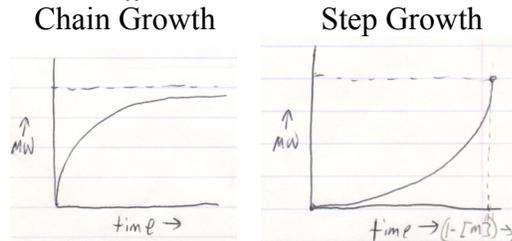


CME 300 Properties of Materials

Homework 7 November 8, 2011

- 1) Show the behavior of molecular weight (number average) as a function of time in step growth polymerization and chain growth polymerization. Explain why these two behaviors differ.



In chain growth a few chains grow initially with a linear dependence in time. As the monomer concentration is depleted the chains grow at a lower rate. In step growth monomers are converted to dimers/trimers etc. immediately. To get high molecular weight the extent of reaction must approach 100%.

The two behaviors differ because chain growth polymerization is based on addition of a single mer unit to the end of a growing chain while step growth polymerization is based on the addition of oligomers to each other similar to the growth of dust particles in a cluster-cluster growth process.

- 2) For the interfacial polymerization of nylon is the behavior described in question 1 followed? Why?

In class we polymerized nylon using interfacial polymerization by extracting a nylon fiber from the interface between an aqueous solution containing a diamine and an oleophilic solution containing a diacid chloride. The reaction was driven to completion by removal of the polymer film so there was a physical means to drive the reaction to completion. The aqueous solution also had NaOH added to remove HCl and further drive the reaction towards completion. The reaction didn't follow the scheme given in question 1 because interfacial polymerization changes the reaction kinetics and because drawing off the polymer serves to also alter the reaction kinetics.

- 3) The synthesis of polydimethylsiloxane by ring opening polymerization has some features of chain growth polymerization and some features of step growth polymerization. Explain this.

PDMS forms from ring opening polymerization so that there are essentially oligomers adding to growing chains rather than monomers adding so this is similar to step growth. There are no condensation products and the reaction kinetics are basically those of chain growth polymerization. Synthesis of PDMS from dichloro dimethoxy silane catalyzed by water proceeds with the kinetics of a step growth polymerization and there is a condensation product of HCl.

4) Polycarbonate is synthesized by a reaction of bisphenol-A and phosgene. Explain the hazards associated with these two organic compounds. Does polycarbonate display any hazards? For a condensation reaction do you expect residual monomer in a polycarbonate polymer?

Form the Wikipedia page on Bisphenol-A:

“Bisphenol A is an [endocrine disruptor](#), which can mimic the body's own [hormones](#) and may lead to negative health effects.^{[27][28][29][30]} Early development appears to be the period of greatest sensitivity to its effects,^[31] and some studies have linked prenatal exposure to later neurological difficulties. Regulatory bodies have determined safety levels for humans, but those safety levels are currently being questioned or under review as a result of new scientific studies.^{[32][33]} A 2011 study that investigated the number of chemicals pregnant women are exposed to in the U.S. found BPA in 96% of women.^[34]”

There are 3 more pages on the health effects of BPA.

Wikipedia:

Phosgene is an insidious poison as the odor may not be noticed and symptoms may be slow to appear.^[15] Phosgene can be detected at 0.4 ppm, which is four times the [Threshold Limit Value](#). Its high [toxicity](#) arises from the action of the phosgene on the [proteins](#) in the pulmonary [alveoli](#), which are the site of gas exchange: their damage disrupts the [blood-air barrier](#), causing suffocation. It reacts with the [amines](#) of the proteins, causing crosslinking via formation of [urea](#)-like linkages, in accord with the reactions discussed above. Phosgene detection badges are worn by those at risk of exposure.^[3]

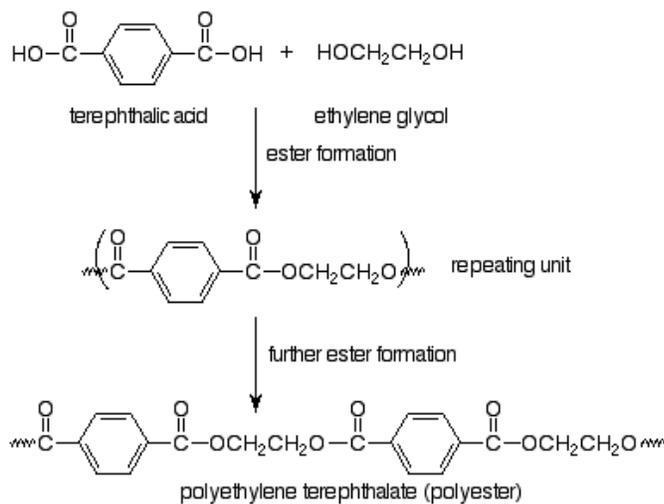
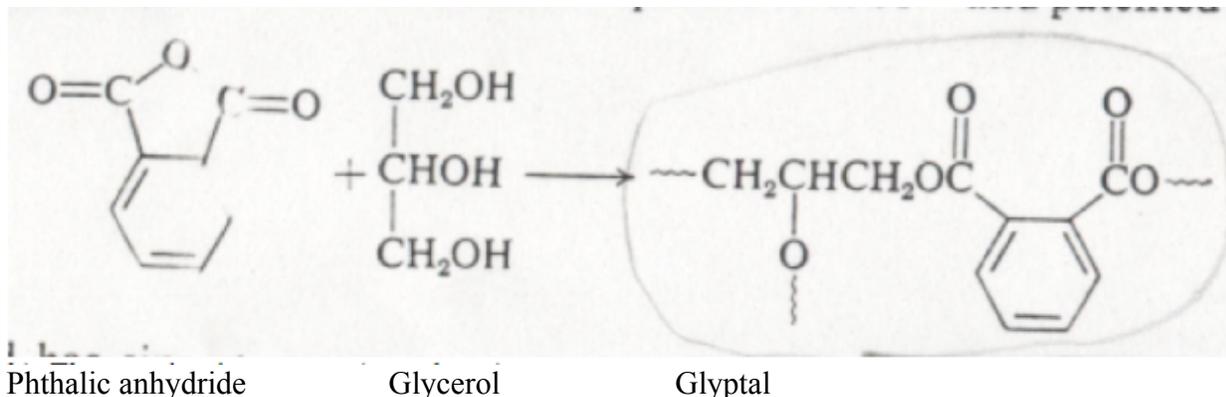
And

Following the extensive use of phosgene gas in combat during [World War I](#), it was stockpiled by various countries as part of their secret chemical weapons programs.^{[10][11][12]}

Phosgene was then only frequently used by the [Imperial Japanese Army](#) against the Chinese during the [Second Sino-Japanese War](#).^[13] Gas weapons, such as phosgene, were produced by [Unit 731](#) and authorized by specific orders given by Hirohito ([Emperor Showa](#)) himself, transmitted by the [chief of staff of the army](#). For example, the Emperor authorized the use of toxic gas on 375 separate occasions during the [battle of Wuhan](#) from August to October 1938.^[14]

Luckily, the phosgene and bisphenol-A are immediately consumed and converted into polycarbonate at early stages of a condensation reaction if things go as planned. Exposure to BPA is mostly from PVC bottles where it is used as an antioxidant in an epoxy where it is a reactant.

5) Give the reaction mechanism for glyptal and for polyethylene terephthalate (PET). Glyptal is a brittle glue like material while PET is the material used to make water bottles. From the molecular structure and functionality explain why these two polymers have different mechanical properties.



Glyptal has a more rigid chain structure because the ortho aromatic substitution can not as easily rotate at the $-O-$ bonds since it is asymmetric. The higher chain flexibility of PET makes the polymer more pliable and less rigid. The higher functionality of glyptal leads to a closely knit network structure while PET is a linear chain. Glyptal is a thermoset resin since it can not be made into a melt by heating. PET is a thermoplastic and it can be injection molded, blow molded, extruded into a fiber or sheet. Glyptal is more or less limited to use as a glue or wood fiber binder.

- 6) Explain what percolation is for a condensation reaction between trifunctional and bifunctional monomers. How can the extent of reaction at percolation, p_c , be determined analytically? Explain how this could be determined in a computer simulation. Explain how this could be determined in an experiment, i.e. what physical property might indicate that percolation had occurred.

Percolation occurs when the reactants have reacted to an extent that there is a pathway across the sample through chemical bonds. For a reaction between trifunctional and bifunctional monomers percolation occurs at 83% conversion following the Carother's equation,

Example
for $2 \text{ A-A} + 3 \text{ B-B}$

$f_{avg} = \frac{2(6)}{5} = 2.4$

$p_c = \frac{2}{2.4} = 83\%$

(Handwritten notes: "Hand groups (or bond groups)" pointing to the 6 in the numerator, and "Molecules" pointing to the 5 in the denominator.)

This can be determined analytically by calculating the point at which the number average molecular weight reached infinity, $p = 2/f_{avg}$

N_0 = initial number of molecules and N = the number of molecules at extent of reaction p .

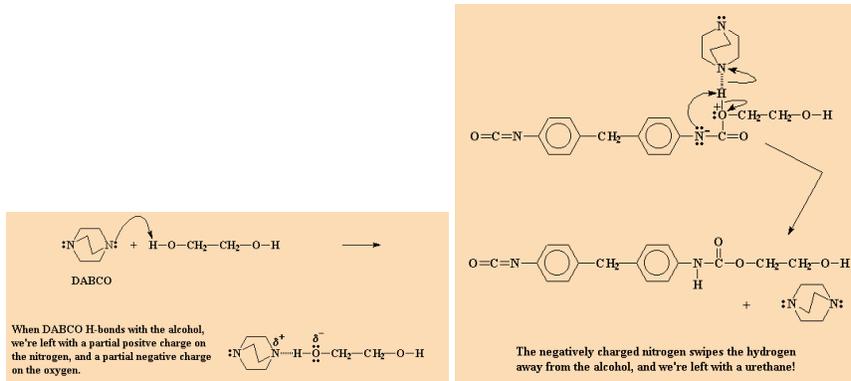
The extent of reaction, $p = 2(N_0 - N)/(N_0 f_{avg})$ since $N_0 f_{avg} (p/2) =$ number of molecules reacted $= (N_0 - N)$. It is $p/2$ since each reacted site involves two units joining. The number average molecular weight is N_0/N so $p = 2(N_0 - N)/(N_0 f_{avg}) = (2 - 2/M_n)/f_{avg}$ and when $M_n \Rightarrow \infty$, $p_c = 2/f_{avg}$.

In a computer simulation you would first check in the vertical direction if you have an occupied site, then go to the next layer to check for an occupied site, if yes then you would continue on until no occupied sites were found testing each possible path. This would be used to identify clusters. If one of these clusters reached the opposite side then percolation would have occurred in the vertical direction. You would need to repeat this for the horizontal direction.

Experimentally, the percolation threshold is found at the gel point where the viscosity goes to infinity.

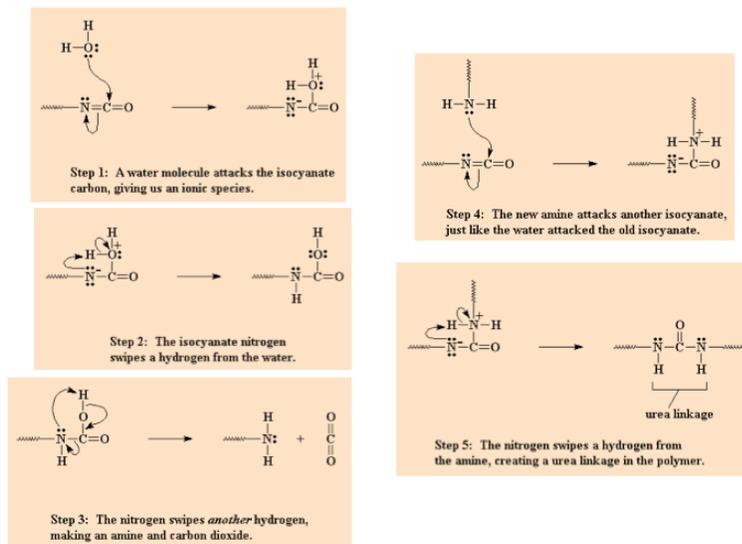
- 7) Why is polyurethane used for furniture finishes? Show the chemical reaction and explain what feature is important to this application.

Polyurethane is used for furniture finishes because it produces a hard and tough material with no byproduct from the step growth reaction. Also, the polyurethane reaction is extremely flexible through manipulation of the chemical composition of the diisocyanate and diol. The reaction is shown below:



There is no condensation byproduct in this reaction.

8) *Why is polyurethane used to make foam? Show what modification of the chemical reaction is needed to produce a foam. How is polystyrene foam made (styrofoam)?*



Reaction of the isocyanate with water produces CO_2 and a urea linkage in the polymer.

9) *What is an aerogel and how is it made? Explain how sol-gel chemistry is used to make an aerogel.*

From Wikipedia:

Aerogel is a **manufactured** material with the lowest bulk **density** of any known porous **solid**.^[1] It is derived from a **gel** in which the **liquid** component of the gel has been replaced with a **gas**. The result is an extremely low-density solid, with a notable effectiveness as a **thermal insulator**. It is nicknamed **frozen smoke**,^[2] **solid smoke**, **solid air** or **blue smoke** due to its **translucent** nature and the way **light scatters** in the material; however, it feels like **expanded polystyrene (styrofoam)** to the touch.

Aerogel was first created by **Samuel Stephens Kistler** in 1931, as a result of a bet with Charles Learned over who could replace the liquid in 'jellies' with gas without causing shrinkage.^{[3][4]}

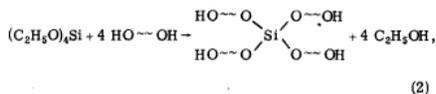
Aerogels are produced by extracting the liquid component of a gel through **supercritical drying**. This allows the liquid to be slowly drawn off without causing the solid matrix in the gel to collapse from **capillary action**, as would happen with conventional **evaporation**. The first aerogels were produced from **silica gels**. Kistler's later work involved aerogels based on **alumina**, **chromia** and **tin oxide**. **Carbon** aerogels were first developed in the late 1980s.^[5]

Silica aerogels (the normal kind) are made by a sol-gel reaction of TMOS or TEOS to produce a SiO₂ network in alcohol. This is solvent exchanged with supercritical CO₂ and this is removed under supercritical conditions to make an aerogel. Under supercritical conditions a “liquid” does not display surface tension so drying can be achieved without pore collapse. (Normal drying would produce a powder.)

10) *Crosslinking of hydroxyl terminated polydimethylsiloxane (PDMS) involves a sol-gel reaction. Sketch how this reaction proceeds.*

End-linking of the chains

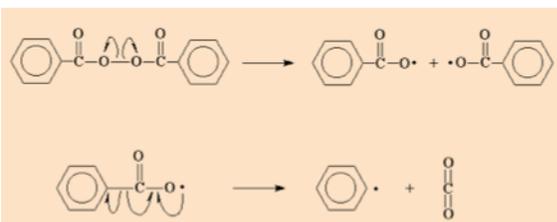
Networks were prepared from each of the six fractions and from unfractionated sample A, using the reaction³⁶



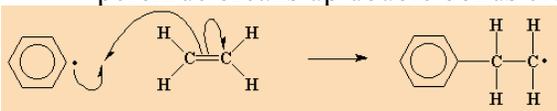
where HO---OH represents the hydroxyl-terminated PDMS chains. (Sample B was excluded because of its

From J. E. Mark, J.L. Sullivan *J. Chem. Phys.*, Vol. 66, No. 3, 1 February 1977

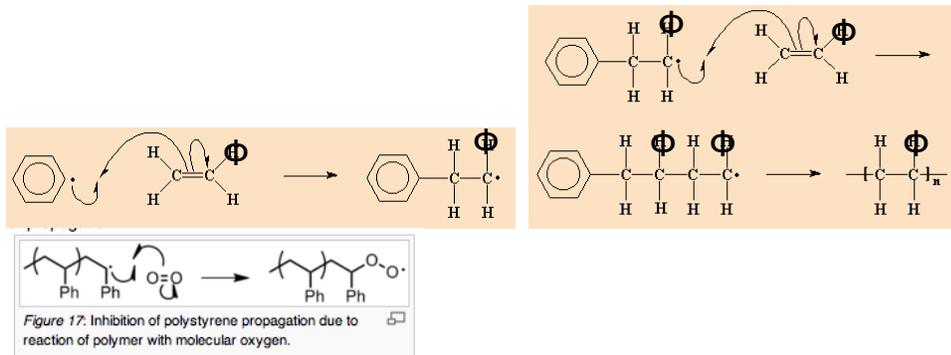
11) *Benzoyl peroxide is used in dishwashing detergents to remove tomato stains from plastic dishes. Explain how this works and what hazards might be involved in the use of benzoyl peroxide. How is benzoyl peroxide used in polymerization reactions?*



Benzoyl peroxide will decompose into a free radical that will attack double bonds in the proteins responsible for tomato stains. This will breakup the molecules. The hazard is that benzoyl peroxide is an explosive as noted on Wikipedia. (It might be a questionable idea to wash dishes with an explosive.) Benzoyl peroxide breaks up double bonds creating a propagating free radical in polymerizations.



12) Sketch the initiation, propagation and termination reactions for the synthesis of polystyrene using free radical chain polymerization.



13) Why is anionic polymerization used to make SBR rubber for tires?

With living anionic polymerization the styrene reaction can be conducted first then, when the styrene monomer is completely reacted, you can add butadiene monomer and continue the living reaction to make a block of styrene and a block of butadiene. You can also add styrene again at the end to make SBS blocks and many other distributions of blocks.

14) What is the advantage of Ziegler-Natta polymerization compared to free radical polymerization? Is Ziegler-Natta polymerization an example of chain growth polymerization? Explain your answer.

Free radical polymerization has no stereo selectivity so you cannot make tactic polymer using free radical polymerization. The termination steps of free radical polymerization include branching reactions.

Free radical polymerization makes branches in polyethylene due to the termination mechanisms. This does not occur with ZN polymerization.

ZN polymerization can lead to a tighter control over the molecular weight distribution.

Polypropylene cannot be synthesized using free radical polymerization since you cannot make a stable propagating species with propylene.

ZN polymerization is an example of chain growth since monomers are added one at a time to a growing chain that is tethered to an active catalyst site.