Chemically Recyclable Elastomers

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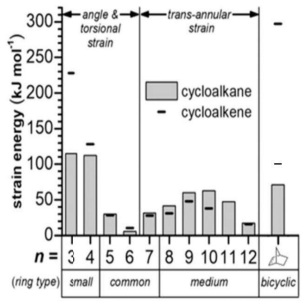
Abstract

This experiment focuses upon the recyclability and functionality of polycyclopentene (PCP). The structure of cyclopentene, a cycloalkene molecule consisting of 5 carbons, has low ring strain energy. In comparison, norbornene, a commonly used bicyclic cycloolefin monomer, has a high ring strain energy. Due to this, polynorbornene is depolymerizable, meaning it cannot return to monomer via metathesis reaction. However, due to the low ring strain energy of cyclopentene, the reaction can be depolymerizable, which allows it to be recycled. Utilizing the process of Variable Temperature Ring Opening Metathesis Polymerization (VT-ROMP), we can achieve a low dispersity and high molecular weight of PCP. To perform VT-ROMP, we initiate cyclopentene with a G1 catalyst (ruthenium type) at ~40°C, following it with a cold propagation at ~0°C. This method, when compared to Ring Opening Metathesis Polymerization (ROMP), allows us to achieve the targeted molecular weight with low dispersity that is necessary for the resulting polymer to remain stable. For the determination of molecular weight, characterization of PCP using nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC) will be utilized.

Introduction

The purpose of our project is to perform VT-ROMP in order to achieve desirable samples of polycyclopentene. By doing so, we can create elastomers that are depolymerizable but remain functional in use.

- **Cyclopentene (CP)** is mainly used to create rubbers and plastics. When polymerized, it is called **polycyclopentene (PCP)**.
- To create chemically recyclable elastomers, we must produce polymers that can break back down into monomers, or **depolymerize**.
- The **Gibbs Free Energy Equation of Equilibrium Polymerization**, $\Delta G_p = \Delta H_p - T\Delta S_p$, measures the maximum amount of energy used by a thermodynamic system when temperature and pressure are kept constant. For a reaction to be considered favorable, this number should be kept as low as possible.
- **Ring-Opening Metathesis Polymerization (ROMP)** converts cyclic olefins to polymeric material, in the presence of a Grubbs catalyst, typically made from ruthenium.
- **Variable-Temperature ROMP (VT-ROMP)** runs the reaction at a low temperature, to keep Gibbs Free Energy as small as possible. This method can polymerize CP with suitable ring strain to high conversion, targeted molar mass, and low dispersity.

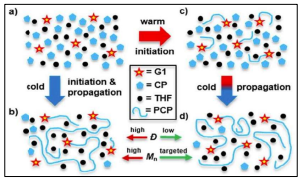


Methods

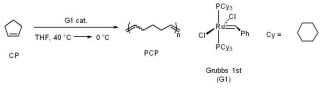
- Polymerize cyclopentene into polycyclopentene using VT-ROMP and a G1 catalyst (ruthenium type).
- To characterize polycyclopentene (PCP) we will use Nuclear Magnetic Resonance (NMR) and Size Exclusion Chromatography (SEC) to determine the molecular weight.

How we perform VT-ROMP:

- Initiate cyclopentene with G1 Grubb's Catalyst (ruthenium type).
- Warm initiation at ~40°C.
- Cold propagation at ~0°C.



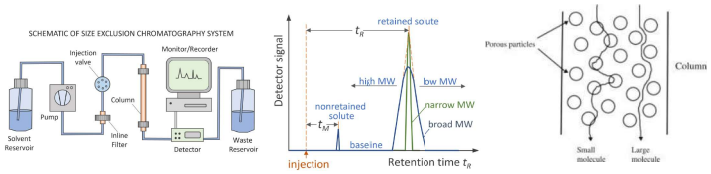
VT-ROMP Synthesis Scheme:



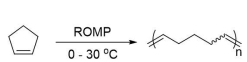
How we perform SEC:

- Dissolve polymer in a good solvent. In our case, we use tetrahydrofuran (THF).
- Allow solution to flow into column.
- As the solution moves throughout the column, small molecules will get stuck within the beads and large molecules will pass through.

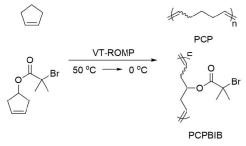
This allows us to separate the polymers based upon size.



Comparison Between ROMP and VT-ROMP



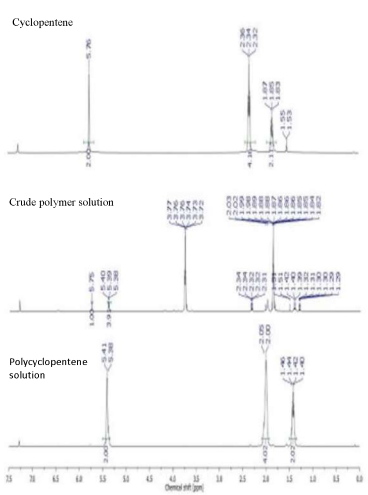
Temp. ()	Time (h)	% Conv.	M_n (kDa)	Đ
0	2	82.2	145.4	1.76
0	5	82.4	122.3	1.88
10	2	75.1	114.7	1.85
20	2	66.2	69.6	1.96
30	2	50.0	31.8	2.07



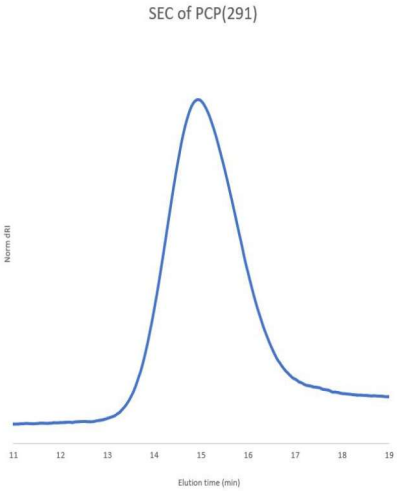
Name	[M]/[I]	Time (h)	% Conv.	$M_{n,theo}$ (kDa)	$M_{n,SEC}$ (kDa)	Đ
PCP(291)	400	2	79.0	21.5	19.8	1.39

Desired target	ROMP	VT-ROMP
High Conv.	Only at cold temp.	✓
Targeted MW	Only at cold temp.	✓
Low Đ (<1.3)	✗	✓

Nuclear Magnetic Resonance



Size Exclusion Chromatography



Results & Further Research

- The polymerization of cyclopentene into polycyclopentene was successful, achieving low dispersity, targeted molecular weight, and high conversion.
- Nuclear Magnetic Resonance revealed that our sample of polycyclopentene had little remnants of linear olefins.
- The sample of polycyclopentene exhibited rubbery behavior, showcasing its potential as an elastomer.
- Further research needs to be done on the rheology of polycyclopentene, to further analyze its ability to withstand different conditions.

References

Fulmer, *et al. Organometallics* **2010**, 29, 2176–2179.
Neary *et al. ACS Macro Lett.* **2019**, 8, 46–56.
Neary *et al. ACS Macro Lett.* **2018**, 7, 1080–1086.
Neary *et al. J Am Chem Soc.* **2019**, 141 (36), 14220-14229.
Neary *et al. Macromolecules.* **2017**, 50, 4935–4941.
Schleyer *et al. J Am Chem Soc.* **1970**, 92, 2377–2386.
Tuba *et al. Polym Chem* **2013**, 4, 3959–3962.

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