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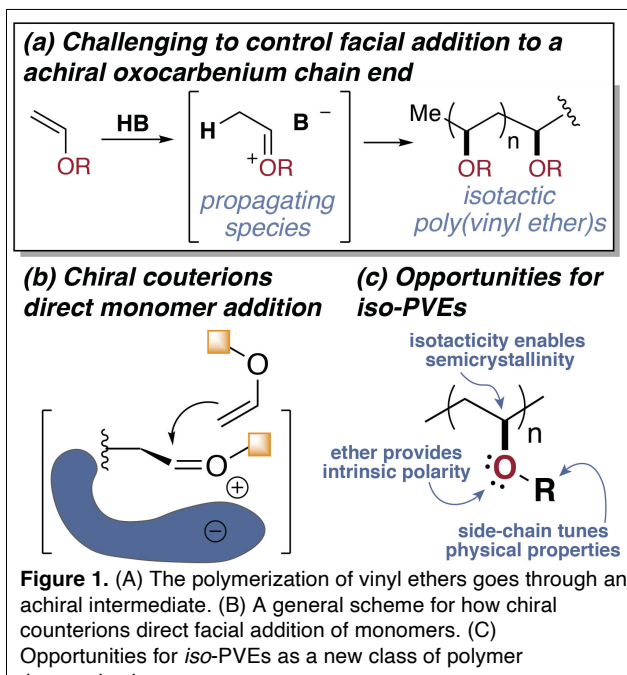
## A modern approach to polar thermoplastics

Polyolefins are high-volume, low-cost thermoplastics with high tensile strength, low density, and excellent processability. Despite their omnipresence, these hydrocarbons are limited by their inability to interface with polar additives, fillers, or other materials. These innate attributes make polyolefins inadequate for many high-performance engineering applications. Chemists have long sought to add polar functionality to polyolefins through either copolymerization or post-polymerization modification, but decades of intense effort have yielded materials ill-suited for demanding applications in composites, coatings, membranes, or adhesives.<sup>1-3</sup> Furthermore, polyolefins are derived from petrochemical resources and hinder progress toward a sustainable plastics economy.<sup>4</sup> A fundamentally new approach is needed.

The stereochemistry of vinyl polymers, known as polymer tacticity, is intimately linked to their resultant material properties. Isotactic poly(vinyl ethers) (*iso*-PVEs), where each ether side-chain is on the same face of a polymer backbone, have exciting potential as a versatile and intrinsically polar class of semicrystalline thermoplastics derived from a readily available but rarely considered monomer class. PVEs are inherently polar due to an ether in each repeat unit and, like polyolefins, have low glass transition temperatures and high thermal stabilities. These materials, however, are typically amorphous at room temperature and thus relegated to niche applications as lubricants and adhesives.<sup>5</sup> Moderately *iso*-PVEs have been reported to have thermal and mechanical properties commensurate with commodity polyolefins, but the lack of viable synthetic methods to control stereochemistry in cationic polymerizations has limited their evaluation as polar polyolefin analogues.<sup>6-7</sup> As a consequence, there remains an enormous chasm between current methods and the selectivity and substrate scope needed to evaluate *iso*-PVEs as a versatile class of semicrystalline thermoplastics.

We propose to develop a general approach for the stereocontrolled polymerization of vinyl ethers to realize a diverse library of *iso*-PVEs as a new class of polar thermoplastics. Previously, difficulty controlling the stereochemical environment of the propagating chain-end during cationic polymerization has hindered progress in achieving highly *iso*-PVEs (Figure 1A). Unlike the Edisonian approaches pursued previously,<sup>7-9</sup> our strategy uses the concept of asymmetric ion-pairing catalysis to *systematically tune the reactivity and chain-end interactions of chiral counterions* to design highly stereoselective catalysts (Figure 1B). The objectives of the proposed studies will: *i*) lead to a molecular-level understanding of viable approaches to stereocontrolled vinyl ether polymerization by elucidating critical factors that control the stereochemistry and dictate the structure of *iso*-PVEs; *ii*) pioneer a platform approach to polar thermoplastics with previously unimagined versatility, where the thermal behavior is dictated by polymer tacticity and the mechanical and interfacial properties are a result of the chosen side-chain (Figure 1C); and *iii*) demonstrate the potential of *iso*-PVEs through a comprehensive evaluation of the thermal, mechanical, and interfacial properties of this diverse new class of polar, semicrystalline thermoplastics.

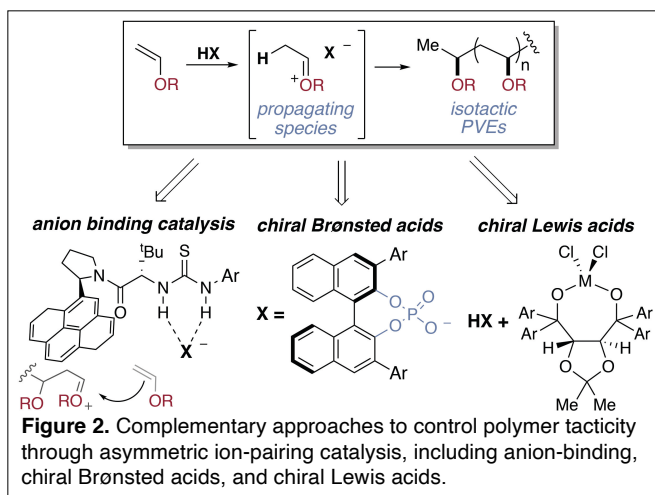
We will accomplish these objectives by pursuit of the following goals:



### Discover a chiral-counterion approach for stereocontrolled vinyl ether polymerization.

Despite the promise of *iso*-PVEs, there have been few contemporary efforts toward stereocontrolled vinyl ether polymerization. The lack of literature precedent can be attributed to the challenge of controlling facial addition of an incoming monomer to an oxocarbenium reactive intermediate, which serves as the propagating chain end during cationic polymerization.

We will pioneer new synthetic methods for the stereocontrolled polymerization of vinyl ethers by designing custom counterions that direct the addition of each monomer unit to the growing polymer. The versatility of our strategy is demonstrated by the three complementary approaches to this challenge that we propose to pursue (Figure 2). The three methods are conceptually similar; *i.e.* the use of a chiral counterion directs the



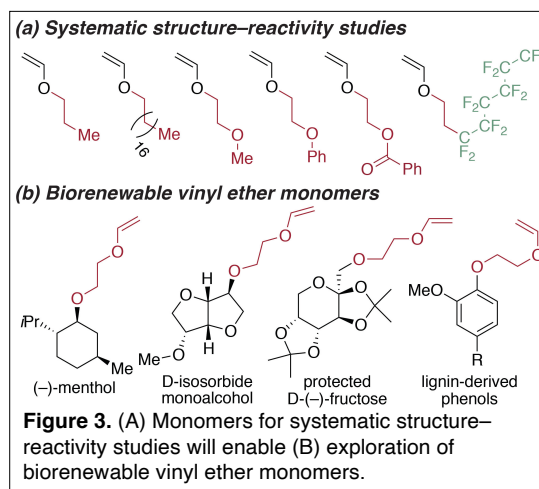
facial addition of the incoming monomer to set the stereochemistry of the last enchainment. Each approach, however, has distinct advantages for different pursuits. Anion binding catalysis, for example, will interface well with known methods to control the molecular weight and molecular weight distribution of PVEs. Chiral Brønsted acid catalysis will enable the systematic modulation of stereoelectronic properties of the counterion for a variety of monomers. Alternatively, chiral Lewis acid catalysis holds greater potential to control the tacticity of commercial vinyl ethers with aliphatic side chains. For each of these strategies, a comprehensive understanding of the underlying thermodynamics and kinetics will facilitate a molecular-level understanding of reaction mechanism and a rational tuning of catalyst structure to realize new approaches to stereocontrolled cationic polymerization and new materials with an expanded set of properties.

**Pioneer a versatile new class of semicrystalline *iso*-PVEs.** A universal drawback to traditional routes toward polar polyolefins is that the addition of polar groups adversely affects the thermal and mechanical properties of the parent material by disrupting crystallinity. Conversely, the intrinsic polarity of *iso*-PVEs allow for their interfacial and physical properties to be decoupled.

The oxygen heteroatom in each repeat unit provides the functionality to interface with polar additives, fillers, and/or surfaces, while the extent of tacticity and side chain identity determine melting temperature, solid-state structure, and mechanical properties.

Detailed structure–reactivity studies on vinyl ethers with diverse side chains will reveal the influence of monomer sterics, functionality and stereochemistry on polymerization behavior. These experimental studies will inform the expansion of this method to include unique vinyl ether monomers with a range of valuable properties. For example, the ease of generating vinyl ethers from alcohols will enable a platform approach to realize semicrystalline thermoplastics derived from biorenewable resources

(Figure 3). Our strategy will provide the ability to tune thermal properties through tacticity control and functionality through the choice of the bioderived subunit, with the goal of realizing



biorenewable soft materials that can compete with petroleum-derived plastics in both cost and performance.

**Develop comprehensive structure–property relationships for *iso*-PVEs.** The ultimate utility of *iso*-PVEs will directly correlate with their thermal and mechanical properties. Our group's interdisciplinary expertise enables us to both develop state-of-the-art synthetic methods and study the resulting physical properties of the novel materials. Thermal properties will be probed by gravimetric analysis and differential scanning calorimetry, while solid state structure will be evaluated by x-ray scattering techniques. Temperature dependent mechanical properties will be probed by rheology and dynamic mechanical analysis, while tensile experiments will provide an understanding of how the materials responds to uniaxial strain.

A detailed understanding of the structure–property relationships for *iso*-PVEs will enable their translation to applications where their intrinsic polarity is beneficial compared to polyolefins. Lap shear experiments with glass, metal, and other polar substrates will inform the utility of these materials for adhesives and composites. Specifically, we aim to study the use of *iso*-PVEs for the development of high-strength composites with cellulose nanocrystals through coextrusion methods. Such an approach would provide a scalable and sustainable alternative to polyolefin–glass or polyolefin–carbon fiber composites with enhanced properties due to the improved interfacial adhesion between the cellulose and the intrinsically polar *iso*-PVEs.

In conclusion, support from the Arnold and Mabel Beckman Foundation will help support my goal of training a diverse group of undergraduates, graduate students, and postdoctoral scholars in the pursuit of the high-risk, high-reward research program outlined herein. Pioneering a general approach to stereocontrolled cationic polymerizations will make significant contributions to the scientific community and the broader population, both in contributing to fundamental knowledge and introducing novel material solutions for contemporary societal challenges.

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