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**RPPR Final Report**  
as of 11-Dec-2019

Agency Code:

Proposal Number: 63803CH

**Agreement Number: W911NF-13-1-0363**

**INVESTIGATOR(S):**

**Name:** Karen I Winey winey@lrsm

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**Principal:** Y

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DUNS Number: 042250712

EIN: 231352685

**Report Date:** 14-Nov-2018

Date Received: 13-Nov-2019

**Final Report** for Period Beginning 15-Aug-2013 and Ending 14-Aug-2018

**Title:** 7.3: Rapid Screening of New Precise Copolymers: Morphology and Ionic Conductivity

**Begin Performance Period:** 15-Aug-2013

**End Performance Period:** 14-Aug-2018

**Report Term:** 0-Other

Submitted By: Karen Winey

Email: winey@seas.upenn.edu

Phone: (215) 898-0593

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 2

**STEM Participants:** 4

**Major Goals:** The primary goals for this project is to rapidly screen new polymers to identify polymers and morphologies with significantly improved ionic conductivity. The secondary objective is to advance the fundamental understanding of ion conduction mechanisms in polymers.

Our work has focused on three sets of polymers: precise polyethylenes synthesized by ADMET, commercial pentablock copolymers with a poly(sulfonated styrene) midblock, and polymerized ionic liquids containing cyclopropenium. We have also explored a nearly precise acid-containing polymer.

**Accomplishments:** The most significant outcome of this project is our Nature Materials paper that demonstrates how the novel morphologies that we have revealed in the precise polyethylenes can provide excellent transport properties. Specifically, a polyethylene with a sulfonic acid on every 21st carbon self assembles into acid layer that swell when exposed to relative humidity. The proton conductivity of these materials is comparable to Nafion at 40C and relative humidities above 60%. This demonstrates our previously hypothesized transport mechanism through the precise polyethylenes. Moreover, these design concepts can be applied to a wider set of materials. Since publication in May 2018, this paper has already been cited 29 times.

This grant substantively contributed to the education of 3 doctoral students (Robert Middleton, Edward Trigg, and Lu Yan) and 1 postdoctoral fellow (Phil Griffin). Robert is working for Exponent, Ted is an NRC postdoc at Wright Patterson, Lu entered law school and Phil is employed at the University of Chicago.

**Training Opportunities:** This grant substantively contributed to the education of 3 doctoral students (Robert Middleton, Edward Trigg, and Lu Yan) and 1 postdoctoral fellow (Phil Griffin). Robert is working for Exponent, Ted is an NRC postdoc at Wright Patterson, Lu entered law school and Phil is employed at the University of Chicago.

Graduate student training included the design of experiments, sample preparation, EIS measurements, X-ray scattering, thermal analysis, and data analysis. For Ted Trigg is also involved all-atom molecular dynamics simulations performed in collaboration with scientists at Sandia National lab. Both Ted and Lu worked with undergraduate students during their studies, which provided opportunities for them to mentor/manage younger scientists.

# RPPR Final Report

## as of 11-Dec-2019

**Results Dissemination:** The grants has been acknowledged 12 journal publications and dozens of invited talks.

### Major Lectures

Distinguished Speaker, New Jersey Institute of Tech.- 2018  
Keynote Speaker, PMSE Symposium, American Chemical Society - 2018  
Plenary Session, American Institute of Chemical Engineers - 2017  
DB Robinson Distinguished Lecture, University of Alberta - 2017  
Plenary Speaker, 2017 Joint CNMS-SNS User Meeting - 2017  
Plenary Lecture, 5th International Symposium Frontiers in Polymer Science - 2017  
IUPAC Lecture, Chemistry Department, University of Montreal - 2017  
Plenary Speaker, Macromolecular Innovation Institute Conference - 2016  
Plenary Speaker, ECNP International Conf. on Nanostructured Polymers & Nanocomposites - 2016

### Honors and Awards:

Honors for Karen Winey  
Trustees Council of PennWomen Award for Undergraduate Advising - 2017  
Fellow, Polymeric Material Science and Engineering, ACS - 2016  
“For outstanding contributions to the understanding of polymer nanocomposites and ion-containing polymers through quantitative scattering and microscopy studies.”  
Visiting Miller Research Professor, University of California, Berkeley - 2014

### Honors for Edward (Ted) Trigg

DOE Office of Science Graduate Student Research Award - 2015  
Geoffrey Belton Graduate Fellowship Award, Univ. of Pennsylvania - 2016  
Finalist, Padden Award, Division of Polymer Physics, APS - 2018  
NRC Postdoctoral Fellowship - 2019

### Protocol Activity Status:

**Technology Transfer:** Nothing to Report

### PARTICIPANTS:

**Participant Type:** PD/PI

**Participant:** Karen I Winey

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Edward Trigg

**Person Months Worked:** 10.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Lu Yan

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

International Collaboration:

**RPPR Final Report**  
as of 11-Dec-2019

International Travel:  
National Academy Member: N  
Other Collaborators:

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)

**Participant:** Phil Griffin

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Robert Middleton

**Person Months Worked:** 6.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Undergraduate Student

**Participant:** Grace Salmon

**Person Months Worked:** 3.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**ARTICLES:**

**Publication Type:** Journal Article

Peer Reviewed: Y

**Publication Status:** 1-Published

**Journal:** Polymer

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.polymer.2017.12.007

Volume:

Issue:

First Page #:

Date Submitted: 11/13/19 12:00AM

Date Published: 12/5/17 7:27PM

Publication Location:

**Article Title:** Solution-Grown Crystals of Precise Acid- and Ion-Containing Polyethylenes

**Authors:** Lu Yan, Karen C. Bustillo, Ouliana Panova, Andrew M. Minor, Karen I. Winey

**Keywords:** polymer crystals, precise polymers, electron diffraction

**Abstract:** Crystals of precise acid- and ion-containing polyethylenes were prepared from solution. While large pendant groups on polyethylene backbones are typically excluded from the crystalline domain, the precisely-placed acid and ionic functional groups are accommodated into the solution-grown crystals. Polyethylene containing carboxylic acid pendant groups on every 21st carbon atom (p21AA) grows into rectangular shaped crystals with an average thickness of 9 nm, which is 3-4 times the all-trans chain length between the functional groups. This thickness indicates that the carboxylic acid groups are incorporated within the crystals. Electron diffraction images and Raman spectra indicate that p21AA backbones are hexagonally packed. Finally, we propose a multi-layer stack of adjacent reentry structures that is consistent with the incorporation of large functional groups into the solution-growth crystals of these precise polyethylenes, in contrast to melt-crystallized p21AA.

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Acknowledged Federal Support: Y

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Macromolecules

Publication Identifier Type: DOI

Publication Identifier: 10.1021/acs.macromol.7b02546

Volume: 51

Issue: 5

First Page #: 1681

Date Submitted: 11/13/19 12:00AM

Date Published: 2/1/18 12:00AM

Publication Location:

**Article Title:** Ion Transport in Cyclopropenium-Based Polymerized Ionic Liquids

**Authors:** Philip J. Griffin, Jessica L. Freyer, Nicholas Han, Noah Geller, Xiaodong Yin, Chirag D. Gheewala, Trista

**Keywords:** ionomers, polymerized ionic liquids

**Abstract:** Ion transport in polymerized ionic liquids (poly-ILs) occurs via a fundamentally different mechanism than in monomeric ionic liquids, and recently progress has been made toward understanding ion conduction in poly-ILs. To gain insight into the nature of ionic conductivity in ionic polymers, we investigate the physical properties of the trisaminocyclopropenium (TAC) ion, as it is an aromatic carbocation with unique structural and electronic properties. Herein, we characterize the thermal properties, local morphology, and dielectric response of a series of monomeric and polymeric TAC ionic liquids with different counterions. We have found that the extent of a "superionic" mechanism depends on the nature of the ion pair and can result in anomalously high conductivity at the calorimetric T<sub>g</sub>. Our results suggest that the molecular volumes of the cationic and anionic species are important parameters that impact ion conductivity in polymerized ionic liquids.

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Soft Matter

Publication Identifier Type: DOI

Publication Identifier: 10.1039/C5SM02053K

Volume: 12

Issue: 4

First Page #: 1133

Date Submitted: 11/13/19 12:00AM

Date Published:

Publication Location:

**Article Title:** Polymerized ionic liquid diblock copolymers: impact of water/ion clustering on ion conductivity

**Authors:** Jacob R. Nykaza, Yuesheng Ye, Rachel L. Nelson, Aaron C. Jackson, Frederick L. Beyer, Eric M. Davis

**Keywords:** ionomers, block copolymers, ionic liquids

**Abstract:** Herein, we examine the synergistic impact of both ion clustering and block copolymer morphology on ion conductivity in two polymerized ionic liquid (PIL) diblock copolymers with similar chemistries but different side alkyl spacer chain lengths (ethyl versus undecyl). When saturated in liquid water, water/ion clusters were observed only in the PIL block copolymer with longer alkyl side chains (undecyl) as evidenced by both small-angle neutron scattering and intermediate-angle X-ray scattering, i.e., water/ion clusters form within the PIL microdomain under these conditions. The resulting bromide ion conductivity in the undecyl sample was higher than the ethyl sample (14.0 mS cm<sup>-1</sup> versus 6.1 mS cm<sup>-1</sup> at 50 °C in liquid water) even though both samples had the same block copolymer morphology (lamellar) and the undecyl sample had a lower ion exchange capacity (0.9 meq g<sup>-1</sup> versus 1.4 meq g<sup>-1</sup>). No water/ion clusters were observed in either sample under high humidity or dry conditions. The resulti

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## RPPR Final Report as of 11-Dec-2019

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Macromolecular Chemistry and Physics

Publication Identifier Type: DOI

Publication Identifier: 10.1002/macp.201700634

Volume: 219

Issue: 11

First Page #: 1700634

Date Submitted: 11/13/19 12:00AM

Date Published: 6/1/18 4:00AM

Publication Location:

**Article Title:** Precision Sulfonic Acid Polyolefins via Heterogenous to Homogenous Deprotection

**Authors:** Taylor W. Gaines, Michael H. Bell, Edward B. Trigg, Karen I. Winey, Kenneth B. Wagener

**Keywords:** ADMET synthesis, precise polymer

**Abstract:** Polyolefins containing precisely spaced sulfonic acid functionality are made. First, precision ethyl sulfonate ester diene monomers are synthesized, which then are converted to acyclic diene metathesis polymers using Grubbs' catalysis. Subsequently, the poly(ethyl sulfonate esters) are deprotected post-polymerization via two successful routes, both using a concept of "heterogenous to homogenous deprotection." The resulting poly(sodium sulfonate) salts are then converted to precise poly(sulfonic acids), where the sulfonic acid functionality is placed either at every ninth or 21st carbon. For comparison, random versions of poly(sulfonates), their salts, and sulfonic acid polymers are synthesized via copolymerization of the "9" sulfonate monomer with 1,9-decadiene. Precision placement of sulfonic acid functionality could lead to materials of potential utility.

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

Acknowledged Federal Support: Y

**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Nature Materials

Publication Identifier Type: DOI

Publication Identifier: 10.1038/s41563-018-0097-2

Volume: 17

Issue: 8

First Page #: 725

Date Submitted: 11/13/19 12:00AM

Date Published: 5/1/18 4:00AM

Publication Location:

**Article Title:** Self-assembled highly ordered acid layers in precisely sulfonated polyethylene produce efficient proton transport

**Authors:** Edward B. Trigg, Taylor W. Gaines, Manuel Maréchal, Demi E. Moed, Patrice Rannou, Kenneth B. Wag

**Keywords:** precise polymers, proton conductivity

**Abstract:** Recent advances in polymer synthesis have allowed remarkable control over chain microstructure and conformation. Capitalizing on such developments, here we create well-controlled chain folding in sulfonated polyethylene, leading to highly uniform hydrated acid layers of subnanometre thickness with high proton conductivity. The linear polyethylene contains sulfonic acid groups pendant to precisely every twenty-first carbon atom that induce tight chain folds to form the hydrated layers, while the methylene segments crystallize. The proton conductivity is on par with Nafion 117, the benchmark for fuel cell membranes. We demonstrate that well-controlled hairpin chain folding can be utilized for proton conductivity within a crystalline polymer structure, and we project that this structure could be adapted for ion transport. This layered polyethylene-based structure is an innovative and versatile design paradigm for functional polymer membranes, opening doors to efficient and selective trans

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Acknowledged Federal Support: Y

Nothing to report in the uploaded pdf (see accomplishments and 12 published papers