Plastics from Pine Sap: Insight into the Ring-Opening Metathesis Polymerization Thermodynamics of Monoterpenes

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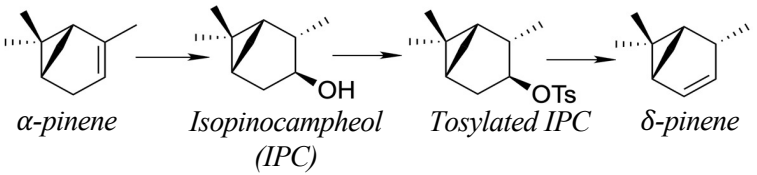
Background

- **Ring-Opening Metathesis Polymerization (ROMP) is** a polymerization reaction of cyclic olefins with high steric & thermodynamic control.
- ***α*-pinene** is a monoterpene that cannot undergo ROMP.
- ***δ*-pinene**[1] is a novel isomer of *α*-pinene with an accessible olefin, capable of undergoing ROMP.

Motivations

- Evaluate the potential for biomass-based chemical feedstocks to replace petrochemicals in plastics.
- Further understanding of ROMP and its steric and thermodynamic requirements.

Monomer Synthesis



α-pinene → *Isopinocampheol (IPC)* → *Tosylated IPC* → *δ-pinene*

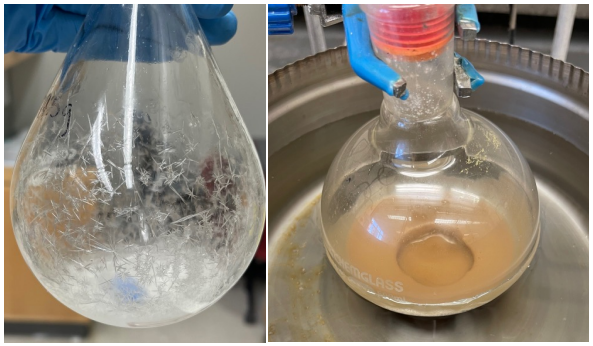
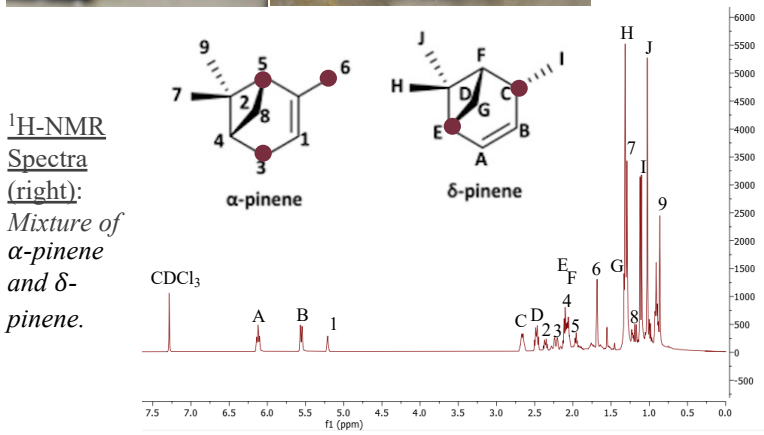


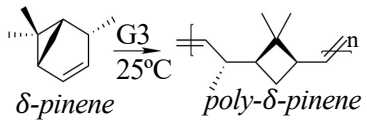
Image descriptions: *Crystallized IPC (left); Tosylated IPC after 48 hours of reacting (right).*



[1]H-NMR Spectra (right): *Mixture of α-pinene and δ-pinene.*

Findings

- Via ROMP:



δ-pinene → *poly-δ-pinene*

Poly-*δ*-pinene properties:

- Monomer RSE: 35.1 kJ/mol
- T_g (DSC): 87–101°C
- Đ (SEC): 1.06–1.35
- M_n (SEC): 4–75 kDa
- Conversion: 83–99%

Prospects: (Co)polymerization (w/ CP, Lactam, etc) and mechanical testing.

References

[1]"Ring-Opening Metathesis Polymerization of δ-Pinene: Well-Defined Polyolefins from Pine Sap." Yarolimek, M.R. et.al; *ACS Macro Letters* **2021** *10*, 760-766