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Understanding the Structure and Dynamics of Conjugated Polymers by Advancing Deuteration Chemistry and Neutron Scattering

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I. ACCOMPLISHMENTS:

Overall Goal of the project

The overarching goal of the proposed work was to set up a partnership between the University of Southern Mississippi (USM) and Oak Ridge National Laboratory (ORNL) to develop novel approaches to measure the backbone rigidity of conjugated polymers (CPs) and understand the critical role of sidechains on the backbone conformation and the materials macroscopic property. The backbone rigidity greatly influences the electronic properties of CPs, which ultimately determines the functionality and performance of these materials. Improvements in the electronic properties of CPs would allow for enhanced charge transport in semiconductor devices, improved photovoltaic performance, recycling of waste heat in thermoelectrics, and discovery of new phenomena that will enable the next generation of energy technologies. Although significant progress has been made to optimize the optical and electronic properties of CPs, largely through Edisonian methodologies, it remains a challenge to experimentally characterize conjugated backbone conformation (chain rigidity, torsion, planarity, and short-range order) and relate these to the fundamental optical and electronic properties (electronic coupling, charge transport, etc.). This has left fundamental gaps in our knowledge of the most basic structure/property relationships within these systems, precluded the study of fundamental physical phenomena, and constrained the design and realization of new electronic and device functionalities. Thus, the major goal of this work is to use novel deuteration methodologies via systematic synthetic approaches, and neutron scattering techniques to comprehensively characterize the structural and dynamic properties of CPs in contrast-matching solvents. Our work would, for the first time, elucidate the relationship between backbone rigidity and macroscopic properties. They will also allow a rational formulation of design principles for next-generation CPs that are resilient to disorder through precise control of the delocalized electrons along the polymer backbone. Overall, this project will advance our understanding of the structure, dynamics, and fundamental physics of these materials, which is crucial for enabling the prediction, design, control, and manipulation of current and emerging material electronic properties.

Additionally, this project will also set up a new partnership between USM and ORNL to leverage each other's core strengths and will boost the scientific impacts, train next-generation scientists and neutron users and foster strong ties between junior faculties at USM and scientists at the DOE laboratory.

Accomplishment of the project

Overview:

During the course of this project, we successfully developed a new conjugated polymer with a deuterated sidechain and performed contrast-matching neutron scattering to study the single-chain conformation and various conjugated polymers. Additionally, we have published several additional works that highlight the important role of the different building blocks from either the backbone or sidechain chain on the chain conformation. We believe this result could benefit the organic electronic community and help them to understand the role of the single chain conformation in designing high-performance materials and ultimately devices.

Major Results:

1. Synthesis of deuterated polymers and contrast variation neutron scattering (Cao, Z.; Li, Z.; Zhang, S.; Galuska, L.; Li, T.; Do, C.; Xia, W.; Hong, K.; Gu, X. Decoupling Poly(3-Alkylthiophenes)' Backbone and Side-Chain Conformation by Selective Deuteration and Neutron Scattering. *Macromolecules* **2020**, *53* (24), 11142–11152. https://doi.org/10.1021/acs.macromol.0c02086.)

Our first major result was done by graduate student Sean Cao, in collaboration with Dr. Kunlun Hong from CNMS, ORNL. It is important to note that experimental characterization of conjugated polymer backbone conformations remains underexplored due to limited techniques that are capable of distinguishing the backbone and side-chain structures at nanoscopic resolution. Thus, relating the electronically functional backbone conformation to the material's macroscopic optoelectronic property was a challenge. Our work showed that using small-angle neutron scattering techniques (SANS) with contrast-variation (CV) experiments can allow us to study poly(3-alkylthiophenes) (P3ATs) with both deuterated and protonated side chains in a mixture of protonated and deuterated solvents to decouple the backbone and side-chain scattering signals. We obtained the form factor of P3ATs' backbone, side chains, and cross-scattering term by deconvoluting their respective scattering signals. The strong scattering signal from long and flexible alkyl side chains leads to a seemingly more rigid conjugated polymer, which is further revealed by coarse-grained molecular dynamics simulations. This work offers a methodology to decouple the scattering contribution from the CPs' backbone and side chains, thus elucidating the inherent conformation of the electronically active conjugated backbone, which provides guidance for the rational design of next-generation polymeric semiconductors.

2. Neutron scattering to study single chain conformation for conjugated polymers with different sidechains. (Cao, Z.; Li, Z.; Tolba, S. A.; Mason, G. T.; Xiong, M.; Ocheje, M. U.; Alesadi, A.; Do, C.; Hong, K.; Lei, T.; Rondeau-Gagné, S.; Xia, W.; Gu, X. Probing Single-Chain Conformation and Its Impact on the Optoelectronic Properties of Donor–Accepter Conjugated Polymers. *J. Mater. Chem. A* **2023**. https://doi.org/10.1039/D2TA09389H.)

In our second work, we discussed the single chain conformation of a donor-acceptor conjugated polymers using neutron scattering, as well as how to obtain a non-aggregated single chain in solution. The chain conformation of donor–acceptor conjugated polymers (D–A CPs) is critical to their optical and electronic properties. However, probing the conformation of D–A CPs (e.g., persistence length and contour length) at a single-chain level is challenging due to the formation of aggregates in a dilute solution, even in a good solvent. In our work, we studied the chain conformation and corresponding optical spectra for high-performance D–A CPs in the single-chain state by multimodal variable-temperature scattering and spectroscopy techniques, as well as by molecular dynamics simulations. We found a critical role of the side-chain length and branch point in the persistence length and optical absorption due to steric effects. Hence, it is important to consider both the chain rigidity and coplanarity of the polymer backbone to achieve desirable optoelectronic properties. Our findings bridge the fundamental knowledge gaps to design new CPs with desired optoelectronic properties via molecular engineering for next-generation electronic devices.

3. The important role of the chain rigidity on the thermal transition signal for semi-rigid polymers (Qian, Z.; Galuska, L.; McNutt, W. W.; Ocheje, M. U.; He, Y.; Cao, Z.; Zhang, S.; Xu, J.; Hong, K.; Goodman, R. B.; Rondeau-Gagné, S.; Mei, J.; Gu, X. Challenge and Solution of Characterizing Glass Transition Temperature for Conjugated Polymers by

Differential Scanning Calorimetry. *J. Polym. Sci. Part B Polym. Phys.* **2019**, *57* (23), 1635–1644. https://doi.org/10.1002/polb.24889.)

In this work, we discussed the important role the chain rigidity on their physical property, particularly the glass transition temperature (Tg). Differential scanning calorimetry (DSC) is commonly used to measure the Tg of polymers. However, many conjugated polymers (CPs), especially donor–acceptor CPs (D–A CPs), do not show a clear glass transition when measured by conventional DSC using a simple heat and cool scan. We discussed the origin of the difficulty in measuring Tg in such type of polymers is due to a more rigid polymer backbone, and we observed restoration of the Δcp at Tg by a factor of 10, confirming that backbone rigidity reduces the Δcp. Additionally, an increase in the crystalline fraction of the CPs further reduces Δcp. We conclude that the difficulties of determining Tg for CPs using DSC are mainly due to the rigid backbone and semicrystalline nature.

4. The important role of backbone rigidity on the thermomechanical property of semiconducting polymers (Galuska, L. A.; McNutt, W. W.; Qian, Z.; Zhang, S.; Weller, D. W.; Dhakal, S.; King, E. R.; Morgan, S. E.; Azoulay, J. D.; Mei, J.; Gu, X. Impact of Backbone Rigidity on the Thermomechanical Properties of Semiconducting Polymers with Conjugation Break Spacers. *Macromolecules* **2020**, *53* (14), 6032–6042. https://doi.org/10.1021/acs.macromol.0c00889.)

In this work, we studied the role of backbone rigidity in the entanglement behavior of semiconductive polymers. We provided the first holistic approach to understanding the fundamental influence of backbone rigidity on n-type naphthalene diimide-based conjugated polymer through the insertion of a flexible conjugation break spacer (CBS). CBS lengths are varied from fully conjugated with zero alkyl spacer (PNDI-C0) to a seven-carbon alkyl spacer (PNDI-C7), with the CBS engineered into each repeat unit for systematic evaluation. Solution small-angle neutron scattering and oscillatory shear rheometry were employed to provide the first quantitative evidence of CBS influence over conjugated polymer chain rigidity and entanglement molecular weight (Me), demonstrating a reduction in the Kuhn length from 521 to 36 Å for fully conjugated PNDI-C0 and PNDI-C6, respectively. We later discovered that backbone rigidity can impact entanglement behavior. For example, for that conjugated polymer with a flexible link, an entanglement molecular weight of 15 kDa was observed. An extraordinary ductility, upwards of 400% tensile strain before fracture, was observed for high-molecular-weight PNDI-C4, which we attribute to a high number of entanglements and disruption of crystallization. This work sheds light on the important role of backbone rigidity in designing flexible and stretchable conjugated polymers.

5. Development of the new mechanical characterization tool for thin film (Galuska, L. A.; Muckley, E. S.; Cao, Z.; Ehlenberg, D. F.; Qian, Z.; Zhang, S.; Rondeau-Gagné, S.; Phan, M. D.; Ankner, J. F.; Ivanov, I. N.; Gu, X. SMART Transfer Method to Directly Compare the Mechanical Response of Water-Supported and Free-Standing Ultrathin Polymeric Films. *Nat. Commun.* **2021**, *12* (1), 2347. https://doi.org/10.1038/s41467-021-22473-w.)

Working with the Oak Ridge National lab scientist, also we developed a new way to make free-standing polymer thin film down to tens of nanometers. In our published work, we presented a way to prepare conjugated polymer thin film, named the shear motion-assisted robust transfer technique, for fabricating free-standing sub-100 nm films and measuring their inherent structural–mechanical properties. We compared these results to water-supported measurements, exploring two phenomena. First, the influence of confinement on mechanics

and second the role of water on the mechanical properties of hydrophobic films. Upon confinement, polymeric thin films exhibit increased strain at failure, and reduced yield stress, while modulus is reduced only for the thinnest 19 nm film. Such work is important for any confined sub-100 nm thin film mechanical property analysis.

6. Understanding the mechanical property for thin film samples with different electron donating groups (Zhang, S.; Ocheje, M. U.; Huang, L.; Galuska, L.; Cao, Z.; Luo, S.; Cheng, Y.; Ehlenberg, D.; Goodman, R. B.; Zhou, D.; Liu, Y.; Chiu, Y.; Azoulay, J. D.; Rondeau-Gagné, S.; Gu, X. The Critical Role of Electron-Donating Thiophene Groups on the Mechanical and Thermal Properties of Donor–Acceptor Semiconducting Polymers. *Adv. Electron. Mater.* **2019**, *5* (5), 1800899. https://doi.org/10.1002/aelm.201800899.)

Building upon our new thin film mechanical characterization tool, we started to measure the mechanical property of sub100nm films used in various organic electronic devices and studied the correlation with their chain rigidity. In this work, we found that chain rigidity does not directly impact the modulus of a conjugated polymer. Thin-film mechanical properties were investigated for diketopyrrolopyrrole (DPP)-based conjugated polymers with varying numbers of isolated thiophene moieties and sizes of fused thiophene rings in the polymer backbone. Interestingly, it was found that these thiophene units act as an antiplasticizer, where more isolated thiophene rings or bigger fused rings result in an increased glass transition temperature (Tg) of the polymer backbone, and consequently elastic modulus of the respective DPP polymers. Using the knowledge gained above, a new DPP-based polymer with increased alkyl side chain density through attaching alky chains to the thiophene unit was engineered. The new DPP polymer demonstrates a record low Tg, and 50% lower elastic modulus than a reference polymer without side-chain decorated on the thiophene unit. This work provides a general design rule for making low-Tg conjugated polymers for stretchable electronics.

Additionally, we also published two review papers from this funded project.

7. A review article of the thin film mechanical property for conjugated polymers were reviewered. (Zhang, S.; Galuska, L. A.; Gu, X. Water-assisted Mechanical Testing of Polymeric Thin-films. *J. Polym. Sci.* **2022**, *60* (7), 1108–1129. https://doi.org/10.1002/pol.20210281.)

In the first review article, we discussed in depth the thin film mechanical analysis tool invented for this project. Thin films with a nanometer-scale thickness are of great interest to both scientific and industrial communities due to their numerous applications and unique behaviors different from the bulk. However, the understanding of thin-film mechanics is still greatly hampered due to their intrinsic fragility and the lack of commercially available experimental instruments. In our review, we discussed the progression of thin-film mechanical testing methods based on the supporting substrate: film-on-solid substrate method, film-on-water tensile tests, and water-assisted free-standing tensile tests. By comparing past studies on a model polymer, polystyrene, the effect of different substrates and confinement effect on the thin-film mechanics is evaluated. These techniques have generated fruitful scientific knowledge in the field of organic semiconductors for the understanding of structure–mechanical property relationships.

8. Qian, Z.; Cao, Z.; Galuska, L.; Zhang, S.; Xu, J.; Gu, X. Glass Transition Phenomenon for Conjugated Polymers. *Macromol. Chem. Phys.* **2019**, *220* (11), 1900062. https://doi.org/10.1002/macp.201900062.

In the second review article, we surveyed the dynamics of the conjugated polymers. Previously, the optical and electronic properties of conjugated polymers have been extensively studied, while their thermomechanical properties, especially the glass transition phenomenon which fundamentally represents the polymer chain dynamics, have received much less attention. Currently, there is a lack of design rules that underpin the glass transition temperature of these semirigid conjugated polymers, putting a constraint on the rational polymer design for flexible stretchable devices and stable polymer glass that is needed for the devices' long-term morphology stability. In this review article, the glass transition phenomenon for polymers, glass transition theories, and characterization techniques are first discussed. Then previous studies on the glass transition phenomenon of conjugated polymers were reviewed and a few empirical design rules are proposed to fine-tune the glass transition temperature for conjugated polymers. The goal of this perspective is to draw attention to challenges and opportunities of controlling, predicting, and designing polymeric semiconductors, specifically to accommodate their end use.

There are another 30 research papers that benefited from the resource provided by this grant. They are listed in the manuscript list.

Student Training and workforce development accomplished in this project.

The project provided training opportunities for one post-doctoral researcher, Dr. Zhiyuan Qian (employed at Modern Meadow), Dr. Haoyu Zhao (Current at the group), graduate students, Dr. Michael Steelman, Dr. Luke Galuska (ExxonMobile), Dr. Zhiqiang Cao (to be employed by ORNL), Guorong Ma, and Yunfei Wang. The project provided important resources for them to carry out their thesis project. The following finished thesis's are a direct result of this grant.

1) Galuska, Luke, "Thermomechanics Of Semiconducting Polymers and Their Morphological Phenomena" (2022). Dissertations. 1985. https://aquila.usm.edu/dissertations/1985
2) Steelman, Michael, "Magnetic Interactions in Open-Shell Conjugated Polymers" (2023). Dissertations. 2117. https://aquila.usm.edu/dissertations/2117
3) Cao, Zhiqiang, "Understanding the Structure and Dynamics of Conjugated Polymers by Deuteration and Neutron Scattering" (2023). Dissertations.

The project also provided important travel resources for them to travel to various DOE national laboratories (NSLS II, and SNS) to perform X-ray and neutron scattering experiments. This provided training resource that otherwise not possible for Mississippian students.

Results published for the communities of interest.

The results were disseminated to polymer science and engineering and the organic electronic communities via conference talks (invited and contributed) by PI Dr. Gu and his research team members, as well as several department seminars. Throughout the project period, 38 publications, and 30 invited and contributed talks are given by the students and PIs on the project. Additionally, one patent was filed and granted from this project. We listed all the presentations in the PRODUCTS **Section.**

PROJECT PRODUCTS

a. Publications, conference papers, and presentations

(i) Publications

(1) Pang, S.; Zhou, X.; Zhang, S.; Tang, H.; Dhakal, S.; Gu, X.; Duan, C.; Huang, F.; Cao, Y. Nonfused Nonfullerene Acceptors with an A–D–A′–D–A Framework and a Benzothiadiazole Core for High-Performance Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2020**, *12* (14), 16531–16540. https://doi.org/10.1021/acsami.0c01850.

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(ii) Conference papers and presentations

Conference talks

1) Xiaodan Gu, Contributed talk, "Combining inelastic neutron scattering and molecular dynamics simulation to probe conjugated polymer dynamics", ACNS meeting, June 5~9, 2022
2) Xiaodan Gu, Contributed talk, Design strategies to predict and control semiconducting polymers' dynamics, organic electronic session, APS March meeting, March 13-18, 2022
3) Luke A. Galuska, Dung T. Tran, Haoyu Zhao, Gage T. Mason, Zachary C. Ahmad, Kundu Thapa, Simon Rondeau-Gagné, Jianguo Mei, Xiaodan Gu, Illuminating the Rigid Amorphous Fraction of Conjugated Polymers, and its Pivotal Influence on Optoelectronic and Performance. ACS - Excellence in Graduate Polymer Research symposium, ACS National Meeting & Exposition, 2022.
4) Luke Galuska; Eric Muckley; Cao Zhiqiang; Dakota Ehlenberg; Zhiyuan Qian; Zhang Song; Simon Rondeau-Gagne; Minh Phan; John Ankner; Ilia Ivanov; Xiaodan Gu, SMART transfer method to directly compare the mechanical response of water-supported and free-standing ultrathin polymeric films; ACS National Meeting & Exposition Virtual, April 06, 2021
5) Song Zhang, Amirhadi Alesadi, Wenjie Xia, Xiaodan Gu; Molecular origin of strain-induced chain alignment in PDPP-based semiconducting polymers; APS National Meeting & Exposition, Virtual, April 14-19; 2021
6) Song Zhang, Amirhadi Alesadi, Wenjie Xia, Xiaodan Gu; Structure-thermal/mechanical property relationship of semiconducting polymer thin films; APS National Meeting & Exposition, Virtual, April 14-19; 2021
7) Nathaniel Prine, Xiaodan Gu; Quantitative Analysis of Isotopic Blends by Infrared Nanospectroscopy, APS National Meeting & Exposition, Virtual, April 14-19; 2021
8) Luke Galuska, Xiaodan Gu; Role of Water on Correlated Structural and Mechanical Response of Water-Supported and Free-Standing Ultrathin Films, APS National Meeting & Exposition, Virtual, April 14-19; 2021
9) Zhiqiang Cao, Xiaodan Gu; Decoupling conjugated polymer's backbone and sidechain conformation by selective deuteration and neutron scattering, APS National Meeting & Exposition, Virtual, April 14-19; 2021
10) Song Zhang, Amirhadi Alesadi, Wenjie Xia, Xiaodan Gu; Towards the prediction and design of low-glass transition Donor-Acceptor semiconducting polymers; MRS Spring Meeting & Exposition, Phoenix, AZ, April 13-17; 2020
11) Luke Galuska, Eric Muckley, Zhiqiang Cao, Song Zhang, Ilia Ivanov, Xiaodan Gu; A Novel Technique for the Characterization of Freestanding Ultrathin Film Deformation Mechanics; MRS Spring Meeting & Exposition, Phoenix, AZ, April 13-17; 2020
12) Luke A. Galuska, William W. McNutt, Zhiyuan Qian, Song Zhang, Sujata Dhakal, Zhiqiang Cao, Jianguo Mei, Xiaodan Gu; Controlling the Backbone Flexibility of Conjugated

Polymer to Achieve Superior Backbone Tensile Alignment; MRS Spring Meeting & Exposition, Phoenix, AZ, April 13-17; 2020

13) Song Zhang, Amirhadi Alesadi, Wenjie Xia, Xiaodan Gu; Towards the prediction and design of low-glass transition Donor-Acceptor semiconducting polymer; APS National Meeting & Exposition, Denver, CO, March 2-6; 2020
14) Luke Galuska, Eric Muckley, Zhiqiang Cao, Song Zhang, Ilia Ivanov, Xiaodan Gu; A Novel Technique for the Characterization of Freestanding Ultrathin Film Mechanics; APS National Meeting & Exposition, Denver, CO, March 2-6; 2020
15) Luke A. Galuska, William W. McNutt, Zhiyuan Qian, Song Zhang, Sujata Dhakal, Zhiqiang Cao, Jianguo Mei, Xiaodan Gu; Controlling the Backbone Flexibility of Conjugated Polymer to Achieve Superior Backbone Tensile Alignment; APS National Meeting & Exposition, Denver, CO, March 2-6; 2020
16) Zhiyuan Qian, Shaochuan Luo, Tengfei Qu, Zhiqiang Cao, Youjun He, Kunlun Hong, Dongshan Zhou, Xiaodan Gu; The effects of branching position on the crystallization of poly(3-alkylthiophene)s using fast scanning calorimetry; ACS National Meeting & Exposition, Philadelphia, PA, March 22-26; 2020
17) Zhiyuan Qian, Luke Galuska, Song Zhang, Daniel W. Weller, William W. McNutt, Jianguo Mei, Xiaodan Gu; The role of backbone rigidity on entanglement behavior for conjugated polymer; ACS National Meeting & Exposition, Philadelphia, PA, March 22-26; 2020
18) Luke Galuska, Eric Muckley, Zhiqiang Cao, Song Zhang, Ilia Ivanov, Xiaodan Gu; Novel In Situ Tensile Platform for Thin-Film Characterization; MRS Fall Meeting & Exposition, Boston MA, December 1-6; 2019
19) Zhiqiang Cao, Song Zhang, Luke Galuska, Tianyu Li, Kunlun Hong, and Xiaodan Gu; The Influence of Side-chain Length on Backbone Rigidity for Conjugated Polymers; Southeast Polymer Forum, Oak Ridge, Jul 11-12, 2019
20) Zhiqiang Cao, Song Zhang, Luke Galuska, Tianyu Li, Kunlun Hong, and Xiaodan Gu; The Influence of Side-chain Length on Backbone Rigidity for Conjugated Polymers; SNS user meeting, Oak Ridge, June 4-5, 2019

Department talks

1) Xiaodan Gu, Invited Talk, 3M technology day, virtual talk, Sept, 27th, 2022
2) Xiaodan Gu, Design strategies to control the backbone conformation of semi-rigid conjugated polymers, Department of Chemistry, Texas A&M University, April 28th, 2022
3) Xiaodan Gu, Harnessing polymer physics to achieve predictable design of soft electronic materials for wearable applications, Department of Materials Science and Engineering, North Carolina State University, Feb 18th, 2022
4) Xiaodan Gu, Design strategies to predict and control semiconducting polymers' dynamics, Department of Chemistry, Georgetown University, Jan 27th, 2022
5) Xiaodan Gu, Design strategies to predict and control semiconducting polymers' dynamics, Dept. of Chemical and Environmental Engineering, The University of Arizona, November 15th, 2021
6) Xiaodan Gu, Strategies to predict and control semiconducting polymers' dynamics, Department of Chemical Engineering, Mississippi State University, October 21th,2021
7) Xiaodan Gu, Rational design of deformable electronic materials through structure and dynamics study of conjugated polymers, Louisiana State University, Department of Chemical Engineering, April 16th 2021
8) Xiaodan Gu, Invited Talk, Rational design of deformable electronic materials through structure and dynamics study of conjugated polymers, University of Washington, Chemical Engineering Department Seminar, March 29th 2021

9) Xiaodan Gu, Rational design of deformable electronic materials through neutron scattering, Chemical Engineering, Stanford University (Virtual visit), CA, June 29th, 2020
10) Xiaodan Gu, Rational design of deformable electronic materials through neutron scattering, Chemical Engineering Departmental Seminar, University of Alabama at Tuscaloosa, AL, January 2020

Inventions, patent applications, and/or licenses

This work resulted in one patent.

Patent name: Methodology and Instrumentation for Thin Film Mechanical Analysis. Patent number: US20190339180A1.

PARTICIPANTS & OTHER COLLABORATING ORGANIZATIONS

List of Individuals worked on the project and their respective roles.

Name: Xiaodan Gu

Project Role: Principal Investigator

Nearest person month worked 1.5 summer months & 2.5 academic month.

Contribution to Project: PI Xiaodan Gu oversaw the entire project, mentored the students and postdocs involved in this project, initiate collaboration with other researchers from acadmic institution or DOE national lab.

Collaborated with individual in foreign country: Yes

Country(ies) of foreign collaborator: China, UK, Taiwan, Canada

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Jason Azoulay

Project Role: Co-Principal Investigator

Nearest person month worked one summer month & one academic month.

Contribution to Project: CO-PI Jason Azoulay oversaw the synthesis of various deuterated conjugated polymers and supervised graduate student Michael Steelman.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: None

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Dr. Zhiyuan Qian

Project Role: Post-doctoral scholar

Nearest person month worked: 6 months.

Contribution to Project: Zhiyuan performed rheology experiment on conjugated polymers.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: None

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Dr. Haoyu Zhao

Project Role: Post-doctoral scholar

Nearest person month worked: 6 months.

Contribution to Project: Haoyu Zhao performed experiment to study the dynamics of conjugated polymers.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: None

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Yunfei Wang

Project Role: Graduate student

Nearest person month worked: 19 months.

Contribution to Project: Yunfei Wang performed thin film mechanical characterization and neutron scattering experiments.

Collaborated with individual in foreign country: Yes

Country(ies) of foreign collaborator: China, UK, Taiwan, Canada

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Michael Steelman

Project Role: Graduate student

Nearest person month worked: 36 months.

Contribution to Project: Michael Steelman performed conjugated polymer synthesis.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: None

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Luke Galuska

Project Role: Graduate student

Nearest person month worked: 30 months.

Contribution to Project: Luke Galuska performed various neutron/X-ray scattering on conjugated polymers.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: None

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Guorong Ma

Project Role: Graduate student

Nearest person month worked: 14 months.

Contribution to Project: Guorong Ma performed various neutron/X-ray scattering on conjugated polymers.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: None

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Zhiqiang Cao

Project Role: Graduate student

Nearest person month worked: 24 months.

Contribution to Project: Zhiqiang Cao performed various neutron/X-ray scattering on conjugated polymers. He also worked at ORNL for deuteration synthesis.

Collaborated with individual in foreign country: Yes

Country(ies) of foreign collaborator: China, UK, Taiwan, Canada

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Sujata Dhakal

Project Role: Undergraduate student

Nearest person month worked: 24 months.

Contribution to Project: Sujata worked under Luke Galuska for morphology characterization.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: none

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

Name: Zachary Ahmad

Project Role: Undergraduate student

Nearest person month worked: 24 months.

Contribution to Project: Sujata worked under Song Zhang and Zhiqiang Cao for morphology characterization.

Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: none

Travelled to foreign country: No

If traveled to foreign country(ies), duration of stay: 0

IV. IMPACT

Impact of the project on the principal discipline of study

The impact of the project is mostly centered around the following aspects:

1) New chemistry was developed for making deuterated conjugated polymers.
2) A new thin-film tensile testing tool was developed for probing the mechanical property of polymeric films down to 20nm.
3) A contrast variation approach using neutron scattering and contrast variation to probe the backbone conformation of the conjugated polymer.

4) New knowledge of the impact of conjugated backbone rigidity on the electronic and mechanical properties of conjugated polymers.

We communicated our work with the science community with 38 journal publications. The majority of those works were published in high-impact journals. Detail of the impact of each published work is listed in section 1.

Impact on other disciplines

The impact on the other disciplines related to this work is the following:

1) General deuteration chemistry based on click reaction could be used in other materials systems for general users in the neutron community.

2) The thin film tensile test tool can be adopted by other disciplines for study materials' mechanical properties under extreme confinement. For example, the mechanical property of 2d materials.

3) The new knowledge related to the rigidity of the polymer backbone can be applied to conjugated polymer for applications in applications in energy generation and storage.

Impact on the development of human resources

This program aided the training of five graduate students and three undergraduate students in Mississippi. This is very important for such jurisdictions to have their future generation educated with state of art instruments and science. Students involved in this work can build a successful career path. The underrate students who worked on this program received recognition on several occasions such as the USM's undergraduate research symposium. Two female undergraduate students continued their graduate studies at Case Western University and the University of Akron. One graduate student, Song Zhang, received the Charles E. Hoyle Memorial Polymer Science Scholarship for his leading role in mentoring undergraduates. Several students have also been recognized for their research work through national and university awards. For example, Song Zhang received the Graduate Student Hall of Fame, as well as the Graduate student research award, both from the University of Southern Mississippi. Luke Galuska received best graduate research award from ACS POLY division. Zhiqiang Cao’s work was recognized by the APS as a finalist for Frank Padden award.

Impact on physical, institutional, and information resources that form infrastructure/

Although this program did not directly provide instrumentations at USM, it provides collaboration opportunities between students and researchers at the Oak Ridge National Laboratory. This gives students an opportunity to access the state-of-art facility at the Spallation Neutron Source and Center for Nanophase Materials. Many of the instrumentations in ORNL are one of their own kind. Without this funding, the student would not have the resource (travel funds) to access them. Another such opportunity is not previously available in EPSCOR jurisdiction. They made a very important impact in helping develop competitive scientific work and retain students in our program.

Impact on technology transfer.

One patent was filed on May 2019 as a result of this program. We are seeking for an opportunity to transfer the technology.

Impact on society beyond science and technology.

The proposed work would provide new knowledge for engineering new higher-performance functional polymers that would impact clean energy generation and storage. We envisioned that the successful execution of this work would provide new pathways to make functional polymers that would more efficiently harvest solar energy and promote charge transport for next-generation flexible computer chips, as well as wearable electronics for health monitoring.