensing, and more.¹⁰²⁻¹⁰⁴ Compared to other stimuli driven actuators, they can be advantageous with large actuation magnitudes and have additional application as thrust actuators¹⁰⁵ and evaporation energy harvesting.^{106,} ¹⁰⁷ The majority of studies involve materials responding to H₂O while some involve a response to organic solvents. These investigations also range from liquid solvent response to gaseous solvent response, i.e., actuation when exposed to water and/or solvent vapors.

Solvent driven actuation can result from a variety of mechanisms. The main mechanism is swelling/deswelling in which a material absorbs/desorbs solvent, causing a change in shape. Moisture sensitive polymer actuators depend on their ability to absorb water. On a molecular level, this depends on the inclusion of hydrophilic functional groups within the polymer chains. Water acts to plasticize the material, allowing polymer chain rearrangement which is accompanied with macroscopic shape change. More complex rearrangements can take place, for example involving dynamic networks or protein folding, to achieve these effects to a large degree.^{3, 26} Solvent swelling operates similarly with appropriate functional groups and polymer chemical structure favoring polymer solvent interaction.¹⁰⁸ The shape change associated with swelling can be translated into bending actuation by introducing asymmetry. Asymmetry in the environment can cause an absorbing film to bend. For example, a film on wet paper is exposed to a gradient of solvent, absorbing more on one side.²⁰ This gradient of stimulus should be distinguished from a structural asymmetry which can be viewed as a separate class of solvent swelling actuators. This group of actuators is arguably more useful in a wider range of environments and applications but may call for more intricate fabrications.

In this chapter DBCOD polymer solvent actuation is studied. Similar to TMA testing of pure film, only the active material without a CNT layer was used in these studies. A wet paper test revealed bending response to many solvents with the strongest effect seen in toluene, DCM, THF, acetone, methanol, and water. A vapor test further revealed that a

gradient of stimulus, or a bilayer design, was not necessary for bending to occur. We hypothesized that a gradient of amide bonds within the films led to uneven solvent absorption. Whether or not this causes simple swelling or a more complex molecular rearrangement in which DBCODs change conformation remains to be determined. The solvents causing the greatest response were rationalized either through their ability to hydrogen bond or by their likelihood of interacting with the polymer through pi-pi stacking and van der Waals interactions.

The results of tests indicate that vapor actuation may not be completely reversible, and the behavior of the films is dependent on the solvent used. Different solvents may have competing effects, and the film's history may play a role in its behavior. The response time of the films can range from seconds to hours. The study also found that moisture actuation is accompanied by molecular rearrangement and ordering, and that heat may be necessary to remove absorbed molecules, but the process is still not fully reversible. Future research is proposed to better understand the sensitivity and behavior of the films to different solvents.

These films could potentially be used as sensors of various organic solvents or multi-stimuli responsive, multi-functional devices. Much fewer multi-stimuli responsive polymer actuators exist. Additional stimuli offer unique advantages such as versatility and/or precision which can eliminate the need to have the best performance in any one of the stimuli. A highly sensitive thermal actuator can be created from this material as described in Ch. 4. Simultaneously being solvent responsive with potentially distinct responses enables more complex behavior capable of more functionality. Independent responses offers a route to a tunable stimulus response, e.g., small temperature actuation in dry conditions but large temperature actuation in humid conditions. To the best of my knowledge, a NIR light, heat, moisture, and at least 5-fold solvent responsive polymer actuator has never been reported. Such materials bring us closer to self-powered autonomous soft robots that mimic the complexity of living systems.

5.2 Methods

5.2.1 Paper Test

A so called paper test was used to screen solvents and films quickly for actuation response. The paper test was inspired by the work of Ma et al. and others who followed suit.²⁰ They created a water absorbing polymer film, and wet paper was used to create a moisture gradient which drove actuation. Because this test provides an exposure gradient, an actuating design, such as a bilayer or an internal structural gradient, isn't necessary.

The tests here took place in a petri dish with a polytetrafluoroethylene (PTFE) layer placed underneath a sheet of paper for its chemical inertness. The paper was used to soak up solvent and expose films to a wet substrate. The petri dishes were covered and the solvent eventually evaporated for all but a few solvents due to high intermolecular interactions and/or substate affinity. This test does not separate the effect of liquid and the effect of vapors. In most cases, the effect of liquid contact was hard to determine due to surface tension, while a clear response was observed after evaporation. **Figure 5.1** shows an example of this test on different films with an apparent surface tension interference. Actuation response was noted qualitatively as "no response", "low", or "high" as shown in **Figure 5.2**.

High responses could not be refuted, but low and no response could not be trusted in the paper test due to only a snapshot being taken. Video recordings during the vapor test showed that a film can respond but return to its starting shape during continued exposure. Therefore, films could simply appear to have not responded but had already undergone changes before the paper test photo was taken. Hence, conclusions could not be drawn by comparing different responses. Additionally, different responses among films could also be due to geometry, age, history, or batch variations.



Figure 5.1. Paper test of various films using water to investigate actuation response.



Figure 5.2. Paper test examples of qualitative response assignments: no response, low, and high.

5.2.2 Vapor Test

A vapor test was used to confirm solvent actuation behavior and make more detailed observations. **Figure 5.3**. shows the vapor test setup. A polymer sample was clamped at one end and held above a beaker of solvent. The setup was covered and sealed to contain solvent vapors and to protect the film from fume hood air flow. This marked time zero for exposure, and the response was recorded. After the film reached its final state, the beaker was removed, purged with nitrogen, and put back on. The film response was recorded to observe recovery motion.



Figure 5.3. Vapor test setup. A polymer film is exposed to solvent vapor and its response is recorded.

Low response could also not be trusted in the vapor test due to the concentration of vapor being unknown. However, since the response was recorded over time, a "no response" is truly a "no response" for the concentration it was exposed to. Different films were exposed to the same concentration, so different films could be compared in this test. Differing results must be due to geometry, age, history, batch variations (Mw, dispersity, morphology, etc.), or variations in the material itself.

Humidity Chamber

A humidity chamber was built and successfully automated to keep within 5% desired relative humidity (RH) as a way of testing water vapor response. Essentially the chamber is an acrylic box connected to a humidifier and de-humidifier which turn on and off to blow humid and dry air into the box until reaching the desired RH. It's controlled and monitored with a raspberry pi and temperature/humidity sensors. The humidifier, a common household appliance, and de-humidifier, simply an air pump passing through desiccant, were re-wired to connect and be automated by the raspberry pi. Fans were installed to increase uniformity and mitigate condensation at high RH. **Figure 5.4** is a photo of the chamber with its components labeled.



Figure 5.4. Humidity chamber with labeled components.

Vapor Pressure

Partial pressure of solvents at different temperatures can be calculated using Eq. 5.1, the Clausius-Clapeyron relation

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(5.1)

where ΔH_{vap} is the heat of vaporization, *R* is the ideal gas constant, and *P*₁ and *P*₂ are equilibrium vapor pressures at *T*₁ and *T*₂, respectively. For example, the partial pressure of toluene at 40 °C was calculated to be 59 mmHg using the heat of vaporization and partial pressure at 25 °C values of 38,010 J/mol and 28.4 mmHg, respectively, taken from the PubChem database.¹⁰⁹

5.2.3 AFM

Atomic force microscopy was performed in the Baykara lab using a commercial AFM (Asylum Research, Cypher VRS) to look at polymer morphology before and after soaking in water. A heated stage was also employed to image films during heating. Films studied in this way were not etched from their Si substrates during fabrication in order to ensure a flat surface. The sequence was as follows. Two pieces of the same PA-DBCOD film were taken for imaging. While one was imaged in ambient conditions, the other was soaked in water for 10 minutes. The soaked film was then dabbed dry and mounted on the stage. It took about 45 minutes to set up and get a good image. The same location was imaged again 10 minutes later and again 10 minutes after that as the morphology was changing over time. Then the film was heated to 50 °C and imaged at elevated temperature before being cooled and imaged again at room temperature.

5.3 Results

5.3.1 Actuation

Different polymer films were tested for solvent actuation in both liquid and vapor form through use of a paper test and vapor test. The paper test was simply an observation of film response on wet paper and was able to screen multiple films at once, quickly testing many solvents. Vapor tests were used to study the polymer film response in more detail. The response was noted qualitatively as no response, low, or high. However, for various reasons null responses were not definitive. Rather, any significant bending observed is indisputable, so high responses were the observations highlighted and attempted to be understood. More details are provided in the methods section.

Paper Test

The paper tests yielded a mix of responses with no apparent trend, e.g., based on solvent polarity. Among the solvents tested, which are listed in **Table 5.1**, high responses were found using toluene, THF, DCM, acetone, methanol, and water (**Figure 5.5**a) which span a wide range in polarity index values.¹¹⁰ These solvents also represent hydrogen bond donor/acceptors, aprotic acceptors, and molecules that don't participate in hydrogen bonding at all.

Solvent	Polarity Index ¹	H- bond donor ²	H-bond acceptor ²	High Response
Hexane	0	-	-	-
Toluene	2.3	-	-	Yes
DCM	3.4	-	-	Yes
DCE	3.7	-	-	-
THF	4.2	-	Yes	Yes
IPA	4.3	Yes	Yes	-
Acetone	5.4	-	Yes	Yes
Acetonitrile	6.2	-	Yes	-
DMF	6.4	-	Yes	-
DMSO	6.5	-	Yes	-
NMP	6.5	-	Yes	-
Methanol	6.6	Yes	Yes	Yes
Water	9	Yes	Yes	Yes

Table 5.1. List of solvents used, their polarities, hydrogen bond capabilities, and whether or not they elicited a relatively large polymer film actuation

1. From reference ¹¹⁰

2. From the Pubchem Database¹⁰⁹

THF, acetone, methanol, and water are all known to hydrogen bond with amides.^{111,} ¹¹² All of the solvents capable of hydrogen bonding are expected to interact with the polyamide polymer which offers both hydrogen bond donors (the amide nitrogen) and acceptors (the amide oxygen). In addition to swelling, this could destabilize the twist-boat conformation by interrupting the intramolecular hydrogen bonds, causing a shift to chair conformation. Even DCM which is considered an aprotic solvent with low polarity can form weak hydrogen bonds.¹¹³ Figure 5.5b shows that DCM molecules remain trapped between DBCODs in their crystal structure.

However, toluene is not capable of hydrogen bonding. This solvent likely interacts with the largely aromatic polymer through pi-pi interactions and dispersion forces. This may also change the energy landscape for DBCOD conformations and needs further study to support non-polar solvent induced conformational change. Otherwise, the solvent polymer interaction is likely allowing swelling of the material and the actuation a result of a greater degree of swelling on the side touching the paper.



Figure 5.5 a) Paper test of high response films before and during exposure to toluene, THF, DCM, acetone, methanol, and water. b) Molecular structure of based on X-ray crystallography showing dichloromethane trapped between DBCODs; carbon (gray), hydrogen (white), oxygen (red), nitrogen (blue), chlorine (green). Reprinted (adapted) with permission from Fu, W., et al., *Arene Substitution Design for Controlled Conformational Changes of Dibenzocycloocta-1,5-dienes.* Journal of the American Chemical Society, 2020. **142**(39): p. 16651-16660.⁷⁷ Copyright 2020 American Chemical Society.

Interestingly, a pre-annealed aramid-*alt*-PEG showed bending behavior in response to THF. **Figure 5.6**. shows images before and during exposure to solvent. The pre-annealed film responded less than DBCOD containing films but responded nonetheless. This means

that DBCOD conformational change cannot be the sole mechanism of solvent actuation here. This was the only solvent with any significant effect on the pre-annealed film and is most likely due to swelling of the film.



Figure 5.6. Paper test of annealed, DBCOD-containing films (left) and a pre-annealed, lacking DBOCD film (right) before and during exposure to THF.

Lastly, the type of motion, i.e., bending or twisting, was film dependent rather than solvent dependent. Twisting could be a result of where the film was cut from and the presence of non-uniform thickness.

Vapor Test

Vapor tests were performed and agreed with all of the high response solvents observed in the paper test with the exception of toluene (**Figure 5.7**). The lack of response to toluene is believed to be due to its low vapor pressure of only 28 mmHg at 25 °C.¹⁰⁹ In an attempt to increase the film's exposure to toluene vapor, the vapor test was conducted on a hot plate at 40 °C. The hotplate could not be raised as heat itself caused actuation, highlighting the limitations of the test. This only raises the vapor pressure of toluene to an estimated 59 mmHg (see Methods for details) compared to the other solvents' vapor pressures of 127-435 mmHg at 25 °C with the exception of water.¹⁰⁹ Although the vapor pressure of water was the lowest among high response solvents, moisture actuation was able to be observed using a humidity chamber.

Vapors



Figure 5.7. Vapor test showing a large solvent actuation response of a pure DBCOD film in response to toluene, THF, DCM, acetone, methanol, and water.

In addition to validating the paper test, vapor testing offered less constraints on film actuation, such as the surface boundary and surface tension, and was recorded in order to observe the actuation behavior more closely. Unexpected behavior was revealed. **Figure 5.8**a shows the actuation behavior of a film over time when exposed to acetone and THF using the vapor test as well as their recovery responses. These tests showed that vapor actuation may not be fully reversible. The resting or unstimulated state might change due to a release of internal stress, by trapped solvent molecules, or by an aging effect. Furthermore, films were capable of multi-step exposure and recovery actuation in which a film could actuate and reverse during a single testing step, e.g., during continuous solvent vapor exposure.

Exposure to acetone exemplified these behaviors. In the first cycle, a two-step exposure action was observed, followed by a two-step recovery that left the initially flat film in a twisted state. In the second cycle, there was a three-step (flatten, twist, flatten) exposure motion, followed by a single-step recovery actuation.

Additionally, these tests revealed that the specific behavior is solvent dependent. For example, when exposed to THF the same film underwent a single-step exposure and dual-step recovery motion in which the initially twisted film twisted tighter, followed by flattening and re-twisting to the initial state upon recovery. This suggests that different solvents may have competing effects, that film history may be important, and/or that they drive different mechanisms. Figure 5.8b summarizes the actuation in response to acetone and THF in terms of the film shape and the type of motion in between each step.

In all multi-step actuations, the first step was relatively fast compared to subsequent steps, also suggesting multiple processes involved in actuation which operate on different timescales. In terms of absolute response time, films could respond within seconds to hours. Due to the nature of the test, recovery time was more representative of film response time as the exposure step was a steady increase in concentration over the course of hours while the recovery step involved a sudden removal of stimulus.



Figure 5.8. a) Actuation behavior of a film over time when exposed to acetone and THF using the vapor test as well as its recovery responses. b) Summary of the actuation in terms of the film shape and the type of motion in between each step.

5.3.2 Morphology

AFM was used to look at PA-DBCOD film morphology after soaking in water. Additionally, a heated stage was used in order to image the film during and after elevated temperature. **Figure 5.9** shows the experimental flow chart and corresponding images. When soaked in water for 10 minutes the film underwent a change to a smoother and more ordered structure. However, while resting in ambient conditions afterwards, the film begins to change back. Upon heating to 50 °C, the film appears to fully revert back to the original structure. Finally, after cooling back to room temperature, the film undergoes additional, less dramatic changes. These results support the notion that swelling is not the only mechanism at play in moisture actuation. Rather, it appears to be accompanied with a molecular rearrangement and ordering. Additionally, heat may be necessary to remove absorbed molecules, but the process is not fully reversible, at least on the first cycle. This data is consistent with actuation behavior.



Figure 5.9. AFM phase images $(0.3 \times 1.2 \mu m)$ of a PA-DBCOD film in ambient conditions, after water soaking, during heating, and after heating.

5.4 Future Studies

DBCOD actuating polymer-solvent interactions have just begun to be studied on both the material level and performance level, and much remains to be done on these fronts. In terms of actuation performance, a sensitivity should be determined for different solvents. However, it is difficult to measure and control the vapor concentration. Since heating causes some actuation, changing the temperature cannot be used to bring different solvents to the same vapor pressure. Perhaps for solvents with high vapor pressures, a set volume could be allowed to fully evaporate at room temperature. The volume would have to be chosen such that the equilibrium vapor pressure is never reached. Different solvents would evaporate at different rates, but once fully evaporated, the vapor concentration would be known and actuation response could be compared. Furthermore, this could be done at elevated temperature in order to include all desired solvents, assuming the added temperature actuation to be consistent in each test. Alternatively, soak tests could be performed in order to determine the maximum response. Practical application will also require appropriate material testing, in particular, testing mechanical properties and how they change upon solvent exposure and over time. Film expansion and contraction may be directly measured as well. Finally, more actuation cycles should be performed and the effect of geometry, process parameters, and aging should be studied systematically.

In terms of understanding solvent driven shape change on the material level, there are also many options. A combination of DFT, NMR, and FTIR, as historically used in DBCOD investigations, could be used to understand DBCOD conformational kinetics and energetics in different solvents. FTIR could additionally be used to observe solvent desorption over time after exposure, as well as moisture exchange with the atmosphere.²⁰

The hypothesis that a gradient exists within films and drives a gradient swelling can also potentially be tested. Perhaps, an environmental SEM would reveal a structural gradient and uneven swelling upon increasing humidity. Furthermore, EDX or XPS could also be used to check for an elemental gradient, e.g., if more amides existed on one side than the other.

Finally, different polymers should be made and compared in all tests. **Figure 5.10** shows the current polymer structure and three additional proposed structures that can potentially be made under the same polymerization conditions in order to compare with and without DBCOD as well as polyester (PE) vs. polyamide (PA). By comparing PA-DBCOD to PA, it can be determined whether or not the solvent effect is related to DBCOD switching. The goal of comparing PA-DBCOD to PE-DBCOD is to help determine the role of hydrogen bonding in solvent induced changes as PA-DBCOD contains many hydrogen bond donors and acceptors whereas PE-DBCOD contains only hydrogen bond acceptors. If hydrogen bonding is involved in PA-DBCOD solvent response, polar aprotic solvents should produce a different response in PE-DBCOD. Lastly, comparing PE-DBCOD to PE-Control could inform whether or not the effect of DBCOD on structure, properties, and response is the same in polyester compared to polyamide.



Figure 5.10. Proposed polymer structures to help understand the material-solvent interactions, including the polyamide DBCOD studied thus far and three additional proposed structures that can potentially be made under the same polymerization conditions in order to compare with and without DBCOD as well as polyester (PE) vs. polyamide (PA).

5.5 Conclusion

DBCOD-based polymer films' response to various solvents was tested. Wet paper tests showed a bending and twisting response to many solvents, with the strongest effect seen in toluene, DCM, THF, acetone, methanol, and water. The response time of the films can range from seconds to hours. Vapor testing further showed that a gradient of stimulus was not necessary for bending to occur in single layer films. We posit that interacting solvents absorb into the film, forming a concentration gradient due to an underlying gradient of amide groups in the film, causing actuation. The solvents causing the greatest response were rationalized as polymer-interacting through hydrogen bonds or pi-pi stacking and dispersion forces.

The paper and vapor tests suggest that the type of actuation was film dependent while the actuation sequence of forward and reverse motions was solvent dependent. The study also found that moisture actuation is accompanied by molecular rearrangement and ordering. Although the process was not fully reversible, heat seemed to help, presumably through removal of absorbed molecules. Whether or not DBCOD conformational change is involved in this molecular rearrangement remains to be determined.

Future research should focus on defining the sensitivity of the films to different solvents and testing the mechanical properties of the films. The effect of geometry, process parameters, and aging should also be studied systematically. The use of various techniques

such as DFT, NMR, and FTIR could help understand the conformational kinetics and energetics of the films in different solvents. Environmental SEM and EDX or XPS could be used to investigate the potential existence of structural or elemental gradients in the films. Finally, comparing different types of polymers in various tests could provide insight into the role of DBCOD and hydrogen bonding in solvent-induced changes. Therefore, polymer structures were proposed to allow comparisons to determine if the solvent effect is related to DBCOD switching as well as whether or not the effect of DBCOD on structure, properties, and response is the same in polyester compared to polyamide.

These materials have potential applications as sensors for organic solvents or as multi-stimuli responsive actuators, toward more complex synthetic systems that respond to their environment in many ways. Studying DBCOD-solvent interaction and solvent driven actuation provides a deeper understanding of these systems which can enable greater control and performance improvements, broadening their potential uses and bringing them closer these applications.

Chapter 6: Conclusions and Future Work

The work in this dissertation has made progress in understanding polymeric DBCOD-containing materials, bringing them one step closer to many promising applications while also contributing to the broader field of stimuli responsive materials. While DBCOD derived polymers with unique properties have received increasing interest since their introduction, no advances had been made prior to this work on one of the original observations: actuation. Similarly, DBCOD polymer-solvent interaction and response has also not been reported prior to this work. However, now robust actuation utilizing DBCOD has been realized, including the possibility for multiple stimuli such as heat, light, moisture, and solvents, for more diverse functionality in applications such as biomedical, soft robotic, and self-powered devices.

In this dissertation, a review of DBCOD-containing polymers was provided since initial reports of anomalous behavior in 2012, through key studies determining the mechanism and criteria for negative thermal expansion, all the way to the present. Chapter 3 provided a detailed description of the synthesis and characterization of the BCB crosslinked DBCOD polymer used by the author. The pre-crosslinked aramid-*alt*-PEG polymers possessed a fibrous self-assembled nanostructure that was crucial to the production of highly sensitive thermally responsive actuating films. By crosslinking DBCOD moieties within the polymers, they exhibited negative thermal expansion as measured by TMA and evidenced by DSC and variable temperature NMR.

Using DBCOD as a method to achieve novel actuation provides multiple benefits including being low-energy driven, having high cycle stability, and the ability to contract rather than expand, offering new possibilities. These properties were exemplified in this work as the most significant actuating DBCOD film to date was revealed in Chapter 4. By use of aligned CNTs in a bilayer composite, a greater degree of DBCOD alignment was attained. This new actuator was able to produce a large shape change in response to a small thermal stimulus. The response was highly cyclable in part by covalent linkages between the layers and in part by the inherent stability of DBCOD. Compared to other thermally responsive materials, no large, unrestrained molecular rearrangement occurs. Additionally, the conformational change can have a much lower activation energy compared to other systems.

The DBCOD bilayer actuator performed at least on par with others in the field, adding to the toolkit for controlled actuation. It was obvious from the fast response, moderate bending, and high sensitivity that this large advancement in DBCOD actuation has brought it to the forefront of thermal actuation with room to improve still. The sensitivity of this bilayer can be exploited for thermal energy harvesting, as was demonstrated by an 86-fold enhancement in energy conversion compared to PVDF alone when coupled together.

In addition to various thermal responsive actuators, moisture and solvent driven actuators can be made from DBCOD based polymers as discussed in chapter 5. These actuators don't require a bilayer structure, but the addition of one could improve performance and dimensionality in terms of stimuli and response tunability, shape, and behavior. Still, large deformations were achieved in a single layer in response to a range of solvents with widely varying properties. These were proposed to cause gradient swelling of the polymer as a result of favorable polymer-solvent interactions with an underlying gradient within the film. Film exposure was accompanied with molecular rearrangement and ordering, and heat assisted in morphology recovery. Large deformations could fully reverse and re-actuate, all during continuous exposure. This behavior (speed, magnitude, direction and sequence) varied by solvent, so multiple mechanisms are expected to be involved including solvent induced conformational change of DBCODs. Future studies were discussed to investigate these mechanisms and performance further.

While unique aspects and benefits of this material have been highlighted, I wanted to also point out some limitations. First, the temperature window is small and fixed, and the modulus is high making the material brittle. It's difficult to draw fair comparisons to existing actuators in the literature when actuating systems vary tremendously and the performance metrics reported are also not standardized. For example, bending performance depends on factors such as thickness, aspect ratio, modulus, energy input, and energy conversion efficiency. If at all possible, these should be reported along with response time and/or power density. Future stimuli responsive DBCOD material studies can fill in these gaps while also exploring new stimuli such as electric current and changing magnetic fields which can be used as heating methods, taking advantage of its heat sensitivity.

One way of categorizing DBCOD polymers is by the type of monomers or origin of DBCOD: linear DBCOD polymers by directly using DBCOD monomers or BCB crosslinked polymers as an indirect route to these unique materials. The work of this dissertation has dealt with BCB crosslinked polymers; however, the use of linear DBCOD polymers in actuating designs offers another direction which may greatly enhance their tunability and performance as multi stimuli responsive materials. Furthermore, strategies for aligning linear DBCOD polymers, e.g., by fiber drawing or liquid crystal incorporation, remain unexplored.

In addition to polymer actuators, the future of DBCOD polymers lies in designing materials for dielectric, high performance (thermal and mechanical), and coefficient of thermal expansion matching applications as well as creation of new types of polymers such as DBCOD elastomers. In any case, a lack of commercially available starting materials and lengthy, inefficient synthesis steps hindering commercial application of DBCOD-based materials needs to be addressed.

Finally, as a materials scientist of the 21st century, I'd like to end with a note on sustainability and how DBCOD-based materials may find their place in a sustainable future. Designing materials has traditionally been with only the materials' use in mind. However, moving forward, materials should be designed with their full life cycle in mind, striving for circularity. This is a paradigm shift from our current linear model in which we take resources from our environment, make devices, and dispose of them after their use is exhausted. The goal of circular economics is to create a closed-loop system where resources are used and reused in a sustainable manner, without depleting natural resources or causing harm to the environment. To meet this goal, we need to develop materials for advanced technology that can either be recycled infinitely or be broken down harmlessly while at the same time coming from a renewable feedstock.

Many DBCOD small molecule variations are naturally found in plants and offer a variety of health benefits. There exists a whole body of research and active efforts

surrounding lignans and their health effects. Perhaps this field will overlap the field of polymeric DBCOD. These biologically available counterparts could be explored theoretically and experimentally for the potential of negative thermal expansion behavior and other desired properties, offering a renewable feedstock to new high performance polymeric DBCOD materials.

Further efforts are needed on the recycling aspect of these materials as well. There are many approaches to recycling plastics that have been thoroughly reviewed.¹¹⁴ Plastic recycling remains below 20%¹¹⁵ with gigatons of plastic waste since 1950 in landfills or the environment, clearly a pressing issue. Many recycling techniques remain extremely inefficient which is a result, in part, of the material design. We will stop adding to the world's plastic problem when materials are made recyclable from conception. Recently, progress has been made to chemically engineer polymers that are infinitely recyclable.¹¹⁶, ¹¹⁷ Future DBCOD-based polymeric endeavors should explore such strategies to develop chemically recyclable materials and close the loop, before commercial production.

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