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4. TITLE AND SUBTITLE Precision Morphology in Sulfonic, Phosphonic, Boronic, and Carboxylic Acid Polyolefins			5a. CONTRACT NUMBER W911NF-09-1-0290		
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6. AUTHORS Ken Wagener			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
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14. ABSTRACT This is the final report for ARO W911NF-09-1-0290. Prior reports on this project give further detailed information. Of greatest importance in this work has been our novel discovery of heterogeneous deprotection of sulfonic acid esters. The consequence will be that we can form precision placed sulfonic acid groups along a polymer chain. This has never been done before. If the morphology arranges as we expect it to (based on what we observed in the case of carboxylic acid precision placement) then we may be able to create conduction channels for protons and other ions in bi-continuous phase polymer systems. From an educational point of view, 9 students have been					
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a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 352-392-4666

Report Title

Precision Morphology in Sulfonic, Phosphonic, Boronic, and Carboxylic Acid Polyolefins

ABSTRACT

This the final report for ARO W911NF-09-1-0290. Prior reports on this project give further detailed information. Of greatest importance in this work has been our novel discovery of heterogeneous deprotection of sulfonic acid esters. The consequence will be that we can form precision placed sulfonic acid groups along a polymer chain. This has never been done before. If the morphology arranges as we expect it to (based on what we observed in the case of carboxylic acid precision placement) then we may be able to create conduction channels for protons and other ions in bicontinuous phase polymer systems. From an educational point of view, 9 students have been impacted by this research, 5 of whom are woman, 1 being a minority.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/31/2012 13.00	Shuichiro Seno, Tatsuhiro Nagamatsu, Satoru Hosoda, Yoshinobu Nozue, Yuya Shinohara, Yoshiyuki Amemiya, E. B. Berda, G. Rojas, K. B. Wagener. Cross Nucleation in Polyethylene with Precisely Spaced Ethyl Branches, ACS Macro Letters, (06 2012): 772. doi: 10.1021/mz300215u
08/31/2012 21.00	Paula A. Delgado, David Y. Liu, Zachary Kean, Kenneth B. Wagener. Synthesis of Poly(3-dodecyl-2,5-thienylene vinylene) by Solid-State Metathesis Polycondensation, Macromolecules, (12 2011): 9529. doi: 10.1021/ma2020529
08/31/2012 20.00	Brian S. Aitken, Patrick M. Wieruszewski, Kenneth R. Graham, John R. Reynolds, Kenneth B. Wagener. Perfectly Regioregular Electroactive Polyolefins: Impact of Inter-Chromophore Distance on PLED EQE, Macromolecules, (01 2012): 705. doi: 10.1021/ma202409k
08/31/2012 19.00	Brian S. Aitken, C. Francisco Buitrago, Jason D. Heffley, Minjae Lee, Harry W. Gibson, Karen I. Winey, Kenneth B. Wagener. Precision Ionomers: Synthesis and Thermal/Mechanical Characterization, Macromolecules, (01 2012): 681. doi: 10.1021/ma202304s
08/31/2012 18.00	James K. Leonard, Yuying Wei, Kenneth B. Wagener. Synthesis and Thermal Characterization of Precision Poly(ethylene-, Macromolecules, (01 2012): 671. doi: 10.1021/ma202233a
08/31/2012 17.00	Lisa M. Hall, Michelle E. Seitz, Karen I. Winey, Kathleen L. Oppen, Kenneth B. Wagener, Mark J. Stevens, Amalie L. Frischknecht. Ionic Aggregate Structure in Ionomer Melts: Effect of Molecular Architecture on Aggregates and the Ionomer Peak, Journal of the American Chemical Society, (01 2012): 574. doi: 10.1021/ja209142b
08/31/2012 16.00	Michael D. Schulz, Kenneth B. Wagener. Solvent Effects in Alternating ADMET Polymerization, ACS Macro Letters, (04 2012): 449. doi: 10.1021/mz200236r
08/31/2012 15.00	Ingo Lieberwirth, Bora Inci, Werner Steffen, Markus Mezger, Robert Graf, Katharina Landfester, Kenneth B. Wagener. Decreasing the Alkyl Branch Frequency in Precision Polyethylene: Effect of Alkyl Branch Size on Nanoscale Morphology, Macromolecules, (04 2012): 3367. doi: 10.1021/ma3002577
08/31/2012 14.00	Clifford R. Bowers, Yuying Wei, Brian S. Aitken, Christopher R. Reeg, Christopher D. Akel, Kenneth B. Wagener. Molecular dynamics in precision deuteriomethyl branched polyethylene from solid-state deuterium NMR, Polymer, (06 2012): 2633. doi: 10.1016/j.polymer.2012.03.055
09/06/2011 9.00	Bora Inci, Kenneth B. Wagener. Decreasing the Alkyl Branch Frequency in Precision Polyethylene: Pushing the Limits toward Longer Run Lengths, Journal of the American Chemical Society, (08 2011): 0. doi: 10.1021/ja2040046
09/06/2011 11.00	Kenneth B. Wagener, Kathleen L. Oppen. ADMET: Metathesis polycondensation, Journal of Polymer Science Part A: Polymer Chemistry, (02 2011): 0. doi: 10.1002/pola.24491

09/06/2011 10.00 Yoshinobu Nozue, Yasutoyo Kawashima, Kouei Suita, Shuichiro Seno, Tatsuhiro Nagamatsu, Kenneth B. Wagener, Bora Inci, Fabio Zuluaga, Giovanni Rojas, James K. Leonard, Satoru Hosoda. Effect of the Sequence Length Distribution on the Lamellar Crystal Thickness and Thickness Distribution of Polyethylene: Perfectly Equisquential ADMET Polyethylene vs Ethylene/?-Olefin Copolymer., *Macromolecules*, (01 2011): 0. doi: 10.1021/ma102072p

11/01/2013 22.00 Chester Simocko, Kenneth B. Wagener. Effects of Boron-Containing Lewis Acids on Olefin Metathesis, *Organometallics*, (05 2013): 0. doi: 10.1021/om400257b

11/14/2013 24.00 Michael D. Schulz, Rachel R. Ford, Kenneth B. Wagener. Insertion metathesis depolymerization, *Polymer Chemistry*, (05 2013): 0. doi: 10.1039/c3py00531c

11/15/2013 25.00 Pascale Atallah, Kenneth B. Wagener, Michael D. Schulz. ADMET: The Future Revealed, *Macromolecules*, (06 2013): 0. doi: 10.1021/ma400067b

11/15/2013 26.00 Janelle E. Jenkins, Michelle E. Seitz, C. Francisco Buitrago, Karen I. Winey, Kathleen L. Opper, Travis W. Baughman, Kenneth B. Wagener, Todd M. Alam. The impact of zinc neutralization on the structure and dynamics of precise polyethylene acrylic acid ionomers: A solid-state ¹³C NMR study, *Polymer*, (08 2012): 0. doi: 10.1016/j.polymer.2012.06.019

TOTAL: 16

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

- 1) 246th ACS National Meeting, September 2013, Indianapolis, IN, Taylor Gaines and Ken Wagener, Functionalized polyethylene containing precisely placed sulfonic acid groups synthesized via ADMET polymerization,
- 2) POLYOLEFINS CONFERENCE, October 15, 2013, Santa Rosa, California
"Polymer Morphology of A Series of Precision Acid Polymer Structures"
- 3) BRASKEM CONFERENCE ON POLYMERS, October 8, 2013, Porto Alegre, Brazil
"Using Metathesis to Control Polymer Morphology"
- 4) HERMAN MARK AWARD SYMPOSIUM, ACS Meeting, September 10, 2013, Indianapolis, IN
"Using Metathesis To Control Polymer Morphology"
- 5) IUPAC WORLD CONFERENCE, August 13, 2013, Istanbul, Turkey
"New Methodology For Preparing Precision Acid Polymer Structures"
- 6) INTERNATIONAL SYMPOSIUM ON OLEFIN METATHESIS, July 16, 2013, Nara, Japan
"New Methodology For Preparing Precision Acid Polymer Structures"
- 7) GORDON CONFERENCE ON POLYMERS, June 12, 2013, Mt. Holyoke, MA
"Synthesis Of Polymers Related To Radionucleotide Chemistry"
- 8) KEYNOTE LECTURE - KING ABDULZILLA CITY FOR SCIENCE & TECHNOLOGY CONFERENCE, May 14, 2-13, Riyadh, Saudi Arabia, "The ADMET Reaction"
- 9) UNIVERSITY OF NEW MEXICO, March 8, 2013, Albuquerque, New Mexico
"The ADMET Reaction"
- 10) POLYCONDENSATION CONFERENCE, September 19, 2012, San Francisco, CA
"Metathesis Solid State Polycondensation"
- 11) FURMAN UNIVERSITY, September 13, 2012, Greenville, SC
"The ADMET Reaction"
- 12) NATIONAL ACS APPLIED POLYMERS AWARD SYMPOSIUM FOR RICHARD TURNER, August 20, 2012
"Solid State Metathesis Polymerization"
- 13) IUPAC MACRO 2012, June 28, 2012, Blacksburg, VA
"Precision Polyolefin Acid Polymers"

Number of Presentations: 13.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
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11/12/2013	23.00	Kenneth B. Wagener, Klaus Müllen, Markus Klapper, Dilyana Markova, Kathleen L. Opper, Manfred Wagner. Synthesis of proton conducting phosphonic acid-functionalized polyolefins by the combination of ATRP and ADMET, Polymer Chemistry (10 2012)
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TOTAL: 1

Number of Manuscripts:

Books

<u>Received</u>	<u>Paper</u>
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TOTAL:

Patents Submitted

Provisional patent filed on July 15, 2013, Serial No 61/846,474 by Taylor Gaines and Kenneth Wagener; Sulfonated Polyethylene

Patents Awarded

Awards

2013 American Chemical Society Herman F. Mark Polymer Chemistry Award

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Taylor Gaines	0.33	
Chester Simocko	0.33	
FTE Equivalent:	0.66	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Kenneth Wagener	0.08	
FTE Equivalent:	0.08	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Taylor Frering	0.15	Animal Reproductive Science
FTE Equivalent:	0.15	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Chester Simocko
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

This is the final report for ARO W911NF-09-1-0290. During the past year we implemented our synthetic program based on the novel discovery of heterogenous deprotection of sulfonic acid esters. This approach is one of the first of its kind and leads to a completely deprotected precise sulfonic ester polymer and leads us into our future work. We synthesized this polymer for complete characterization and to send samples to Professor Karen Winey at the University of Pennsylvania for morphological characterization. We worked to determine what molecular weight is sufficient in order to produce suitable mechanical properties. Since sulfonic acids are strongly hydrogen bonded, we anticipated lower molecular weights to be better than higher ones from a processing point of view, where processing will mean conversion into various material forms such as fibers, films, and membranes. We reached the stage where we can begin to consider these possibilities, since they are important to the basic science at hand.

During the past year we had a visiting Japanese graduate student from Kyoto University spend several months with us, and during this time he served as extra labor in the synthesis of precisely spaced sulfite containing polymers. These polymers were made and await complete characterization before sending them to Professor Winey for morphological characterization. We will also send these polymers to the Max Planck Institute for Polymer Research in Mainz, where we have had a strong working relationship over 20 years.

Boronic acid research was completed over the past year, where the synthesis of boronic acids were polymerized in ionic liquids. High molecular weights were observed during this chemistry. In an interesting observation we discovered the boronic Lewis acids reduce isomerization in resulting alkenes in small molecule metathesis, which provides a valuable insight into metathesis catalysis in general. The boronic acid polymers that have been made displayed unique properties during melting. These precision boronic acids were also cross linked, yet displayed distinct melting points. Even more interesting, each subsequent melt occurred at a higher temperature than the previous melt.

We were pleased to be able to work on this research and appreciate the Army Research Office for providing the support necessary to achieve these results.

Technology Transfer