UNC
COLLEGE OF ARTS AND SCIENCES
Chemistry

Stereoselective Cationic Polymerization of Cycloaliphatic Vinyl Ethers

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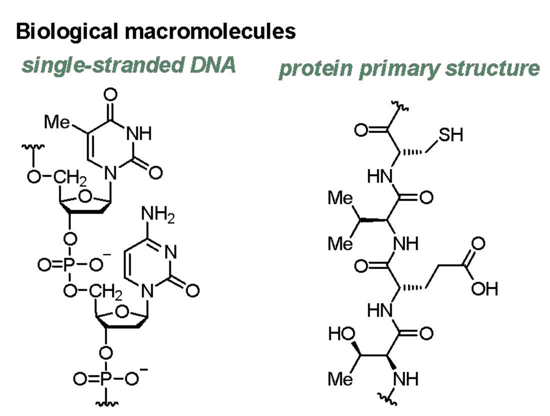
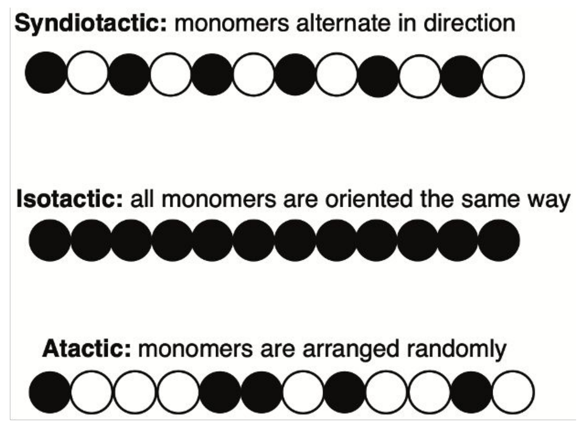
Background





Isotactic polymers are used in...

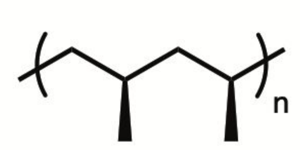
Tacticity describes the orientation of a polymer's individual units, or *monomers*, relative to each other. Tacticity affects the **material properties of a polymer**. For example, biological macromolecules have specific functions related to their tacticity. Similarly, Isotactic or stereoregular polymers have properties that make them ideal for use in many fields.

Experimental Goals:

- Investigate the effects of changing pendant groups on polyvinyl ether (PVE) properties including:
  - glass transition temperature (Tg)
  - dispersity (Đ)
  - decomposition temperature
  - 1H and 13C NMR spectra
  - number average molecular weight (Mn)

Global Plastic Consumption

*isotactic polypropylene (**iPP**)*



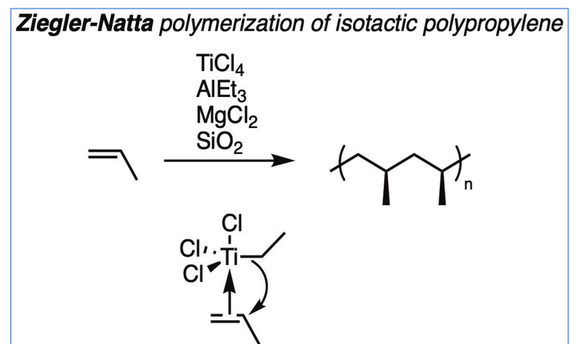
Polypropylene (PP) is the largest volume commodity thermoplastic in the world, accounting for about **20 percent of global plastics** materials consumption.

Why?

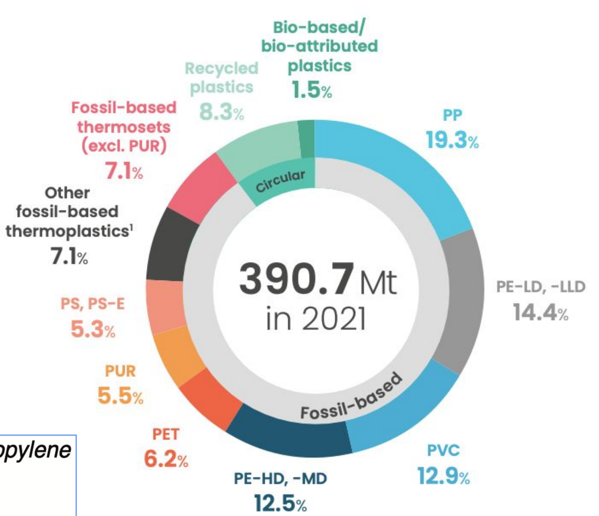
- *Cheap starting material (propene)*
- *Efficient polymerization (Ziegler-Natta)*
- *Versatile material properties*

= High demand and large-scale production capabilities

***Ziegler-Natta** polymerization of isotactic polypropylene*



involves alkene binding and insertion into metal-carbon bonds



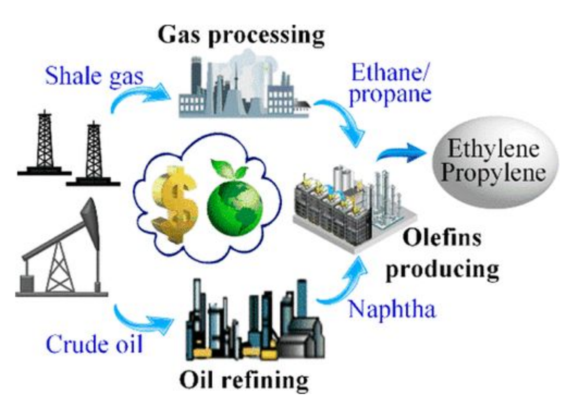
Distribution of global plastics production by type, 2021

- ***90.2%** petroleum-based*
  - ***19.3%** polypropylene*

Plastics - The Facts 2021, PlasticsEurope. **2021**, 1-81
Uekert et. al. ACS Sustainable Chem. Eng. **2023**, 11, 965–978

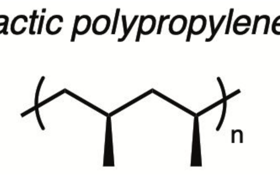
Property Differences: iPP vs. PVE

As iPP is **considerably more difficult** to recycle than PVE, producing an isotactic PVE with material properties comparable to iPP could **increase plastic recycling.**



Polypropylene is one of the most ***widely used*** and ***least recycled*** commodity plastics in the world.

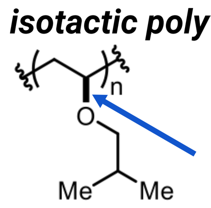
*isotactic polypropylene (**iPP**)*



Disadvantages:

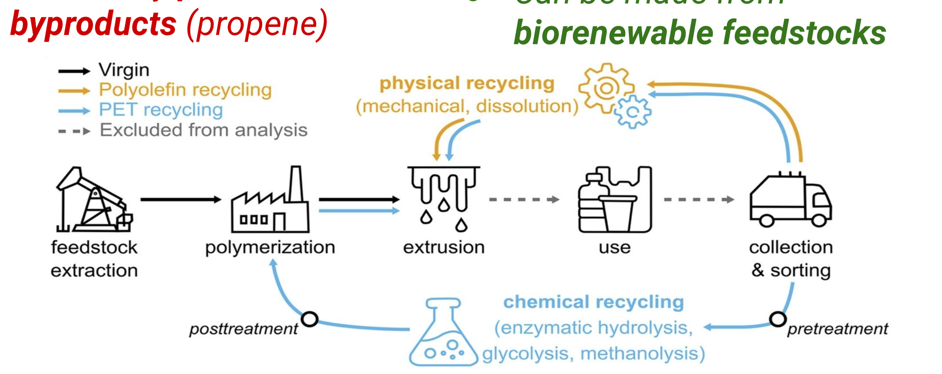
- *Hard to recycle*
- *Inferior adhesion*
- *Non-renewable feedstock, exclusively **petroleum byproducts** (propene)*

*isotactic polyvinyl ether (**iPVE**)*



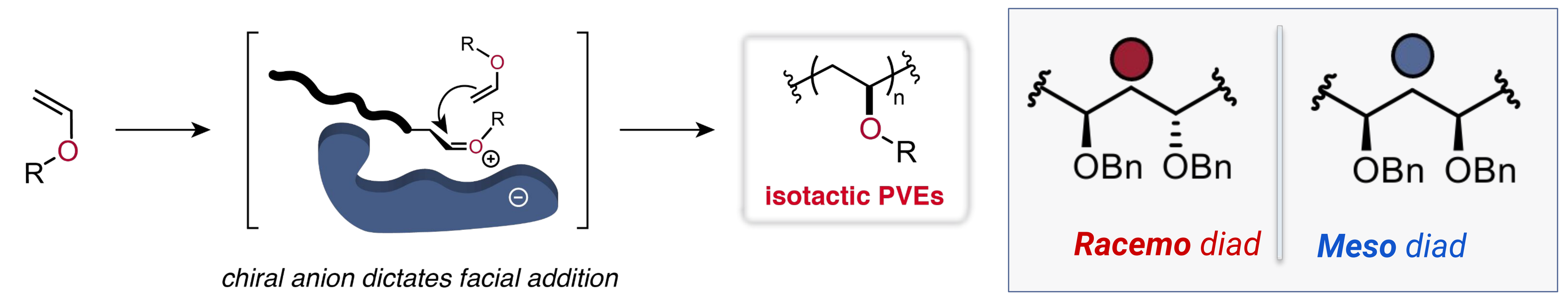
Advantages:

- *Easier to recycle*
- *Better adhesive properties due to H-bonding*
- *Can be made from **biorenewable feedstocks***



Yang et. al. Ind. Eng. Chem. Res. **2017**, 56, 4038-4051
Isogai et. al. Nanoscale. **2010**, 3, 71-85
Polypropylene Plastic. Polychem USA. **2018**

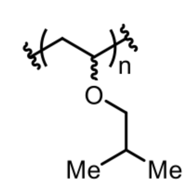
Review of Stereoselective Cationic Polymerization

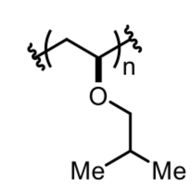


Stereoselective cationic polymerization achieves isotacticity in polyvinyl ethers by using a large negatively-charged counterion to force all monomers into the same orientation.

Atactic poly(vinyl ether), 68%m

- *Amorphous*
- *Flexible*
- *Lower melting point*





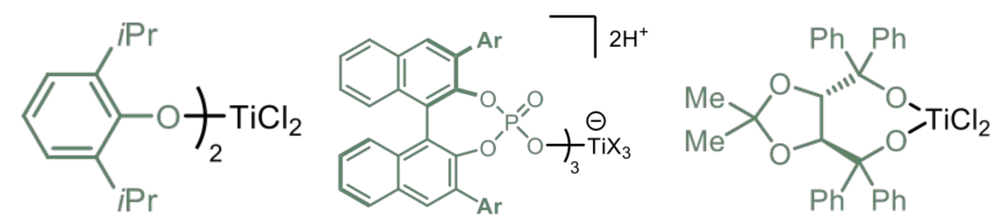
Isotactic poly(vinyl ether), 91%m

- *Crystalline*
- *Rigid*
- *Higher melting point*

***Ziegler-Natta** polymerization cannot be applied to PVEs*

Then what catalysts can we use to synthesize isotactic PVEs?

Catalysts *previously* used to achieve isotacticity (≥90% *meso* diads) **in PVEs:**



All ligated Titanium Lewis acids

Disadvantages:

- Harsh/unsafe reagents
- Residual metals
- Incompatible with many functional groups

How can we eliminate these issues with a novel catalyst?

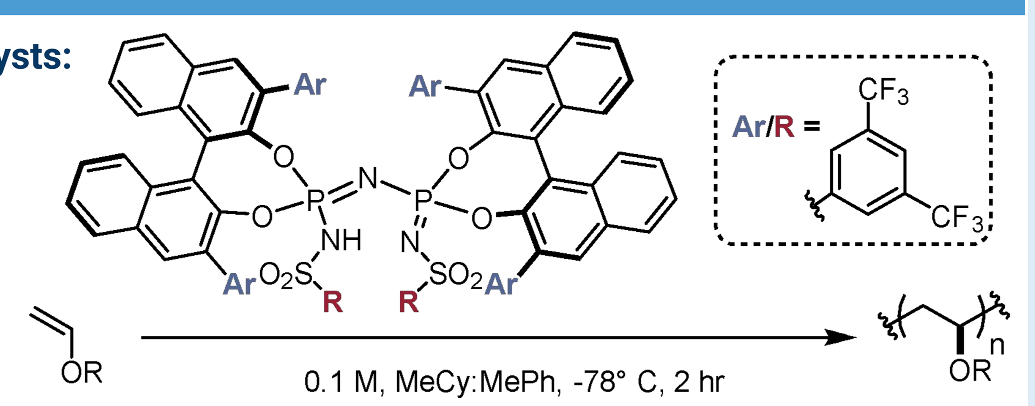
Ouchi et al. Macromolecules. **1999**, 32, 6407-6411.
Teator et al. Science. **2019**, 363, 1439-1443.
Watanabe et al. Polym. Chem.. **2020**, 11, 3398-3403

Brønsted Acid Catalyzed Stereoselective Polymerization

Imidodiphosphorimidate (*IDPi*) catalysts:

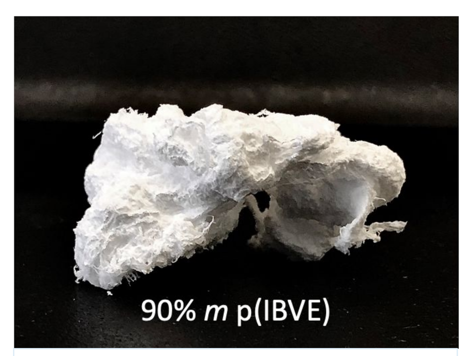
Advantages:

- Milder reaction conditions
- Metal-free
- Broad substrate scope
- Tunable catalyst structure allows for a range of tacticities

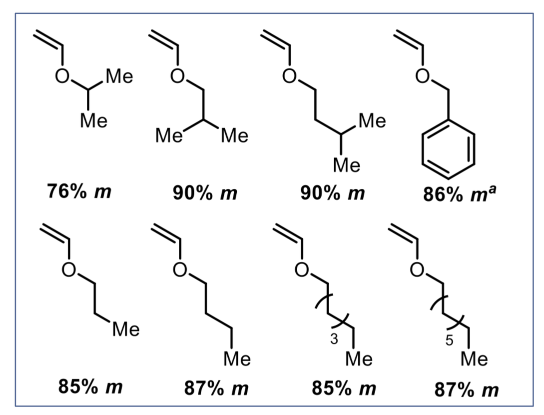


IDPi has achieved ***remarkably high %m*** with a **wide range of substrates.**

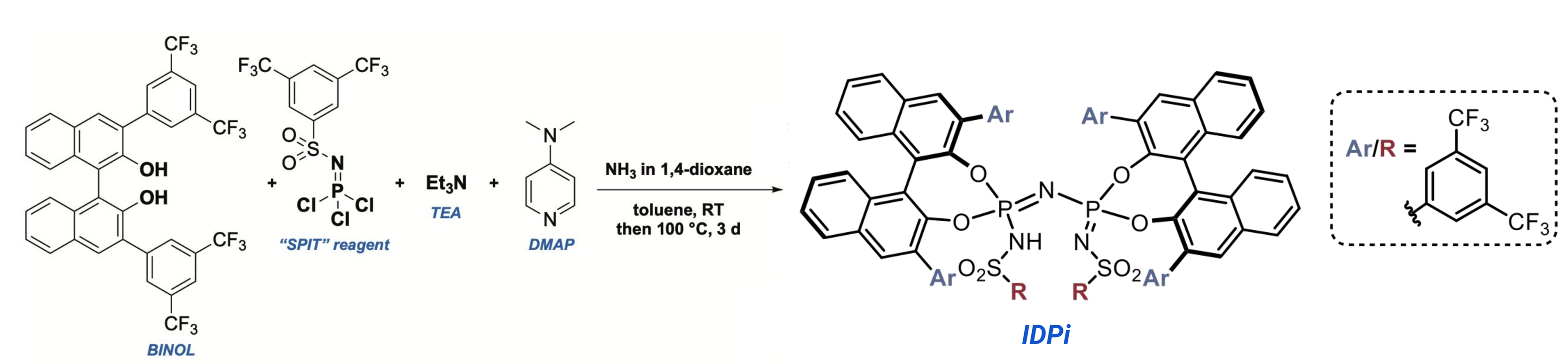
***%m**: the percentage of polymer diads that are **meso**. High %m indicates a **high degree of isotacticity**.*



The highest reported isotacticity for p(IBVE)!



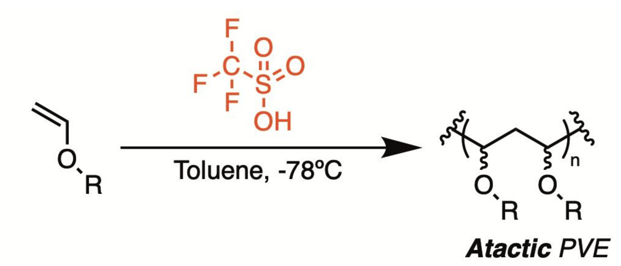
IDPi Synthesis Method:



Knutson et al. J. Am. Chem. Soc. **2021**, 143, 16388-16393.
Sama et. al. ScienceDirect. **2021**, 3, 2666-5425

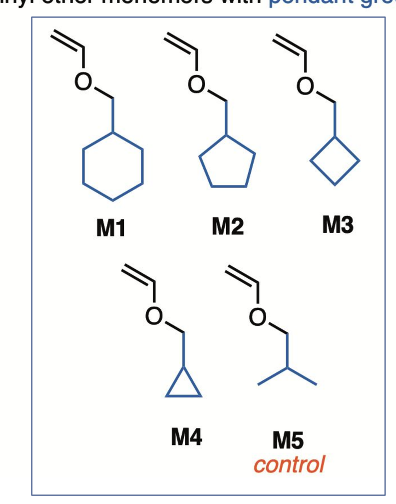
Screening Cycloaliphatic Monomers

Non-stereoselective triflic acid catalyst

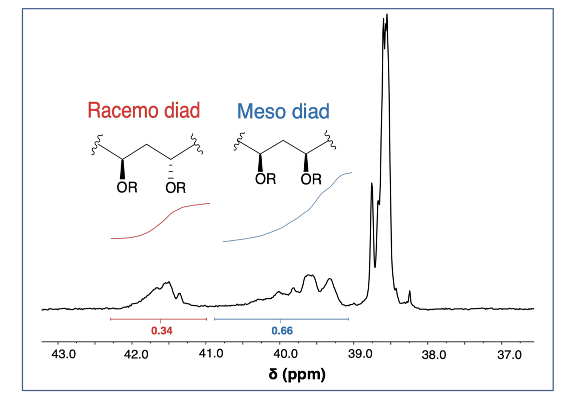


Monomer	*Mn, theo* (kDa)	*Mn, SEC* (kDa)	Đ	% m
M1	-	14952	1.8	69
M2	–	–	–	–
M3	–	?	–	–
M4	–	?	?	?
M5	?	?	?	?

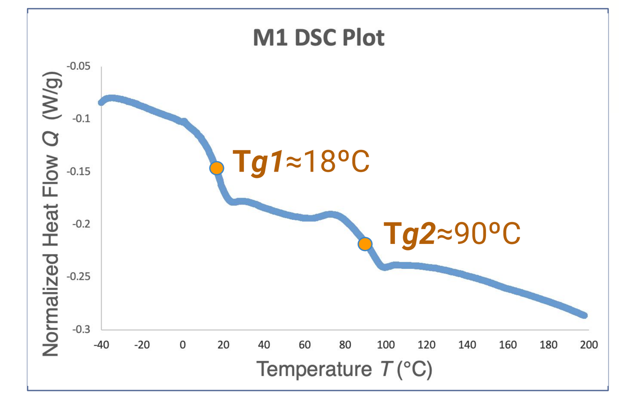
Vinyl ether monomers with pendant groups



Example Characterization of M1:



- **13C NMR** derivation of **%m** from ratio of **meso:racemo diad** peak integrals

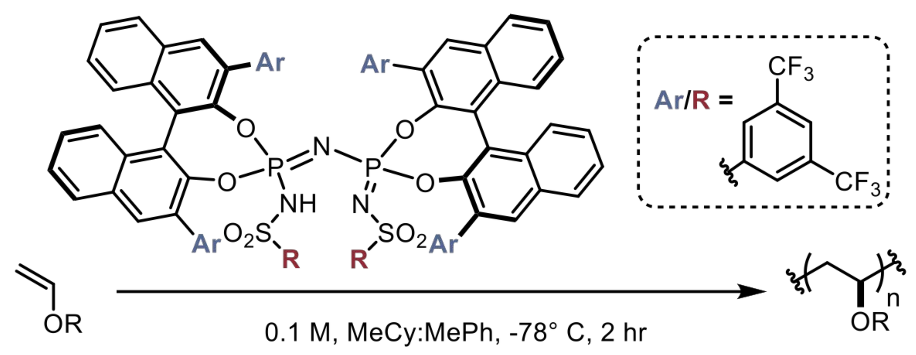


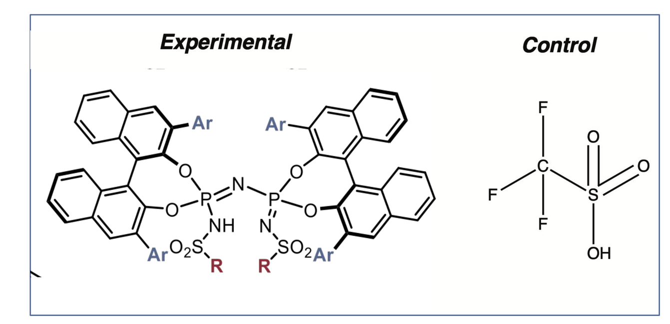
- **Differential Scanning Calorimetry** (DSC) conducted on sample for ***glass transition temperatures, Tg1*** and ***Tg2*** (°C)
  - *Tg=inflection point*

Monomer substitution alters polymer properties...

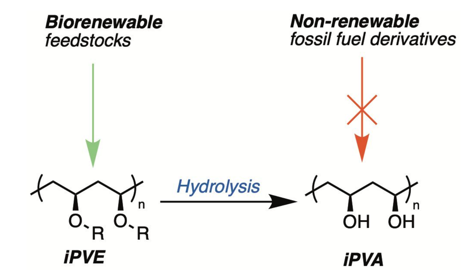
- ***Insight into structure-property relationships***
- ***Optimization of polymer design and synthesis***

Future Work





- *Use **IDPi** with the same 4 experimental **pendant group monomers** & iBVE control monomer*
  - *Elucidate **stereoselective capabilities** of IDPi, expand substrate scope*
- *Determination of **thermomechanical properties** (DSC, %m, tensile testing, etc.)*
- ***Post-polymerization functionalization** of iPVEs*



Sama et. al. Giant. **2021**, 3, 100047-100058
Sorensen et. al. ACS Catal. **2023**, 13, 5, 3272–3284

Conclusions

The stereoselective polymerization of isotactic polyvinyl ethers (**iPVEs**) presents a promising avenue for the development of renewable and sustainable polymers. The ability to derive iPVEs from **biorenewable feedstocks** is a **significant advantage** over traditional polymers which rely on unsustainable fossil fuel derivatives. The **IDPi catalyst** represents a **significant improvement** over ligated titanium-based catalysts due to its superior selectivity, control over polymerization, and metal-free nature, aligning with principles of **green chemistry**. Future work can explore **post-polymerization functionalization** and the use of other monomers, making this research area promising for the development of **new and exciting polymeric materials**.

Acknowledgements

This material is based on work that would not have been possible without the support of Ph. D. candidate Caleb Kozuszek, P.I. Dr. Frank Leibfarth, the members of the Leibfarth Group, Connie Pei, and the UNC Department of Chemistry's NMR Core Laboratory, which provided expertise and instrumentation that enabled this study.