

Week 6

???

6.1 Ring-Opening Polymerizations

2/6:

- Relevant reading: Odian, Chapter 7.
- **Ring-opening polymerization:** The conversion of cyclic monomers into polymers via a ring opening process. *Also known as ROP.*
- Introduction.
 - The impact of size is very important in ROP.
 - You need a way to *kinetically* open the ring.
 - There can be an *equilibrium* between macrocyclic and linear species.
 - This equilibrium is big.
 - In order to induce polymerization, the equilibrium has to be driven toward the linear side.
 - Not every ring can be polymerized; one of the big things in this class is learning how to determine which rings can be polymerized.
 - A monomer require ring strain (thermodynamic) and a nucleophilic site (kinetic).
- Monomers that can be polymerized via ROP.
 - We'll talk about most of the monomers on this slide.
 - First half: Polymerizing ethers and ester.
 - Then different ones.
 - Poly- ϵ -caprolactam is nylon!
 - There is a polymer called polysulfur that is just a bunch of sulfur atoms in a chain!
- General mechanism (two basic types).
 1. Cationic ROP.
 - We get a positive charge (e.g., oxonium) and then the charge transfers after nucleophilic attack.
 2. Anionic ROP.
 - The anion on the growing chain attacks the monomer.
- Major driving force: Ring strain.
 - This is a more thermodynamic factor and is the relative stability of the cyclic monomer vs. linear polymer.

- We *can* use entropy to drive this, but most often, we take $\Delta H \ll 0$.
- ...
- Bond angle distortion.
 - This is the primary way to drive polymerization.
 - 3- and 4-membered rings have the most distorted bond angles and are very reactive toward polymerization.
 - **Transannular strain** increases strain in an 8-membered ring.
 - 8-membered rings are actually *great* to polymerize.
 - A 6-membered ring is the most thermodynamically stable; except for a *few* known exceptions, these do not polymerize.
 - Example: Trioxane; the oxygens get us away from ideal bond angles because of their lone pairs!
 - Thus, *en toto*, the thermodynamic feasibility for polymerization in terms of ring number is

$$3, 4 > 8 > 5, 7 \gg 6$$

- Kinetic factors.
 - Require functionality (a nucleophile) in the ring, which allows propagation to occur.
 - The rate of polymerization depends on both the reactivity of the monomer and active species.
 - The question is, “which is more important?” The *nucleophilic* nature of the monomer and the *electrophilic* nature of the active species.
 - Aziridine is more nucleophilic than cyclopropoxide because the nitrogen is less electronegative than the oxygen.
 - In general, the higher the basicity of the parent monomer, the lower the reactivity of the active species derived from this monomer toward the standard monomer.
 - The rate constant k_p of homopropagation overall decreases as the nucleophilicity of Z in the monomer increases because the activity of the active species controls the rate of homopropagation.
 - This tells us that in the transition state, the bond breaking is more advanced (it’s driving the polymerization) than the bond making.
- Thermodynamics of polymerization of cyclic ethers and acetals.
 - Observe that 3- and 4-membered cyclics are comparable to those for alkenes.
 - Substitution on the ring generally decreases tendency to polymerize because of sterics.
 - 6-membered rings are generally difficult to polymerize.
 - Generally, the larger the ring, the lower the entropic cost.
- Comparison to olefin chain and step-growth polymerization.
 - Initiators required, similar to cationic and anionic initiators used in olefin polymerizations.
 - Shows similar characteristics to those described for ionic olefin polymerizations: Effect of solvent, counterion, propagation by different species (covalent, ion pair, free ions).
 - Growth process similar to chain polymerization in that only monomer adds to growing chain.
 - However, rate constants are closer to step-growth polymerizations and there is a slower build up of molecular weight...
 - This means that it’s easier to get living polymerizations with this technique because the reactions are less fast.

- The following kinetics are almost identical to the alkene case.
- Thus, Rowan will focus more on the *chemistry* than the *kinetics*.
- Chemistry of ROPs.
 - Very similar to step-growth polymerizations, but with no condensation product.
 - ...
 - In THF, the positive charge converts oxygen into a good leaving group and we just do S_N2.
 - Aside: You should never use a strong cation in THF solvent because the cation will just polymerize it!
- Cationic Ring-Opening Polymerization (CROP).
 - Propagation with a *cationic* species.
 - General characteristics.
 - The cyclic monomers require a nucleophilic site. In general, the nucleophilic site in ROP is more nucleophilic than a double bond.
 - Shows most of the characteristics of vinyl cationic polymerization.
 - ...
- Initiation.
 - Similar to cationic!
 - Use a Brønsted (protic) acid.
 - Stable organic salts work well.
 - Lewis acids can also help out.
 - You can also do initiation with a covalent compound.
 - Use strong alkylating or acylating agents.
 - Depends on the nature of the nucleophile in the ring.
 - RBr is good for amines and oxazolines.
 - ROSO₂CF₃ is good for acetals or ethers (O); it's a *very* good **methylation agent**.
 - This also means that you should not use an alkylating agent in THF!
 - We can think of CF₃SO₃ as an almost *dormant* species, because once it is bound to a chain end, it can just react with THF again!
- Propagation.
 - Three possible propagation mechanisms.
 1. Activated chain-end (ACE) mechanism (ionic species).
 2. Activated chain-end (ACE) mechanism (covalent species, pseudocationic).
 3. Activated monomer (AM) mechanism.
 - Which propagation mechanism occurs depends on the nucleophile in the ring and the initiator.
 - Examples of ACE and AM.
 - Both ACE and AM can occur simultaneously in the polymerization process. The AM mechanism (which reduces the amount of cyclics formed during polymerization) can predominate if the ratio of [Monomer]/[HO⁻] is kept low, i.e., slow addition of monomer to the reaction mixture.
 - We can get backbiting in AM mechanisms; polymerizing ethylene oxide cationically just gets you a bunch of dioxane, which is just a thermodynamic well that you fall into.
 - Adding a small smidge of alcohol in will preferentially react with the activated monomer.
 - Not the best ever; ACE will still be actively generating dioxane. But not bad.

- Transfer and termination.
 - Almost all analogous to cationic alkene polymerization.
 - Chain transfer to polymer.
 - Probably the most common mode of transfer in this case.
 - If intermolecular, we'll get some mixing of molecular weights as chains exchange their growing fragments.
 - We can get intramolecular backbiting, too.
 - Termination by irreversible recombination.
 - Three different nucleophiles can react with the active cationic species.
 1. Monomer (leads to propagation).
 2. ...
 - Termination with polymer.
 - We can get branched structures that are fairly stable and don't react further.
 - Termination by counterion.
 - Termination by reactions with other compounds in the system: Solvent and impurities.
 - Termination by water does occur. However, it is less important than in vinyl cationic polymerization on account of the cyclic monomer being more nucleophilic than the vinyl monomer.
 - Termination by reaction of more reactive species existing in equilibrium with stable onium species.

6.2 ???

- 2/8: • I was at the CCRF national scholars luncheon.