Week 2

???

2.1 ???

• Finishing up from last time's lecture to start.

- Regio- and geometric isomers.

  – Some monomers can react at two different sites (e.g., 1,4-butadiene).

  – There's also *cis* and *trans* isomerism when double bonds are in the polymer.

  – Three types of potential isomers.

    ■ Structural isomers: 1,2- or 1,4-addition; this depends on the regiochemistry of the polymerization.

    ■ ...

- **Copolymer**: A polymer in which two or more different monomers are incorporated into the polymer chain.

  – **Terpolymers** and **tetrapolymers**, as well.

  – **Statistical/random** vs. **alternating** copolymers.

- **Terpolymer**: A copolymer with 3 different monomer repeat units.

- **Tetrapolymer**: A copolymer with 4 different monomer repeat units.

- **Statistical** (copolymer): A copolymer in which the comonomers appear in irregular, unspecified sequences along the chain. *Also known as* **random**.

- **Alternating** (copolymer): A copolymer in which the comonomers occur in alternation.

- **Block** (copolymer): A copolymer in which a long, linear sequences of polymer A is joined to a long, linear sequence of polymer B.

- **Graft** (copolymer): ...

- Polymer end groups.

  – For a linear polymer, there are two end groups.

  – The more branches, the more end groups.

  – End group chemistry is often important and allows us to do fun stuff.

  – For addition and some ROPs, one end group comes from the initiator and the other from the termination process.

- ■ "If we know how it dies, maybe we can keep it from dying a bit longer. A little bit of autopsy on the polymer allows us to keep it alive and growing for longer"
      - For step-growth polymers, the end groups are determined by the monomer.
      - Knowledge of the structure of the end groups allows. . .
        - ■ Determination of molecular weight (up to about 30,000 because after that, they're just too small to characterize).
        - ■ Synthesis of block copolymers.

- Key points of lecture 1, in summary.

  - Many definitions related to macromolecules.
  - Different macromolecular...
  - Main takeaways:
    - ■ Mainly definitions.
    - ■ If you understand the definitions, it will make everything else easier!

- Reminder that this first lecture content is introducing us to stuff that we'll see throughout the rest of the course!

- Moving onto today's lecture!

- The next 2-3 lectures will be about radical polymerization of olefins.

  - We could easily do 10 lectures on this stuff!
  - There's so much and so many things we can control and play with.

- We'll be focusing on radical addition polymerization and the general propagation mechanism.

  - Works for most olefin monomers.

- **Radical polymerization**: ...

- This method produces a lot of synthetic plastics.

- Examples:

  - PE (LDPE, LLDPE, HDPE).
  - PP.
  - PVC.
  - PS.
  - Acrylates and fluoropolymers (e.g., teflon).
  - *More in the slides.*

- Olefin substituents.

  - Isobutene and vinyl ethers don't really work, but pretty much everything else can.
  - Anything with a strong EDG won't work.
  - This is useful to remember when he gives us a monomer and wants us to tell him how to polymerize it!

- Overview of free radical process.

  - Key: The *rate*.
    - ■ Difficult to measure because there are a ton of different reactions at different points all happening in the same one pot.

- Initiation, propagation, termination.
  - ■ We'll talk about each of these separately, plus their kinetics, and then pull everything back together.

- The mechanism of radical polymerization.

  - Initiation step: Throw a radical progenerator into the reaction, heat it up so that it splits into two radicals that *then* do the reaction.
  - Reaction.

$$\text{I} \xrightarrow{k_d} 2\,\text{R}\cdot$$

  - k_d is given by the Arrhenius equation

$$k_d = A\mathrm{e}^{-Ea/RT}$$

  - ...

- Thermal initiators.

- AIBN.

  - AIBN (2,2'-azobisisobutyronitrile) will be found in almost every polymer lab. *screenshot*
  - The reaction goes because N_2 is a thermodynamic sink, and because the nitrile group acts as an EWG to stabilize the radical.
  - Where do k_d and E_a come from?
  - We can measure time vs. nitrogen evolution and know that the two will have a logarithmic relationship so t vs. $\ln(l_0/l)$ will be linear.

- Benzoyl peroxide.

  - This one is even slightly stronger than AIBN.
  - The weak $O-O$ bond is the driving force for this decomposition.
  - Same stuff as in acne creme and tooth whiteners!

- There are hundreds of examples of thermal initiators! *table*

  - Which one you uses depends.
  - For one, you want your initiator to be soluble in the monomer.
  - If the monomer boils below the initiation temperature, that's not good!
  - Oftentimes, polymer chemists get so caught up in the kinetics that they forget practical things like, "is my initiator soluble in my monomer?"

- Key takeaways on thermal initiators.

  1. The difference in the decomposition rate...

- Initiator half-lives.

  - We don't need to memorize this table, but it's good to know!
  - We should be able to look at a chemical structure and know which of two initiators initiates faster.

- Two ways to do the course: Memorize absolutely everything, or understand how to work things out.

- The fate of free radicals.

  - A small percentage of benzoyl radicals will decarboxylate and give you the phenyl radical.

- – Most of the reaction will react via the middle route because the radical there can be stabilized by resonance delocalization into the aromatic ring (vs. 2) and we're not breaking aromaticity (vs. 3).
  - – Not all radicals initiate new chains; a big waste product is BPO, which is when two radicals react. This brings us to the next topic.

- **Initiation efficiency**: The fraction of radicals formed in the primary step of initiator decomposition which are successful in initiating polymerization. *Denoted by f. Given by*

$$f = \frac{\text{radicals incorporated into the polymer}}{\text{radicals formed by the initiator}}$$

  - – Temperature- and solvent-dependent.
  - – ...
  - – Primary reasons $f < 1$.
    - ■ **Solvent cages**.
    - ■ Increasing viscosity of the reaction medium.
  - – Viscosity.
    - ■ This is chain-growth, so we get HWt polymers really quickly.
    - ■ Increasing viscosity means that the lifetime of radicals in solvent cages increases.
    - ■ Example: AIBN for polystyrene decreases from 0.75 to 0.2 as conversion increases from 30% to 60%.

- **Solvent cage**: An ephemeral, transient group of solvent molecules that forms around radicals.

  - – The presence of a solvent cage traps radicals and increases rate of recombination... basically molecules in solution act like they are encapsulated.
  - – This is an explanation of why our f might be crappy, but we don't really worry about it or do anything about it.

- Mechanism and kinetics of initiation.

  - – Two reactions: Decomposition and addition to monomer.
  - – Decomposition is the RDS (think of the long half-lives!).
    - ■ Typical values for $k_d = 10^{-3}\,\text{s}^{-1}$...
    - ■
  - – Thus, the rate R_i of initiation will equal the rate R_d of decomposition, yielding the differential equation

$$R_i = R_d = -2\frac{\text{d}[\text{I}]}{\text{d}t} = \frac{\text{d}[\text{R}\cdot]}{\text{d}t} = 2k_d[\text{I}]$$

  - – Taking f into account,

$$R_i = 2k_d f[\text{I}]$$

- Initiation is the easy step, and you see how much that was!

- We now move into propagation.

- Mechanism and kinetics of propagation.

  - – k_{p2} is the rate of monomer to dimer.
  - – k_{p3} is the rate of dimer to trimer.
  - – Instead of having to consider thousands of rate constants, the rate of reaction is independent of molecular weight to a very good approximation.

– Thus, a general scheme is

$$R(M)_n \cdot + M \xrightarrow{k_p} R(M)_{n+1}$$
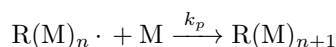
– It follows that the rate of propagation is

$$R_p = k_p[M][M\cdot]$$

– Typical values for $k_p = ...$
– The fact that the propagation kinetics work so well implies that there's no reason to do polymerizations at high temperature *except* for the issue of the initiator.

• Mechanism and kinetics of termination.

• *cnc = [H] command*

– Several mechanisms.
– You can have termination via combination. This is k_{tc}:

$$R_{tc} = 2k_t[M\cdot]^2$$

– You can have termination via disproportionation.
– *Similar kinetics.*
– There are other forms of death (such as reacting with an initiator radical), but these two are dominant.
  ■ For example, the concentrator of initiator is so much lower than that of growing polymers that it is much more likely for two growing polymers to mutually terminate.
– These varying forms of death imply that you don't have control over chain ends in a radical mechanism.
– Overall rate of termination:

$$R_t = 2k_2[M\cdot]^2$$

• The rate of propagation is faster than the rate of termination because the rate of propagation depends on [M], which is very large (much larger than [M·]).

– This is true even though $k_t \gg k_p$; it's just that $[M\cdot] \lll [M]$.

• ...

• Olefin substituents.

– Free radical polymerizations can be carried out with most vinyl monomers.
– Radical stabilization of the growing polymer happens with most species.
– However, there are exceptions.
  1. Strong EDGs.
  2. 1-alkyl olefins and 1,2-dialkyl olefins.
– Remember: Propylene, for example, cannot be polymerized under free radical conditions.
  ■ This is because of delocalization/resonance because an allyl radical is much more stable than the polymer radical.
– Reactivity. *scale*
  ■ Reactive monomers have substituents which stabilize the polymeric radical by resonance stabilization.
  ■ So styrene is one of the most reactive monomers.
  ■ The greater the gain in stability, the greater the incentive for the monomer to react.

■ There are exceptions: We can polymerize ethylene, even though its substitutents don't help; styrene will always react first with a radical.

■ It's flipped with growing radical stability, though: A radical generated in the middle of building PE will react much more quickly than a radical generated in the middle of building PS.

- Thus, overall, polymerization rate is determined by a compromise between monomer and polymer reactivity.

  – Example: Vinyl acetate goes super fast.

  – Most reactive radical and most reactive monomer go the fastest.

    ■ What does this mean tho?? Because won't a vinyl acetate radical immediately bind to a styrene radical and then not react with vinyl acetate again?

- Olefin substituents: Structural isomerization.

  – ...

  – Tacticity.

    ■ **Meso diads** vs. **racemic dads**.

    ■ Lead to the 3 tacticity types...

  – The racemic form is usually slightly preferred over the meso structure because of sterics and/or electrostatic repulsion...

- W 9:30-10:30 in the morning is a second discussion section.

- Th class will be virtual.

- 300-level class has papers, plus 25% of exam.

2.2   ???

1/11:   - More on the importance of tacticity.

  – Isotactic PP is very common; it's a durable material.

  – Atactic PP is just a goo.

  – T_m vs. T_g.

- Polymerization kinetics.

  – Last class, we derived the rates of initiation, propagation, and termination.

  – How do we look at the overall rate of reaction?

    ■ Propagation is the RDS, so that's what's most important!

  – Rates of initiation and termination are essentially the same; this is the **steady state approximation**.

    ■ This allows us to say

$$R_i = R_t 2k_d f[\text{I}] \qquad\qquad = 2k_t[\text{M}\cdot]^2$$

$$[\text{M}\cdot] = \left(\frac{k_d f[\text{I}]}{k_t}\right)^{1/2}$$

    ■ Substituting, we obtain

$$R_p = k_p[\text{M}][\text{M}\cdot] = k_p[\text{M}]\left(\frac{k_d f[\text{I}]}{k_t}\right)^{1/2} = k'[\text{M}][\text{I}]^{1/2}$$

where k' combines all constants.

- To confirm that this math is valid, let's look at some experimental data.

  - The plot of R_p vs. $[\mathrm{I}]^{1/2}$ is linear.
  - The plot of R_p vs. $[\mathrm{M}]$ is linear.

- Linear systems work well, but only to a point, leading to...

- Autoacceleration. *picture*

  - Deviations from the general kinetic expressions do occur. ONe type of deviation is referred to as the **gel effect**.

- **Gel effect**: Generally, one would expect from the standard kinetic expression that R_p would decrease with increasing time/conversionas both $[\mathrm{M}]$ and $[\mathrm{I}]$ decrease; however, particularly in bulk or concentrated solutions, a sharp increase in R_p is observed. *Also known as* **Tommsdorff effect**, **Norris-Smith effect**, **Norris-Tommsdorff effect**.

  - This happens because of chain entanglements, which reduce the mobility of the polymer chain radicals.

    - Chain entanglement, like wet spaghetti, dramatically increase viscosity.

  - In such viscous media, the diffusion rates of the polymer become very low and k_t is dramatically reduced. Thus, from the equation above, an increase in both R_p and X_n occurs.

    - Recall that all termination steps require two polymer chains to come together! If they're diffusing more slowly, they're less likely to come together.

- The above allows us to think about kinetics at the molecular level.

- Other types of initiators: Redox.

  - Many redox reactions can be used to generate radicals which initiate polymerization.
  - AdvantageA: Radical rpoduction occurs at a reasonable rate over a broad range of temperatures.

    - Consequence: Lower temperatures are accessible (0-50 °C) than with thermal homolysis of initiators.

  - Peroxides in combination with a reducing agent are frequently employed.

    - Hydrogen peroxide + ferrous ion: $\mathrm{H_2O_2} + \mathrm{Fe^{2+}} \longrightarrow \mathrm{HO^-} + \mathrm{HO}\cdot + \mathrm{Fe^{3+}}$.
    - ...
    - ...
    - Other reductants can be employed instead of $\mathrm{Fe^{2+}}$; it depends on the system!
    - Solubility can be an issue for these redox systems; these are mostly used in *aqueous* or emulsion systems.

  - If you're thinking of doing a redox polymerization, there are some changes to the rate...

- Redox initiation.

  - Return to the equation

$$R_p = k_p[\mathrm{M}] \left(\frac{R_i}{2k_t} \right)^{1/2}$$

  - For redox initiation, we have

$$R_i = k_d[\text{reductant}][\text{oxidant}]$$

  - Thus, the polymerization rate R_p of a free radical polymerization initiated by a redox reaction is...
  - Note that in this type of initiation, only *one* radical is produced, not two!

- Other types of initiators: Photochemical.

  - Photochemical initiation[1].

  - Light absorption by some compound in the system either. . .

    ■ Directly causes the compound to decompose into radicals;

    ■ Leads to an excited species which transfers its energy to a second compound, which in turn decomposes into radicals.

  - Advantages.

    ■ Polymerization can be carried out in a spatially directed manner by irradiating selective zones: ...

- **Photochemical initiation**: When radicals are produced by irradiation of the reaction system with UV or visible light.

- Photochemical initiators.

  - Typically UV curable.

  - Consider solubility, absorption spectrum, **quantum yield**, etc.

  - Type 1: **Cleavage**.

    ■ 2,2-dimethoxy-2-phenylacetophenone is a super common one.

    ■ So is benzoin.

  - Type 2: **Abstraction**.

- **Quantum yield**: How well does the compound absorb photons going into the system?

- **Cleavage**: Unimolecular bond cleavage upon irradiation.

- **Abstraction**: Bimolecular mechanism where excited molecule reacts with a second molecule (coinitiator) to generate free radicals, e.g., benzophenone amine.

- **Kinetic chain length**: The number of monomer molecules consumed per active species (radical) which initiates a chain. *Denoted by ν. Given by*

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[\text{M}][\text{M}\cdot]}{2k_t[\text{M}\cdot]^2} = \frac{k_p[\text{M}]}{2k_t[\text{M}\cdot]} = \frac{k_p^2[\text{M}]^2}{2k_t R_p} = \frac{k_p[\text{M}]}{2(k_t f k_d[\text{I}])^{1/2}} = k''[\text{M}][\text{I}]^{-1/2}$$

  - How big the polymer is going to get.

  - The kinetic chin length is very related to the degree of polymerization.

  - Tells you what you can control to get heavier polymers!

  - Note: An increase in the rate of polymerizatino by increasing the radical concentration will decrease the kinetic chain length.

- **Number-average degree of polymerization**: The average number of repeat units contiained in a macromolecule. *Denoted by $\overline{X}_n$.*

  - Related to the ν.

  - If the termination process is by combination, then $\overline{X}_n$.

  - If the terminatio process is by disproportionation, then $\overline{X}_n = \nu$.

  - If a is the fraction of chains which terminate by combination, then $\overline{X}_n = 2\nu/(2 - a)$.

  - Most polymer radicals appear to terminate predominantly by coupling (almost exclusively: styrene, methyl acrylate, acrylonitrile).

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[1]Like in the Lin lab!

– Disproportionation increases when the propagating radical is sterically hindered or features many β-hydrogens available for transfer (methyl methacrylate undergoes termination by combination 33% with 67% disproportinoation at $25\,^{\circ}\mathrm{C}$).

- **Number-average molecular weight**: The following quantity. *Denoted by* $\overline{\boldsymbol{M}}_{\boldsymbol{n}}$. *Given by*

$$\overline{M}_n = M_0 \overline{X}_n$$

- Chain transfer in radical polymerizations.

  – A premature termination process that accounts for lower-than-expected M_n.

  – Chain transfer agents may be monomer, initiator, solvent, or another substance. Sometimes we want to promote this!

  – The rate of chain transfer is given by

  $$R_{tr} = k_{tr}[\mathrm{M}\cdot][XA]$$

  – Chain transfer differs from termination in that it results in the formation of a new radical which can initiate a new polymer chain.

  – ...

- Effect of the chain transfer on molecular weight.

  – The degree of polymerization for a polymerization which has chain transfer is

  $$\begin{aligned}
  \overline{X}_n &= \frac{R_p}{(2-a)(R_t/2) + R_{tr,M} + R_{tr,S} + R_{tr,I}} \\
  &= \frac{R_p}{(2-a)(R_t/2) + k_{tr,M}[\mathrm{M}\cdot][\mathrm{M}] + k_{tr,S}[\mathrm{M}\cdot][\mathrm{S}] + k_{tr,I}[\mathrm{M}\cdot][\mathrm{I}]}
  \end{aligned}$$

  where a is the fraction of chains which terminate by combination; 100% combination implies $a = 1$.

- **Chain transfer constant**: The ratio of the rate of chain transfer k_{tr} of the propagating radical with the substance to the rate of propagation of the radical. *Denoted by* $\boldsymbol{C}$. *Given by*

$$C_M = \frac{k_{tr,M}}{k_p} \qquad\qquad C_S = \frac{k_{tr,S}}{k_p} \qquad\qquad C_I = \frac{k_{tr,I}}{k_p}$$

- **Mayo equation**: ...

  – If a solvent otherwise works but has a very high chain transfer constant, you may not want to use it!
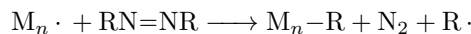
- The chemistry of chain transfer.
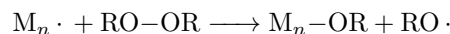
- Chain transfer to monomer.

  – C_M is generally small because the reaction usually involve breaking the stronger vinyl $\mathrm{C-H}$ bond.

  – The largest monomer transfer constants are generally observed when the propagating radicals have very high reactivites, such as with ethylene, vinyl acetate, and vinyl chloride.

  – We often have head-to-tail cheistry, but here we have some more head-to-head chemistry??

  – Vinyl chloride's high value of C_M is also related to a reaction sequence that originates in a propagating center formed by head-to-head addition.

  – C_M is really what places the upper limit on the polymer molecular weight. For example, the high C_M of vinyl chloride limits the M_n of PVC to 50,000-100,000, whereas with polyethylene, we can get into the millions.
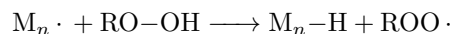
- Chain transfer to initiator.

    - Greater than chain transfer to monomer.
    - However, transfer to initiator is governed by C_I, [I]/[M], and [I] is usually small (10^{-4}-10^{-2} M).
    - Azo initiator:
    $$\mathrm{M}_n\cdot + \mathrm{RN{=}NR} \longrightarrow \mathrm{M}_n{-}\mathrm{R} + \mathrm{N}_2 + \mathrm{R}\cdot$$
    - Peroxides:
    $$\mathrm{M}_n\cdot + \mathrm{RO{-}OR} \longrightarrow \mathrm{M}_n{-}\mathrm{OR} + \mathrm{RO}\cdot$$
    - Hydroperoxides:
    $$\mathrm{M}_n\cdot + \mathrm{RO{-}OH} \longrightarrow \mathrm{M}_n{-}\mathrm{H} + \mathrm{ROO}\cdot$$
    - You have to take into account the nature of the polymer radical as well!

- Chain transfer to chain transfer agent.

    - If transfer to the chain transfer agent dominates, then the Mayo equation simplifies to
    $$\frac{1}{\overline{X}_n} = \left(\frac{1}{\overline{X}_n}\right)_0 + C_S \frac{[\mathrm{S}]}{[\mathrm{M}]}$$
    where $(1/\overline{X}_n)_0$ is the value of $1/\overline{X}_n$ in the absence of the chain transfer agent.

- Reactivity of chain-transfer agent.

    - Aliphatic hydrocarbons have strong C$-$H bonds, hence show low transfer constants.
    - Benzene has an even lower transfer constant because of the stron C$-$H bonds in this aromatic and the instability of the aryl radical.
    - The presence of more weakly bound hydrogen atoms in toluene, ethylbenzene, etc. leads to higher C_S values for these species when compared to benzene. The benzylic proton is readily abstracted because of resonance stabilization.
    - Primary halides such as n-butyl chloride and n-butyl bromide behave similar to aliphatics and feature low C_S values; by contrast, the weak C$-$I bond in n-butyl iodide leads to an increased C_S value.
    - Acids, carbonyl compounds, ethers, amines, and alcohols have highet transfer constants,corresponding to breakup of the C$-$H bond and stabilization of the radical by an adjacent O, N, or carbonyl group.
    - The weak S$-$S bond leads to high C_S values for disulfides.
        - Note that disulfides are good chain transfer agents, but not good initiators because the radical is more stable.
    - The high C_S values fro carbon tetrachloride and carbon tetrabromide are due to the excellent resonance stabiliaation of the trihalocarbon radicals.
        - The weaker C$-$Br bond in CBr$_4$ leads to a substantial increase in C_S.
    - Thiols have the largest C_S values of any known compounds, due to the weak S$-$H bond.
    - Transfer agents...
    - Use of the Mayo equation once again for moderation??

- Chain transfer to a polymer.

    - Can create a propagation site anywhere along the polymer chain, which can lead to a branched polymer.
    - Becomes important when the polymerization is carried out to high conversion.

- Example: polyethylene.
    - ■ Two main types of branches: Long and short.
    - ■ Long branches are formed as before from reactions between disparate chains.
    - ■ Short branches outnumber the longer branches by 20-50 tiemes. These form via **backbiting**.

- **Backbiting**: The radical site of propagation moving back a few carbons in a stable, six-membered ring. *picture*

    - Typical PE produced by radical polymerization contains 5-15...
    - May seem small, but has a massive effect on properties.
    - Gives you LDPE.
    - HDPE is *not* mede free-radically! It's made using insertion catalysts, which we'll cover later.

- **Retardation** and **inhibition**.

    - Quinones are example inhibitors.
        - ■ They inhibit the reaction until the concentration is fully consumed, then polymerization resumes.
    - Nitrobenzene is an example retarder.

- **Inhibitor**: An agent that *prevents* radical polymerization by reacting with the initiating and propagating radicals and converting them to nonradical species or radicals of reactivity too low to undergo polymerization.

- **Retarder**: An agent that *slows* radical polymerization by reacting with a fraction of the initiating and propagating radicals and converting them to nonradical species or radicals of reactivity too low to undergo polymerization.

- The class that Rowan thought would be virtual in a couple weeks *should* be in-person. All the rest should be as well!