COVER PAGE

Project Title: Collaborative Research: Polymer Macrocycles: A novel topology to control dynamics of rubbery materials	
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ACCOMPLISHMENTS

1. What are the major goals of the project?

Understanding the dynamics of polymers of different topologies is an important field of study and one of the most important unanswered questions in this field is "how do circular polymers move," particularly in the melt state. New information suggests that molecular topology, specifically circular rings, impacts the response of materials in nanometer-scale confinement. The work performed here tackles these subjects through a collaboration in which specialists in polymer synthesis, polymer rheology and scattering methods, and in the physics of nanoconfinement work together to investigate the thermophysical behavior of circular macromolecules. The project goals are to use a novel synthesis method of "green" oxidative polymerization to produce high purity macrocycles and to investigate their linear viscoelastic behavior in order to fully characterize the dynamics of circular macromolecules to sizes that correspond to linear molecule entanglement densities higher than previously obtainable with synthetic polymers. Chemical chain end characterization and critical edge fractionation coupled with direct visualization of the prepared polymers through the use of polymer amplification methods are proposed in order to quantify the numbers of circular and linear molecules in each sample. The study of the linear viscoelastic response of blends of linear and circular molecules is also to be undertaken in the project. Nonlinear viscoelastic measurements, including extensional viscosity, are to be made.

Strong differences in behavior between linear chains and circular ones also provides an important opportunity for new technology to break the "magic triangle" for tires: it is believed that improving one of the three key attributes—traction, wear, rolling resistance—necessarily sacrifices at least one of the others. Rubber made from cyclic polymers has the potential to break out of this triangle by reducing the so-called Payne effect in reinforced rubbers because circular macromolecules are less sensitive to nanoconfinement than their linear counterparts. The work has as one objective to characterize the impact of nanoconfinement on the behavior of large circular macromolecules. In addition, the dynamics of carbon black filled circular macromolecules are to be studied to test the hypothesis that the resulting rubbery materials will exhibit a reduced Payne effect.

2. What was accomplished under these goals?

University of Akron

The major goals of our part of the project are polymer synthesis and characterization and supplying samples to Texas Tech (TTU) and Caltech (CT).

Polymer synthesis. After the start of the project we sent 2 samples to TTU. It was noticed that during rheological testing drifts occurred. The samples were sent back for SEC analysis that verified molecular weight increase in the samples. Disulfide bonds are relatively easy to break, especially in the presence of thiols (mixture of linear polymers with thiol end groups and rings with no end groups). This could lead to recombination into larger rings and linear molecules. We also sent an additional sample (M_w ~ 100,000 g/mol) that has proven to be quite stable. A sample was also sent to CT.

We then carried out an experimental design (17 polymerizations) to investigate the effects of reaction conditions on the

synthesis of poly(DODT). The polymers were analyzed by SEC, NMR, Raman spectroscopy and MALDI-ToF. We have found that less than stoichiometric amounts of triethylamine (TEA) and hydrogen peroxide relative to the SH groups of the monomer DODT leads to low molecular weights (~ 2000 g/mol) and linear chains with <5% rings. Excess TEA and hydrogen peroxide led to high molecular weights (> 200,000 g/mol). The high MW samples were shown to be mostly rings – no end groups were found by NMR, but it should be mentioned that NMR has a detection limit of about 5-10% (higher at higher molecular weights). Thus, we can conclude that based on chemical analysis these high molecular weight polymers have at least 90% rings. We sent representative samples to TTU. After rheological testing they were sent back to us for analysis – we are currently summarizing the results. We also made samples with medium molecular weights that were a mixture of ring and linear polymers, based on chemical analysis. We are currently working on the synthesis of cyclic oligomers that are very difficult to isolate.

Separation of linear and ring molecules. In the literature dealing with ring polymers separation was carried out using critical edge fractionation. Originally, we also proposed this approach. Literature search also revealed affinity chromatography in which thiol-containing polymers can be captured on a column. However, the special column is extremely expensive (mostly used to capture thiol-containing proteins). We have developed a new method that may be patentable after demonstration of its effectiveness. We have ordered the material for the column that will be functionalized for capturing the linear polymers with thiol end groups, thereby yielding pure cycles. Separation of the high molecular weight polymers will especially be challenging.

The functionalization chemistry led us to a chemical method to check the purity of ring polymers. This would be the first chemistry-base method – in the literature only indirect tests are available such as the critical edge chromatography, rheology or simulation. The chemical test is based on colorimetry. Dipyridyl disulfide reacts with thiols, releasing a thion with intense yellow color. We are working on the establishment of the methodology and the lowest detection limit.

Texas Tech University (TTU)

The major accomplishments during this period at TTU were two-fold. First, we studied the linear viscoelastic properties of several early stage University of Akron (UA) samples using dynamic mechanical measurements and analysis. This work lead to a surprising result that the rings created at UA were "living" in the sense that their behavior continued to evolve towards that of higher molecular weight materials. This was subsequently shown to be the case upon further analysis at UA of returned samples. The result was that the synthesis and the subsequent treatment of the samples was changed to assure sample stability.

Second, UA made new macrocyclic polyDODT materials which were shown by their methods to be at least 90% ring molecules. The sample had a nominal molecular weight of 85,000 g/mol and its viscoelastic response was measured over a range of temperatures and frequencies. The results were suggestive of one of two possibilities. Either the extremely high molecular weight rings behave in the dynamics much like entangled linear polymers, or the 10% contaminant of such high molecular weight rings by the linear counterpart leads to sufficient entanglement that the behaviors of ring and linear polymers become similar. The challenge remaining is to establish how the mixtures of rings and linear chains behave, so that the response can be extrapolated towards zero linear chains. To this end, we have also examined the linear viscoelastic response of mixtures of ring and linear chains provided to us by UA. In this case samples of M_n=26,700 g/mol mixed with 30% linear counterparts and a M_n=13,900 g/mol mixed with 50% linear counterpart were tested. These samples exhibited behavior expected for entangled systems, with the lowest molecular weight system showing evidence that the entanglement coupling was weakening as evidenced by a high phase angle minimum at the rubbery modulus value in a van Gurp-Palmen representation of the data. These aspects are under continuing investigation.

In addition to the above investigations, we also carried out several nonlinear viscoelastic tests on the early stage sample that showed evidence of evolution of properties, but now with the intent of determining whether or not the material with primarily ring-structures behaved in the same way as linear macromolecules in the two-step test protocols used in such characterizations. The preliminary findings suggest that there are differences and the work will continue once more stable samples are available.

Because the present polymer synthesis route produces somewhat higher quantities of ring molecules than prior methods (i.e., the potential exists for tens of grams in ordinary laboratory preparations), we also have begun developing the methods needed to study the behavior of circular macromolecules in concentrated (entangled) solution. This investigation is of importance because the nature of entanglements is such that one would expect that linear chain entanglement would possibly have a different concentration dependence from that of the circular systems. The results of our work to date are inconclusive.

Finally, one goal of the first year of the project was to procure an extensional rheometer fixture in order to carry out extensional rheometry on the circular macromolecules. This fixture has been purchased and has been set up to show that

it functions properly by testing performed on a low density polyethylene material and on an SBR rubber material.

California Institute of Technology

The goal is to obtain rings with linear content as low as 0.1%. The initial plan was to use AFM imaging and analysis to count the number of linear molecules per 1000 molecules imaged. Slow progress in that direction led us to develop an alternative method using covalent capture. The thiol groups at the ends of linear pDODT species opens several options for grafting the linear chains onto particles or polymers. The advantage of covalently bonding pDODT to a dissimilar polymer as a method to quantify the number of linear contaminants present is that the initial screening can be performed using gel permeation chromatography (GPC) and the method holds promise for pulling even scarce linear contaminants out of a sample. Polystyrene (PS) and poly(n,n-dimethyl-acrylamide) (pDMA) were selected as candidate "capture polymers": precipitation of pDODT under conditions that keep PS in solution did not occur cleanly; precipitation of pDODT occurs cleanly using methanol. We have synthesized a protected maleimide initiator for ATRP polymerization; from it, we have synthesized pDMA with protected maleimides at each end. The deprotection reaction was not completed at the time of this writing; as soon as the maleimide end groups of the pDMA are exposed, we plan to dissolve maleimide-ended pDMA and pDODT in chloroform (a good solvent for both) and allow coupling to occur between any exposed thiols and maleimides. Examination of the GPC traces of the individual reagents (pDODT and maleimide-ended pDMA) in comparison with those of the product of the coupling reaction should show a high molecular weight peak consistent with coupling pDODT to PDMA. If present, we will separate it using methanol to drive precipitation of the pDODT. This will enable us to separate linears and rings and to quantify the mass fraction of linear pDODT.

The discovery at TTU that the molecular weight of the rings can increase over time in the melt led to the hypothesis that the rings were fusing by disulfide exchange and we reasoned that in dilute solution molecular weight would reverse as small rings would pinch off from large ones and the probability of ring fusion would be low in dilute solution. We confirmed that is indeed the case. We then evaluated the factors influencing the rate of disulfide exchange. We found the kinetics to be insensitive to temperature over the range tested (-4C to +60C). The rate was also not affected by oxygen. The primary determinant of the rate of reaction was light: even indoor room light substantially accelerates the disulfide exchange reaction.

3. What opportunities for training and professional development has the project provided?

University of Akron

The project so far trained one Ph. D. student. She became familiar with synthetic methodologies and characterization techniques such as SEC, NMR, MALDI-ToF and Raman spectroscopy. She will defend her thesis in June of this year. The project also provided development opportunities for a research professor and a visiting scientist. They will be moving to the Ohio State University with the PI and continue working on the project. The original inventor with the PI, a former Ph. D. student, also participated in the project as a consultant and the new findings provided development opportunities for her as well.

Texas Tech University

The project is training two Ph.D. students. One student is actively focusing on the linear viscoelastic characterization of the materials and has been working on the project since its inception. He is also learning the non-linear rheology of step-strain histories in the evaluation of the constitutive behavior of polymeric fluids. The second student just began working on the project in March, 2019 and will be learning how to perform the rheological characterization of the materials, with emphasis on the extensional viscometry aspects of the project. She is also learning how to carry out thermal analysis of

ultrathin polymer films related to the portion of the project related to confinement effects on material behavior. One undergraduate student is also working on the project under the guidance of the senior graduate student and is learning linear viscoelasticity.

California Institute of Technology

Two Caltech Ph.D. students have contributed to this collaborative research. One student brought AFM experience for detection of linear chains in the presence of linears. The second student has been increasingly involved in the development of chemical methods to assay and separate linear contaminants. On his own initiative, that student launched a suite of experiments to understand the evolution of pDODT ring size and ring:linear ratio. Both of them are eager to learn more from Puskas regarding "green polymers" and from McKenna regarding the dynamics of cyclic and linear polymers and their blends.

4. How have the results been disseminated to communities of interest?

University of Akron

The results are being incorporated into the Ph. D. thesis of the graduate student. Several interim reports were written and will be compiled for potential peer-reviewed publications.

Texas Tech University

The results have been reported in the form of a poster presentation by a graduate student and the PI made to the Annual Meeting of the Society of Rheology held in Houston, Texas in October 2018. The poster was: Dongjie Chen, Gregory B. McKenna, Judit E. Puskas, Carin A. Helfer, Zhiyuan Qian, and Julia A. Kornfield, "A study of the linear and nonlinear viscoelastic properties of cyclic poly(3,6-dioxa-1,8-octanedithiol) (polyDODT)." SOR 90th Annual Conference, Houston, TX October 14-18, 2018. The graduate student Dongjie Chen also made a presentation of this poster at the 2019 International Polyolefins Conference held in Houston, TX Feb. 24-27, 2019.

California Institute of Technology

Nothing to report.

5. What do you plan to do during the next reporting period to accomplish the goals?

Ohio State University (co-PI Puskas moved from the University of Akron to Ohio State University)

A new Post-doctoral fellow and a new Ph. D. student will start working on the project on August 1 at the Ohio State University. The equipment from the Akron lab will have been relocated to the Wooster lab. Hopefully the grant will have been transferred to OSU with a revised budget.

Polymer synthesis. We plan to synthesize a series of DODT polymers with various molecular weights. We will isolate the ring molecules by column chromatography using our new method. We will then try to break just one disulfide bond, yielding a linear molecule with the same molecular weight. The polymers will be characterized by SEC, NMR, Raman and MALDI-ToF when applicable. OSU has an 850 MHz NMR that will be very useful for end-group characterization of high molecular weight polymers. Full SEC characterization (conformation, size, viscosity) will be carried out with selected polymers.

Separation of linear and ring molecules. We will develop our new affinity chromatography and use to separate ring polymers on a g scale.

Visualization by AFM. We will also proceed with the visualization plan. Copolymers will be made with lipoic acid and the structures will be amplified so AFM analysis could be carried out.

Texas Tech University

Linear viscoelastic characterization: Linear viscoelastic characterization of the sample will continue both to further understand the samples and to guide the synthesis efforts in the quest to achieve pure ring molecules. These studies will continue also in making measurements on blends of linear and ring molecules as well as in the investigation of the concentration dependence of the dynamic properties of rings in solution.

Nonlinear viscoelastic characterization: Pure ring samples will be investigated using the two-step protocol that is an important basis for the evaluation of nonlinear constitutive responses of macromolecular melts. In addition, the high purity rings will be investigated for the elongational viscosity behavior.

Confinement behavior. The impact of nanoconfinement on the glass transition temperature of the macrocycles will be investigated by differential scanning calorimetry using rapid chip methods. In addition, the TTU nanobubble inflation method will be used to characterize the rubbery stiffening behavior of the poly(DODT) macrocycles. Work on the Payne effect in filled macrocyclic rubber systems will be started.

California Institute of Technology

Quantification and removal of linears from rings using maleimide-thiol coupling: Based on promising preliminary results, the Kornfield group will synthesize maleimide-ended pDMA, co-dissolve it at relatively high concentration (ca. 5% in chloroform) with a pDODT sample of interest, allow it to react in the dark overnight, and precipitate in methanol to recover pDODT that is free of thiols (intended to be pure rings). Kornfield will use GPC to characterize the changes in the molecular weight distributions of the pDODT (due to removal of linears) and the pDMA (due to conversion of some of them to diblock copolymers formed by capture of linear-pDODT); and will use NMR to quantify the amount of pDODT that became grafted to pDMA (using the distinctive 1H-NMR peaks of pDMA and pDODT. Based on the precise mass of pDMA that was introduced in the coupling reaction, the NMR spectra will enable calculation of the precise mass of pDODT that was captured. In turn, the mass of linear impurity and the precise mass of the pDODT that was introduced to the coupling reaction will be used to compute the mass fraction of linear pDODT that was present. This method will have sufficient sensitivity to detect and quantify as little as 0.1%wt linear in an otherwise cyclic sample. This work will be pursued in close coordination with both McKenna and Puskas: McKenna will measure the changes in relaxation dynamics as a function of trace linear content; Puskas will critique Kornfield's chemical coupling method and interpretation of the results.

Study of kinetics of ring growth and reversion to lower molecular mass: Kornfield will continue to investigate the kinetics of the changes in ring size that may prove useful in creating responsive elastomers and open new routes to recovery, repurification and resynthesis of pDODT elastomers. This would be pursued in close collaboration with Puskas, building on her vision of green elastomers and her discoveries regarding the roles of amine and peroxide in controlling the stability of pDODT.

PRODUCTS - DETAILS

PUBLICATIONS DETAIL

1. Conference Paper/Presentation: A study of the linear and nonlinear viscoelastic properties of cyclic poly(3,6-dioxa-1,8-octanedithiol) (polyDODT)	
Conference Name: 2019 International Polyolefins Conference	**Conference Location:** Houston, Texas
Publication Status: Presented	**Conference Date:** 02/25/2019
Author(s): Dongjie Chen, Zhiyuan Qian, Carin A. Helfer, Judit E. Puskas, Julia A. Kornfield, and Gregory B. McKenna	
Acknowledgement of DOE Support: Yes	

2. Conference Paper/Presentation: A study of the linear and nonlinear viscoelastic properties of cyclic poly(3,6-dioxa-1,8-octanedithiol) (polyDODT).	
Conference Name: Society of Rheology 90th Annual Conference	**Conference Location:** Houston, Texas
Publication Status: Presented	**Conference Date:** 10/17/2018
Author(s): Dongjie Chen, Gregory B. McKenna, Judit E. Puskas, Carin A. Helfer, Zhiyuan Qian, and Julia A. Kornfield	
Acknowledgement of DOE Support: Yes	

INTELLECTUAL PROPERTIES DETAIL

There are no intellectual properties to report.

TECHNOLOGIES AND TECHNIQUES DETAIL

There are no technologies or techniques to report.

OTHER PRODUCTS DETAIL

There are no other products to report.

PARTICIPANTS AND OTHER COLLABORATING ORGANIZATIONS

PARTICIPANTS DETAIL

1. Participant: Mr. Dongjie Chen		
Project Role: Graduate Student (Research Assistant)	**Person Months Worked**: 12	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Mr. Chen is a graduate student working on the project since its inception. He is performing the linear viscoelastic characterization of the materials and some of the nonlinear viscoelastic measurements.		
International Collaboration: No		
International Travel: No		

2. Participant: Ms. Shuang Jin		
Project Role: Graduate Student (Research Assistant)	**Person Months Worked**: 3	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: Ms. Jin will be responsible for the studies of confinement effects on the behavior of the macrocyclic polymers and will work, also, with graduate student Donjie Chen on the elongational viscosity measurements.		
International Collaboration: No		
International Travel: No		

3. Participant: Prof. Gregory B McKenna		
Project Role: Principal Investigator/Project Director	**Person Months Worked**: 1	**Funding Support (if other than this award)**: Not Provided
Contribution to the Project: PI on project. Coordinating with co-PIs Puskas and Kornfield. Also supervising the research at Texas Tech University that is being carried out by graduate students D. Chen and S. Jin. This also involves supervising the activities of an undergraduate student working on the project during the spring semester of 2019.		

International Collaboration: No
International Travel: No

4. Participant: Mr. Rene Troche-Baez		
Project Role: Undergraduate Student	**Person Months Worked**: 1	**Funding Support (if other than this award)**: pays own tuition.
Contribution to the Project: Mr. Troche-Baez is an undergraduate student who is enrolled in a research credit class with the intent to evaluate whether or not research is a good avenue for him to pursue. He is working to learn how to perform the linear viscoelastic measurements on the macrocyclic polymers under the direct guidance of graduate student Dongjie Chen.		
International Collaboration: No		
International Travel: No		

PARTNERS DETAIL

There are no partners to report.

OTHER COLLABORATORS DETAIL

There are no other collaborators to report.

IMPACT

1. What is the impact on the development of the principal discipline(s) of the project?
Nothing to report yet.
2. What is the impact on other disciplines?
Nothing to report yet.
3. What is the impact on the development of human resources?
Student training towards Ph.D. as well as undergraduate student learning experience about research.
4. What is the impact on physical, institutional, and information resources that form infrastructure?
Nothing to report yet.
5. What is the impact on technology transfer?
Nothing to report yet.
6. What is the impact on society beyond science and technology?
Nothing to report yet.
7. Foreign Spending
Not Provided

CHANGES - PROBLEMS

1. Changes in approach and reasons for change

University of Akron/Ohio State University

No changes in the research plan were made. The budget was changed internally to include a Ph. D. student.

Texas Tech University

No changes in research plan were made.

California Institute of Technology
Kornfield needed an alternative to AFM as a method to detect trace linear contaminants; one of the members of her group devised a chemical route that has provided encouraging preliminary results. Therefore, we plan to move forward using covalent capture as the method of choice for removing linears from rings and quantitatively analyzing even a small fraction of linear contaminants.

At the inception of the project we did not know that pDODT would open the way to rings that may be amenable to systematic increase in size (via disulfide exchange in the melt) or systematic decrease in size (via disulfide exchange in solution). Kornfield would like to investigate this new direction with a level of effort that does not interfere with fulfilling the commitment to quantify linear contaminant and contribute to methods of removal of trace linears from rings.

2. Actual or anticipated problems or delays and actions or plans to resolve them

University of Akron/Ohio State University

Some delays were encountered due to the change of affiliation of the PI – she accepted a tenured full professor position at Ohio State University (OSU) effective January 1, 2019. The Size Exclusion Chromatography (SEC) computer crashed in December. The whole set-up has already been moved to OSU. A new computer was purchased, and a new software was installed free of charge by Wyatt Technologies who also supervised the relocation. The set-up was fully operational by March 7. All equipment will be moved by June 30. The problems encountered at the University of Akron related to the transfer of the grant and moving all equipment hopefully will be resolved soon – As per the instructions of the program officer, very recently Akron submitted the request for PI change at Akron, followed by the transfer request. The program manager has concurred to this request.
Texas Tech University

No problems

California Institute of Technology

Kornfield's analysis of linear contaminants has been delayed; the plan to resolve the bottleneck is to use covalent capture (described above).

3. Changes that have a significant impact on expenditures

All Institutions:

Expenditures were not affected by the changes discussed.

4. Significant changes in use or care of human subjects, vertebrate animals, and/or biohazards

N/A

5. Change of primary performance site location from that originally proposed

University of Akron/Ohio State University

The primary performance location will change starting July 1, 2019. Y1 plans will be completed at the University of Akron.

Texas Tech University

N/A

California Institute of Technology

N/A

6. Carryover Amount
Estimated carryover amount for the next budget period: $0.00