

050929 Quiz 1 Introduction to Polymers

- 1) In class we discussed a hierarchical categorization of the terms: macromolecule, polymer and plastics, in that plastics are polymers and macromolecules and polymers are macromolecules; but all macromolecules are not polymers and all polymers are not plastics.
 - a) Give an example of a macromolecule that is not a polymer.
 - b) Give an example of a polymer that is not a plastic.
 - c) Define polymer.
 - d) Define plastic.
 - e) Define macromolecule.

- 2) In class we observed a simulation of a small polymer chain of 40 flexible steps. The chain was observed to explore configurational space.
 - a) Explain what the phrase "explore configurational space" means.
 - b) Consider the two ends of the chain to be tethered with a separation distance of about 6 extended steps. If temperature were increased would the chain ends push apart or pull together the tether points? Explain why.
 - c) If one chain end is fixed in Cartesian space at $x = 0$, what are the limits on the x-axis for the other chain end as it explores configurational space?
 - d) What is the average value of the position on the x-axis?

- 3) Polymer melts are processed at high rates of strain, $\frac{d\gamma}{dt}$, in an extruder, injection molder, or calander.
 - a) Sketch a typical plot of polymer viscosity versus rate of strain on a log-log plot showing the power-law region and the Newtonian plateau at low rates of strain.
 - b) Explain using this plot why polymers are processed at high rates of strain.
 - c) Using your own words propose a molecular model that could explain shear thinning in polymers.
 - d) Sketch a plot of log viscosity versus log strain rate for a series of polymers of different molecular weight showing the effect of molecular weight on this plot.

- 4) The zero shear rate viscosity, η_0 , displays power-law behavior in molecular weight in two distinct and universal regimes.
 - a) Sketch log viscosity versus log of molecular weight showing these two regimes and give the slope of the curve in these two regimes.
 - b) Explain why two regimes are observed
 - c) How does this plot relate to the definition of a plastic given in question 1?
 - d) Why would similar behavior be seen in viscosity versus concentration for high molecular weight polymer solutions?

ANSWERS: 050929 Quiz 1 Introduction to Polymers

1) a) A protein in its native (folded) state is not a polymer because its structure does not explore configurational space.

b) A low molecular weight polymer below the entanglement molecular weight is a polymer but not a plastic since it does not display entanglements.

c) Polymer is usually a long chain molecule that displays thermal equilibration through exploration of configurational space. Polymers do not display a fixed size but show a statistical size, that is they are constantly changing size as they equilibrate thermally.

d) Plastic is a polymer that displays chain entanglements. Plastics are polymers with molecular weights larger than the entanglement molecular weight.

e) A macromolecule is a large molecule, probably greater than about 1000 Daltons.

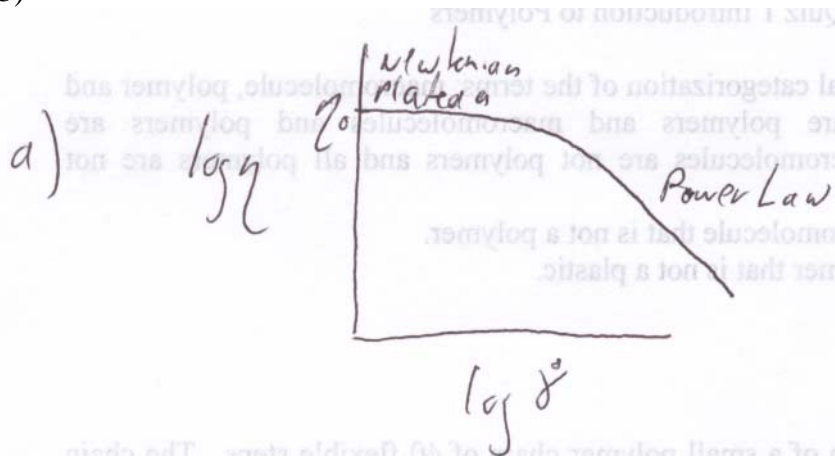
2) a) Explore configurational space means that the chain structure is constantly changing and the sum of energetic interactions associated with changes in bond rotational angle and steric interaction between chain units is compared/equilibrated with the available thermal energy, kT .

b) When the temperature increases the thermal motion of the chain units increases. This results in longer mean free paths for each unit which translates to a tightening of the ends of the chain, i.e. the chain ends are pulled together at higher temperatures. (You can consider that this is as if you had an ideal gas and could couple a linear path of the atoms together into a chain.)

c) The limits for the other chain end are -40 steps and + 40 steps for the fully extended chain in two directions.

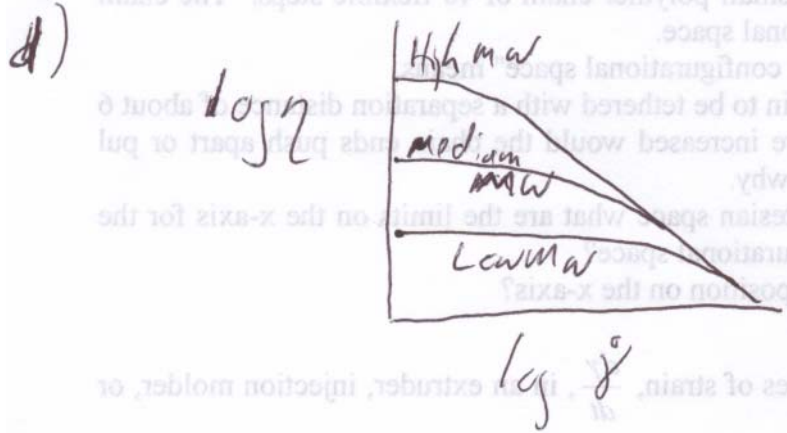
d) The average value of the position on the x-axis is 0. This means that the first moment or mean is useless to describe chain size.

3)

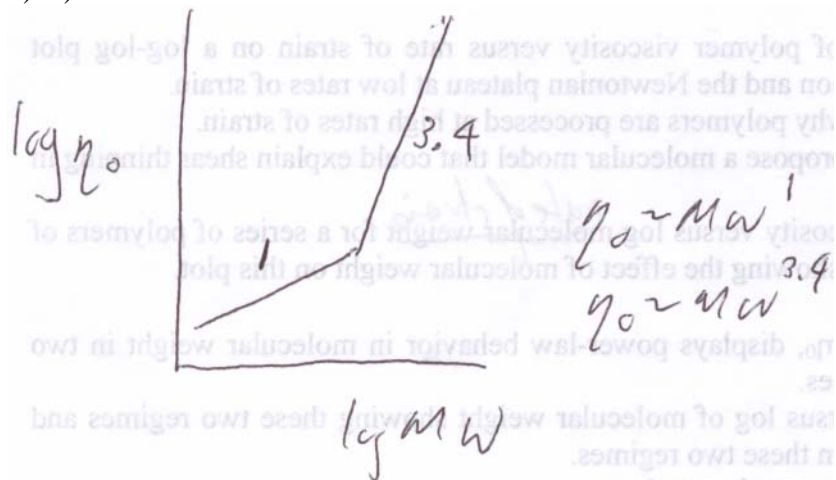


b) At high rates of strain the viscosity drops so it becomes easier to process. This is called shear thinning.

c) In class we discussed that at high rates of strain we are effectively detangling the entanglements and lowering the viscosity. The higher the rate of strain the larger is this disentanglement. You could also consider that the chains straighten out and become like uncooked spaghetti which will flow easily out of the box, for instance.



4) a)

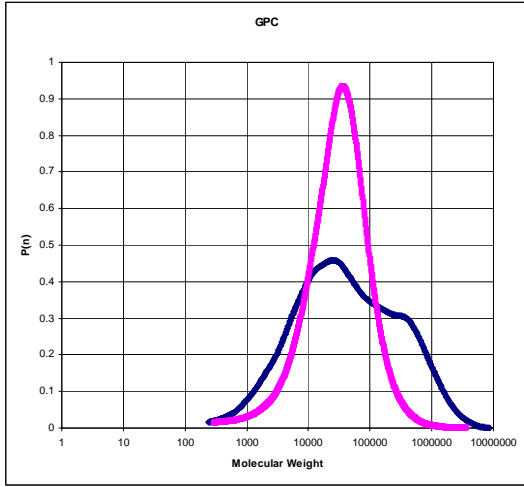


b) Below the entanglement molecular weight, increasing molecular weight is additive, that is viscosity is linear in molecular weight. Above the entanglement molecular weight there is a much stronger dependence on molecular weight.

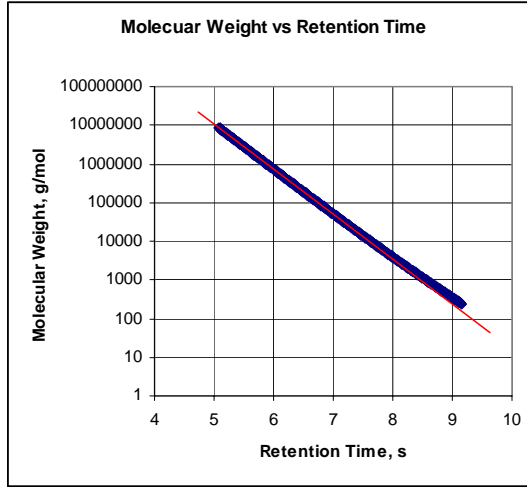
c) Plastics are found to the right of the entanglement molecular weight. Below this molecular weight are found high molecular weight organics.

d) The behavior seen in "a" is related to the presence or absence of entanglements. Entanglements can be removed by diluting the polymer chains in direct analogy to increasing the molecular weight.

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(a)



(b)

1) In Plot "(a)", Pick 5 or 6 equally spaced points in molecular weight including the peak position(s) for the *unimodal* curve and make a table of P(n) and n. Use this table to calculate a) the mean (number average, n_1), b) second moment, n_2 , c) weight average, n_w , d) the polydispersity index, PDI, and e) the standard deviation, σ , about the mean.

2) a) What is *retention time* in Plot "(b)". (Explain by describing the GPC measurement.)
 b) Gel Permeation Chromatography is also called Size Exclusion Chromatography (SEC) and High Pressure Liquid Chromatography (HPLC). Explain the origin of the terms GPC, SEC and HPLC by explaining how the GPC works.

3) Figure "(b)", above, indicates a relationship between Molecular Weight and Retention time.
 a) Propose a function for the relationship between n and retention time, t , for the line in plot "(b)".
 b) How many unknown parameters must be determined to use the function you have proposed?
 c) Explain how *low-PDI* samples are used to obtain a t to n conversion function.
 d) How many *low-PDI* standard samples are needed for a calibration master curve in this case?

4) The 3D-Gaussian function describes the probability of a chain of length N having an end-to-end distance R,

$$P_{Gaussian}(R) = \left(\frac{3}{2\pi\sigma^2} \right)^{3/2} e^{-\frac{3(R-\langle R \rangle)^2}{2\sigma^2}} \quad (1)$$

where $\sigma = N^{1/2} l$ and l is the chain's step size.

- Equation (1) is symmetric about the mean $\langle R \rangle$. Explain why.
- What is the effect of increasing σ on the distribution curve? (You may want to sketch $P(R)$ versus R for variable σ to show this.)
- What effect does the term in brackets (first term after "=") have on the shape of the distribution curve?
- How would you calculate $\langle R^2 \rangle$ in general? (Give an equation.)
- What is the value of $\langle R^2 \rangle$ (in terms of N and l) using this equation (1)?

ANSWERS: 051006 Quiz 2 Introduction to Polymers

1) Unimodal Curve

n	P(n)	nP(n)	n ² P(n)
10 ³	0.02	20	20,000
10 ⁴	0.4	4000	4 x 10 ⁷
5x10 ⁴	0.92	46,000	2.3 x 10 ⁹
10 ⁵	0.5	50,000	5 x 10 ⁹
5x10 ⁵	0.08	40,000	2 x 10 ¹⁰
Sum	1.92	140,020	2.734 x 10 ¹⁰

- a) $n_1 = 140,020/1.92 = 72,927 \text{ g/mol}$
 b) $n_2 = 2.734 \times 10^{10}/1.92 = 1.42 \times 10^{10} \text{ (g/mol)}^2$
 c) $n_w = 1.42 \times 10^{10}/72,927 = 195,300 \text{ g/mol}$
 d) $PDI = 195,300/72,927 = 2.677$
 e) $\sigma = 72,927 \text{ g/mol} (2.677-1)^{1/2} = 94,450 \text{ g/mol}$

2) a) GPC involves pumping under high pressure through a gel in a tubular column a dilute polymer solution. The effluent is measured, for index of refraction for instance, as a function of time after injection of the solution. This time is the retention time.

b) This is termed Gel Permeation Chromatography because you pump a solution through a gel and the solution permeates the gel. It is called Size Exclusion Chromatography because the largest molecules exit first, they are excluded from the gel due to size. It is called High Pressure Liquid Chromatography to distinguish it from gel chromatography used to separate DNA and Proteins. The instrument uses a high pressure pump that distinguishes the technique from plate chromatography using gels.

3) a) You should notice that the molecular weight scale is a log-scale (from last week) while the retention time is on a linear scale. Then $\ln(n) \sim -t$. A reasonable function might be,

$$\ln(n) = K_2 - K_1 t \quad \text{or} \quad n = \exp(K_2 - K_1 t) = \exp(K_2) \exp(-K_1 t) = K_3 \exp(-K_1 t)$$

n displays an exponential decay in time.

- b) Two unknowns, K_3 and K_1 .
 c) If you run *low-PDI* samples the constants K_1 and K_2 can be determined so you can construct a conversion function between retention time and molecular weight.
 d) For two constants you would require two standards so the number of unknowns and number of equations (one per standard) are equal.

4) a) It is symmetric about $\langle R \rangle$ because the term $(R - \langle R \rangle)$ is squared so the sign of this term doesn't matter. This is true for all even powers but is not true for any odd power.

b) Increasing σ broadens the distribution function and lowers the peak value.

c) The first term has no effect on the shape, it re-scales the y axis.

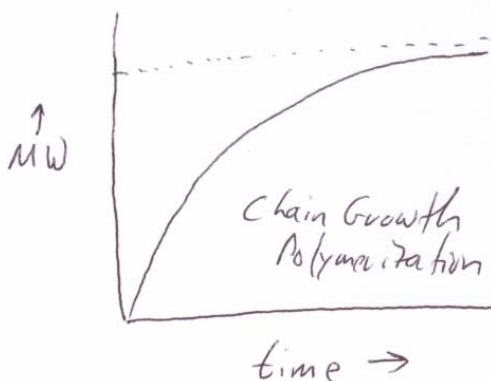
d) $\langle R^2 \rangle = \frac{\sum (R - \langle R \rangle)^2}{N - 1}$ or $\langle R^2 \rangle = \frac{\int P(R)(R - \langle R \rangle)^2 dR}{\int P(R)dR}$

e) $\langle R^2 \rangle = Nl^2$ so $R \sim N^{1/2}$

051013 Quiz 3 Introduction to Polymers

This week we saw a demonstration of nylon synthesis, we generally discussed step-growth (or condensation) and chain-growth (or addition) polymerization and went through a list of about 30 common polymers and copolymers including their chemical structure.

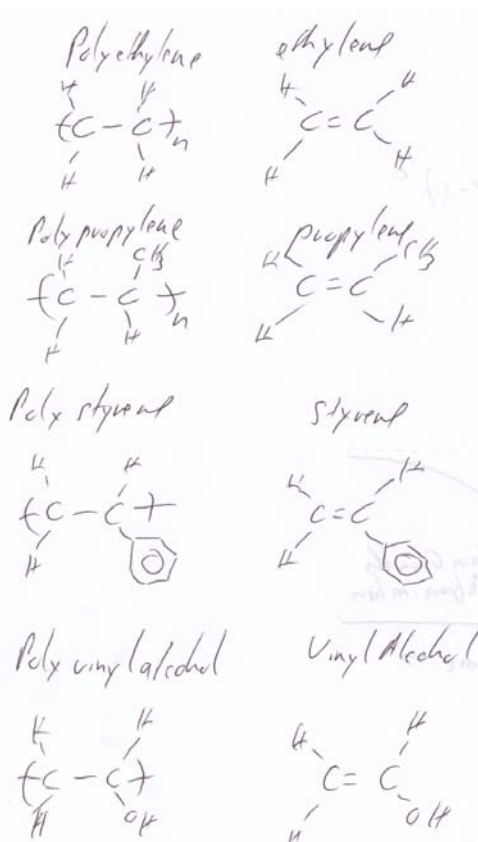
- 1) Vinyl polymers are generally made by addition polymerization.
 - a) Give 4 vinyl polymers and their chemical structure.
 - b) Give the 4 monomers used for the addition polymerization and their chemical structure.
 - c) By comparing the monomer to the polymer repeat unit explain why these polymers are not made by condensation (step) polymerization.
- 2) Nylon is commonly made by step-growth polymerization. In class we made nylon 6,10.
 - a) Give the structure of Nylon 6,10 circling the chemical group that defines this polymer as nylon.
 - b) Draw the structure of the two chemicals that were used in class to make nylon 6,10.
 - c) Explain why this is a condensation polymerization and what molecule condenses (is a byproduct). What is added to the reaction mixture to neutralize this molecule?
 - d) How is this reaction driven to completion and why is driving the reaction to completion important to condensation polymerizations?
- 3) The following three statements are true of Chain Growth (Addition) Polymerization. Make 3 contradictory statements for Step Growth Polymerization (e.g. the Nylon reaction from class).
 - a) Mechanism: Initiation step followed by Propagation steps followed by a Termination step.
 - b) Monomer Concentration: Monomer is left even at the end of the reaction.
 - c) Polymer Molecular Weight Graph:



- 4)
 - a) Give a function that describes the relationship between n_1 and the extent of reaction p for a step growth polymerization (this is called the "Most Probable Distribution").
 - b) Explain how this function is obtained by i) writing an expression for the extent of reaction, p , in terms of the original number of molecules N_0 and the number of molecules at a given time of reaction, N ; ii) writing an expression for n_1 in terms of N and N_0 . iii) Relating n_1 and p .
 - c) n_w for a bifunctional monomer (2 reactive atoms) made by step-growth is, $n_w = (1+p)/(1-p)$. What is the polydispersity index (PDI) for a step growth polymerization that has fully reacted, $p = 1$? What is the standard deviation, σ , for this polymer in terms of n_1 ?
 - d) The *Most Probable* distribution is also found for a randomly degraded (cleaved) polymer, regardless of initial distribution. Can you explain why this might be the case? (Hypothesize what the similarity is between random cleavage and step growth polymerization.)

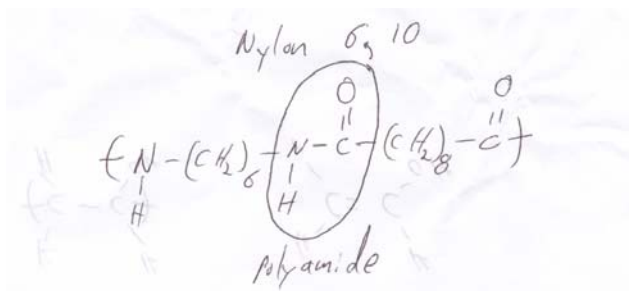
ANSWERS: 051013 Quiz 3 Introduction to Polymers

1) a&b)

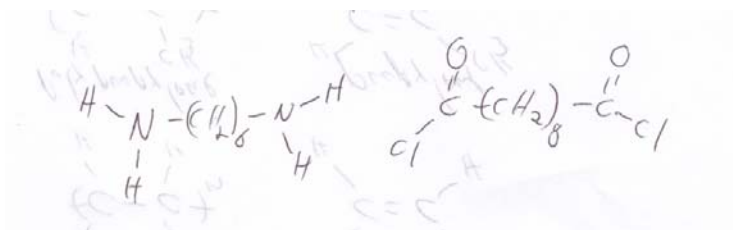


c) The polymers are not made by condensation (step-growth) because no mass is lost to a byproduct in the polymerization reaction. (monomer and repeat unit have the same molar mass).

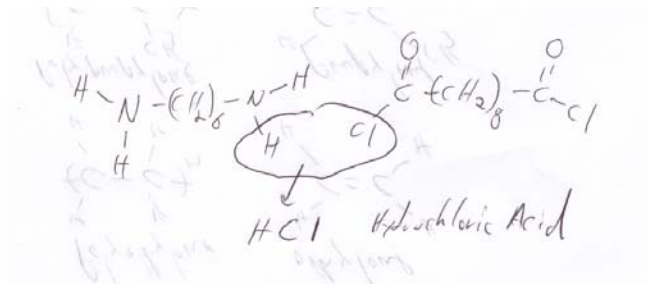
2). a)



b)



c) It is a condensation reaction because HCl is condensed (appears as a byproduct) during the polymerization. HCl is neutralized by NaOH which is added to the aqueous phase to produce water and NaCl salt.

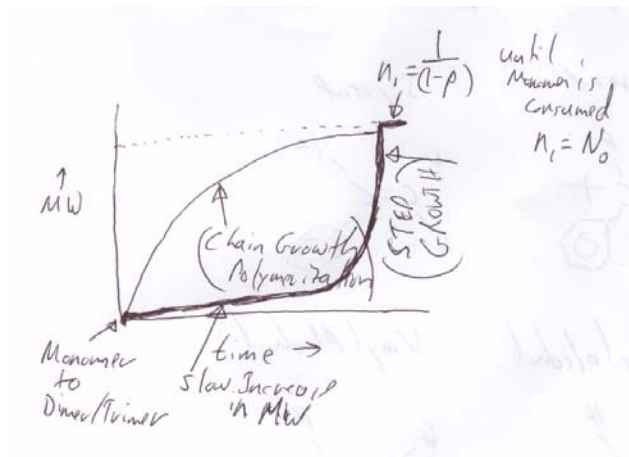


d) Removing the product (Nylon) and byproduct HCl drives the reaction to completion at the interface between the organic and aqueous phase.

3) a) There is only one reaction in step growth, the reaction terminates when the last condensation occurs.

b) Monomer in the step growth reaction is consumed almost immediately as it is transformed into dimers and trimers.

c)



4) a) $n_1 = 1/(1-p)$

b) i) The extent of reaction is given by $p = 1 - N/N_0$

ii) $n_1 = N_0/N$

iii) $p = 1 - 1/n_1$ or $n_1 = 1/(1-p)$

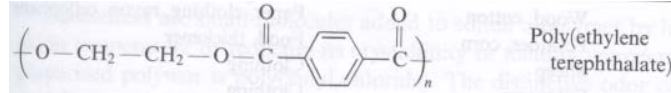
c) $\text{PDI} = 2$ and $\sigma = n_1$

d) In random cleavage the largest chains are more likely to break by a factor of $(N_{\text{large}}/N_{\text{small}})$. For step polymerization smaller chains are more likely to react on a per mass basis by the same factor since the number density of reactive chain ends is $2/N$. The same distribution results from chain cleavage and step growth because the same probability factor governs both reactions. (This is a difficult question intended as a test of your reasoning using what we covered in class.)

051020 Quiz 4 Introduction to Polymers (Chemistry)

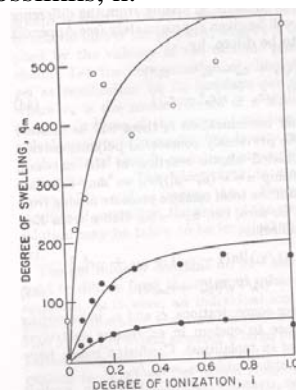
This week we looked at synthesis of a polyester network polymer "glyptal", Carother and Flory/Stockmayer (Miller/Macosko)'s interpretation of network formation and the swelling of a hydrogel (sodium polyacrylate).

- 1) PET or PETE is a polyester. Propose a synthesis for PETE based on the synthesis of glyptal in class.



For your synthesis propose

- i) monomer(s),
 - ii) reaction conditions (temperature etc.) and
 - iii) suggest the PDI that might result from this synthesis.
 - iv) How might you qualitatively monitor the extent of reaction, p , in this system?
- 2) i) If a network polymer was desired what monomer could be added to your PET synthesis?
ii) What would be the average functionality, $\langle f_{\text{avg}} \rangle$ for this system (write an equation)?
iii) Using the Carothers equation what would be the critical extent of reaction based on your equation for average functionality?
- 3) i) How would you measure/observe when the system forms a gel? (Define a gel) That is how did we determine the system was a gel in class? (Sketch a plot of this versus reaction time).
ii) Give three definitions of a gel based on molecular weight and topology (network structure). These are due to Carothers; Miller/Macosko; and Flory/Stockmayer.
iii) Percolation is a feature of many disordered, complex systems. Percolation was first seriously considered in polymers by Flory and Stockmayer. Explain in your own terms what "percolation of a network" means .
- 4) The hydrogel we observed in class can swell more than 100 times ($q_m = 10,000!$) its volume with water. The plot below, from Flory's first book, shows the swelling ratio of an early polyacrylic acid hydrogel as a function of the degree of ionization (ionized fraction) and molecular weight between crosslinks, n .

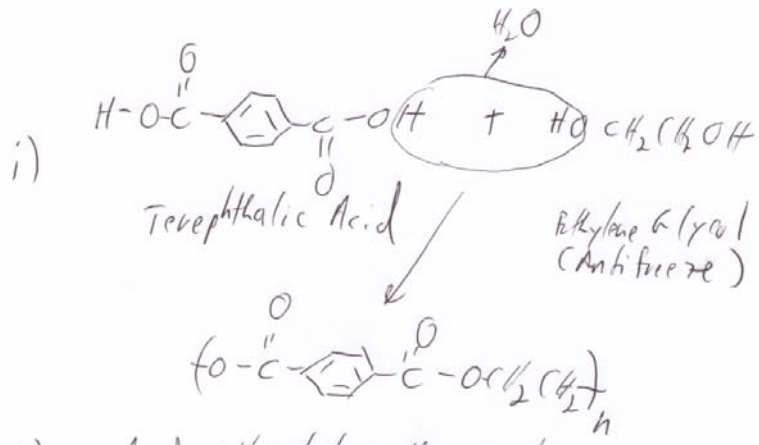


- i) Explain in your own words the behavior as a function of n (top curve is highest n).
- ii) Explain in your own words the behavior as a function of Degree of Ionization, i .
- iii) Guess at the reason for the plateau in swelling ratio.
- iv) Why does salt make the hydrogel deswell?

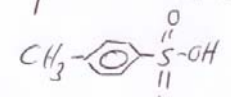
ANSWERS:

051020 Quiz 4 Introduction to Polymers (Chemistry)

1) i) You would use terephthalic acid and ethylene glycol in a condensation reaction,

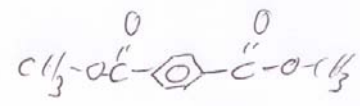


ii) Acid will catalyze this reaction
 (typically p-toluene sulfonic acid)



Raise Temperature to drive off water $T > 100^\circ\text{C}$

If you use



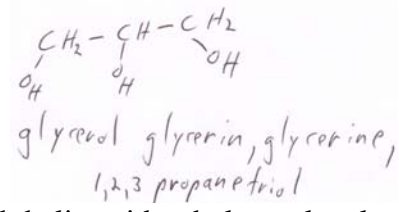
You make CH_3OH $T_{\text{boil}} = 65^\circ\text{C}$
 So it's easier to drive reaction
 (Methanol is toxic)

Typically 150°C

iii) PDI = 2 for condensation

iv) As the reaction proceeds water is produced and acid is consumed so the reaction could be monitored by the pH of the system.

2) i) Glycerol (glycerin) can be added to give branching.



ii) If the mole fractions of terephthalic acid, ethylene glycol and glycerin are A, B and C, then the average functionality is $\langle f_{\text{avg}} \rangle = 2(A+B) + 3C$

iii) $p_c = 2/\langle f_{\text{avg}} \rangle$. If C = 0.1 then $\langle f_{\text{avg}} \rangle = 2.1$ and $p_c = 0.95$.

3) i) The (low shear rate) viscosity becomes infinite for a gel as shown in Flory's Plot.

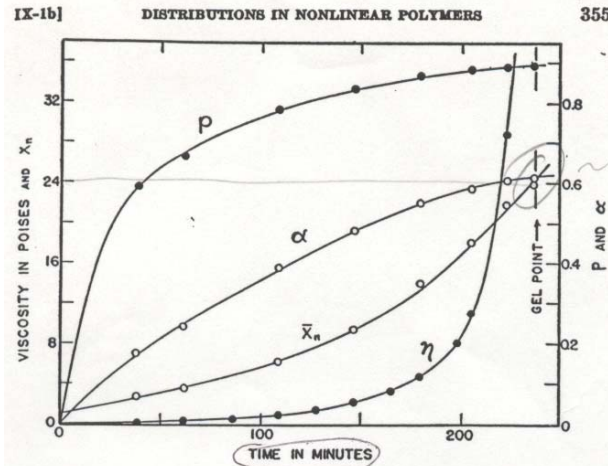


FIG. 62.—The course of a typical three-dimensional polyesterification.¹ The results shown are those for the third experiment reported in Table XXXI.

ii) Carothers: $n_1 \Rightarrow \text{infinity}$

Miller/Macosko: $n_w \Rightarrow \text{infinity}$

Flory/Stockmayer: $\alpha \Rightarrow 1$

where α is a way to measure when you have reached the percolation threshold, that is when the network connects across the sample. α is the average number of bonds a crosslink site sees in looking away from a networked chain.

iii) Percolation means that there is a connecting pathway across the system in 3d.

4) i) The functionality can be described by the Flory-Rehner equation:

$$\ln(1 - v_2) + v_2 + \chi v_2^2 = \frac{V_1}{n} \left[\frac{v_2}{2} - v_2^{1/3} \right] K_{\text{dangling chain}}$$

where n is the molecular weight between crosslinks, v_2 is $1/q_m$, χ is the interaction parameter and V_1 is the molar volume of the solvent. q increases with n because the elastic response of the network to swelling is smaller for longer chains, that is the single chain modulus or spring constant k_{spring} is proportional to kT/n . With a smaller elastic response the enthalpic attraction of ionic groups and water drives more swelling.

ii) The more ionic groups the stronger the enthalpic interaction and the greater the swelling.

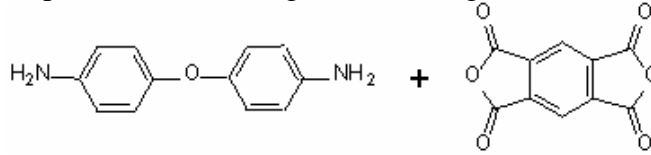
iii) Several reasons, the elastic response of the network is non-linear at high extensions, at high charging levels the charging is screened (as described by Debye) and the effect of addition of more charges is diminished, the Flory Rehner equation is non-linear.

iv) The addition of salt effectively blocks the ionic groups so salt reduces the average interaction parameter between the polymer and water.

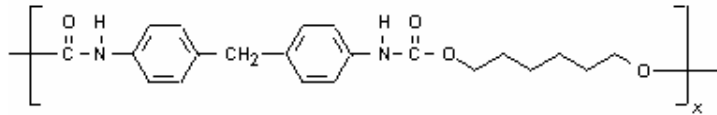
051027 Quiz 5 Introduction to Polymers (Chemistry)

1) Explain the statement "polyimide synthesis is like a double polyamide synthesis."

- a) Show the monomers and product for Nylon 6, 10
- b) Show a two step reaction involving the following monomers:

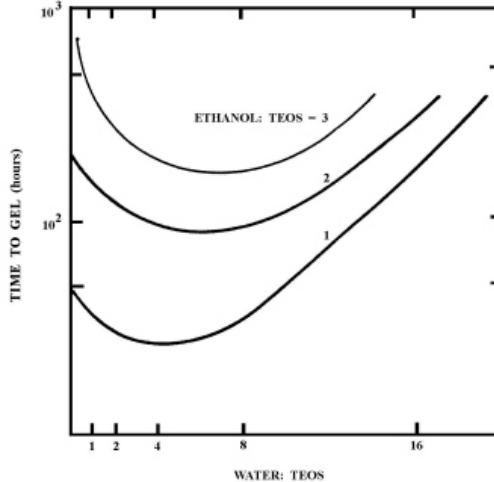


- c) Explain the relationship between part a and part b.
 - d) Why is the polymer made by this synthesis heat and flame resistant (speculate)?
- 2) a) Explain how the polyurethane shown below is a hybrid of a polyester and a polyamide.



- b) What monomers would be used to make this polymer?
 - c) What is the byproduct of this reaction?
 - d) Why might your answer to part "c" be important to a coating application?
- 3) Hydrolysis/condensation reactions are the basis for a wide range of ceramic and polymer synthesis reactions. Show how silica (SiO_2) is made from TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and water in a two step reaction.

- a) Sketch the chemical structure of the reactants and products.
- b) What catalyst is used in this reaction?
- c) What is a byproduct from this reaction?
- d) Explain the following graph from Mauritz's web page: (What is the role of Ethanol?)



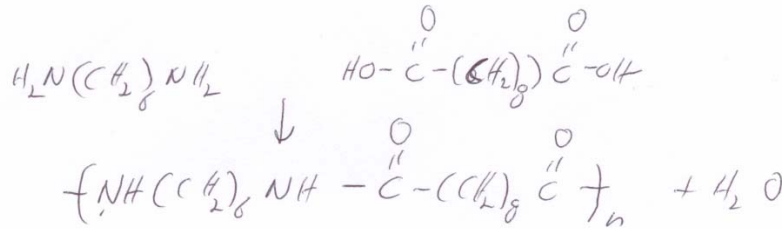
4) In class we crosslinked Hydroxyl terminated polydimethyl siloxane (PDMS) using TEOS.

- a) Sketch the crosslinking reaction mechanism between TEOS and PDMS.
- b) In addition to the rate of the hydrolysis/condensation reaction, what governs the rate of crosslinking for PDMS networks?
- c) What is the critical extent of reaction for this reaction to form a gel? (Stoichiometric)
- d) Would you use a pre-polymer above or below the entanglement molecular weight for this reaction? Why?

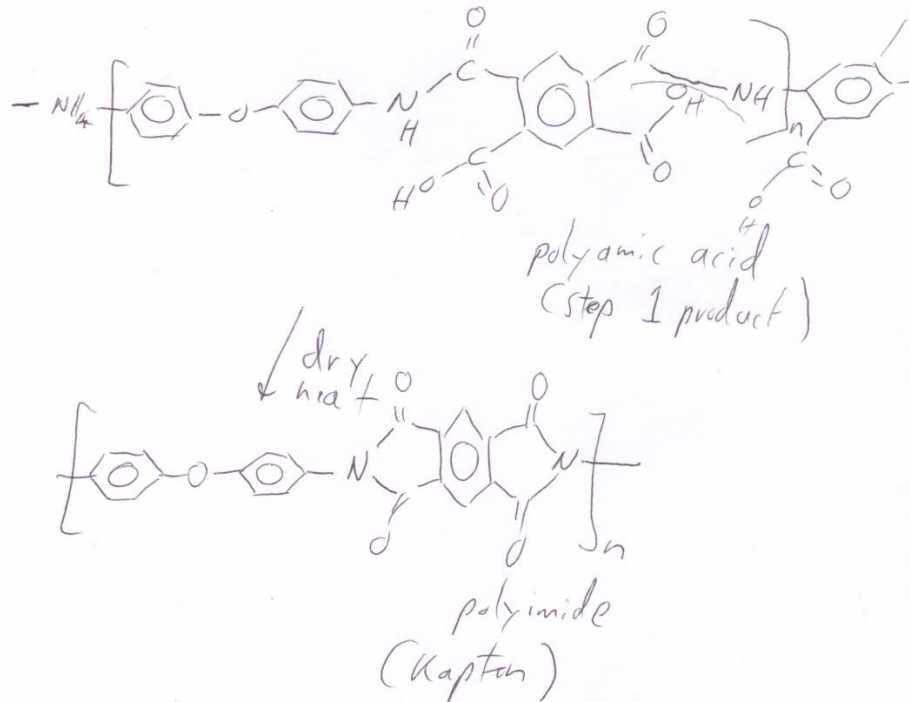
ANSWERS:

051027 Quiz 5 Introduction to Polymers (Chemistry)

1) a)



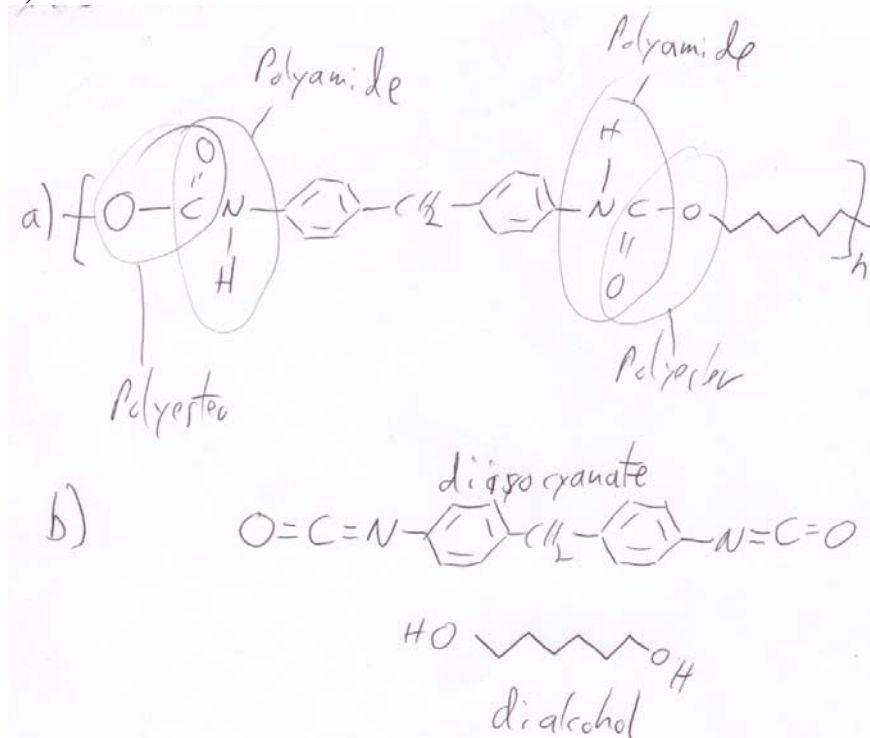
b)



c) Both involve condensation reaction of a diamine and a dicarboxylic acid or an anhydride. For the polyimide the reaction occurs twice.

d) There doesn't seem to be a clear answer to this in the literature. Basically, it is heat resistant because the aromatic ring structures are stable and the OC bond that would normally be easy to break is stabilized by the ability of the double aromatic rings to donate electrons. The imide structure has resonance structures where the double bonds switch around the triple ring structure. It is flame resistant because it makes a dense and copious ash. This is because the byproducts are solid for the most part and not gaseous. Solid byproducts because there is a lot of unsaturated carbon in the structure and not much hydrogen and oxygen. $\text{C}_{22}\text{O}_5\text{N}_2\text{H}_{10}$ so the combustion product is 5 H_2O (gas), 22 C (soot), 1 N_2 (gas), lots of soot. Some of the soot turns to CO_2 but probably not much.

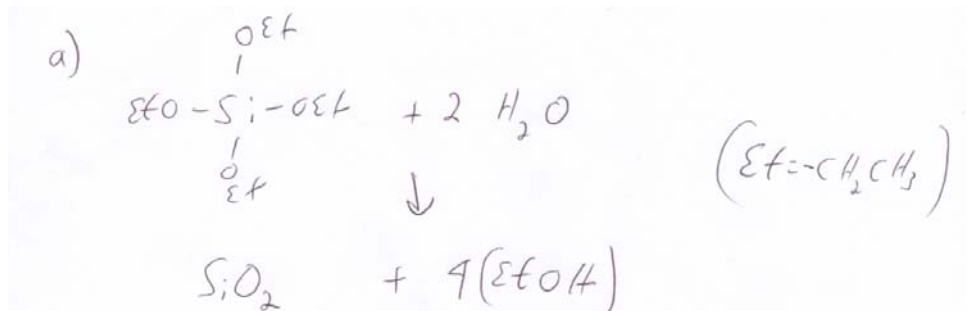
2)



c) There is no byproduct.

d) With no byproduct there is no solvent to phase separate and produce domains or flaws in a coating. The product does not need to dry after reaction.

3)

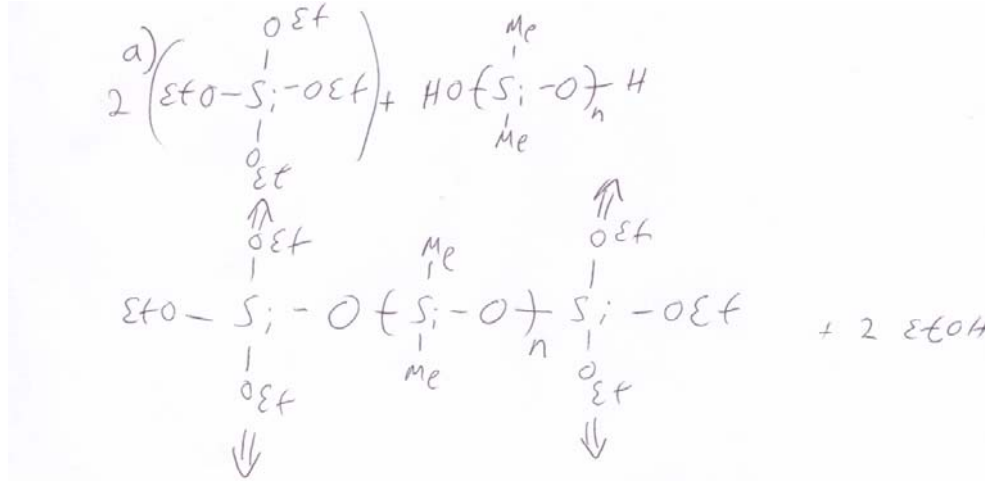


b) Acid or base can be used as a catalyst. The structure of the product is different for acid and base.

c) Ethanol.

d) TEOS and water don't mix. However, TEOS mixes in ethanol and water is miscible in ethanol (the latter is the basis of beer). So ethanol can be used to mix TEOS and water. The plot shows that the reaction of TEOS and water varies with the relative fraction of water to TEOS with a maximum rate between 4 and 8 for [Water]/[TEOS]. Stoichiometrically this ratio is 2 as noted above so more water than is used in the reaction is needed (water acts like a catalyst for the hydrolysis step). Adding more ethanol relative to TEOS at fixed TEOS water ratio decreases the reaction rate. This is primarily an issue of dilution of the reactive groups.

4)



b) Diffusion of TEOS and hydroxyl end-groups to the reaction site. This is governed by the viscosity of the reaction mixture. Transport becomes a problem for high molecular weight prepolymers.

c) $\langle f_{\text{avg}} \rangle = 2.67 = (2*2+1*4)/3$ so $p_c = 2/\langle f_{\text{avg}} \rangle = 0.75$

d) For a crosslinking reaction prepolymers well below the entanglement molecular weight are used to reduce the viscosity, increase the rate of reaction and make the material processable prior to crosslinking, so it can fill a mold for instance.

051103 Quiz 6 Introduction to Polymers (Chemistry)

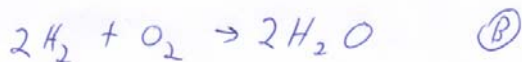
- 1) Methane (CH_4) or hydrogen (H_2) can be burned with oxygen (O_2).
 - a) Write a stoichiometric reaction for each of these with water and carbon dioxide as products.
 - b) What "order" is each of these reactions in oxygen? (First, second, third, fourth, etc. order)
 - c) Write an expression for the rate of combustion using methane and using hydrogen.
 - d) Which reaction would be more sensitive to the concentration of oxygen? (Sketch a plot of rate versus concentration of oxygen for both reactions on the same plot.)
 - e) Explain what the idea of order has to do with the probability of finding an ideal gas atom per volume of a reacting system such as a flame combustion process.

- 2) For free radical polymerization of polystyrene using benzoyl peroxide:
 - a) Write a stoichiometric expression for the three reactions involved in this chain polymerization.
 - b) Write an expression for the rate of reaction for each of the three reactions in terms of monomer concentration, initiator concentration and free radical concentration.
 - c) Sketch a plot of overall rate versus time and show where steady state occurs
 - d) How is steady state defined in terms of the rates listed in part b?
 - e) Assuming that the reaction is at steady state write an expression for the overall rate of polymerization in terms of monomer and initiator concentrations.

- 3)
 - a) Explain what the kinetic chain length is, ν . (describe this in words)
 - b) Give an expression for the kinetic chain length if the monomer concentration is M and the initiator concentration is I . The answer should include a function of 3 rate constants, I and M .
 - c) List the two main mechanisms for termination of chain growth.
 - d) How will the molecular weight be related to the kinetic chain length for these two conditions of termination reaction?

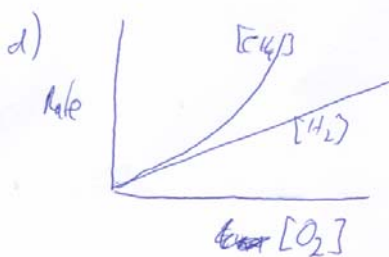
- 4) The enthalpy of polymerization of styrene, ΔH , is -20 kcal per mole.
 - a) If the ceiling temperature is observed to be 310 °C calculate the entropy, ΔS , of polymerization.
 - b) Comment on the sign, + or -, of ΔS . Is the sign for polystyrene normal for polymerizations?
 - c) Would you think that heating the reaction mixture would enhance polymerization? Explain your answer.

ANSWERS :051103 Quiz 6 Introduction to Polymers (Chemistry)



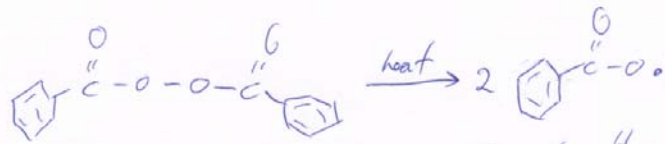
- b) (A) is second order in O_2
(B) is first order in O_2

c) Rate $\text{CH}_4 = k_{\text{CH}_4} [\text{CH}_4] [\text{O}_2]^2$
Rate $\text{H}_2 = k_{\text{H}_2} [\text{H}_2] [\text{O}_2]$

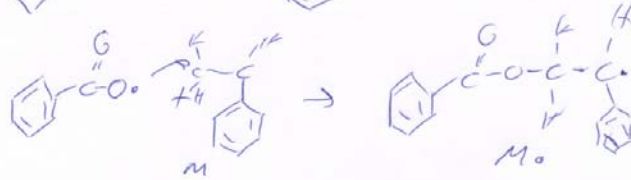


e) The probability of reacting methane involves finding two oxygen molecules. The probability to find one oxygen is proportional to the concentration of the oxygen so the probability to find two is proportional to the square of the concentration. This is then second order in oxygen concentration.

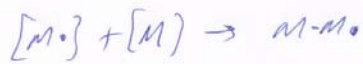
2) a)



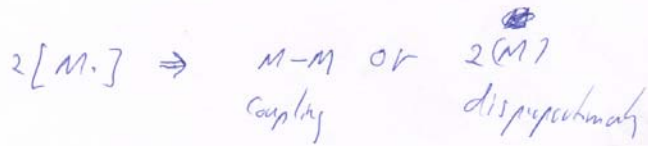
Inisiatif



Propagasi



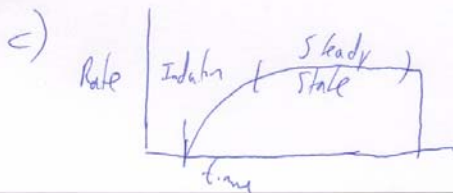
Terminasi



b) Rate inisiatif = $k_i [I]$

Rate Propagasi = $k_p [M][M\cdot]$

Rate Term = $k_t [M\cdot]^2$



$$2) d) R_i = R_t = k_i [I] = k_t [M\cdot]^2$$

e) Assume $R_{op} = R_{rxn} = R_{atf}$

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

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

$$3) a) T_c = \frac{\Delta H}{\Delta S}$$

$$\Delta S = \frac{\Delta H}{T_c} = \frac{-20 \text{ kcal/mol}}{(310+273) \text{ K}} = -0.0343 \frac{\text{kcal}}{\text{mol K}}$$

b) The entropy change is negative because the polymer is less random than the free monomer. This is the norm for polymerization.

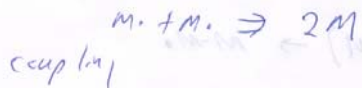
c) Heating would not enhance polymerization since the free energy change would be lower when heated since $\Delta G = \Delta H - T \Delta S$ and ΔH and ΔS are negative.

3) a) The kinetic chain length is the rate of propagation divided by the rate of initiation.

$$b) \nu = \frac{R_{atf}}{R_{atf}} = \frac{k_p \left(\frac{k_i}{k_t}\right)^{1/2} [I]^{1/2} [M]}{k_i [I]}$$

$$\nu = \frac{k_p [M]}{(k_t k_i)^{1/2} [I]^{1/2}}$$

c) disproportionation



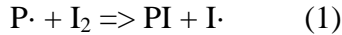
d) coupling $n_i \cong 2\nu$

disproportionation $n_i \cong \nu$

051110 Quiz 7 Introduction to Polymers (Chemistry)

1) Termination of chain growth can occur by coupling/disproportionation *or* through a variety of chain transfer reactions.

- What does chain transfer mean?
- Does chain transfer affect the rate of consumption of monomers (rate of propagation)?
- Chain transfer to initiator $[I_2]$ involves the reaction,



write an expression for the rate of chain transfer to initiator using the initiator concentration $[I_2]$ and the concentration of propagating species $[P\cdot]$.

- At steady state $[P\cdot] \sim [I_2]^{1/2}$. Write an expression for the kinetic chain length, $\nu = R_p/R_t$, where R_t includes all reactions that end chain growth.
 - Explain why $1/\nu$ is a more useful function than ν from part d.
 - Write an equation for the rate of chain transfer to polymer and explain why this might be important to the quality of polymer product.
- 2) Critique the following polymerization of polystyrene (PS) that contains BHT (butylated hydroxyl toluene *or* t-butylcatechol):
To a small amount of PS we add benzyl peroxide (DBP) and expose at room temperature to UV radiation.
- What is BHT and why/how can it be removed?
 - Does DBP initiate when exposed to UV? How is DBP initiated?
 - When bulk polymerization of PS was successful a viscous liquid with about 60% conversion and a molecular weight of about 4000 g/mole resulted. Is this surprising? Explain the problems with bulk polymerization that can lead to this result.
 - When adding solvent to polymerization of MMA, below, the conversion versus time shows several characteristic features. Write an equation that explains the decrease in rate with increasing solvent added to the reacting system.

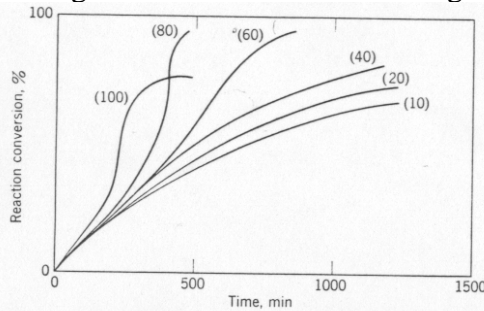


Figure 11-4. Effect of dilution on rate of polymerization of methyl methacrylate at 50°C. Curves are labeled for per cent concentration of monomer in solvent.¹⁷⁴

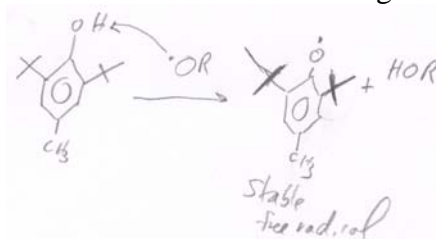
From R. W. Lenz's book.

- Why does the plot show a change in shape of the conversion vs time curve for 80 and 100% concentrations? (A steep increase after about 1/2 of the reaction time and plateau).
- 3) As an alternative to bulk polymerization it is possible to run polymerization reactions in the presence of solvent and under several other unique conditions. List 7 types of chain polymerization and briefly describe how these reactions differ and what advantages and disadvantages they may have. (We haven't gone through in detail so guess advantages/disadvantages based on what you know.)

ANSWERS :051110 Quiz 7 Introduction to Polymers (Chemistry)

- 1) a) "Chain transfer" is the name for chemical reactions where a radical group is transferred from the propagating chain to another species in the reaction mixture such as initiator, monomer, other polymer chains, and solvent. In chain transfer the radical is not terminated and will proceed to initiate either another polymer chain or a branch on an existing polymer chain.
- b) Chain transfer does not affect the rate of propagation since the radical is not consumed.
- c) $R_{ctI} = k_{ctI} [I_2][P\cdot]$
- d) $v = R_p/R_t$ and $R_p = k_p [P\cdot][M]$ and $R_t = k_t [P\cdot]^2 + k_{ctI} [I_2][P\cdot]$ so
 $v = k_p [P\cdot][M] / (k_t [P\cdot]^2 + k_{ctI} [I_2][P\cdot]) = k_p [M] / (k_t [P\cdot] + k_{ctI} [I_2])$
 $v_0 = k_p [M] / (k_t [P\cdot])$ so
 $1/v = 1/v_0 + k_{ctI} ([I_2]/[M])$ (2)
- e) $1/v$ is easier to consider since it separates the effects of various chain transfer mechanisms into a sum of terms.
- f) $R_{ctP} = k_{ctP} [P\cdot]^2$, which will add to equation (2) the term $k_{ctP} [P\cdot]/[M]$. Chain transfer to polymer leads to long chain branched polymers.

- 2) a) BHT is an inhibitor that reacts with free radicals through the following reaction:



- It is added to increase the shelf life of styrene monomer. It can be removed with "activated" alumina, Al_2O_3 . Alumina powder is heated with a Bunsen burner extensively and then cooled. The alcohol group bonds to the activated alumina structure and is trapped when the monomer is filtered through activated alumina. Alternatively the monomer can be distilled.
- b) DPB will not initiate under UV irradiation. Styrene monomer can self-initiate under UV but with a low efficiency. DPB should be initiated using heat (60 °C).
- c) Problems with bulk polymerization include, over heating due to concentration of reactive monomers, high viscosity (gel) that leads to no termination and chain transfer to polymer that leads to branching, chain transfer to monomer that leads to low molecular weight. For our polymerization the gel point and chain transfer to monomer are the dominant problems that lead to low molecular weight polymer.
- d) The rate polymerization follows the rate of propagation, $R_p = k [M] [I]^{1/2}$. Increasing the solvent content decreases $[M]$ and also decreases $[I]$ so the rate of reaction (slope of conversion versus time) should decrease as is seen from 10 to 40 %.
- e) The change in shape is related to the Tromsdorf effect (gel effect) where the reaction displays auto-acceleration (steep curve). The gel effect is associated with a dramatic decrease in the rate of termination associated with low transport rates of chains. In the absence of strong termination the conversion becomes much faster and is self accelerating since the reaction is exothermic.

- 3) **Bulk Polymerization:** Disadvantages: Over heat/gel effect/chain transfer to polymer. Advantage is simple reaction stoichiometry and high concentrations of product. Generally higher reaction rates due to high concentrations.

Solution Polymerization: Both monomer and polymer are soluble in solvent. More controlled polymerization with lower reaction rates and temperatures. Disadvantage is the need for separation of product polymer from solvent and slow reaction kinetics. Chain transfer to solvent can be a problem in some systems.

Precipitation Polymerization: Monomer is soluble in solvent but polymer is not depending on molecular weight and temperature of the solvent. Free radical is trapped in a droplet of precipitated polymer chain. Similar to solution polymerization in terms of advantages and disadvantages except that product separation is not a problem.

Suspension Polymerization: Monomer and polymer are immiscible in solvent (water usually). Product is fine grain beads which are separated easily from water. The system does not have the problem of heat buildup that is seen in bulk polymerization. Droplets are less well defined and larger than in emulsion polymerization, typically on the order of 1 mm in size. The catalyst is dissolved in monomer and the monomer dispersed in water with the help of a dispersing agent such polyvinylalcohol, polyacrylic acid or using inorganic materials such as clay, aluminium hydroxide and phosphates.

Emulsion Polymerization: The catalyst is dissolved in the solvent phase (water) the monomer is the organic phase of a soap micelle. Catalyst diffuses to the micelle and initiates usually one chain per micelle which is on the order of 5 to 50 nm in diameter. The size of a micelle ensures that only one initiator per micelle is present and termination is not possible by combination or disproportionation so emulsion polymerization follows different kinetic equations compared to bulk and other solution polymerizations. Rate depends on number of micelles and monomer concentration but not on the initiator concentration. Advantage is controlled molecular weight and good heat removal from concentrated nanodroplets.

Gas-phase Polymerization: Monomer forms an aerosol which is a cloud of monomer droplets on the order of 1-10 micron diameter. Initiation is generally by UV light.

Solid-state Polymerization: Crystallize monomer and irradiate with UV, x-rays or electron beams to initiate. Heat transfer is an issue but there may be some advantages for some monomers.

051117 Quiz 8 Introduction to Polymers (Chemistry) (Figures from Heimenz *Colloid Sci.*)

1) Surfactants are amphiphilic molecules (molecules having one end hydrophobic and the other hydrophilic) and are often represented in figures as a circle and a line. We used such a soap molecule in class to emulsion polymerize styrene. Amphiphilic molecules will locate at the free surface of water and form a *monolayer* if sufficient concentration is present. The surface concentration, moles/area, can be increased by dragging a metal paddle across the surface to reduce the area, see the first figure below. The force on the paddle divided by the area of the monolayer is a measure of the "surface pressure", π , within the monolayer. A plot of π versus the area per surfactant molecule, σ , $1/(\text{surface density})$ or specific area (like specific volume), may show discrete transitions.

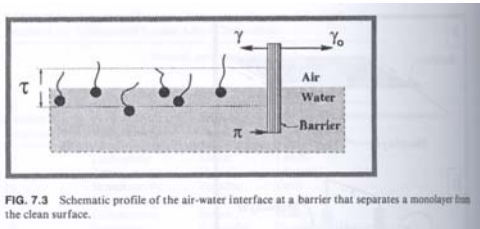


FIG. 7.3 Schematic profile of the air-water interface at a barrier that separates a monolayer from the clean surface.

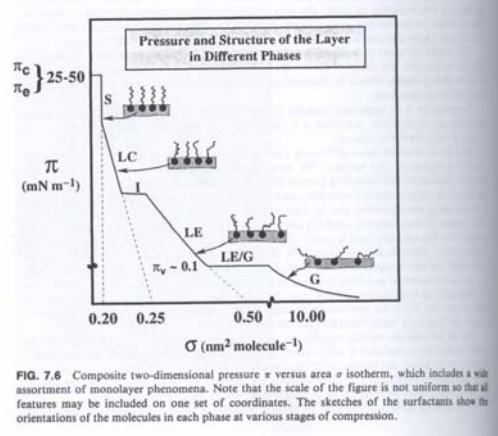
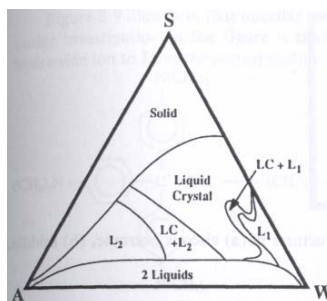


FIG. 7.6 Composite two-dimensional pressure π versus area σ isotherm, which includes a wide assortment of monolayer phenomena. Note that the scale of the figure is not uniform so that all features may be included on one set of coordinates. The sketches of the surfactants show their orientations of the molecules in each phase at various stages of compression.

- Sketch the molecular structure of the amphiphilic molecule used in class.
- Explain what a monolayer is.
- Compare the transitions seen in the second figure above with liquefaction and crystallization of a gas with increasing density.
- If the surfactant molecules have some solubility in water, explain what can occur structurally in the soap solution with increasing bulk (3d) soap concentration.
- Explain how soap can remove "oily" dirt.
- What is the difference between a surfactant molecule in a micelle and the same molecule in a monolayer?

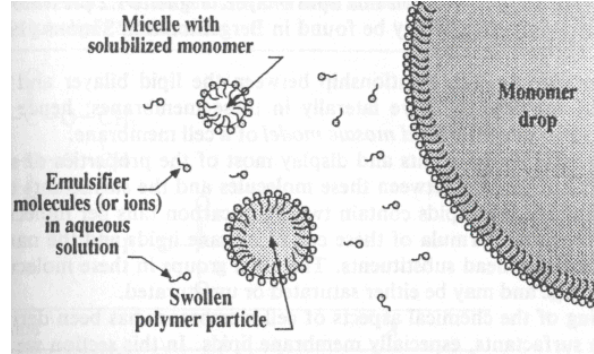
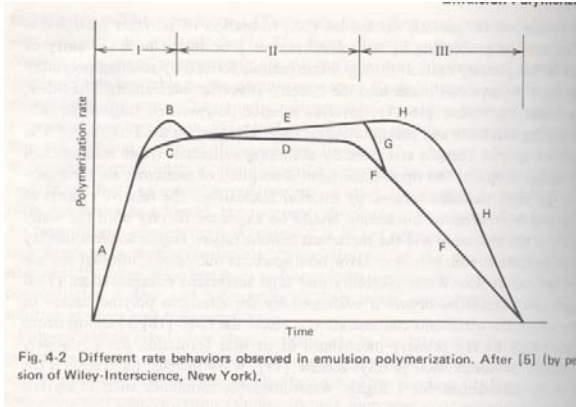
2)



In the figure above, S is SDS, A is styrene and W is water.

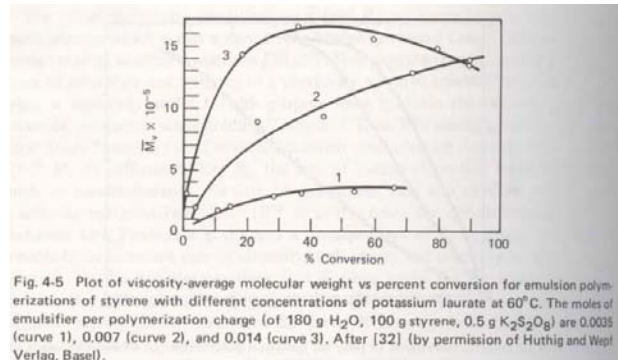
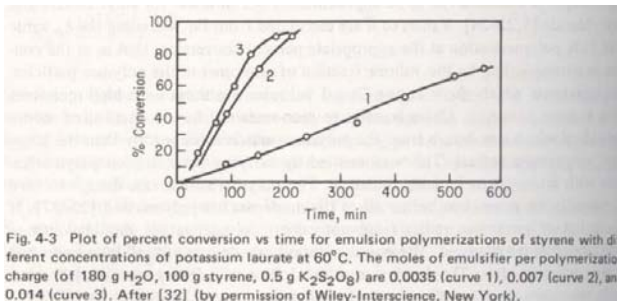
- Explain where you would find an equal mixture of water, styrene and SDS in this plot. Where would you find a 50:50 mixture of styrene and water with no SDS?
- Which of these two mixtures is a stable emulsion?

- c) In class we made a mixture of about 3/4 water, 1/4 styrene and a small amount ~1% SDS. Is the phase diagram above consistent with your idea of the system morphology?
 d) What was the catalyst used in the emulsion polymerization and in which phase did it reside?



- e) The figure above shows three regimes for emulsion polymerization and a schematic of the structure of the reaction media. Explain the difference between regimes I, II, and III in terms of the presence of a droplet phase, the change in the number of micelles with time, and the fraction of micelles with an active radical. (Explain the polymerization.)

3)

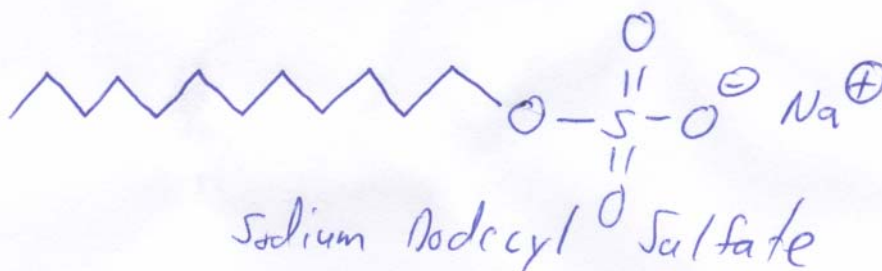


The first figure above shows the conversion versus time for emulsion polymerization with variable surfactant concentration while the second shows the molecular weight versus conversion for different surfactant concentrations.

- a) Write an expression for the rate of polymerization, R_p , that shows the behavior of the first figure and compare this with R_p for a suspension polymerization.
 b) Write an expression for the first moment of the molecular weight that shows the behavior of the third figure.
 c) What assumptions are needed to obtain these expressions?
 d) Which Regime in question 2 do these two equations correspond with?
 e) Why can it be said that a micelle is binary reactor, either totally on or totally off?
 f) How can the average molecular weight drop for the third curve in the third figure?

ANSWERS :051117 Quiz 8 Introduction to Polymers (Chemistry)

1) a)



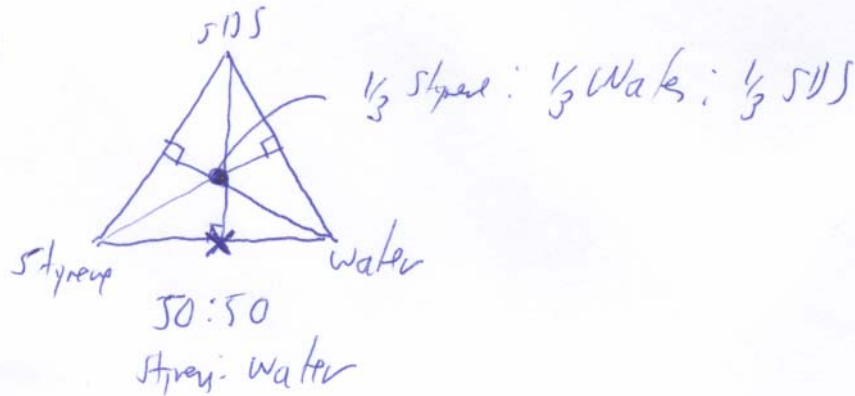
- b) A monolayer is a surface layer with a surface concentration that equals the $1/(\text{molecular cross-sectional area})$. This is called the overlap concentration in 3d solutions.
- c) There is a direct analogy between surface density effects and transitions of gas atoms with increasing pressure or decreasing specific volume. At low density, high specific volume, the gas and the surfactant are free to move as independent atoms or molecules. This is the gas state signified by G in the figure. At higher densities or lower specific area/volume, the molecules pack just as gas atoms pack into a liquid. This occurs when there is sufficient density for frequent molecular collisions. When density reaches a critical value the system must crystallize. For the surfactant liquid crystalline ordering is possible with the molecules aligned parallel to the surface for instance, or at a fixed tilt angle.
- d) As the bulk solution concentration increases the critical micelle concentration is reached where micelles spontaneously form. This is called self-assembly since it requires no external input other than an increase in concentration.
- e) Soap removes dirt since the inside of the micelle is organophilic (oily) while the outside is hydrophilic (watery). The micelle can encapsulate oil and make it soluble as an emulsion in water.

f)



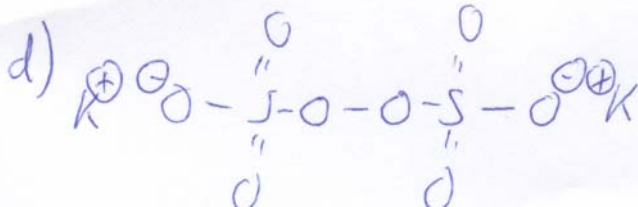
The difference between a surfactant in a micelle and a monolayer has to do with the packing geometry. The packing of tail groups is tighter in a micelle for the same head group packing as a monolayer. This balance of head group and tail group cross sectional area with enthalpic interactions decides the thermodynamically optimal micelle diameter (and shape).

2) a)



b) The equal mixture of Styrene/Water/SDS is a stable emulsion since it is away from the two phase regime.

c) The phase diagram indicates two liquid phases for this mixture, indicating that droplets of styrene exist in the water phase. The diagram does not indicate the presence of SDS micelles which are an important minor component of the polymerization mixture.



The catalyst was potassium persulfate which resided in the water phase.

e) Droplet phase is present in I and II but not in III this leads to depletion of monomer in the water phase and the decline in polymerization rate in regime III. The number of micelles is very large at the start of the reaction but only a very few are initiated. The initiated growing polymer micelles require more surfactant to stabilize the polymer particles which they obtain from non-initiated micelles. When an equilibrium number of polymer/micelle particles form for the system initiation and termination of micelles offset each other and the micelles are either on or off in terms of growth. This is regime II.

3) a) b) $R_p = k_p [M] \left(\frac{N}{2}\right)$ Emulsion (Regime II) $N = \# \text{ of micelles}$

$$n_i = \frac{k_p [M]}{R_i} \left(\frac{N}{2}\right)$$

$$R_i \sim [I_2]$$

Suspension

$$R_p = k [M] [I_2]^{1/2}$$

$$n_i = k \frac{[M]}{[I]^{1/2}}$$

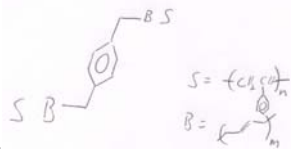
- c) The assumptions are those involved in Regime II, constant number of micelles, unlimited monomer reservoir in droplets, micelles are either on or off in terms of propagation and half the micelles are on at any given time. Sufficient initiator is present so that a significant propagation life time for micelles/polymer particles exists (about 10 seconds).
- d) The equations correspond with Regime II.
- e) With typical concentrations of surfactant and initiator the life time of two free radicals in a micelle is about 2 ms while the time between initiator species colliding with micelles is about 10 s.
- f) The first moment of the distribution can drop if the system produces lower molecular weight polymers or if the high molecular weight polymers degrade in molecular weight. In emulsion polymerization at high conversions it is possible for a radical to transfer to polymer and to lead to chain degradation lowering the molecular weight due to the high concentration of polymer within polymer particles.

051129 Quiz 9 Introduction to Polymers (Chemistry)

- 1) Polyacrylamide is soluble in water as is the monomer acrylamide.
 - a) Use the words *ferric* and *ferrous* to describe the initiator system for this polymerization.
 - b) Why is this called a *redox system*?
 - c) When hydrogen peroxide was added to the reaction mixture it turned from a faint bluish green to red (rust color). Why did it change color?
 - d) How was polymer separated from the viscous reaction mixture after polymerization?
 - e) Explain the disadvantage of solution polymerization compared to emulsion polymerization.
 - f) Why is there dissent on the internet over the current widespread use of polyacrylamide as a soil enhancing agent for food crops in dry-land farming? Do you agree with this dissent?
- 2) Stereochemistry (tacticity) can be controlled in polymerization by two main routes, we have now glimpsed at one (heterogeneous catalysis using organo-metallic oxides or chlorides such as Ziegler-Natta catalysts) which has resulted in two Nobel prizes (Ziegler-Natta and Grubbs-Schrock during this quarter) as well as remaking the polyolefin industry with metallocene catalysts. However, the first stereo-regular polymerization was performed using a homogeneous reaction at very low temperatures and is still used on an industrial scale to produce poly vinyl ethers and butyl rubber.
 - a) What is a poly vinyl ether?
 - b) What catalyst can be used to initiate a cationic polymerization in liquid propane?
 - c) Explain what is a racemic diad.
 - d) What triad tacticity is associated with *mm* diad combination?
 - e) Sketch the water/polyvinylmethyl ether phase diagram
 - f) What water temperature is best to clean up a sticky polyvinyl methyl ether mess?
- 3) Free radical and step-growth polymerizations could be improved by :
 - i) Higher molecular weight/controlled molecular weight
 - ii) Lower polydispersity/controlled polydispersity
 - iii) Higher tacticity/control over tacticity
 - iv) Ability to make controlled block copolymer structure for engineered materials
 - v) Ability to make controlled branch structure

Ionic polymerization can address all of these issues.

- a) Why is there no real termination for ionic polymerizations (i.e. no coupling or disproportionation)?
- b) What does *living polymerization* mean?
- c) Why are most *living polymerizations* conducted using anionic polymerization?
- d) How can you terminate an ionic polymerization? Give an example.
- e) Briefly outline how you would produce Kraton Rubber which is a block copolymer



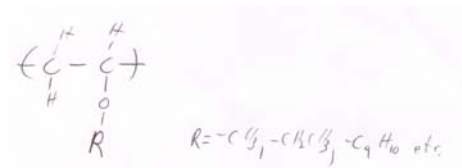
with the structure:

- f) How would you make a 4-arm star polymer of polystyrene using a similar polymerization to part e?

ANSWERS :051129 Quiz 9 Introduction to Polymers (Chemistry)

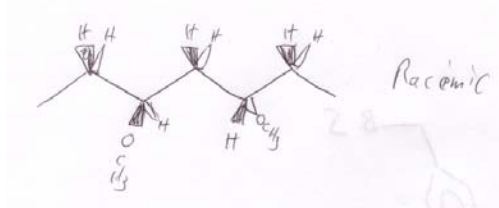
- 1) a,b,c) To deionized water we added ferrous sulfate. Ferrous sulfate is a blue/green crystal so the solution became slightly blue/green. When hydrogen peroxide was added the solution immediately turned redish brown indicating the oxidation of ferrous sulfate, Fe+2 to Ferric sulfate, Fe+3 (or iron (III)). The hydrogen peroxide was reduced to produce two hydroxyl radicals and the iron (II) was oxidized to iron (III), Fe+3, or ferric sulfate. This is called a redox system because hydrogen peroxide is reduced (gains electrons) and iron is oxidized (loses electrons).
- d) Polymer was separated from the viscous polyacrylamide/water solution by pouring the polymer solution in acidified propanol which is a non-solvent for the polymer but is miscible with water. The acid terminates the remaining free radicals. The polymer is then filtered out.
- e) The main disadvantage is that copious amounts of solvent are produced. Usually this is a toxic solvent mixture rather than water and propanol. In this reaction 1 gram of polymer was produced using about 300 ml of solvent so a 50 kilogram bag of polymer would produce 15,000 liters of waste solvent.
- f) Polyacrylamide has residual monomer (about 1%) and the monomer is a degradation byproduct in UV radiation. The monomer is a neurotoxin and a human carcinogen as well as producing sterility in men and several other nasty things. The polymer is completely non-toxic. I would say a risk assessment and consideration of comparative risk and risk/benefit analysis would be appropriate. That is, how does this toxicity compare the toxicity of moth balls for instance, pumping gasoline, nail polish remover, and hair spray. Also, are there alternatives and what is the impact on food production?

2) a)



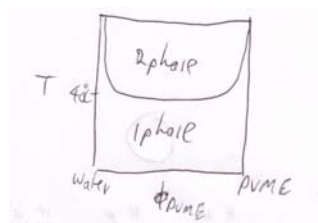
b) Boron trifluoride etherate (BF₃ OCH₂CH₃)

c) A racemic diad is composed of two monomers with opposite *handedness*.



d) A pair of *mm* diads is an isotactic triad.

e)



f) You would need to use cold water to clean up PVME (see phase diagram above).

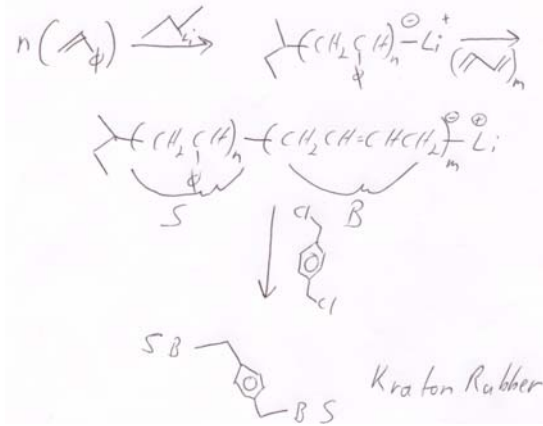
3) a) The propagating species is charged and two of these groups repel each other electrostatically.

b) *Living polymerization* means "A chain polymerization from which chain transfer and chain termination are absent. In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization." (<http://www.iupac.org/goldbook/L03597.pdf>)

c) Living could be done with cationic or anionic but cationic has problems with chain transfer such as chain transfer to monomer, expulsion of the propagating ion pair (spontaneous termination), combination of the propagating cation with a counter ion, backbiting reaction, chain transfer to polymer. None of these transfer reactions exist for anions.

d) Adding water generally terminates an ionic polymerization.

e) This is produced anionically in a living polymerization that is used on an industrial scale.



f)

