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| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER 352-392-4666 |

# RPPR Final Report
as of 29-Jun-2021

Agency Code: 21XD

Proposal Number: 63768CH **Agreement Number: W911NF-13-1-0362**
**INVESTIGATOR(S):**


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**Principal:**

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**Phone Number:** 3523924666
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**Report Date:** 14-Nov-2020 Date Received: 26-May-2021
**Final Report** for Period Beginning 15-Aug-2013 and Ending 14-Aug-2020
**Title:** Extending Morphology Control to Sophisticated Precision Polymer Systems (ARO Polymer Chemistry)
**Begin Performance Period:** 15-Aug-2013 **End Performance Period:** 01-Mar-2021
**Report Term:** 0-Other


Submitted By: Kenneth Wagener Email: wagener@chem.ufl.edu
Phone: (352) 392-4666



**STEM Degrees:** **STEM Participants:**

**Major Goals:** 1. Fully understand the chemistry involved in precision aliphatic polysulfone synthesis
2. Apply provisionally patented research to the synthetic work
3. Conduct large scale polymerizations with newly-purchased high vacuum mechanical stirring apparatus
4. Examine material and chemical properties of precision polysulfones in different applications (i.e. fibers and membranes)

**Accomplishments:** Our group continued investigating the synthesis of large-scale high temperature bulk polycondensation of sulfone diene monomers. The catalyst which enables high temperature polycondensation is a derivative of a Hoveyda-Grubbs second generation catalyst, which has been shown to be stable for metathesis reactions up to 200 deg C with limited olefin isomerization events. The result is precision polysulfones which exhibit high melting points (>160 deg C) and sharp crystallization exotherms. Building on work conducted previously, our group further optimized the synthesis of precision polysulfones on a multi-gram scale to prepare high molecular weight polymers (Mw up to 70 kg/mol) on a time scale of hours, not days. Evolution of high molecular weights in short time scales is enabled by the improved mass transfer resulting from mechanical stirring in combination with high vacuum conditions. Initial attempts at spinning fibers from saturated precision polysulfones yielded uniform fibers with modest tensile properties.

**Training Opportunities:** Trained two undergraduate students and one visiting graduate student in bulk ADMET polymerization and polymer characterization. Specifically, training included organic synthesis and purification, characterization techniques including thermal analysis, spectroscopy, and mechanical testing, and interpretation of these results. Samantha McDonald- UF undergraduate (now pursuing a PhD at Duke University), Sarah Wheeler- UF undergraduate, Katharina Kluthe- visiting PhD student from Max Planck Institute for Polymers.

**Results Dissemination:** Nothing to Report

# RPPR Final Report
as of 29-Jun-2021

**Honors and Awards:** Charles G. Overberger International Prize for Excellence in Polymer Research (Ken Wagener)
ACS Award in Polymer Chemistry (Ken Wagener)

**Protocol Activity Status:**

**Technology Transfer:** Patents have been acquired to protect the technology. Possible use for soldier thermal protection is being considered. Interaction with Army/Natick is possible.

**PARTICIPANTS:**

**Participant Type:** PD/PI
**Participant:** Kenneth Wagener
**Person Months Worked:** 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Julia Pribyl
**Person Months Worked:** 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Undergraduate Student
**Participant:** Samantha McDonald
**Person Months Worked:** 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Undergraduate Student
**Participant:** Sarah Wheeler
**Person Months Worked:** 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Katharina Kluthe
**Person Months Worked:** 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**ARTICLES:**

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**Journal:** Macromolecules
Publication Identifier Type: DOI Publication Identifier: 10.1021/ma4013175
Volume: 46 Issue: 22 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Morphological Trends in Precise Acid- and Ion-Containing Polyethylenes at Elevated Temperature
**Authors:**
**Keywords:** Ion-containing polyethylenes
**Abstract:** ABSTRACT: The morphologies at elevated temperatures (T > Tg, Tm) of 12 precise, polyethylene (PE) -based copolymers with acrylic acid (AA), phosphonic acid (PA), and 1- methylimidazolium bromide (ImBr) groups were studied via X-ray scattering. These precise copolymers enable direct comparisons focusing on the length of the spacer between the functional groups and the type of functional group. The polar groups in these materials self-assemble into microphaseseparated aggregates dispersed throughout the nonpolar PE matrix. At high temperatures the PE segments are amorphous, such that the aggregates are distributed in a liquid-like manner in 11 of these precise copolymers. The correlation distances between aggregates increase with the following: carbon spacer length between pendant groups, size and volume fraction of the pendant species, and functional group configuration (single vs geminal substitution). In addition, comparisons are made between precise copolymers and pseudorandom copolym
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**Journal:** Synthetic Communications
Publication Identifier Type: DOI Publication Identifier: 10.1080/00397911.2014.899606
Volume: 44 Issue: 16 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Large-Scale Preparation of Long-Chain ADMET Synthons
**Authors:**
**Keywords:** ADMET; alkenyl synthons; homologation; precision polymers
**Abstract:** Abstract We report a convenient process with minimal purification to produce large quantities of a,x-alkenyl alcohols. These reagents are indispensable precursors in ADMET chemistry. Icos-19-en-1-ol, nonacos-28-en-1-ol, and octatriacont-37-en-1-ol were produced effortlessly in large quantities (up to 45 g in a single batch) from undec-10-en-1-ol. By extension of the method, any desired methylene run length in the ADMET precursor can be achieved.
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**Journal:** Macromolecular Chemistry and Physics
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Volume: 215 Issue: 12 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Extending the Methylene Spacer Length of ADMET Hydroxy-Functionalized Polymers
**Authors:**
**Keywords:** ADMET, Grubbs catalyst
**Abstract:** Solution acyclic diene metathesis (ADMET) polymerization using Grubbs' fi rst-generation catalyst leads to the direct synthesis of polymers containing hydroxyl groups. Secondary alcohols are placed precisely at specifi c intervals on an unsaturated hydrocarbon backbone. Increasing the number of methylene spacers decreases the frequency of the pendant groups from every 15th carbon to every 21st carbon. The complete hydrogenation of the unsaturated polymers yields model representatives of well-defi ned ethylene–vinyl alcohol copolymers. Despite the decrease in branch frequency in both the homopolymers and randomized versions of such polymers, surprisingly, the precision does not have an infl uence on the thermal properties, and they are all similar in nature. It is concluded that hydrogen bonding dominates the polymer behavior, rather than the precision in hydroxyl-group placement along the polyethylene chain.
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**Journal:** Macromolecular Rapid Communications
Publication Identifier Type: DOI Publication Identifier: 10.1002/marc.201300672
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Date Submitted: Date Published:
Publication Location:
**Article Title:** Systematic Studies of Morphological Changes of Precision Polyethylene
**Authors:**
**Keywords:** Metathesis, poymerizations
**Abstract:** ABSTRACT: Metathesis step-growth polymerizations in ionic liquids (ILs) was explored to take advantage of the high boiling points of ILs, thereby permitting the use of low pressures at high temperatures. Optimization reactions found that high polymers form efficiently using small amounts of catalyst and short reaction times. For example, high molecular weight main-chain triptycene polymers with high triptycene incorporation were synthesized. This new methodology is applicable to various metathesis reactions that require removal of volatile byproducts as a driving force, including acyclic diene metathesis (ADMET).
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Volume: 2 Issue: 12 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Metathesis Step-Growth Polymerizations in Ionic Liquid
**Authors:**
**Keywords:** Metathesis, polymerization
**Abstract:** ABSTRACT: Metathesis step-growth polymerizations in ionic liquids (ILs) was explored to take advantage of the high boiling points of ILs, thereby permitting the use of low pressures at high temperatures. Optimization reactions found that high polymers form efficiently using small amounts of catalyst and short reaction times. For example, high molecular weight main-chain triptycene polymers with high triptycene incorporation were synthesized. This new methodology is applicable to various metathesis reactions that require removal of volatile byproducts as a driving force, including acyclic diene metathesis (ADMET).
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**Journal:** Organometallics
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Volume: 32 Issue: 9 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Effects of Boron-Containing Lewis Acids on Olefin Metathesis
**Authors:**
**Keywords:** boron-containing Lewis acids, metathesis
**Abstract:** ABSTRACT: Boron-containing Lewis acids have shown a profound effect on the cross-metathesis reaction of 1-hexene. Grubbs first-generation catalyst shows over 100% improvement in conversion in some cases, while the yields increase by up to 50% with Grubbs second-generation catalyst. With the inclusion of boron-containing Lewis acids, compounds prepared using Grubbs second-generation-type catalysts display significantly reduced levels of isomerization.
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**Journal:** Macromolecules
Publication Identifier Type: DOI Publication Identifier: 10.1021/ma400608q
Volume: 46 Issue: 11 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Influence of Branch Incorporation into the Lamella Crystal on the Crystallization Behavior of Polyethylene with Precisely Spaced Branches
**Authors:**
**Keywords:** branch incorpoaration, lamella crystal, polyethylene
**Abstract:** ABSTRACT: Depending on the degree of short chain branch (SCB) incorporation, the crystallization behavior and resultant crystalline structure drastically change in polyethylene with precisely spaced branches. In polyethylene with hexyl branches precisely spaced on every 21st carbon (HB21), only crystallization mediated by a transient hexagonal phase without incorporation of the SCB was observed. On the other hand, in polyethylene with ethyl branches precisely spaced on every 21st carbon (EB21), crystallization behavior was strongly dependent on the crystallization temperature. A thin lamella was formed through crystallization mediated by a hexagonal phase and no thickening occurred at 5?8 °C, while thickening of the transient hexagonal lamellae occurred at 10?15 °C, and one SCB seemed to be incorporated into a crystal stem. At 17 °C, no thickening of the hexagonal phase occurred and a hexagonal phase with sufficient lamella thickness was directly formed from the melt. At 21?28 °C, crys
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**Journal:** Macromolecules
Publication Identifier Type: DOI Publication Identifier: 10.1021/ma400067b
Volume: 46 Issue: 12 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** ADMET: The Future Revealed
**Authors:**
**Keywords:** admet, olefin metathesis
**Abstract:** ABSTRACT: Olefin metathesis has been embraced by polymer chemists as a method for creating well-defined polymers. In particular, ADMET and ROMP have emerged as the primary modes of metathesis polymerization. ADMET reactions are now common, found in textbooks, and easy to perform if the proper techniques are chosen. Much remains to be done, however, with work now focusing on silicon chemistry, direct control of tacticity in precision polymers, biological applications, modeling crystal lattices in common polyolefins, exploring solid-state metathesis reactions, and creating water-soluble ADMET polymers.
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**Journal:** Polymer Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1039/c3py00531c
Volume: 4 Issue: 13 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Insertion metathesis depolymerization
**Authors:**
**Keywords:** Insertion metathesis depolymerization
**Abstract:** We have successfully depolymerized polybutadiene via an insertion metathesis mechanism. This new concept involves the irreversible depolymerization of unsaturated polymers with electron deficient olefins. The product of the degradation was characterized by NMR and GC-MS.We also explored the use of copper iodide as an additive. We observed significant reduction of molecular weight under a variety of conditions with the most extensive depolymerization occurring with the use of Grubbs 2nd generation catalyst with CuI. Finally, polybutadiene was converted to a polyamide by performing insertion metathesis depolymerization with acryloyl chloride and subsequently reacting with 1,6-diaminohexane, demonstrating the potential of polymer-to-polymer conversions with this chemistry.
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**Journal:** Polymer Chemistry
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Volume: 4 Issue: 5 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Synthesis of proton conducting phosphonic acid-functionalized polyolefins by the combination of ATRP and ADMET
**Authors:**
**Keywords:** ADMET, ATRP
**Abstract:** Well-defined copolymers of various compositions possessing polar polyphosphonate brushes precisely placed on an unsaturated polyethylene backbone were obtained by a combination of ADMET and ATRP. Both a macromonomer and macroinitiator approach were explored along with conversion to requisite poly(vinylbenzyl phosphonic acid) (PVBPA)/polyolefin graft copolymers. All polymers were quantitatively deprotected to the corresponding free phosphonic acid-containing PVBPA/polyolefin graft copolymer electrolytes. The thermal behavior and the phase transitions of these materials showed amorphous behavior that was exploited in subsequent proton conductivity experiments. Proton conductivity properties of the PVBPA/polyolefin graft copolymers in anhydrous as well as in humidified conditions reached magnitudes of 10 ┌2 S cm ┌1 with particular architectures.
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Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.macromol.5b01410
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** ADMET Polymers Containing Precisely Spaced Pendant Boronic Acids and Esters
**Authors:**
**Keywords:** No keywords
**Abstract:** Precise aryl boronic ester- and acid-containing polymers have been synthesized via acyclic diene metathesis. High-molecular weight phenyl boronic acid polymers were synthesized. Cross-linked phenyl boronic acid polymers were also synthesized and demonstrate a unique crystallization behavior not usually seen in cross-linked polymers.
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Volume: 6.0E+000 Issue: 3.3E+001 First Page #: 0
Date Submitted: Date Published:
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**Article Title:** Unveiling the hyperbolic thermal behaviour of poly(p-phenylene alkylene)s
**Authors:**
**Keywords:** None
**Abstract:** A series of poly(p-phenylene alkylene)s with methylene run lengths ranging from 8 to 40 were obtained by ADMET polymerization of symmetrical ?,?-diene monomers and subsequent exhaustive hydrogenation. ADMET polymerizations were conducted using dibenzyl carbonate as solvent for the first time, providing materials with high molecular weights as compared with those obtained in standard solvent-free conditions. The thermal properties of both the unsaturated and saturated series were investigated. Poly- (p-phenylene alkylene)s exhibit an unprecedented thermal behaviour when considering the fusion temperature as a function of the number of methylene spacers. Solid state 1H MAS and 1H–13C correlation experiments demonstrated that the melting behavior is marked by the gradual disruption of the ring ?–? interactions with increasing methylene chain length. The higher crystallization tendency of longer alkyl chains was detected by the characteristic broadening of the corresponding solid-state 1H
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Volume: 4.0E+000 Issue: 6.0E+000 First Page #: 0
Date Submitted: Date Published:
Publication Location:
**Article Title:** Precise Sulfite Functionalization of Polyolefins via ADMET Polymerization
**Authors:**
**Keywords:** None
**Abstract:** Copolymers containing sulfite functionalities precisely placed between run lengths of 8, 14, and 20 methylene units were synthesized via ADMET with weight-average molecular weights up to 40?500 g/mol (PDI = 1.89). No such polymer structures have been observed previously. The primary polymer structures and precise nature were characterized by 1H NMR, 13C NMR, and IR spectroscopy. Thermal degradation temperatures up to 310 °C were observed through TGA, and melting points typical of similar unsaturated ADMET polymers were determined by DSC. X-ray scattering was used to compare the polymers to ADMET polyethylene (PE), and when the polymers have 20 carbons between sulfites, the functional groups self-assemble into layers. Higher carbon content incorporation leads to an increase in crystallinity and thermal stability for these polysulfites.
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Date Submitted: Date Published:
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**Article Title:** Microwave-assisted ADMET polymerization
**Authors:**
**Keywords:** Microwave-assisted synthesis; ADMET polymerization; Polyolefins
**Abstract:** A variety of complex materials have been created via ADMET polymerization, including various types of branched polyethylenes,1, 2, 3 and 4 and polyolefins functionalized with hydroxyls,5 carboxylics,6 phosphonics, 7 and halogens,8 to name a few. Many of these materials are synthesized in a precise manner in which functional groups are placed in exact locations along polymer backbones. Precision results from the selective ADMET reaction of symmetrical ?,?-diene monomers (Fig. 1) using tolerant and robust catalysts. Effective control of polymerization conditions eliminates unintentional side reactions and defects, yielding precision materials. We now report the expansion of ADMET's versatility, using microwave irradiation, a technique synonymous with control.9

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**Journal:** Macromolecular Rapid Communications
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Date Submitted: Date Published:
Publication Location:
**Article Title:** Spectroscopic Examinations of Hydrogen Bonding in Hydroxy-Functionalized ADMET Chemistry
**Authors:**
**Keywords:** ADMET chemistry;fourier transform infrared (FT-IR);hydrogen bonding;wide-angle X-ray scattering (WAXS);polyethylenes (PE)
**Abstract:** Wide-angle X-ray scattering (WAXS) and temperature-dependent Fourier transform infrared spectroscopy (FTIR) spectroscopy are used to study hydrogen bonding interactions of a hydroxyl-functionalized polyethylene (PE) prepared by acyclic diene metathesis (ADMET) chemistry. The hydroxyl polymer exhibits an orthorhombic unit cell structure with characteristic reflection planes at (110) and (200), comparable to pure crystalline PE. These data unequivocally demonstrate that the OH branch is excluded from the PE lamellae. Furthermore, the polymer melts 100 °C higher than all previous analogous polymers possessing precision placed long aliphatic branches that also are excluded from PE lamellae. Temperature-dependent FTIR spectroscopy from ambient to 150 °C, followed by cooling to 125 °C supports exclusion of the hydroxyl group from the crystalline lattice. It is concluded that these hydroxyl groups form stable physical networks in the amorphous region via hydrogen bonding and are important for

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Date Submitted: Date Published:
Publication Location:
**Article Title:** Direct Comparisons of X-ray Scattering and Atomistic Molecular Dynamics Simulations for Precise Acid Copolymers and Ionomers
**Authors:**
**Keywords:** None
**Abstract:** Designing acid- and ion-containing polymers for optimal proton, ion, or water transport would benefit profoundly from predictive models or theories that relate polymer structures with ionomer morphologies. Recently, atomistic molecular dynamics (MD) simulations were performed to study the morphologies of precise poly (ethylene-co-acrylic acid) copolymer and ionomer melts. Here, we present the first direct comparisons between scattering profiles, I(q), calculated from these atomistic MD simulations and experimental X-ray data for 11 materials. This set of precise polymers has spacers of exactly 9, 15, or 21 carbons between acid groups and has been partially neutralized with Li, Na, Cs, or Zn. In these polymers, the simulations at 120 °C reveal ionic aggregates with a range of morphologies, from compact, isolated aggregates (type 1) to branched, stringy aggregates (type 2) to branched, stringy aggregates that percolate through the simulation box (type 3). Excellent agreement is found betw
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Volume: 217 Issue: First Page #: 2351
Date Submitted: 12/15/16 12:00AM Date Published: 9/2/16 5:39AM
Publication Location: Weinheim, Germany
**Article Title:** High Melting Precision Sulfone Polyethylenes Synthesized by ADMET Chemistry
**Authors:** Taylor W. Gaines, Edward B. Trigg, Karen I. Winey, Kenneth B. Wagener
**Keywords:** ADMET, Polyolefins, Polysulfone, Crystalline polymers
**Abstract:** A series of aliphatic polysulfones is synthesized via ADMET polymerization in which a sulfone group is located precisely after every 8th, 14th, and 20th carbon. Primary structural characterization is accomplished using 1H NMR, 13C NMR, and IR. Polymer morphology is studied by DSC and X-ray scattering, which reveals layered morphologies comprised of polyethylene crystallites along with sulfone groups arranged in sheets. In contrast to other precision polymers with functional groups synthesized by ADMET, this morphology is found at all spacer lengths. Prior to hydrogenation the sulfone polymers show Tm decreasing with increasing sulfone concentration,a typical phenomenon attributed to the mix of cis and trans configurations producing defects in the crystals. However, following hydrogenation, the melting temperature increases as the sulfone group concentration increased rather than decreased, with the highest Tm being 175 °C. This is an increase of 45 °C relative to linear polyethylenes.
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Volume: 217 Issue: First Page #: 2351
Date Submitted: 12/15/16 12:00AM Date Published: 12/15/16 7:49PM
Publication Location: Weinheim, Germany
**Article Title:** High Melting Precision Sulfone Polyethylenes Synthesized by ADMET Chemistry
**Authors:** Taylor Gaines, Edward Trigg, Karen Winey, Kenneth Wagener
**Keywords:** Sulfone Polyethylenes ADMET
**Abstract:** A series of aliphatic polysulfones is synthesized via ADMET polymerization in which a sulfone group is located precisely after every 8th, 14th, and 20th carbon.
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Acknowledged Federal Support: **Y**

**Partners**

,

I certify that the information in the report is complete and accurate:
Signature: Kenneth Wagener
Signature Date: 5/26/21 9:12AM

# Project Summary: Bulk High Temperature Metathesis Polycondensation

**Prof. Ken Wagener, The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, FL**

## Introduction

This work described here represents a departure from all previous acyclic diene metathesis (ADMET) chemistry. The typical ADMET reaction is done in solution at either ambient temperature or with mild heating (<40 °C). The story of this chemistry began from interest in the properties of commercially-produced aryl polysulfones. Aryl polysulfones exhibit excellent chemical, thermal, and mechanical properties. Fully aliphatic precision polysulfones (the first of their kind) were first synthesized via solution-based ADMET polymerization.[1] The ADMET-prepared polysulfones exhibited high melting temperatures resulting from the combination of crystalline polyethylene segments and secondary interactions between precisely spaced sulfone groups (Figure 1A). Notably, the sulfone groups are integrated into the polymer backbone, eliminating stereogenicity which may perturb crystallization. As the sulfone concentration was increased in the fully saturated polymers, the melting point increased compared to the unsaturated analog; a trend observed only in aliphatic polysulfones or polyamides so far.[2] While interesting, poor solubility of the unsaturated polysulfones in organic solvents limited the molecular weights that could be achieved.

Recent work focused on preparing aliphatic polysulfones (Figure 1A) via ADMET polymerization in the bulk (no solvent) and above the melting point of the resulting unsaturated polymer. Use of a new cyclic alkyl amino carbene (CAAC) ligand containing Grubbs catalyst[3] (Figure 1B) was the key to performing the ADMET polymerization above 100 °C. Precision polysulfones with $M_w$>80 kg/mol were prepared according to Scheme 1. Benzoquinone was used as a 1,2-olefin isomerization inhibitor (this type of isomerization would result in the loss of precision). Maintenance of high melting points in the saturated polymers (175 °C for $SO_2$8) indicated that the precision placement of sulfone groups was conserved at these high polymerization temperatures.[4]

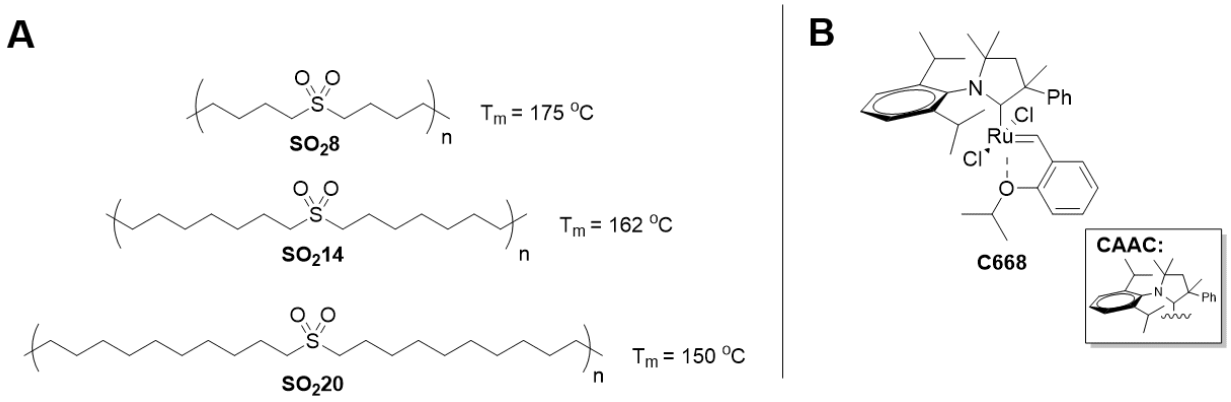



**Figure 1.** (A) Precise aliphatic sulfones that have been prepared by ADMET polymerization. A sulfone group was placed after every 8th, 14th, or 20th carbon, so structures are labeled $SO_2$ to represent the sulfone and the number corresponds to the number of methylene spacers between groups. (B) High-temperature stable Grubbs catalyst (Materia C668) used to perform high temperature ADMET polymerization, with CAAC ligand (inset).

## Results and Discussion

The latest work focused on performing bulk high temperature ADMET polymerization on a large (multi-gram) scale using a mechanically stirred vacuum reactor shown in Figure 2A. Aliphatic polysulfones have been prepared on a multi-gram scale (Figure 2B) with $M_w$ up to ~70 kDa using this reactor and the chemistry described in Scheme 1. The resulting unsaturated polymers were solution cast into films which were highly flexible (Figure 2C).

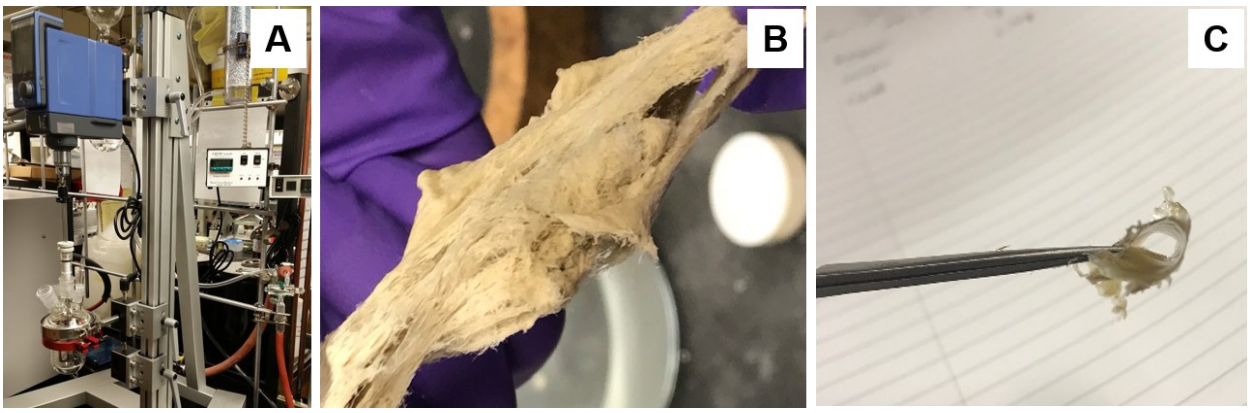
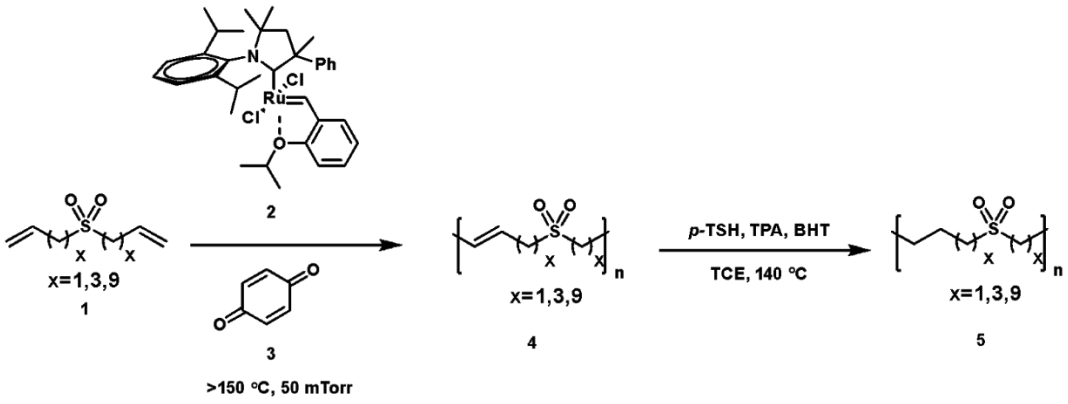



**Figure 2.** (A) Mechanically stirred vacuum reactor (B) Polysulfone ($SO_2$8) prepared via bulk ADMET polymerization (as-synthesized, $M_n$= 14.7 kg/mol $M_w$= 69.2 kg/mol Đ= 4.6) (C) Flexible film of unsaturated polysulfone prepared via bulk ADMET polymerization

The key to successful high temperature bulk polymerization of symmetric α,ω-diene sulfones (**1**) was the use of a specific catalyst, the cyclic alkyl amino carbene (CAAC) ligated Ru-complex (**2**). Polymerizations can be done in excess of 150 °C.[4] As in the small-scale studies, the addition of a small amount of benzoquinone (**3**), prevented olefin migration (which would lead to loss of precision). Hydrogen saturation yielded the saturated aliphatic polysulfone (**5**) which melting as high as 175 °C. High molecular weight polymers ($M_w$=69 kDa, $M_n$=15 kDa) were obtained in as little as 3 hours rather than the typical ADMET reaction time which is on the order of days.




**Scheme 1**. General synthetic strategy to prepare aliphatic polysulfones (*p*-TSH = *para*-toluenesulfonyl hydrazide, TPA = tripropylamine, BHT = butylated hydroxytoluene, TCE = 1,1,2,2-tetrachloroethane)

No loss of precision was observed in the scaled-up of the synthesis of precision polysulfones to multi-gram quantities. After saturation of the internal olefin bonds, the aliphatic polysulfones exhibited a sharp melting endotherm beginning at 175 °C, and a sharp crystallization exotherm at 160 °C (indicating precision spacing of the sulfone groups along the polymer backbone), each measured by DSC (Figure 3A). The saturated polysulfone exhibited a fairly high main-degradation temperature mode at ~400 ºC (Figure 3B).

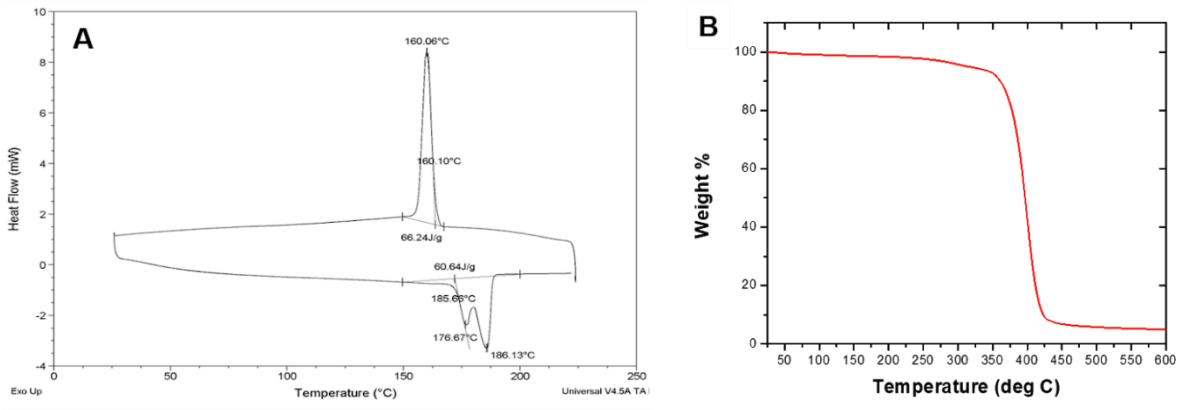



**Figure 3.** (A) Differential scanning calorimeter (DSC) curve of saturated polysulfone. Trace shown is the second heat/cool cycle at a heating rate of 10 ºC/ min. (B) Thermogravimetric analysis (TGA) of saturated polysulfone

Powder x-ray diffraction analysis further corroborated that the large-scale bulk synthesis of aliphatic polysulfones did not cause a loss of precision spacing between sulfone groups (Figure 4). Lower angle reflections near 2θ ≈ 9º indicate the lamellar spacing of the polysulfones (~1 nm). A small shift in the peak at 2θ ≈22º indicates tilting of the lamella to accommodate the large sulfone groups (resulting in a distorted orthorhombic type unit cell). For comparison, orthorhombic polyethylene would display peaks at 2θ = 21.7º and 24º. These results were consistent with small-angle x-ray scattering data which suggests the inclusion of the sulfone groups in the unit cell, thereby creating an extended-chain morphology where the sulfone groups are neatly stacked in the crystalline regions of the polymer.[1]

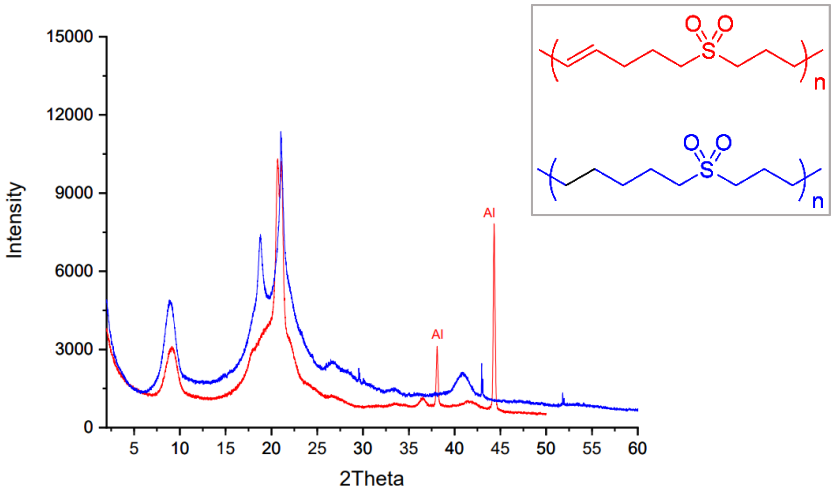



**Figure 4.** Powder x-ray diffractograms of unsaturated $SO_2$8 (in red) and saturated $SO_2$8 (in blue).

The combination of the sharp crystallization exotherm close to the melting point and the conservation of precision sulfone-group spacing in the large-scale reactions indicated that these materials may be suitable for forming fibers. First, some basic studies of the stress/strain properties of saturated $SO_2$8 were conducted (Figure 5A). At the force limit of the instrument (18 N), the sample did not exhibit much elongation and did not break. A temperature sweep at a frequency of 1 Hz was conducted on the same instrument, and a glass transition was observed at approximately 40 °C, as well as two other subtle β-transitions on either side of the glass transition as observed in the tan delta curve in Figure 5B.

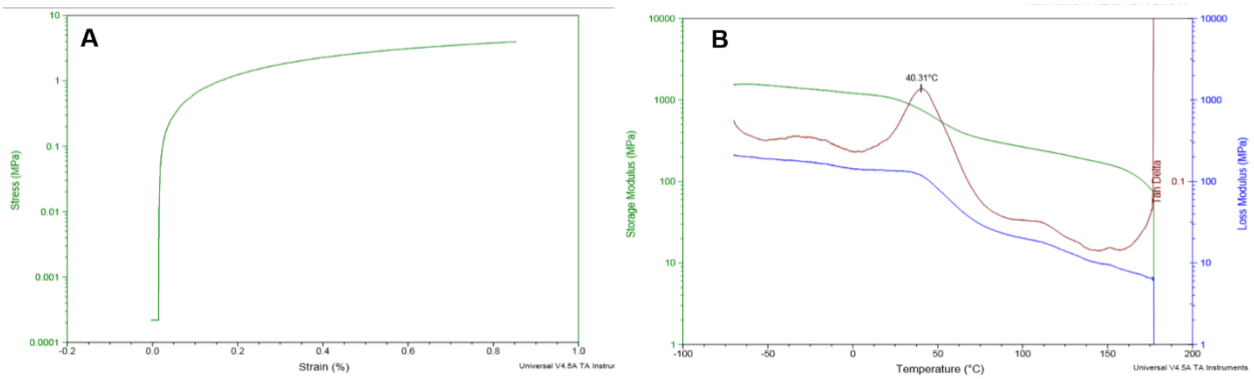



**Figure 5.** (A) Stress/Strain curve of saturated polysulfone (B) Dynamic mechanical analysis (DMA) temperature sweep at 1 Hz

Preliminary wet spinning into fibers (as done for Kevlar™) showed it is possible to spin precision polysulfone fibers *with no change in the commercial spinning process whatsoever*. The most notable result of this fiber-spinning work was the ability to prepare uniform diameter fibers were achieved, though they exhibited modest tensile strength (Figure 6).

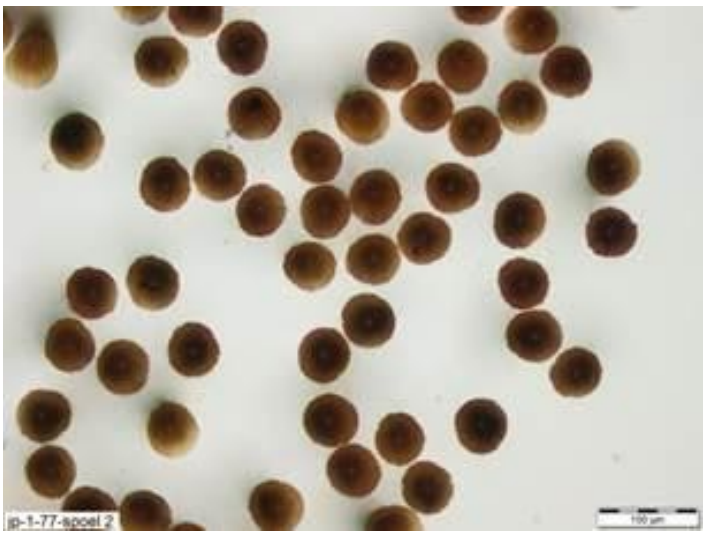



**Figure 6.** Uniform cross section, wet spun precision polysulfone fibers. (Scale bar is 100 μm)

## Conclusion

Based on the results presented here, we have demonstrated the ability to prepare precision aliphatic polysulfones via bulk high temperature ADMET polymerization. In general, the bulk polycondensation process is remarkably similar to commercial processes used for decades to prepare polyesters. From an industrial point of view, we have demonstrated that the ADMET process can be successfully scaled-up to create materials with conserved precision spacing. Further processing of aliphatic polysulfones prepared on a multi-gram scale were successfully spun into fibers without any deviation from the commercial wet spinning process. These results present a significant opportunity for ADMET polycondensation to become a promising tool to prepare high-value precision polymers on an industrial scale.

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