080407 Quiz 1 Introduction to Polymers
(*Please answer each question even if you guess*)

This week we explored the definition of a polymer in terms of properties.

1) The flow of polymer melts and concentrated polymer solutions display features that are distinct from low molecular weight materials.
   a) Sketch a plot of log of shear viscosity versus log of molecular weight showing shear thinning behavior for a polymer.
   b) Sketch a plot of log of the viscosity at low shear rate (from part "a" for instance) versus log of the molecular weight for oligomers and polymers indicating the transition from oligomer to polymer.
   c) Give an example of the first normal stress difference observed in polymer flow (that is stress generated at a right angle to the direction of flow).
   d) Give a short explanation based on the structure of a polymer melt that can explain the observed behavior in parts a, b and c.
   e) At higher temperatures polymers under shear act as if they were subjected to a lower shear rate, that is, they behave more Newtonian at higher temperatures. Explain why you think high temperatures would be associated with a reduction in the feature you describe in part d.

2) Paul Flory stated that *"...perhaps the most significant structural characteristic of a long polymer chain… (is) its capacity to assume an enormous array of configurations."*
   a) Explain how butane (4 carbon chain) can assume 3 isomeric conformations (configurations) using a Newman projection and a plot of molecular energy versus rotation angle.
   b) For a polymer chain explain how the environmental energy, kT, controls molecular motion through an energy plot similar to that of part a.
   c) If you fix a reference frame at one end of a polymer chain what function would describe the probability p(R) for the other end of the chain to be a distance R from the first end of the chain? (Write a function and sketch p(R) versus R.)
   d) Compare this function with the Boltzman probability, $p(R) = \exp(-E_{chain}/kT)$ to obtain an expression for the energy of a polymer chain, E_{chain}.
   e) How do you think E_{chain} might be related to the isomeric states for the polymer chain similar to the states for butane in part a? (This is the subject of Paul Flory's second book, *The Statistical Mechanics of Chain Molecules* for which he won the Nobel Prize.)

3) Metals and ceramics are purely elastic materials since at low strains they return exactly to their original shape with no loss of energy, that is they act as Hookean springs, $dF = k_{spr}\, dR$, where k_{spr} is a spring constant (similar to a modulus). Low molecular weight liquids, like water, are purely viscous materials since at low strains they show no return to their original shape. A change in force leads to a proportional change in velocity as governed by the friction factor f (similar to a viscosity), $dF = f\, du$, where u is the velocity.
   a) How are these viscoelastic properties of importance to the production of a nylon fiber in a fiber spinning process?

b) Explain how the rubber ball displayed both viscous and elastic features as it warmed from -196 ºC (liquid nitrogen) to room temperature. Describe the glassy, and rubbery states as well as the behavior at T_g.

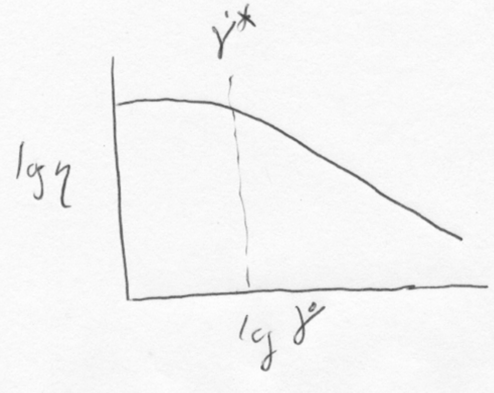
c) How does this temperature dependence of viscoelastic response relate to the energy plot of question 2 a?

d) Temperature is one way to change the viscoelastic behavior of polymers. Describe two other ways that the vicoelastic properties can be manipulated.

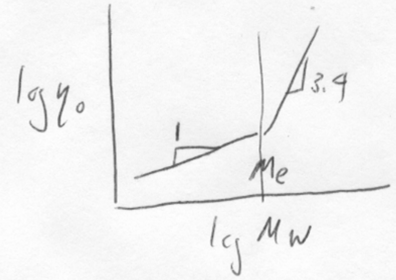
e) A rubber seal is functional only well above the glass transition temperature (> 50ºC above T_g) where it displays rubber-like elasticity. What kinds of problems would you consider for a rocket engine seal subject to vibrations at 50,000 Hz during liftoff on an exceptionally cold morning?

ANSWERS 080407 Quiz 1 Introduction to Polymers

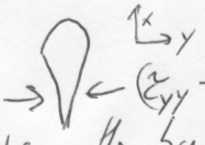
1) a)



b)



c) A bubble in a polymer melt is shaped like a tear. This is due to normal stresses



$\leftarrow (\tau_{yy} - \tau_{xx}) = \Psi_1$

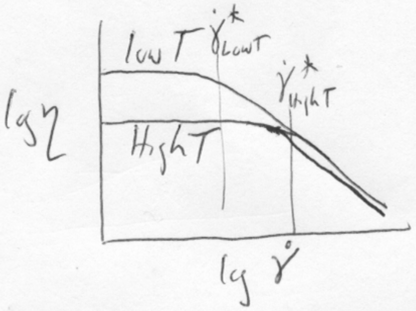
squeezing the bubble.

d) The polymer chains spring back displaying some Hookean characteristic leading to a normal force in the fluid in part c. In part b the short chains are not entangled. In part a the chains display a characteristic time τ.

~~e) The elasticity is related to a time constant~~

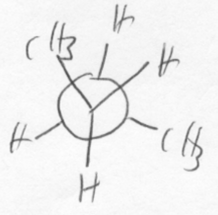
Rate of strain $\dot\gamma$ has units of 1/time. At the transition from the plateau to the power-law fluid the imposed strain rate $\dot\gamma^* \sim \frac{1}{\tau}$ where τ is the characteristic time for the polymer.

e) At high T the chain relaxes faster so τ is smaller & the transition in "a" occurs at a higher $\dot{\gamma}^* \sim \frac{1}{\tau}$

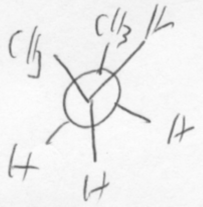


$\dot{\gamma}^* = f(T)$

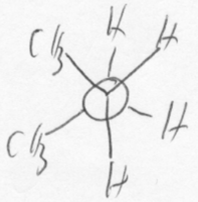
2) a)



trans

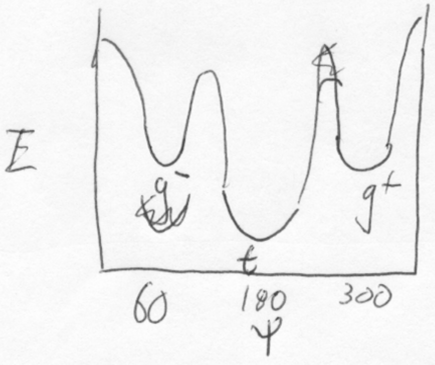


gauche+



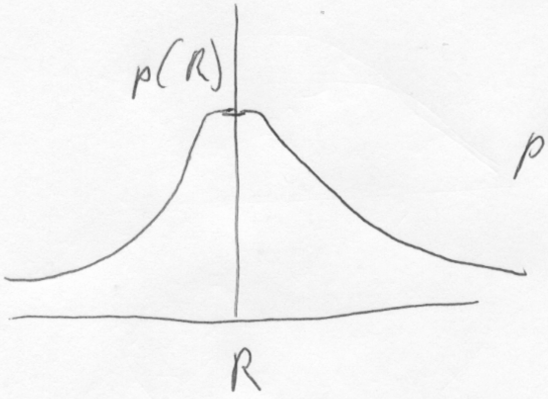
gauche−

Ψ 180



b.) As temperature increases the KT energy overcomes the barrier energy allowing easy rotational function of the chain. This means the chain has overall more motion.

c)



$p(R) = K \exp\left(\frac{-3R^2}{2N\ell^2}\right)$

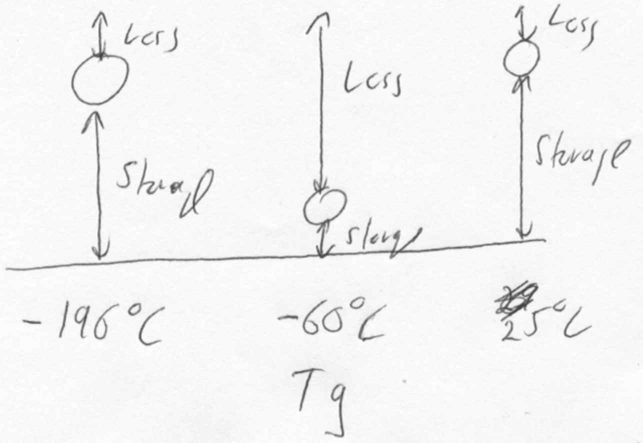
d)

$$\Delta E_{chain} = \frac{3KTR^2}{2N\ell^2}$$

e) E_{chain} is calculated by considering all possible bond rotations that can lead to a given end-to-end separation distance R. As bonds rotate the chain energy changes.

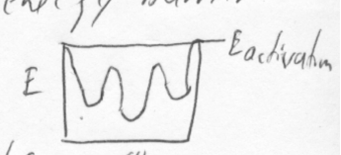
3) a) The formation of a fiber requires melt strength, that is, the melt must display both viscous & elastic properties.

b.)



The bounce is composed of motion lost to heat through viscous flow & bounce retained through anelastic response. (see above). At low temperature the ball is glassy & we observe some small loss but mostly bounce. Near Tg the material absorbs all energy & the response is mostly loss. Above Tg the rubber displays rubber-like elasticity.

c) At low T the chain is well below the energy barrier so $KT << E_{activation}$ So chain can not easily move.



At Tg $KT_g \sim E_{act}$ So Chain Absorbs All Energy

Above Tg $KT >> E_{activation}$ So Chain freely moves.

d) ① Happy & Sad Ball's show that chemistry can change viscoelastic behavior

② Speed of impact of the ball or shear rate in polymer rheology effects the behavior.

e) Low Temperature + very short times i.e. high frequency could make the seal act like a glass & cause failure of the engine seal.

080416 Quiz 2 Introduction to Polymer Science

1) Low molecular weight materials display a single value for the molar mass but synthetic polymers display a spectrum of molar mass.

   a) Why do you think a single molecular weight isn't seen for polymers (we didn't go through this in class so just guess from what you know and thinking of the mechanisms of initiation of growth, growth and termination of growth for a polymer chain). You may want to describe the conditions that could lead to a monodisperse polymer (PDI = 1) in answering this question.

   b) Describe the difference between a unimodal molecular weight distribution and a bimodal or multimodal distribution. Why might a bimodal distribution be seen in polyethylene?

   c) Other than GPC name two methods that could be used to measure the molecular weight of a polymer and what moments of the molecular weight distribution they measure.

2) a) Briefly explain what a GPC is and how it measures molecular weight.

   b) How is retention time or retention volume converted to a molecular weight scale? Include what must be measured and how you would go about using these measurements to convert retention time to molecular weight.

   c) Describe a detector used in a GPC.

3) a) Explain how the third moment of a distribution *P(M)* is obtained.

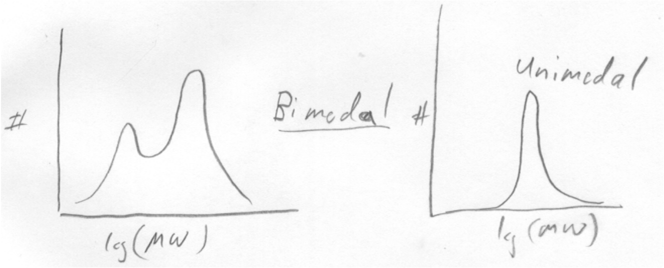
   b) What is the weight average molecular weight?

   c) How is the polydispersity index, *PDI*, related to the standard deviation, σ, of a distribution?

ANSWERS: ***080416 Quiz 2 Introduction to Polymer Science***

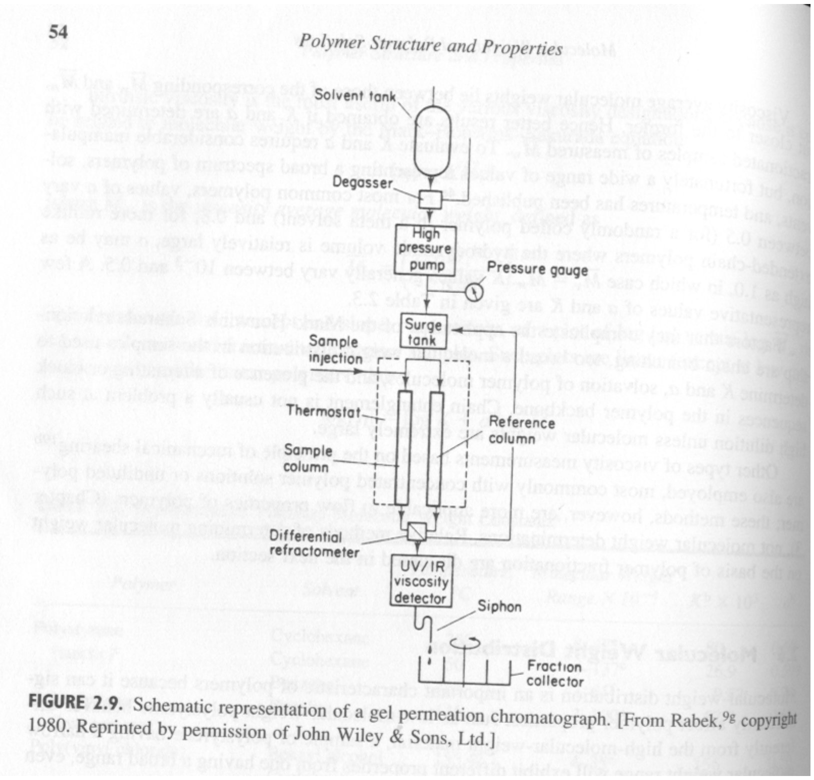
1) a) If polymers initiate simultaneously, grow by chain-growth polymerization with no termination during growth and if termination happens at the same time in a controlled manner then a monodisperse polymer results with almost no polydispersity, i. e. $PDI = 1$, $\sigma = 0$. If polymerization begins sporatically rather than spontaneously, if termination occurs throughout growth and branching occurs during growth and if the termination event is not a coordinated event, i.e. if it does not occur at the same time for all chains, then a polydisperse polymer results.

b) A unimodal population has one peak in the distribution. A bimodal has two peaks and a multimodal has many peaks. A bimodal population in polyethylene could arise due to branching of chains by macromolecular addition where the branched chains form a high molecular weight fraction when long chain radicals attach the polyethylene chain and add to the chain making a three arm star polymer structure.



c) Titration of end groups is a colligative method (counting method) and leads to the number average.
Light Scattering yields the weight average molecular weight.
Membrane osmometry measures number average molecular weight.
Viscosity from dilute solution leads to a viscosity average (high moment).
Melt viscosity (melt index) gives an index that decreases with molecular weight.

2) a) A GPC is composed of a chamber with a dilute ($c < c^*$) solution that is pumped through a high pressure pump through columns filled with a gel (like jello) that might be composed of polystyrene swollen in the solvent used to make the solution, typically tetrahydrofuran (THF) or toluene. After elution from the gel a detector (such as an IR detector or an index of refraction detector) quantifies the amount of polymer in the fluid as a function of retention time or retention volume.



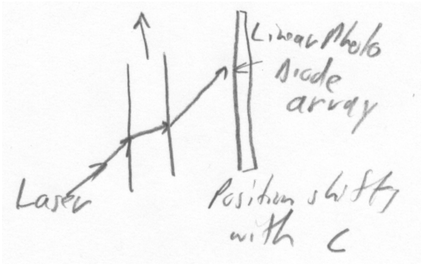
54 *Polymer Structure and Properties*

FIGURE 2.9. Schematic representation of a gel permeation chromatograph. [From Rabek,[9g] copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

From our textbook, Stevens Polymer Chemistry

b) The GPC requires the use of standards since it is a secondary technique. Primary techniques that do not use standards include light scattering, viscosity and membrane osmometry, but these do not yield the entire polydispersity curve. Monodisperse polymers are injected in the same solvent as the polymer to be measured. If monodisperse samples do not exist the column is often calibrated using monodisperse polystyrene and the molecular weight is termed the polystyrene equivalent molecular weight. There is basically an exponential relationship between elution time and molecular weight of the form, $M = K_1 \exp(-K_2 t)$, so a minimum of two standards are needed to calculate the conversion function. Generally 4 to 5 standards of variable molecular weight are mixed in the same standard solution since the peaks are discernable from each other for narrow enough molecular weight standards. Then the exponential equation is fit to the data to yield K_1 and K_2. This equation can then be used to convert retention time to molecular weight.

c) Index of refraction detector measures the refraction of laser light which increases with concentration.



3)

a) $$M_3 = \frac{\int_0^\infty P(m)\, m^3\, dm}{\int_0^\infty P(m)\, dm}$$

b) $$M_w = \frac{M_2}{M_1} = \frac{\int P(m)\, m^2\, dm}{\int P(m)\, m\, dm}$$

c) $$PDI = \frac{M_w}{M_n} = \frac{M_2}{(M_1)^2}$$

$$\sigma = \frac{\int P(m)\,(m - M_1)^2\, dm}{\int P(m)\, dm} = \frac{\int P(m)\, m^2\, dm}{\int P(m)\, dm}$$

$$- \frac{2 M_1 \int P(m)\, m\, dm}{\int P(m)\, dm}$$

$$+ \; M_1^2 \frac{\int P(m)\, dm}{\int P(m)\, dm}$$

$$\sigma = M_2 - 2 M_1^2 + M_1^2$$

$$\boxed{\frac{\sigma}{M_2} = 1 - \frac{1}{(PDI)}}$$

080426 Quiz 3 Polymer Properties

We discussed the two main mechanisms for polymerization and a list of polymers and their structure this week.

1) Consider a mind experiment where you pop corn, but each time a corn kernel pops it joins with another kernel or with another chain of kernels.

a) How would you expect the average number of kernels in a chain to change with time in such a situation? What would be the effect of old maids (unpopped kernels) on the average number of kernels in a chain? What happens if there are no old maids?

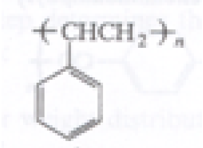
b) Which of the two main mechanisms for polymerization does this popping resemble?

c) Give an example of a polymer that is polymerized by this mechanism.

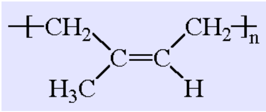
2) Draw the structure or give the name of the following polymers and indicate which of the two types of polymerization could be responsible for this polymer. Indicate, where appropriate, the polyester, polyamide or polyurethane linkages.

a) polyethylene terephthalate

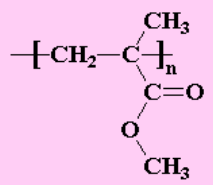
b)



c)



d)



e) Poly vinyl alcohol

3) Polyethylene and polypropylene are the two most prevalent polymers due to their low cost and ease of synthesis.

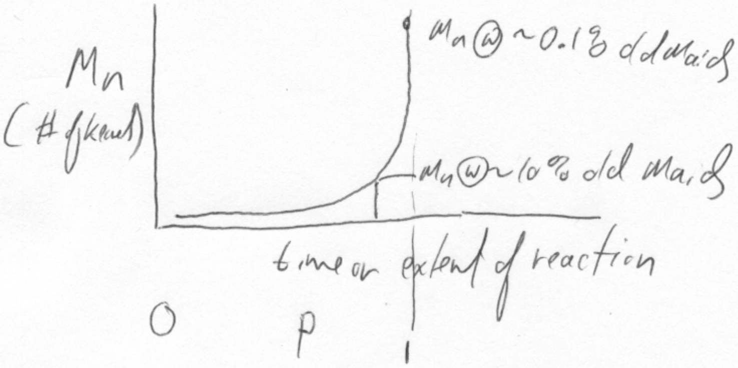
a) List the 4 types of polyethylene that are commonly used in industry.

b) What is the difference in chain structure between these types?

c) What two types of polyproplyene are commonly seen in industry and what is the difference in chain structure for these two types?

ANSWERS: 080426 Quiz 3 Polymer Properties

1) a)

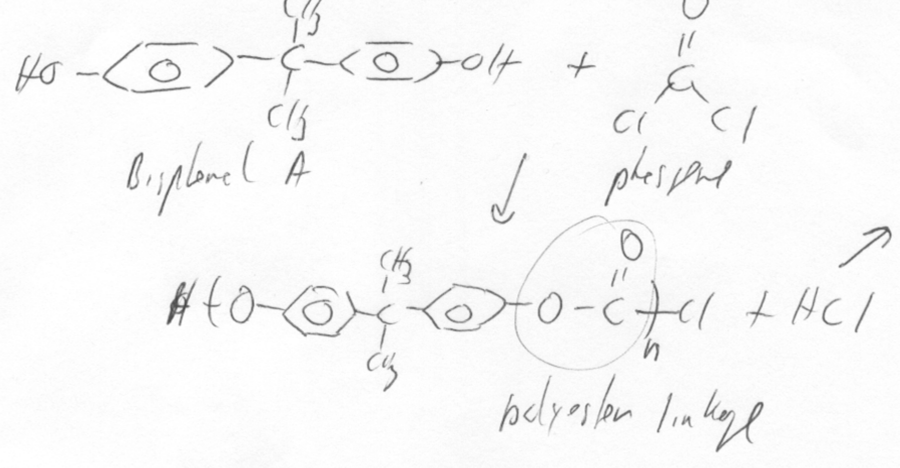


A few old maids makes the $\langle M_n \rangle$ much lower because the slope is steep at the end of polymerization.

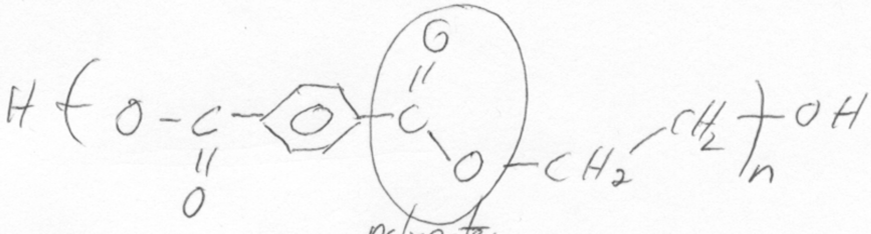
with no old maids the entire system is one chain.

b) Step growth polymerization

c) Polyester like polycarbonate



2) a) PET is a polyester made by step growth



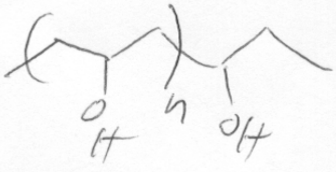
polyester

b) Polystyrene is a vinyl polymer made by chain growth

c) Polyisoprene is a diene polymer made by chain growth

d) Polymethylmethacrylate is an acrylic made by chain growth

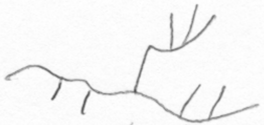
e)



a vinyl polymer made by chain growth

3.) a) LDPE Low density

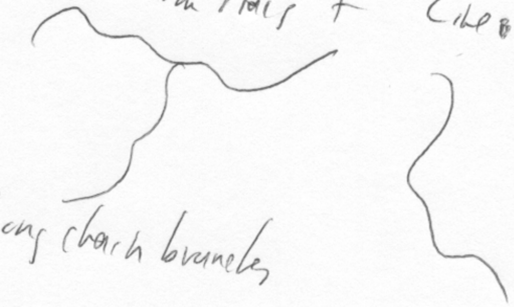
b)



short + Long chain branches

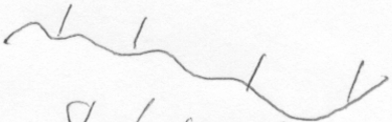
HDPE High density

3-arm stars + Linear



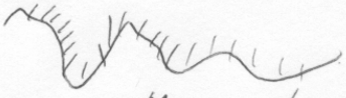
Long chain branches

LLDPE Linear Low Density Polyethylene



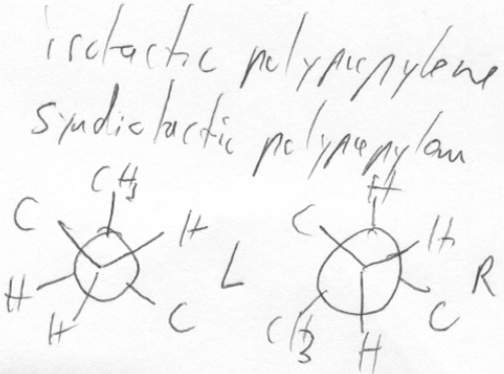
Short chain branches

Metallocene PE



Many short chain branches
Very low density
elastomeric PE

c) isotactic polypropylene ZN catalyst
syndiotactic polypropylene metallocene catalyst



isotactic = LLL or RRR triads
syndiotactic = LRL or RLR triads

080505 Introduction to Polymer Science, Polymer Chemistry Quiz 4

1) In class we synthesized nylon using a Schotten-Baumann interfacial polymerization method. According to wikipedia:

The name "Schotten-Baumann reaction conditions" is often used to indicate the use of a two-phase solvent system, consisting of water and an organic solvent. The base within the water phase neutralizes the acid, generated in the reaction, while the starting materials and product remain in the organic phase...

a) How does the nylon synthesis used in class reflect Schotten-Baumann conditions?

-Give details of the organic solvent and base that are used and specify what acid is neutralized.

-Does the product remain in the organic phase?

-Do the the starting materials remain in the organic phase?

b) Give an advantage and a disadvantage for the interfacial reaction used to make nylon compared to the glyptal reaction.

c) What determines the rate of reaction in an interfacial reaction? (e.g. concentration, reaction rate constants, transport, byproduct or product removal etc.)

2) We also synthesized glyptal polyester in class which has some similarities to the condensation synthesis of polyethylene terephthalate (PET or PETE, i.e. water bottles).

a) Why is phthalic anhydride used rather than phthalic acid in the glyptal synthesis?

b) Give two reactions that phthalic anhydride undergoes in the polymerization and 3 ways that it can be incorporated into the growing polyester chain.

c) Give two reactions that sodium acetate can undergo in this reaction.

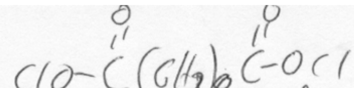
3) In addition to inventing nylon, polyesters, and neoprene, Carothers developed a method to calculate the number and weight average molecular weight for step growth polymerization using the extent of reaction p, as well as a method to predict the gel point in terms of the critical extent of reaction p_c for multifunctional reactants.

a) Give Carothers' equation for the number average degree of polymerization, M_n, in step growth polymerization and sketch a plot of M_n versus p from this equation. (The number average molecular weight is this value times the molecular weight of a monomer, M_0.)

b) The number average degree of polymerization, M_n, is given by the number of monomers in the reacting system, $N(0)$, divided by the number of polymer chains and monomers at time t, $N(t)$. Show how you can obtain the equation of part a) by defining p in terms of $N(0)$ and $N(t)$ and then substituting M_n for $N(0)/N(t)$ and rearranging.

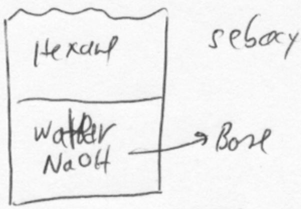
c) Write an expression for p for a system with an average functionality f_{avg} and show that when M_n goes to infinity, p goes to $p_c = 2/f_{avg}$.

1) a)



$ClO-\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}-OCl$

sebacoyl chloride



) HCl Acid

$NH_2-(CH_2)_6-NH_2$

hexamethylene diamine

Starting materials are in each of the two phases rather than remaining in the organic phase

Product is removed from system as a solid.

b) Advantages

Low temperature

Rapid Reaction

Disadvantages

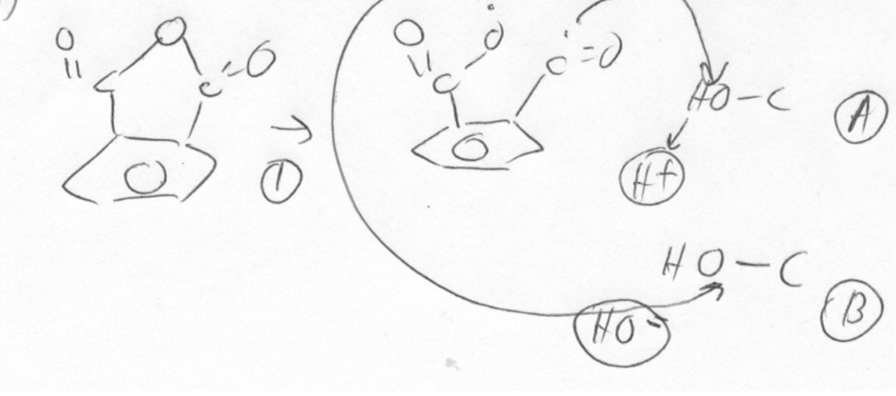
Solvent waste

c) Diffusion of reactants to the interface + interfacial area govern rate.

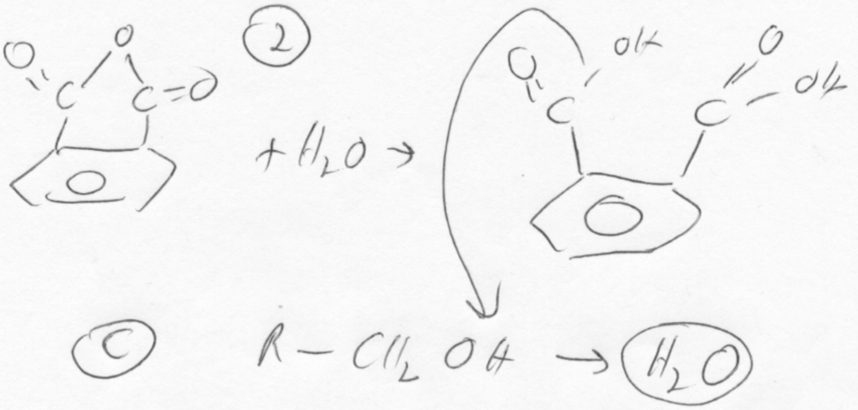
2) a) Tm 131°C vs. 210°C

\+ Ring strain ⇒ polymer formation

b)



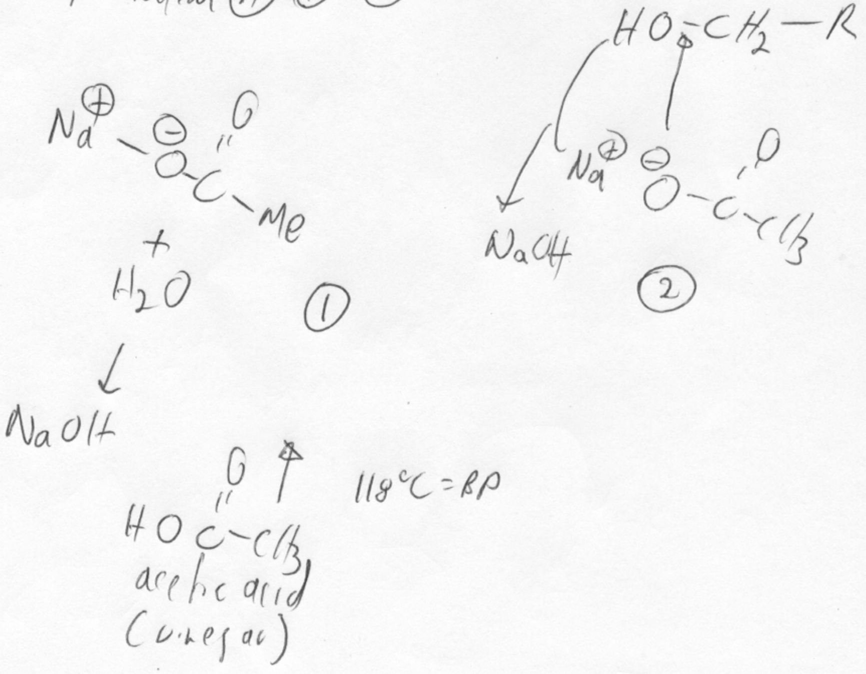
②



Reaction ①, ②

Polymerization Ⓐ Ⓑ Ⓒ

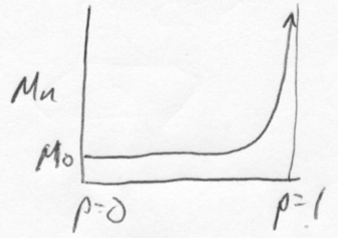
Ⓒ



③

③ $$\frac{1}{1-p} = M_n$$

a)



b) $$M_n = \frac{N(0)}{N(t)}$$

$$p = \frac{N(0) - N(t)}{N(0)} = 1 - \frac{1}{M_n}$$

so

$$M_n = \frac{1}{1-p}$$

c) for functionality f_{avg}

$$p = \frac{2\,(N(0) - N(t))}{f_{avg}\;N(0)}$$

$$= \frac{2}{f_{avg}}\left(1 - \cancelto{0}{\frac{1}{M_n}}\right) \quad \text{at } M_n \Rightarrow \infty$$

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

080512 Quiz 5 Introduction to Polymer Science

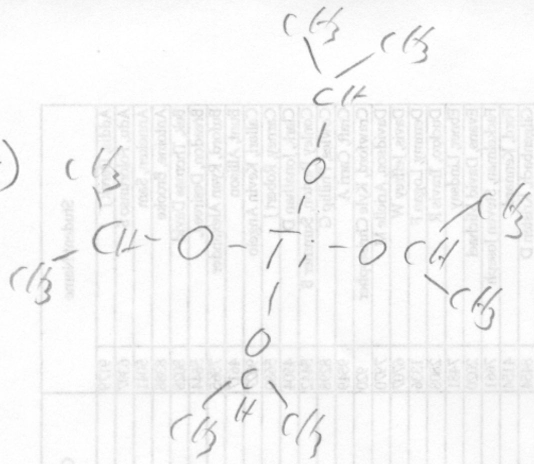
In class we used TTIP (titanium tetraisopropoxide) to crosslink hydroxyl terminated PDMS (polydimethyl siloxane). Often, PDMS is crosslinked using TEOS (tetraethoxy silicate). TEOS or TTIP can also be used to make a ceramic gel in a sol-gel reaction. This is the first step in the production of an aerogel.

1) a) Give the structure of TTIP.
   b) Give the structure of TEOS
   c) Show the reaction scheme (including stoichiometry) for hydrolysis of TEOS or TTIP.
   d) Show the reaction stoichiometry for the condensation of tetra hydroxy silicate or titanate to silica (SiO_2) or titania (TiO_2).
   e) Explain how water can act as both a catalyst and a reactant in the hydrolysis/condensation reaction of TEOS.

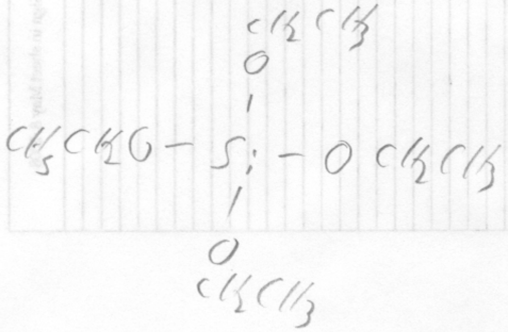
2) In crosslinking reactions to produce a rubber from hydroxyl terminated PDMS and TEOS or TTIP, HMDSO or HMDS (hexamethyldisiloxane) is often added to reduce the functionality of TEOS or other crosslinking agents.
   a) Give the structure of HMDSO (guess if you do not know, it has two silicon atoms bonded by an oxygen).
   b) Show the hydrolysis reaction scheme for HMDSO.
   c) Show the condensation production of hydrolyzed HMDSO with a hydroxyl group such as on tetrahydroxyl silicate (hydrolyzed TEOS) or hydroxyl terminated PDMS.
   d) How can this condensation reaction reduce the functionality of the network? (Functionality means the average number of bonds at a crosslink site.)
   e) Why is PDMS rubber used as an aerospace sealant materials?

3) In class we also made a silly putty from hydroxyl terminated PDMS mixed with boric acid.
   a) Give the structure of boric acid.
   b) Show the hydrolyzed structure of boric acid in water.
   c) If boric acid (61.8 g/mole and 1.44 g/cc were used in a stoichiometric ratio with hydroxyl terminated PDMS of 20,000 g/mole 0.965 g/cc) roughly how much tetrafunctional Boric acid would be needed to end link the PDMS chains? (Give a guesstimate assuming boric acid is trifunctional; PDMS is bifunctional.)
   d) How does this compare with the amount of Boric acid needed to make a reasonable silly putty material?
   e) Guess at the reason for the difference in amounts.

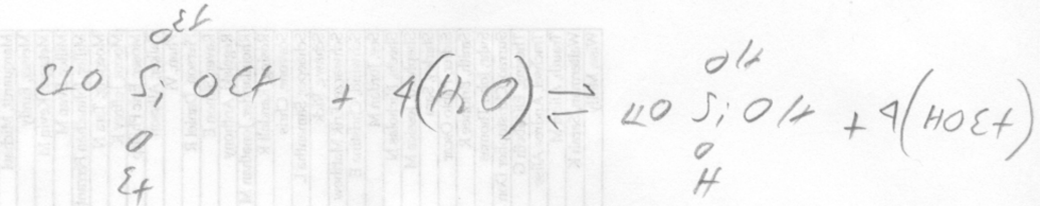
1) a)



b)



c)



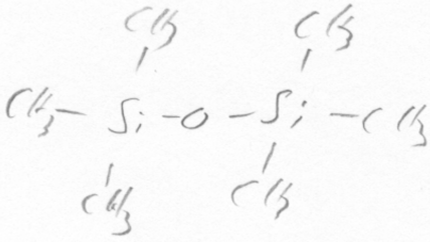
$$\mathrm{EtO\,\overset{OEt}{\underset{OEt}{Si}}\,OEt} + 4(H_2O) \rightleftharpoons \mathrm{HO\,\overset{OH}{\underset{OH}{Si}}\,OH} + 4(HOEt)$$

d)

$$Si(OH)_4 \rightleftharpoons \underset{\text{silica(s)}}{SiO_2} + 2(H_2O)$$

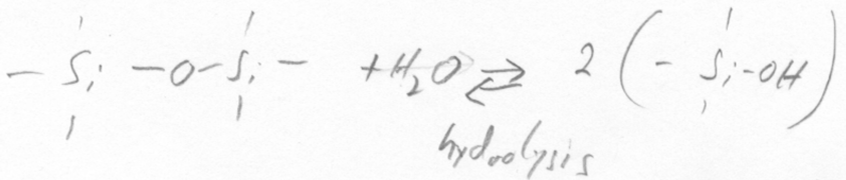
c) in "c" 4 waters are used; while in "d" 2 waters are produced so 2 waters act as catalysts & are regenerated while 2 water molecules act as reactants and are consumed.

2) a)



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_3$$

b)



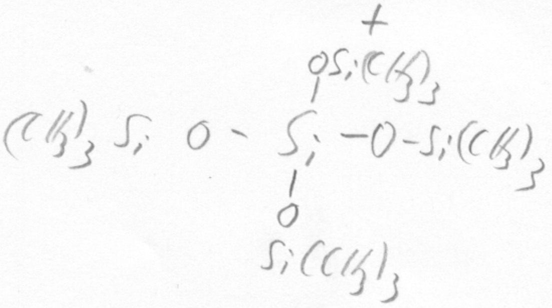
$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O \underset{\text{hydrolysis}}{\rightleftarrows} 2\left(-\overset{|}{\underset{|}{Si}}-OH\right)$$

$Si(CH_3)_3(OH)$

c)

$$Si(OEt)_4 + 4(Si(CH_3)_3(OH)) \rightleftarrows 4(EtOH)$$

+

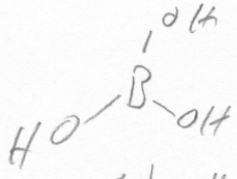


$$(CH_3)_3Si\,O-\overset{\overset{OSi(CH_3)_3}{|}}{\underset{\underset{Si(CH_3)_3}{\overset{|}{O}}}{Si}}-O-Si(CH_3)_3$$

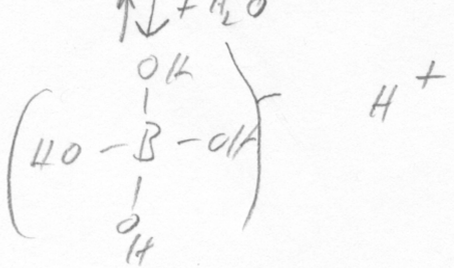
d) The $-OSi(CH_3)_3$ sits do not further bond in the network.

e) Low Tg & high degredation temperature lead to
$-127\,^{\circ}C$ 400°C
a wide range where properties are stable $-55\,^{\circ}C$ to $200+\,^{\circ}C$

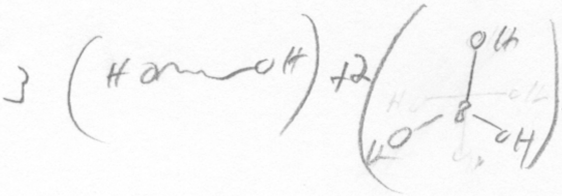
3) a)



b)



c)



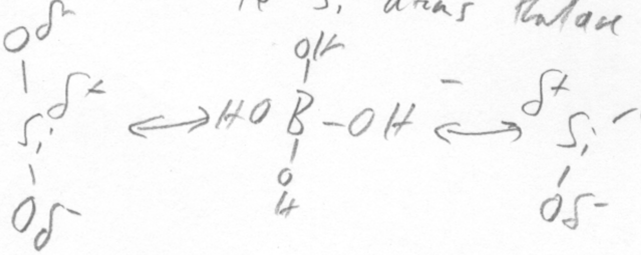
Assume tri-functional

$$\frac{0.965\ g/cc}{1.44\ g/cc}\ \frac{2\,(61.8\ g/mole\ BA)}{3\,(20{,}000\ g/mole\ PDMS)} = 0.0014\ \text{Volume Ratio}$$

0.14 % by volume BA
i.e. almost none

d) We added quite a bit. Silly Putty has more BA than PDMS.

e) BA must bond weakly along the chain perhaps with the Si atoms that are weakly positively charged



to link the chains.

080519 Quiz 6 Introduction to Polymers

1) Polyurethane in the video shown in class is formed from two liquids that are mixed. After mixing the solution foams and expands fairly rapidly forming a solid foam after a few minutes.
   a) One of the liquids contains MDI. Give the full name and structure for MDI.
   b) What is the reactant (co-monomer) in the second liquid?
   c) Name a catalyst (give acronym) that might be in the second liquid.
   d) What role would water play if it were present in the second liquid?
   e) What happens if a diamine is used rather than what you listed in part b?

2) On Friday we made a novolac polymer
   a) What two reactants were used to make the novalac?
   b) How do these reactants differ from those used to make a resole polymer?
   c) For the novolac what condition is needed?
   d) Outline the reaction scheme for formation of the novolac polymer.
   e) Why was the novolac pink?

3) We also discussed polyimides and epoxys last week.
   a) Give the structure of an imide bond.
   b) Give the reactants that form a cyclic polyimide such as kapton.
   c) Show the two reaction steps to form a polyimide
   d) Give the structure of epichlorohydrin.
   e) Give the structure of a glycidyl ether.

1) a) methylene 4,4' diphenyl diisocyanate

b) A diol

ethylene glycol

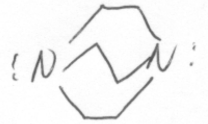
$HO-CH_2CH_2-OH$

or

poly ethylene oxide

$HO\left(CH_2-CH_2-O\right)_n H$

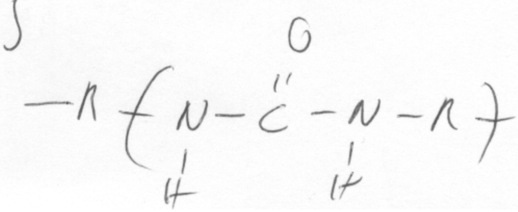
c) DABCO



d) Water + isocyanate $\Rightarrow CO_2(g)$ $\underset{H}{\overset{H}{}}\!N-R$

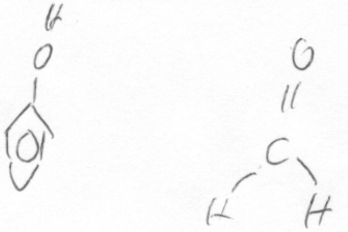
$CO_2(g) \Rightarrow$ Foaming

e) You form a Poly Urea



$$-R\left(\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-R\right)$$

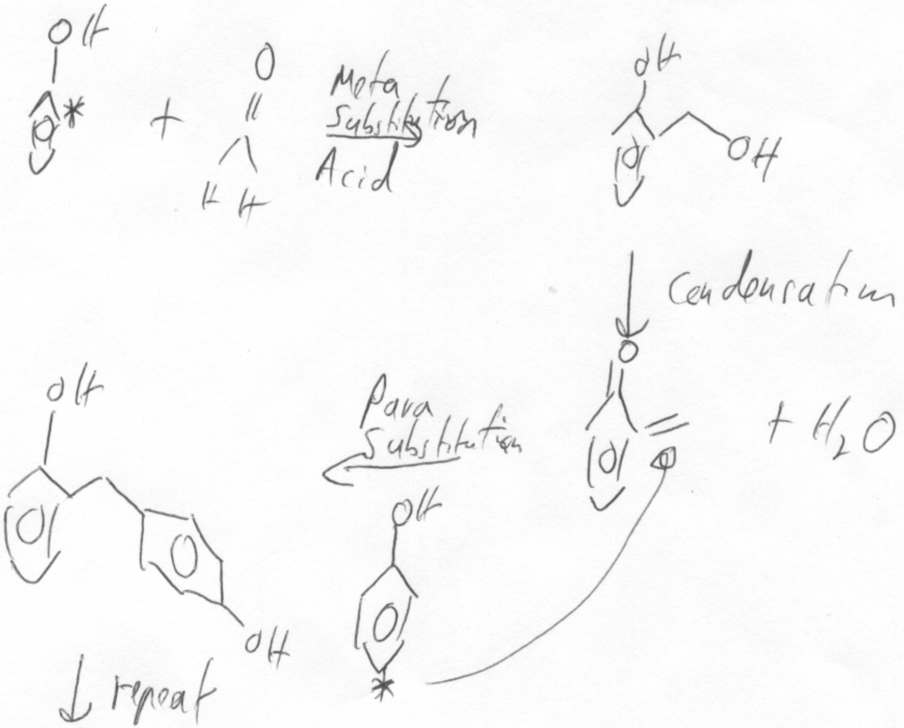
2) a) Phenol & Formaldehyde

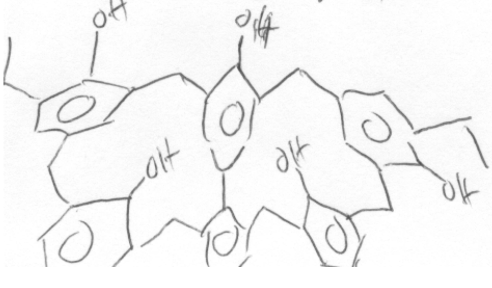


b) Same reactants for a resole

c) Acid we used Acetic acid + HCl

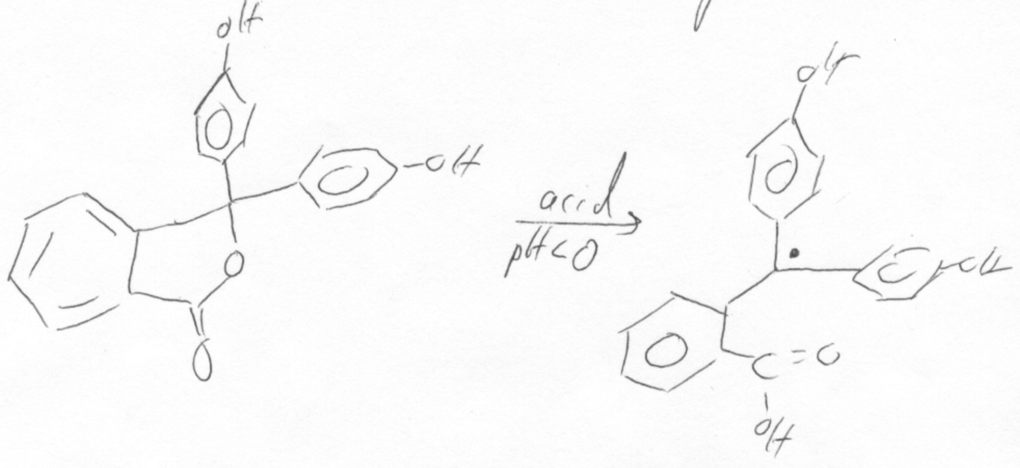
d)





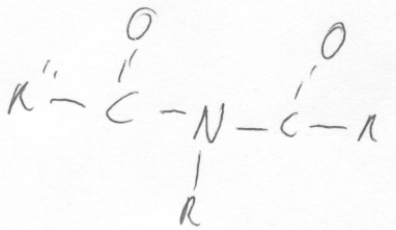
ortho + para substituted phenols

e) Structure is similar to the structure of Phenolphthalein



orange

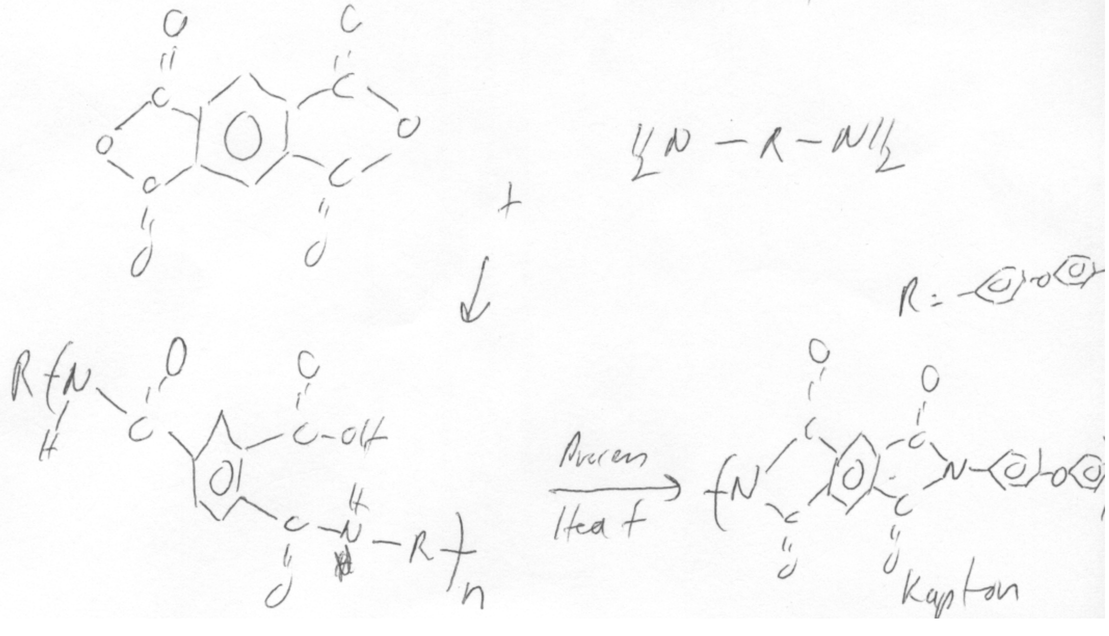
3) a)



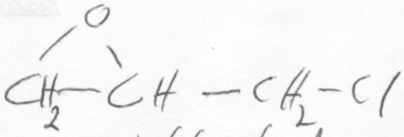
$$R'-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-R'$$

b) pyromellitic anhydride diamide

c)

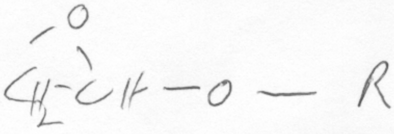


d)



epichlorohydrin

e)



glycidyl ether

080602 Quiz 7 Introduction to Polymers

Last week we made polyacrylamide by concentrated solution (similar to bulk) and by solution polymerization.

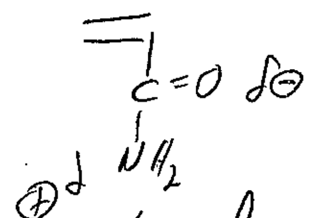
1) a) Give the chemical structure of the monomer and explain why it is soluble in the solvent used.
b) What initiator can be used to polymerize this monomer and under what conditions?
c) Compare the extent of reaction "*p*" that is needed to make a high molecular weight polymer for this chain growth polymerization compared to that needed for high molecular weight in a step growth polymerization.
d) How was the polymer separated from the reaction solution? (Why was a small amount of HCl used?)
e) Compare the reaction when the monomer concentration was very high to the reaction when the monomer concentration was moderate in terms of scale-up to an industrial synthesis (consider heat, ability to separate polymer and waste solvent byproduct).

2) a) For a solution reaction such as the polymerization of polyacrylamide, write the reaction equation for the propagation reaction and the rate equation for propogation.
b) Write the reaction equations and the rate equation for initiation.
c) Write the reaction equations and rate equation for termination.
d) Sketch the overall conversion rate versus time for such a free radical chain growth reaction and state the relationship between the rates of termination and initiation for most of this reaction.
e) Calculate an expression for the kinetic chain length based on the monomer concentration and the initiator concentration.

3) In addition to single phase polymerizations we considered two phase reactions.
a) Describe the reaction scheme for a suspension polymerization (give number of phases, phase composition, process that determines droplet size, location of initiator, kinetic chain length compared to solution polymerization).
b) Describe the reaction scheme for an emulsion polymerization (give number of phases, phase composition, process that determines droplet size, location of initiator, kinetic chain length compared to solution polymerization).
c) Write the rate of propagation for an emulsion polymerization.
d) Calculate the kinetic chain length for an emulsion polymerization.
e) How does the kinetic chain length equation for an emulsion polymerization differ from that of a suspension polymerization?

QUIZ 7

1) a)



acrylamide

Solvent is water

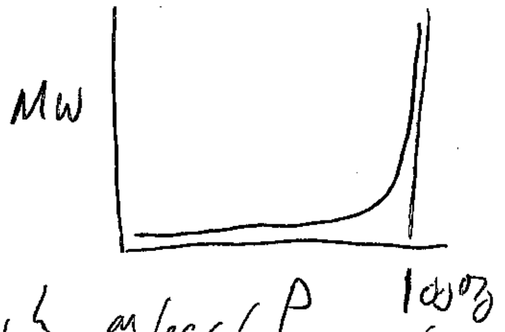
Acrylamide has two polar groups that enhance its water solubility

b) Free radical initiator we used a redox free radical initiator using hydrogen peroxide as the reduction of $H_2O_2 \rightarrow HO^{\ominus} \cdot OH$ by the oxidation of $Fe^{+2} \rightarrow Fe^{+3}$

Ferrous Ferric

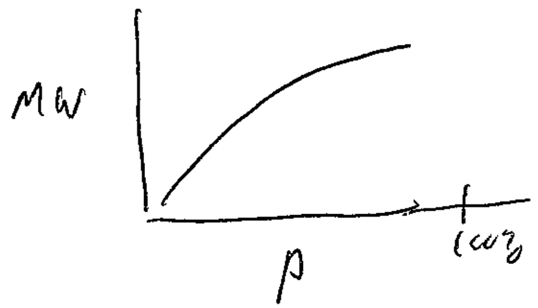
Rust

c) For a step growth you need almost 100% conversion to



obtain high molecular weight polymer

For chain growth much lower conversions lead to high molecular

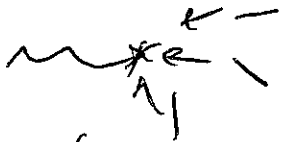


weights.

②

d) The polymer precipitated out of a dropwise addition to propanol with a slight trace of HCl. HCl neutralized ^{-}OH and removed $HO\ddot{}^{-}$ & $\cdot OH$ from the system terminating the reaction.

e) For high concentrations the reaction got very warm. In scale-up the reaction might become hotter & uncontrolled chain reaction might occur since termination becomes difficult in a high concentration system. That is, long chains cannot quickly diffuse while monomers

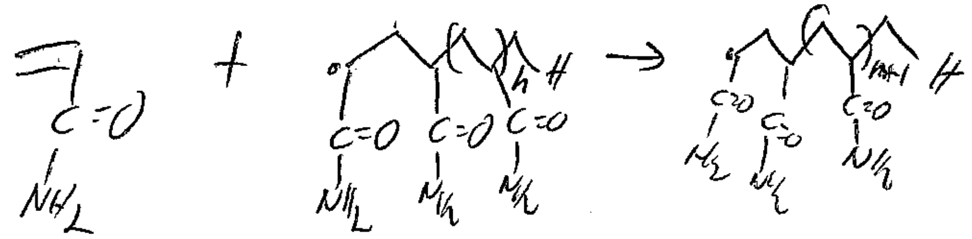


can easily approach the growing chain so low termination ~~rates~~ result & a runaway reaction (~~Tromsdorf~~ effect). The dilute system didn't an heat.

For high concentrations the reaction resulted in a stiff gel & the water could not be separated from the polymer. For dilute the polymer was easily separated by percipitation in acidified propanol.

The concentrated system used little solvent but the dilute system produced about 5X as much solvent as polymer.

2) a)



$$M + \cdot M_n \underset{}{\overset{k_p}{\rightleftarrows}} \cdot M_{n+1}$$

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

monomer Concentration

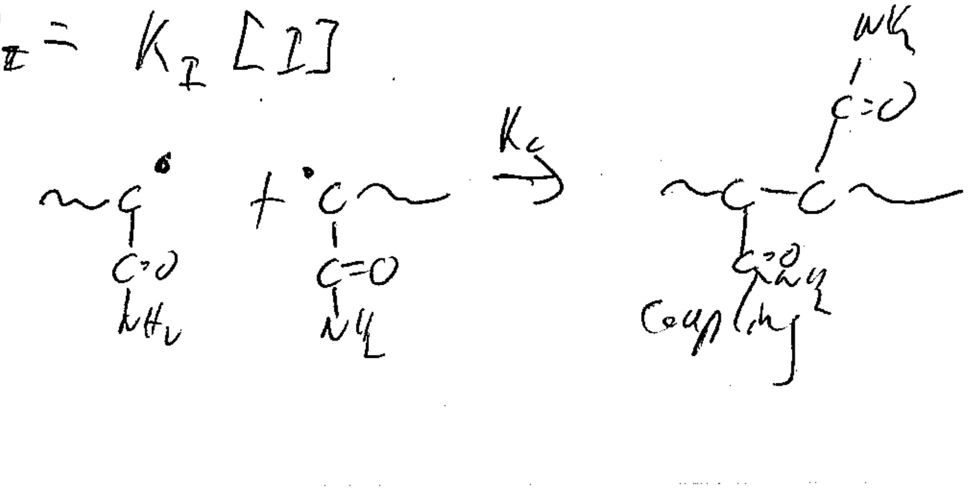
Propagating Radical Concentration

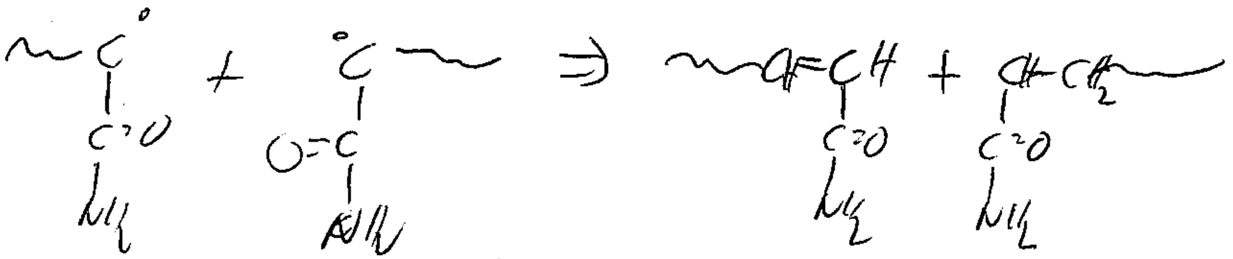
b)

$$HO{-}OH \xrightarrow[Fe^{+3}\ \curvearrowright\ Fe^{+2}]{} HO\!:^- + HO\cdot$$

$$R_I = K_I [I]$$

c)

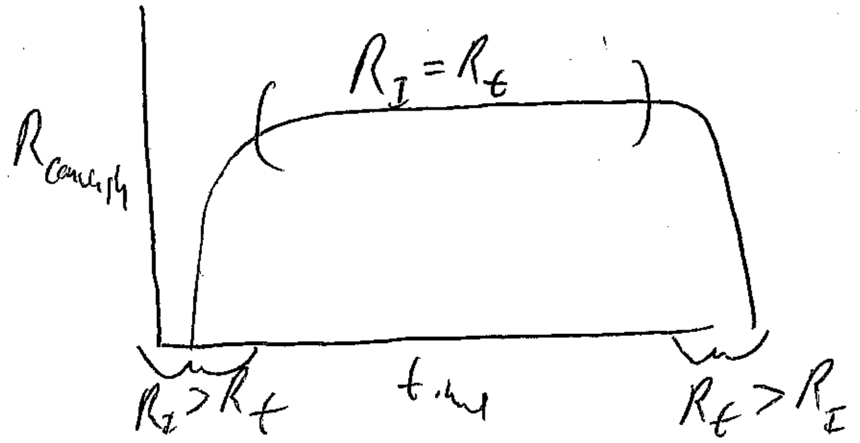




dispropotionation

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

d)



For most of the reaction $R_I = R_t$

e) $$\bar{\nu} = \frac{R_p}{R_t} = \frac{R_p}{R_I} = \frac{K_p[M][M\cdot]}{K_t[M\cdot]^2}$$

from $R_I = R_t$ we have

$$[M\cdot] = \sqrt{\frac{K_I[I]}{K_t}}$$

$$\bar{\nu} = \frac{K_p[M]}{\sqrt{K_t K_I [I]}}$$

3) a) Suspension:

2 phase

Monomer & Solvent

Initiator is soluble in the Monomer Phase

Particle size is determined by strength of agitation & presence of polyvinyl alcohol

Kinetics Match Bulk Polymerization

$$\bar{\nu} = \frac{k_p [M]}{\sqrt{k_t k_d [I]}}$$

b) Emulsion:

2 phase

Monomer & Solvent

Particle size is fixed by surfactant

N = # Particles is determined by surfactant concentration

Initiator is soluble in Solvent (Water)

Kinetics differ from Bulk/Solution

$$\bar{\nu} = \frac{N k_p [M]}{2 f k_d [I]} \leftarrow \text{Monomer Conc. in Micelle}$$

c) $$R_p = N k_p [M]$$

# of Micelles

Monomer Conc in Micelle

d) $$\bar{\nu} = \frac{k_p [M]}{\rho}$$

← Rate in one Micelle

termination probability for a micelle

$$\rho = \frac{2 f k_d [I]}{N}$$

$$\bar{\nu} = \frac{N k_p [M]}{2 f k_d [I]}$$

e) $\bar{\nu}$ is controlled by N & concentration of surfactant in Emulsion polymerization

Stronger dependence on [I] for Emulsion Polymeriza