

Week 9

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9.1 ???

- 2/27:
- Bisphenol A Polycarbonate.
 - Good optical properties (clarity).
 - When you microwave baby bottles with it, though, you get leaching.
 - Polycarbonate synthesis.
 - Interfacial polycondensation.
 - Rapidly stirred mixture of solvent (e.g., DCM, PhCl, DCE), aqueous NaOH, bisphenol A, phosgene, a tertiary amine catalyst, and a monofunctional end-capper for MW control.
 - IN the aqueous phase, there are some reactions. In the organic, there are others. At the interface, there are still more.
 - You can also do transesterification.
 - Melt of Bisphenol A, diphenylcarbonate, sodium bisphenolate catalyst.
 - High temperature and low pressure.
 - You get some undesired side reactions.
 - Polyamides (nylons).
 - Linear aliphatic polyamides will be our focus.
 - The first one was “Polyamide x,” aka Perlon™.
 - “Polyamide x,y” was Nylon™.
 - Polyamides History.
 - Kirby and Carothers (1930) failed to polymerize caprolactam, and put this result in writing in JACS stating that it couldn’t be done. German IG Farben was then able to do it and patent it.
 - ...
 - Peterson in Carothers’ lab made polyamide 5-10 with even better characteristics.
 - Triggered by the business people at DuPont, who were concerned that polyamide 5-10 was too expensive to make, Carothers’ group started to screen...
 - 1935: Berchet prepared the first sample of polyamide 6,6. The polymer had exciting properties (although the high melt temperature suggested possible problems due to degradation upon processing) and the economics of the monomers were right, so that in summer 1935, polyamide 6,6 was selected as the commercial candidate.
 - The “solidification” was a cold crystallization.

- 1939: Polymer brought to market.
- Polyamide.
 - List of properties.
 - Moderate to high crystallinity.
 - High water uptake (wet nylon is softer).
 - The keratin in our nails is polyamide, too, with some side groups. Thus, it has high water uptake, too. That's why our nails get soft in the bath!
 - Few solvents: Hexafluoro-2-propanol, formic acid, *m*-cresol.
 - ...
- Application of polyamides.
- Polyamide fibers.
 - We get a lot of hydrogen bonding that stops chains from slipping past each other.
 - Hydrogen bonding is stronger than the dipole interactions in polyesters (use in gen-chem review??), creating ordered crystalline polymer chains.
- Polyamide 6,6 synthesis.
 - The nylon rope trick, forming nylon via interfacial polymerization.
 - If the rate of reaction is faster than the rate of pulling up the polymer, you'll get a nice long rope.
 - Melt polycondensation.
 - Steps to do it.
- Polyurethanes.
 - Very easy to make.
 - You can do the reverse reaction with catalysts above 180 °C.
 - Most polymerization is done with a catalyst under 100 °C, though.
 - These can be made as either fibers or foams.
 - Lists a number of possible di(isocyanates) and diols.
 - There are literally thousands of polyurethanes.
 - Some are very stiff, e.g., polyurethanes are used in bowling balls.
 - Some are very soft and stretchy, e.g., spandex and shower curtains.
 - Polyester leisure suits in the '70s, spandex in the '80s. As a polymer chemist, with great power comes great (fashion) responsibility.
- Polyurethane fibers.
 - Commercially, the most important polyurethane fibers are those that result in a blocky copolymer structure (e.g., spandex).
 - To make these, a low molecular weight polymeric diol ($M_n = 2000 - 3000$) is reacted with excess isocyanate to result in isocyanate-terminated polymer which is then reacted with a diamine chain extender.
- Polyurethane foams.
 - ...
- Aromatic polymers.

- Polysulfone (PSU) is a rigid, high-strength, semi-tough thermoplastic that has a **heat deflection temperature** of 174 °C and maintains its properties over a wide temperature range.
 - Synthesized via a nucleophilic substitution-type mechanism.
- Polyetheretherketone (PEEK).
- EWGs to pull electrons up before they kick back down are critical in the synthesis for both of these.
- Poly(imide).
 - Really good strong materials.
 - Nucleophilic aromatic substitution mechanism here, too.
 - You go through a **polyamic acid** intermediate. This is solution processible. Then when you “heat the bajesus out of it,” you form the polyimide.
- Poly(ether imide).
 - Same NAS mechanism.
- Poly(phenylene oxide).
- Poly(phenylene sulfide).
- **Heat deflection temperature:** The temperature at which a polymer starts to “soften” under a fixed load.
- Reminder: Most polymer chemistry is done under extreme conditions that we wouldn’t ordinarily find in the lab.
 - We often try to use more mild conditions when we have more functional groups, as in polyurethanes, though.
- Branched and network polymers.
 - We’ll start this today, finish it on Thursday, and then half the class will be left. Rowan is open to any activity we want to propose. He can go over anything again, etc.
- Reactions with monomers with more than two functional groups.
 - All the step-growth polymerizations so far have focused on monomers with only two reactive groups which lead to the formation of either linear polymers or rings.
 - Consider the polymerization of A–B monomer in the presence of a small amount of A... **functionality**
- Crosslinking.
 - Reacting A–B with A_f in the presence of B–B leads to branching and crosslinking.
 - Crosslinking also occurs with

$$A-B + B_f \longrightarrow A-A + B-B + B_f \longrightarrow A_f + B_f \longrightarrow$$
 - Crosslinking is distinguished by the occurrence of **gelation** during the polymerization.
 - At this gel point, an insoluble polymer fraction (**gel**) is formed.
 - It’s all just one big ass molecule.
- Networks: Definitions.
- **Junction:** Point where three or more strands emanate.
- **Functionality** (of a junction): The number of strands connected to it. *Denoted by f*.
- **Strand:** A polymer chain that bridges two junctions.

- **Loop:** A network defect that begins and ends at the same junction point and is not fully elastically active.
- **Dangling chain end:** A network defect that is free to relax and as such does not contribute to the network elasticity.
- Loops and dangling chain ends are *defects*.
- **Sol fraction:** This is the fraction of polymer that is not part of the infinite network either as a linear polymer or as part of a cluster.
 - If put in a good solvent, the sol fraction would dissolve and the **gel fraction** would not.
 - After you synthesize your polymer, you identify the gel fraction by washing it, drying it, and weighing it.
- **Networks:** A class of polymers that consists of an infinite crosslinked architecture.
 - The linkages prevent flow of the material, and as such, these materials are solids.
 - Two main classes of networks: **elastomers** and **thermosets**.
- **Elastomer:** ...
- **Thermoset:** ...
- **Gel point:** The point during the polymerization at which gelation occurs.
 - A key property of crosslinked polymers is that they never dissolve. They may swell, but they will never dissolve unless we break bonds.
 - Definition of the **sol**.
 - Once the gel point is reached, the polymer will no longer flow (even at high temperatures). Thus, processing needs to be completed before gelation sets in.
 - Thus, the **prepolymer** is processed before gelation is reached, and polymerization/crosslinking is completed after processing.
 - Three stages for thermosetting polymers or thermosets.
 1. Polymer soluble and fusible.
 2. Polymer still fusible but close to the gel point.
 3. Polymer highly crosslinked...
- **Sol:** Any non-gel portion of the polymer which remains soluble.
- Network synthesis.
 - It is important to understand the relationship between extent of reaction and gelation. This can be done based on calculating when either \bar{X}_n and \bar{X}_w reach an infinite size.
 - Carothers equation: $\bar{X}_n \rightarrow \infty$.
 - You have to think about the stoichiometric amount of reagents.
 - This is based on the average functionality of the monomer mixture, i.e., the average number of functional groups per monomer molecule:

$$f_{\text{avg}} = \frac{\sum N_i f_i}{\sum N_i}$$

- Recall that N_i is the number of molecules of monomer i with functionality f_i .
- Example: For 2 mol of glycerol (triol) and 3 mol of phthalic acid (diacid), then

$$f_{\text{avg}} = \frac{12}{5} = 2.4$$

- For the system where the number of A and B groups are equal, the number of monomers...
- ...
- Combining equations, we get

$$\bar{X}_n = \frac{2}{2 - pf_{\text{avg}}}$$

- Rearranging, we obtain

$$p = \frac{2}{f_{\text{avg}}} - \frac{2}{\bar{X}_n f_{\text{avg}}}$$

- This relates the extent of reaction and degree of polymerization to the average functionality in the system.
- The gel point is where $\bar{X}_n = \infty$. Thus, the **critical extent of the reaction** p_c when gelation occurs is

$$p_c = \frac{2}{f_{\text{avg}}}$$

- ...
- When the two functional groups are not at stoichiometry, then the average functionality of the molecules is twice that of the amount of the functional group not in excess divided by the number of molecules, i.e., the extent of crosslinking (if it occurs) depends on the deficient functionality.
- Example: *picture of glycerol and phthalic acid*.
 - ...
- Extension to nonstoichiometric reactant mixtures.
- The average functionality of a system containing more than two monomers can be calculated in a similar manner.
- Consider a three component system...
- Experimental gel points.
 - The Carothers (and statistical theoretical approaches not covered here) differ in their predictions of extent of reaction, p_c .
 - The gel point is usually determined experimentally as the point in the reaction at which the mixture loses fluidity (as indicated by the failure of bubbles to rise).
 - The data shows that gelation usually happens a bit before the Carothers prediction and after the statistical prediction.
 - ...

9.2 ???

- 2/29: • I was at KHS Immersion Weekend.