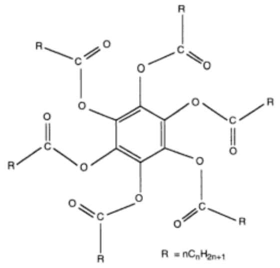
090109 Quiz 1 Introduction to Polymers

In class we discussed the definition of a polymer first by comparing polymers with metals and ceramics and then by noting certain properties of polymers that distinguish commercial polymers from low-molecular weight materials particularly pertaining to rheology.

1) Long-chain molecules crystallize in asymmetric crystals that mimic the asymmetry of the molecule.
   a) Describe the crystal shape of a moderate molecular weight alkane (wax/parafin) crystal such as dodecane. Show how the chain fits into the crystal.
   b) Sketch a plot of crystal size versus number of alkane units from butane (4) to polyethylene (1000). Explain the behavior.
   c) What determines the crystalline size for polyethylene?
   d) While alkanes display rod-like structure in the crystals you described in 1a, benzene-hexa-n-alknoate, shown below, is a macromolecule with discoidal structure. What shape crystal do you expect from such a 2 dimensional molecule?

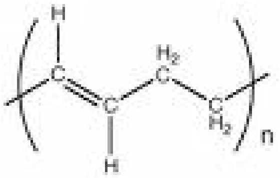


$$\text{Crystal} \xrightarrow{81.2°C} \text{Columnar hexagonal phase} \xrightarrow{87°C} \text{Isotropic liquid}$$

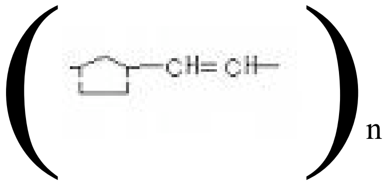
Fig. A.III.12 Homologous series of BHn (benzene-hexa-n-alkanoates). It is to this series that the first columnar phase belongs, discovered in 1977. The phase sequence presented is that of BH7 (from ref. [7]).

2) The mechanical properties of materials are usually described relative to two linear constitutive equations, Hooke's Law for linear elastic materials and Newton's Law for linearly viscous materials.
   a) Give two equations that describe a linear elastic and a linearly viscous material.
   b) A linear elastic material is characterized by the Young's modulus, E, measured in a tensile measurement. Sketch a tensile measurement defining the tensile stress and tensile strain
   c) A linearly viscous material is characterized by the melt viscosity, η, measured in a shear viscometer. Define the shear stress, rate of strain and velocity gradient in a sketch of simple shear flow.
   d) Show a plot of log of viscosity versus log of the velocity gradient for a typical high molecular weight polymer. Indicate where the fluid is Newtonian and where it displays power-law fluid behavior.
   e) Show a plot of log of the zero shear rate viscosity versus log of the molecular weight for oligomers (low-molecular weight) and polymers (high molecular weight). Indicate the slopes.

3) In class we froze a rubber ball using liquid nitrogen and observed changes in the mechanical properties as the ball warmed up to room temperature. We also observed differences in behavior between a polybutadiene (happy) and a polynorbornene (sad) rubber ball.



polybutadiene



polynorbornene

a) Plot the ratio of the viscous or loss (heat) to the elastic or storage (bounce) response of the rubber ball as it warms up.

b) Explain why there is a peak in this plot, that is, why is the ratio low at low temperature, low at high temperature and high at an intermediate temperature?

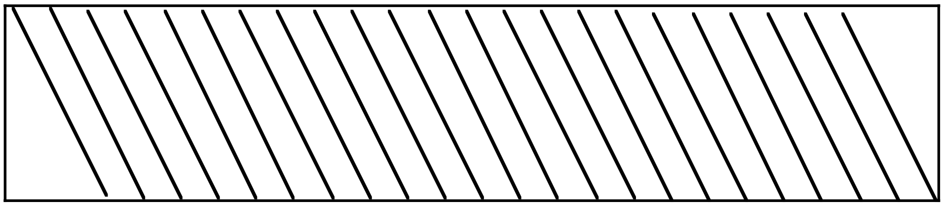
c) Explain why the happy ball is happy and why the sad ball is sad.

d) How does frequency effect this behavior and why.

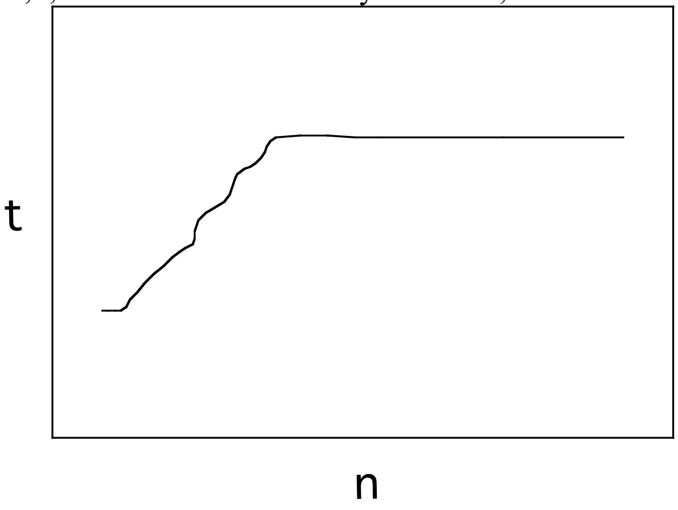
e) Tires have a maximum safe velocity and a minimum use temperature. Explain why tires might have a miximum velocity and minimum use temperature while other components of a car such as the springs or axle do not.

ANSWERS: 090109 Quiz 1 Introduction to Polymers

1) a) Alkanes crystallize into sheet like crystals with the major molecular axis at a tilt (usually) to the sheet surface.



b) Crystalline thickness, t, versus number of methylene units, n.



c) The crystallization temperature, T_c, governs the crystalline thickness following the Hoffman Lauritzen Equation (Gibbs Thompson Equation).

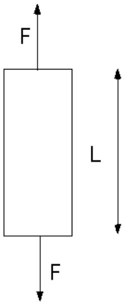
$$t = \frac{2\gamma T_\infty}{\Delta H(T_\infty - T_c)}$$

where γ is the surface energy ΔH is the enthalpy of crystallization, T_∞ is the equilibrium melting temperature.

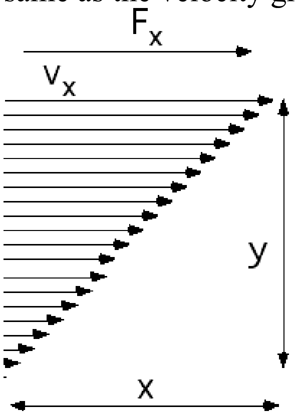
d) 1-d molecules form 2d crystals, 2d molecules form 1 crystals. Benzene-hexa-n-alknoate forms columnar crystals (liquid crystals).

2) a) Linear elastic: tensile stress is proportional to tensile strain with the Young's Modulus as the scaling coefficient $\sigma = E\varepsilon$. Linearly viscous: shear stress is proportional to the shear strain rate with the viscosity as the scaling coefficient $\tau = \eta\dot{\gamma}$.

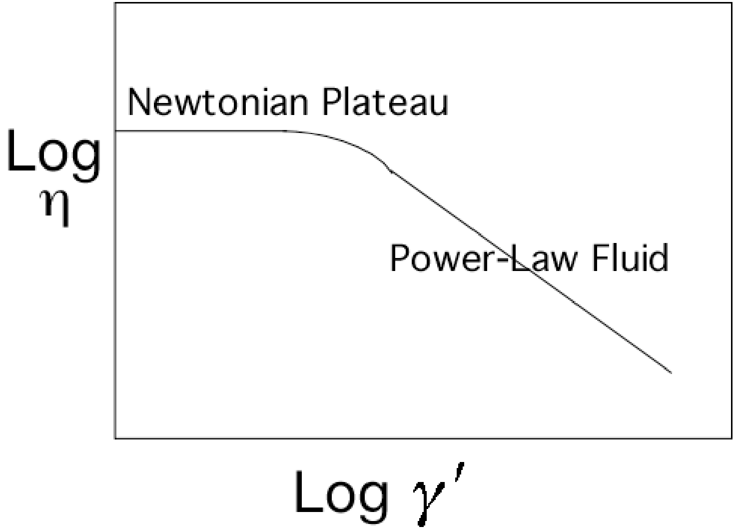
b) A force is applied to the surface normal to the force. The length changes in the same direction as the force. $\sigma = F/A$ and $\varepsilon = \Delta L/L$



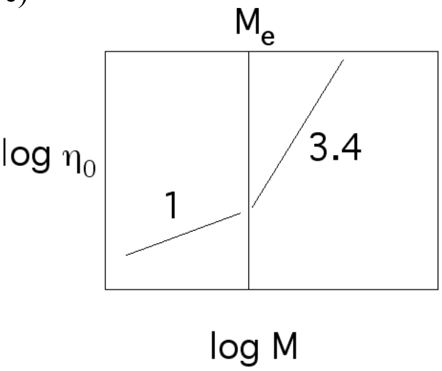
c) A force is applied to a surface whose normal is perpendicular to the direction of the force. The ratio of the stress to the area is the shear stress, τ. The length changes in the direction of the force with a gradient normal to the force. The ratio of the length change with respect to the gap or gradient distance is the shear strain, γ. We usually consider a dynamic shear process where the gradient of the x-velocity in the y-direction is the rate of shear strain. The rate of strain is the same as the velocity gradient.



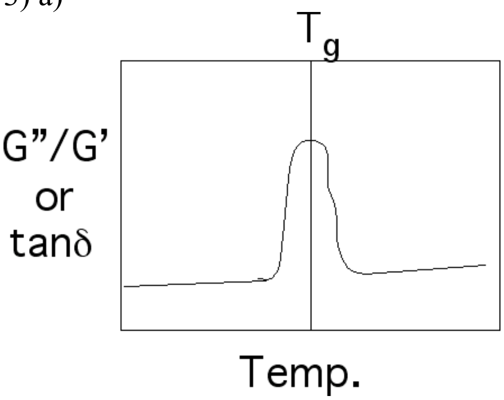
d)



e)



3) a)



b) The polymer chain has a characteristic time, τ, that is needed for it to vibrate. This time is associated with the time for coordinated bond rotation at a local level (9 mer units). There is also a characteristic energy, E_a, associated with this molecular motion. In a temperature ramp the point at which the energy associated with temperature, kT, equals the energy needed to move the polymer, E_a, we observe close to complete conversion of mechanical energy to heat, that is the loss or G" is maximum relative to the storage G'. At temperatures (or frequencies) lower than this characteristic temperature or glass transition temperature, T_g, there is insufficient energy for coordinated motion of the polymer chains. At these temperatures the material is a glass. The elastic modulus is large compared to the storage modulus. At high temperatures the chains move freely and because the chains are tethered to each other through crosslink's in a rubber we see rubber elasticity where mechanical energy is stored in chain deformation relative to the random state. The existing motion of the chains at high temperature does not allow for much of the mechanical energy added in bouncing to be converted to heat.

c) The happy ball is happy because polybutadiene has a glass transition temperature at about -60C. The sad ball is sad because polynorbornene has a glass transition at room temperature. The difference in chemical structure leads to differences in the energy required to rotate bonds. Polynorbornene has a stiffer backbone so a higher glass transition temperature, requiring more thermal energy to cause bond rotation.

d) There is a characteristic temperature at a fixed frequency of mechanical deformation (speed of ball impact). For higher frequency the material acts as if the temperature were dropped. A rubber ball will act like a glass at sufficient speed.

e) Basically the tire rubber could approach T_g or worse the glassy state at high frequencies or at low temperatures. Near the glass transition the tires would dissipate a lot of heat and would give bad fuel efficiency. Below T_g you would get a very rough ride of the tires might exploded.

090116 Quiz 2 Introduction to Polymers

1) Synthetic polymers generally do not display a single molecular weight. Consider the polymerization process that includes chemical steps for initiation, propagation and termination.

a) Explain how the nature of initiation (sporatic versus spontaneous) can affect polydispersity.

b) Explain how the nature of propagation (linear, branched, uniformity of rate of propagation etc.) might affect polydispersity.

c) Explain how the nature of termination (combination of two propagating species versus combination with a low molecular weight species etc.) could affect polydispersity.

d) How could a bimodal distribution result in a polyethylene sample? (Explain a possible synthetic scheme that could lead to a bimodal distribution of molecular weight.)

e) Describe a synthetic scheme that could lead to a monodisperse polymer including a description of initiation, propagation and termination.

2) Proteins are bio-polyamides that have a single value for molecular weight. Nylon is a synthetic polyamide that generally has a polydispersity index of about 2.5.

a) What is the polydispersity index for a protein?

b) What are the units of the polydispersity index?

c) Polydisperse polymers generally have better properties compared to monodisperse polymers. The modulus of a polymer chain is inversely proportional to the molecular weight and the extensibility increases with molecular weight. Explain why polydispersity might help mechanical properties. Is high or low molecular weight better for mechanical properties?

d) Viscosity depends on the molecular weight to the 3.4 power. Explain why a polydisperse polymer might be better for processing (flow) properties for a polymer. (The formation of fibers and films in processing requires high "melt-strength" meaning that the melt displays elastic properties.) Is high or low molecular weight better for processing?

e) Do you think a protein would have very good engineering properties compared to nylon?

3) a) Explain how a membrane osmometer measures the molecular weight of a polymer.

b) How does a GPC measure molecular weight.

c) How would you calculate the molecular weight measured in the membrane osmometer if you had the GPC curve for a polymer.

d) How is the standard deviation related to the polydispersity index.

e) GPC's are sometimes equipped with a viscometer and index detector. What is the advantage of using these two detectors on the GPC rather than just an index of refraction detector. (The index of refraction is proportional to the concentration.)

ANSWERS: 090116 Quiz 2 Introduction to Polymers

1) a) If initiation starts sporatically, that is at random points during time, and if growth occurs for the same length of time, then the chains will have differing lengths.

b) If there is variability in the rate of propagation or if chains branch by formation of multiple growth sites on the same chain structure a polydisperse molecular weight distribution can result.

c) Termination can occur by destruction of the active site, by combination with a low-molecular weight material or by combination of two chains of different or the same molecular weights. Variability in the conditions of termination can lead to polydispersity.

d) One mechanism for a bimodal distribution is formation of some chains with branches by combination at the termination step. Chains that do not combine to make a branched polymer will have about 1/3 the molecular weight of chains with one branch for instance.

e) Initiation would need to be spontaneous (occurring at one time), propagation would need to be of a fixed rate with no branching, termination would need to occur spontaneously and by the same mechanism for all growing chains.

2) a) PDI = 1

b) PDI is unitless

c) Contributions from high and low modulus chains can lead to a tough material that has high modulus and some extensibility due to contributions of different chain lengths. Low molecular weight is good for high modulus and high molecular weight is good for high extensibility.

d) High molecular weight gives "melt strength" for fiber formation and for coherency of the melt, low molecular weight eases flow with low viscosity. A blend of the two is needed for processing since you want melt strength as well as lower viscosity.

e) A protein would have poor engineering properties from a synthetic polymer perspective because it would be basically a brittle highly viscous material with low melt strength.

3) a) Two baths are separated by a semi-permeable membrane that allows solvent to pass but not polymer. One side has a dilute polymer solution and the other has only solvent. Solvent will flow from the low to high concentrated sides in an attempt to dilute the polymer solution leading to an increase in the pressure. This increase is called the osmotic pressure, π. We can thing of the osmotic pressure, in the first order approximation, as being caused by the suspended particles acting as a gas. Then the osmotic pressure is given by the ideal gas law, $\pi = cRT$ where c is the number of polymer molecules in the volume of the polymer bath. If we know the mass that was added and the volume of the bath then we can calculate the mass per polymer by dividing the added mass/vol by the measured number/vol. This results in a number average molecular weight.

b) A GPC measures molecular weight by a size exclusion principle. A high pressure pump pumps a dilute solution of a polymer through a swollen gel such as a polystyrene gel. Large molecules can only probe large pores which make up a small volume of the gel so large molecules pass through the gel quickly. Small molecules probe into the gel structure at a smaller scale and can visit a much larger volume of the gel so the residence time of small molecules is much higher. The GPC/SEC/HPLC separate molecules based on their "hydrodynamic" size, meaning the size they present during flow.

c) If the GPC curve is P(M) versus M, the number average, measured in membrane osmometry, is calculated by,

$$M_1 = \frac{\int_0^\infty MP(M)dM}{\int_0^\infty P(M)dM}$$

d) The standard deviation is given by,

$$\sigma = \frac{\int_0^\infty (M - M_1)^2 P(M)dM}{\int_0^\infty P(M)dM} = \frac{\int_0^\infty M^2 P(M)dM - 2\int_0^\infty MM_1 P(M)dM + M_1^2 \int_0^\infty P(M)dM}{\int_0^\infty P(M)dM}$$

$$= M_2 - M_1^2 = M_1^2\left(\frac{M_2}{M_1^2} - 1\right) = M_1^2\left(PDI - 1\right)$$

$$= M_2\left(1 - \frac{M_1^2}{M_2}\right) = M_2\left(1 - \frac{1}{PDI}\right)$$

e) The viscometer yields the viscosity average molecular weight in an absolute measurement. For a narrow fraction in the GPC all of the molecular weight moments are equal so that the viscosity average is an absolute measure of the molecular weight for a narrow fraction and can be used to internally calibrate the GPC curve without the use of secondary standards. The viscometer measures the intrinsic viscosity, [η] which is proportional to kM^a, where the values of k and a can be obtained in the Polymer Handbook. k and a are known as the Mark-Houwink constants. a varies from 0.5 to 2 with 0.8 being the expected value for a dilute solution.

090126 Introduction to Polymers

1) The following is from an article about research at Livermore-Berkley National Laboratories that came out last week:

> *In their latest research, Ritchie and the team expanded on advances made two years ago, when researchers developed a method to improve the strength of bone substitutes through a technique that involves freezing seawater. The freeze-casting technique has been refined and applied to an alumina/PMMA hybrid to create large porous ceramic scaffolds that closely mirror the complex hierarchical microstructure of nacre, or mother of pearl.*
> *The next step in creating tougher ceramics, say the researchers, is to improve the proportion of ceramic to polymer in their composites, and to replace the PMMA with a better polymer. Ultimately the aim is to eventually replace the polymer content with metal.*
> *http://www.industryweek.com/ReadArticle.aspx?ArticleID=18185*

a) Draw the structure of PMMA and give one common application.

b) Describe a synthesis of PMMA using free radicals.

c) What might be a better polymer than PMMA for this application? Explain why and give the structure of your replacement polymer.

d) The last sentence indicates that the polymer binder can be replaced with “metal”. Comment on the feasibility of such a simple replacement.

e) Give the structure of one polyester and give the name of this polymer, its common acronym, the monomers used to synthesize it and a common application.

2) There are two main mechanisms for polymerization.

a) Name these two mechanisms and give an example of a polymer made by each.

b) Describe the difference between the two mechanisms.

c) Sketch a plot of the number average molecular weight as a function of time for the two mechanisms.

d) Give a function for the number average molecular weight as a function of the extent of reaction p.

e) Give a function for the polydispersity index as a function of the extent of reaction, p.

3) In class we made nylon 6,10 using an interfacial polymerization following a Schotten-Baumann Reaction (http://en.wikipedia.org/wiki/Schotten-Baumann_reaction).

a) What are the monomers used to synthesize nylon 6, 10?

b) What solvents are used in the interfacial polymerization and in which solvent is each monomer dissolved?

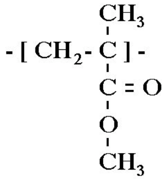
c) How is the polymer separated from the reaction mixture in this reaction?

d) How is this reaction driven to a high extent of reaction, p => 1?

e) Typically a step growth polymerization, such as the reaction of epoxy glue, proceeds through a low viscosity stage (application of the glue), a viscous stage (early stages of setting/tacky glue) and finally a solid stage (cured glue). The interfacial nylon synthesis does not display these stages. Is this really a step growth polymerization? Explain your answer.

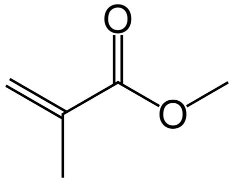
ANSWERS: 090126 Introduction to Polymers

1) a) Plexiglas, Lucite, Perspex (plastic windows and clear tabletops etc.)



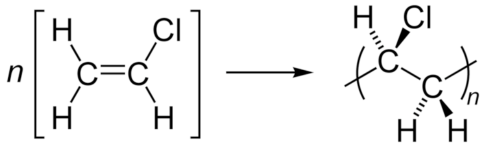
$$-[\,CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle \underset{\displaystyle CH_3}{O}}{C=O}}{C}}\,]-$$

b) Methylmethacrylate



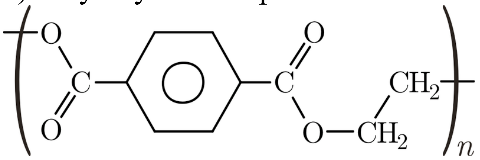
is the monomer it is initiated in a chain growth polymerization with a free radical initiator such as benzoyl peroxide in a solvent such as toluene at an elevated temperature (~ 90ºC). The reaction can be terminated with water.

c) A more polar polymer might be better for interaction with the ceramic. One example is polyvinylchloride,

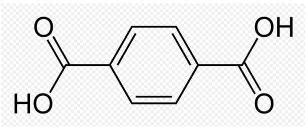


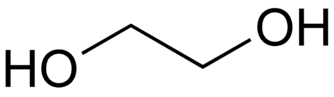
d) The process and product would be completely different for a metal binder. Basically it couldn't work in the same way so the comment about a metal is ridiculous. First a metal could only be used in the melt which is a low viscosity fluid at elevated temperature, probably hot enough to sinter the ceramic particles into a precipitated phase. The metal would crystallize when it cooled forcing further exclusion of the ceramic phase from the metal matrix. The ceramic and metal would not have good interfacial properties so it is most likely a powder would result if the suspension could be made uniform. The polymer melt is an ideal dispersant for the ceramic powder and a metal just couldn't perform this function.

e) Polyethylene terephthalate used for water and soda bottles (PET or PETE).



This is made from terephthalic acid and ethylene glycol in a step growth polymerization.



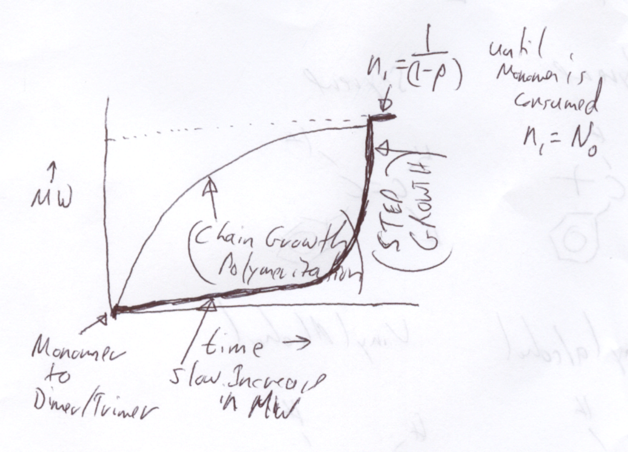


2) a) Step growth, polyurethane. Chain growth, polystyrene.

b) Step growth involves reaction of all monomers at once that combine to make dimers/tetramers etc. All monomers are consumed immediately when the reaction begins and the molecular weight growth is slow. You need a extent of reaction of 1 for this reaction to yield high molecular weight polymers.

Chain growth involves initiation using an initiator and propagation of the polymer as a chain with a propagating chain end. High molecular weight is achieved early on and polymer is produced even at moderate extents of reaction. There is monomer present even at the end of the reaction that must be removed from the polymer generally.

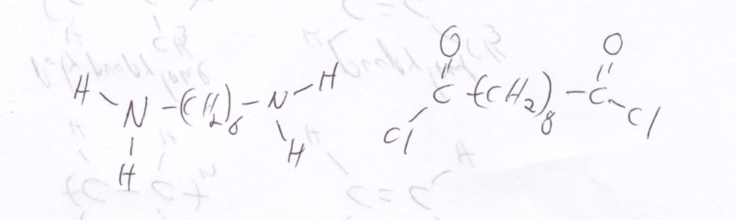
c)



d) $n_1 = n_n = 1/(1-p)$; $n_w = (1+p)/(1-p)$

e) PDI = $n_w/n_1 = (1+p)$

3) a) Hexamethyldiamine and adipic acid chloride



b) Hexane is used for the adipic acid chloride and water for the hexamethlydiamine.

c) The polymer precipitates at the interface of the two immiscible solvents.

d) The reaction is driven to p => 1 by removal of the polymer product and removal of the HCl byproduct by reaction with NaOH to form NaCl that dissolved in the water phase and H_2O.

e) It is really a step-growth polymerization because it proceeds through a step-growth mechanism. It does not seem to be the same kind of reaction as epoxy glue because the products are removed to drive the reaction rapidly and because the polymerization takes place in solvents which leads to a faster transport rate for reactants and an overall higher reaction rate.

090204 Quiz 4 Introduction to Polymers

I class we synthesized Glyptal, swelled and deswelled hydrogels and made and reversed a PVA network.

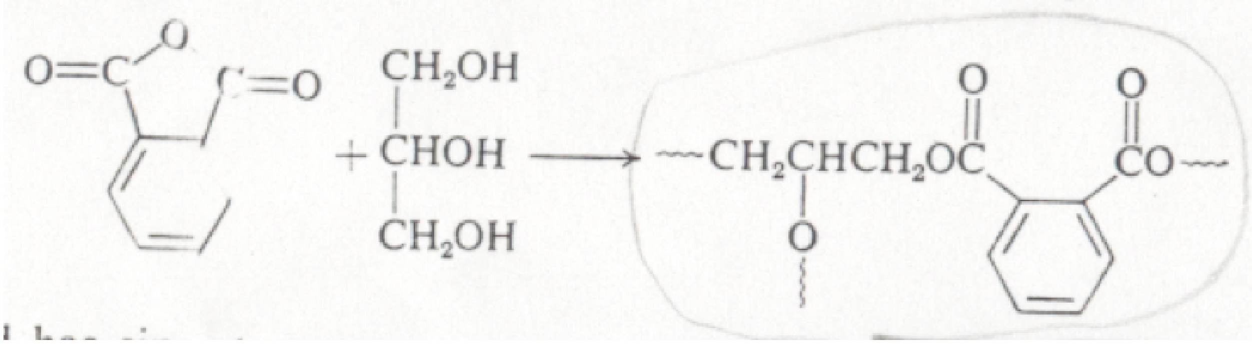
1) The synthesis of glyptal involves a trifunctional and a difunctional reactant in a condensation reaction.
   a) Give the monomers involved in glyptal in a stoichiometric chemical reaction equation. (Draw the structure and give the number of these monomers involved in a stoichiometrically balanced reaction.)
   b) What solvent is used to make glyptal?
   c) Draw the structure of sodium acetate and explain why it was used in this reaction.
   d) Give a sequence of events that occur chronologically in the reaction to form Glyptal.
   e) Give the structure of glyptal and the structure of PET (PETE) and comment on the difference in properties between these two similar polyesters based on the difference in chemical structure.

2) a) Give the structure of PMMA and the structure of the polyacrylate used in the hydrogel. Compare the two and explain the differences in properties between PMMA and polyacrylate associated with this structural difference, i.e. why isn't PMMA a superabsorbent?
   b) What happened when uncrosslinked polyacrylate was added to water? Explain this.
   c) The swelling ratio Q for the hydrogel was about 100 to 500. Write an equation for the swelling ration as a function of the interaction parameter, χ, and the molecular weight between crosslinks, n.
   d) If you wanted a more robust gel what n would you choose.
   e) What happens to χ when salt is added to the hydrogel? Explain what happens to the hydrogel.

3) a) Draw the structure of PVA and boric acid.
   b) The combination of PVA and boric acid yields slime, but when NaOH is added a rubbery elastomer results. Explain this in terms of the percolation model for gelation.
   c) What happens to the molecular weight between crosslinks when NaOH is added? What about when HCl is added?
   d) Gellation occurs at a fixed value of the extent of reaction, p_c, where c indicates the critical extent of reaction. A critical point is where some feature of the system goes to infinity. What feature of a gelling system goes to infinity at p_c, the gel point? Make a rough plot.
   e) Give a function that relates the critical extent of reaction with the structure of a stoichiometric network and calculate p_c for the glyptal system using this function.

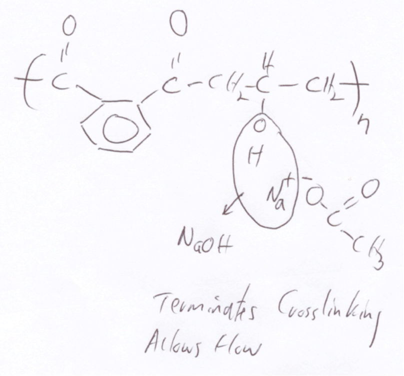
ANSWERS: 090204 Quiz 4 Introduction to Polymers

1) a) **3** phthalic anhydride + **2** Glycerol



b) The reaction is fun neat (no solvent).

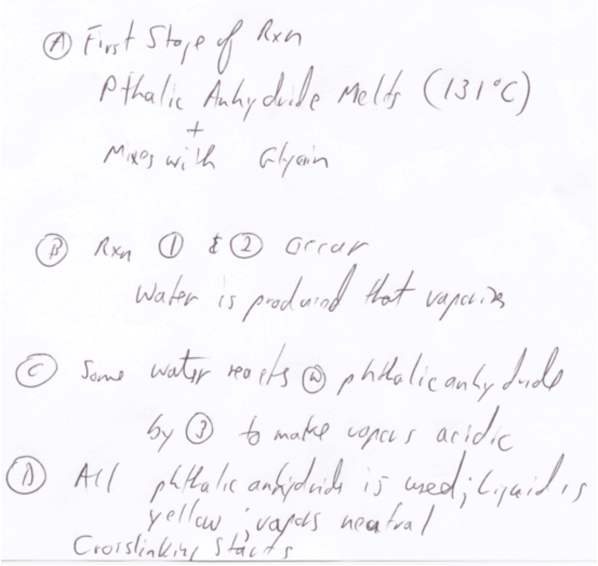
c) The overall extent of reaction relies on the functionality of the monomers and the viscosity (kinetics) of the reacting system. If the system forms a glass too early the reaction ends since molecular mobility is needed for the reaction to occur. Sodium Acetate is used to decrease the functionality of the system to make the system less viscous during the reaction and yielding an overall higher extent of reaction.



Terminates Crosslinking

Allows Flow

d)



Ⓐ First Stage of Rxn

Pthalic Anhydride Melts (131°C)

+

Mixes with Glycerin

Ⓑ Rxn ① & ② occur

water is produced that vaporizes

Ⓒ Some water reacts ⓦ phthalic anhydride

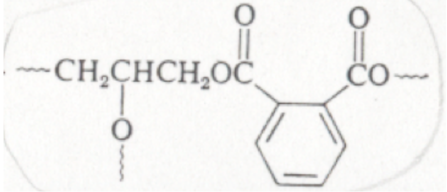
by ③ to make vapors acidic

Ⓓ All phthalic anhydride is used; Liquid is

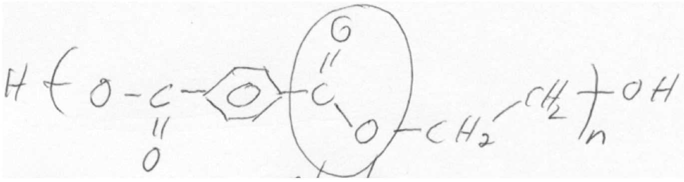
yellow; vapors neutral

Crosslinking Starts

e) Glyptal

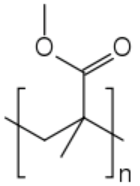


PET (PETE)

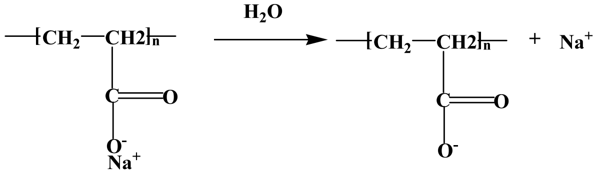


Glyptal has di ortho carboxylic substutited aromatic group and PET has di para substituted aromatic group. This makes PET more flexible than glyptal. Also, the trifunctionality of glycerin versus the difunctionality of ethylene glycol leads to a network structure that is more rigid compared to PET.

2) a) PMMA



Sodium Polyacrylate



PMMA doesn’t have an ioniazable group and it has a more bulky structure that allows it to form a glass. Polyacrylate has a more flexible structure and a highly ionizable group that will have a highly negative interaction parameter with water.

b) The uncrosslinked sodium polyacrylate just dissolved in water and formed a viscous solution. Crosslinked polyacrylate swelled because the network structure opposed the solvation. The network structure retains a solid form for the gel despite the polymers desire to dissolve.

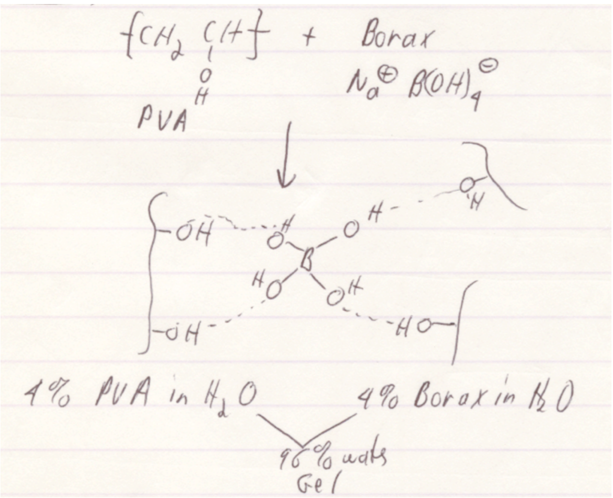
c) V_1 is the molar volume of the solvent.

$$Q = \frac{1}{v_2} \sim \left[\frac{-n\chi}{V_1}\right]^{3/5}$$

d) A more robust gel would be formed with a lower n because the gel modulus is proportional to kT/n following rubber elasticity theory.

e) Salt increases the value of χ (chi parameter) making the swelling ratio drop. If sufficient salt is added χ become positive and the gel desorbs water (the gel collapses).

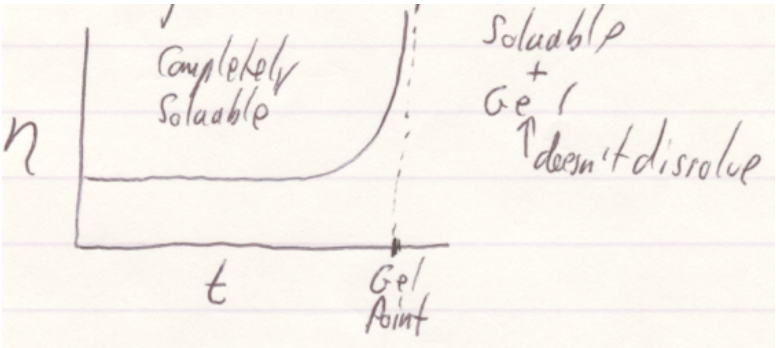
3) a)



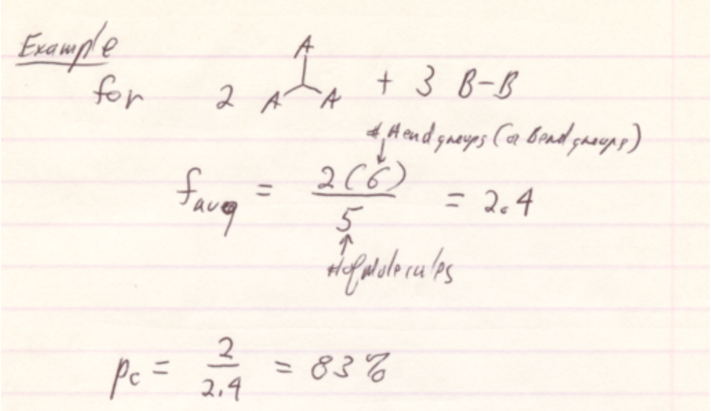
b) The Na ion forms a bridge between OH groups in boric acid and in PVA. When only a few Na ions are present a loose network forms that is still a liquid, that is percolation has not occurred, that is, there is no connecting pathway through the entire system. When NaOH is added there are sufficient Na ions to link PVA molecules through boric acid groups to percolate across the gel.

c) As NaOH is added the molecular weight between crosslinks decreases and the gel becomes more rigid. As HCl is added this molecular weight becomes larger and the gel loosens.

d) The viscosity goes to infinity at the gel point. The viscous liquid becomes a solid at the gel point.



e) $p_c = 2/f_{avg}$ define f_{avg}



Example

for 2 A(A)A + 3 B–B

A end groups (or B end groups)

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

# of molecules

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

080512 Quiz 5 Introduction to Polymer Science

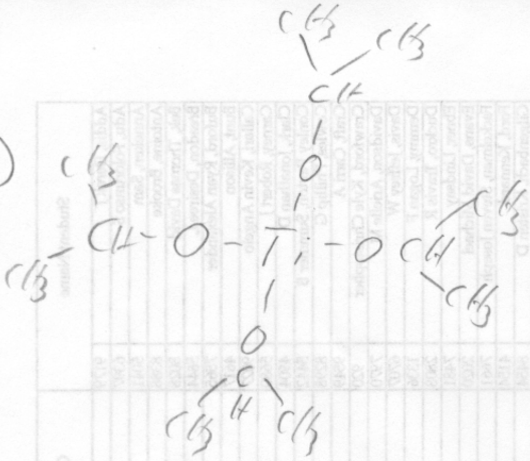
In class we used TTIP (titanium tetraisopropoxide) to crosslink hydroxyl terminated PDMS (polydimethyl siloxane). Often, PDMS is crosslinked using TEOS (tetraethoxy silicate). TEOS or TTIP can also be used to make a ceramic gel in a sol-gel reaction. This is the first step in the production of an aerogel.

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.

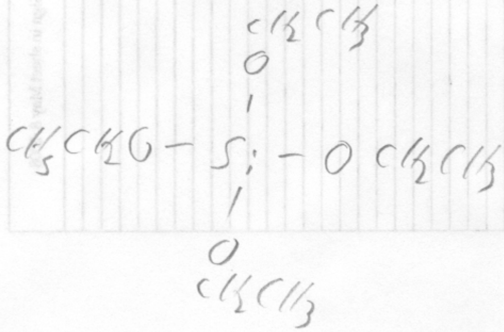
2) In crosslinking reactions to produce a rubber from hydroxyl terminated PDMS and TEOS or TTIP, HMDSO or HMDS (hexamethyldisiloxane) is often added to reduce the functionality of TEOS or other crosslinking agents.
   a) Give the structure of HMDSO (guess if you do not know, it has two silicon atoms 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.

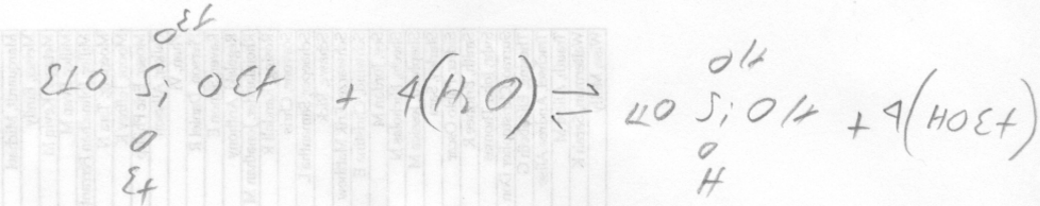
1) a)



b)



c)



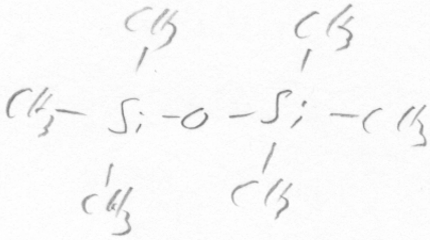
$$\mathrm{EtO}\,\overset{\mathrm{OEt}}{\underset{\mathrm{OEt}}{\mathrm{Si}}}\,\mathrm{OEt} + 4(H_2O) \rightleftharpoons \mathrm{HO}\,\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{Si}}}\,\mathrm{OH} + 4(\mathrm{HOEt})$$

d)

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

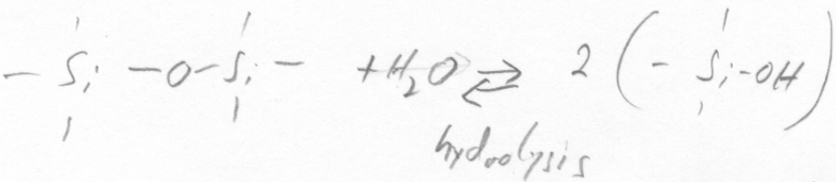
e) in "c" 4 waters are used; while in "d" 2 waters are produced so 2 waters act as catalysts & are regenerated while 2 water molecules act as reactants and are consumed.

2) a)



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

b)



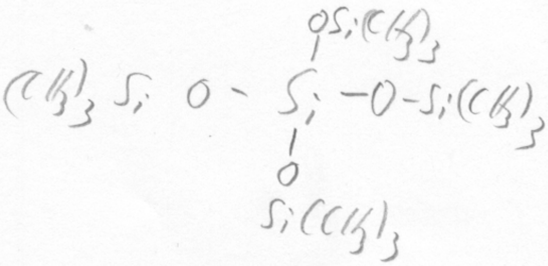
$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- \; + H_2O \underset{\text{hydrolysis}}{\rightleftarrows} 2\left(-\overset{|}{\underset{|}{Si}}-OH\right)$$

$Si(CH_3)_3(OH)$

c)

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

$+$



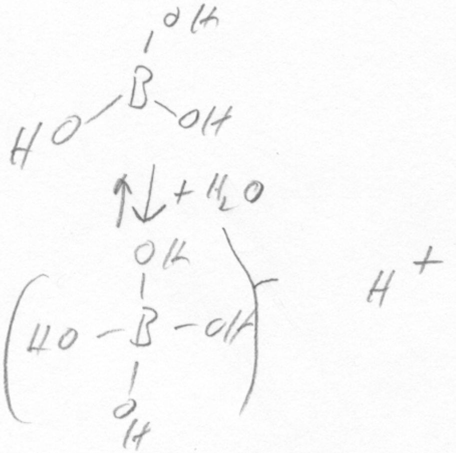
$$(CH_3)_3Si\,O-\overset{OSi(CH_3)_3}{\underset{\underset{Si(CH_3)_3}{O}}{Si}}-O-Si(CH_3)_3$$

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

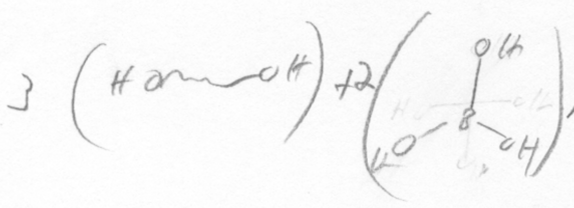
e) Low Tg & high degradation temperature lead to
−127 °C 400°C
a wide range where properties are stable −55 °C to 200+ °C

3) a)

b)



c)



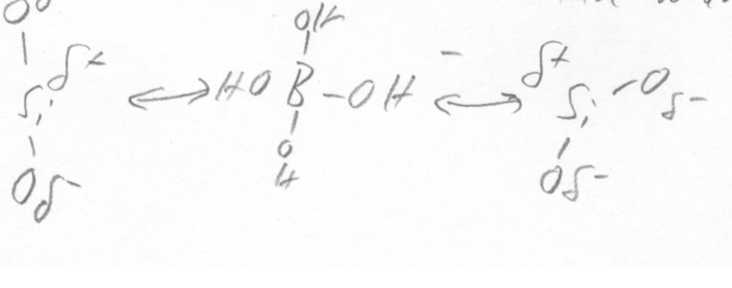
Assume tri-functional

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

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.

090218 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) In class 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 is the novolac procedure easier to demonstrate than the resole procedure?

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

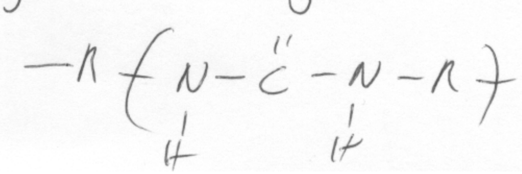
$HO \left(CH_2 - CH_2 - O \right)_n H$

c) DABCO

d) Water + isocyanate $\Rightarrow CO_2(g)$ H_2N-R

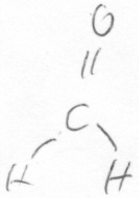
$CO_2(g) \Rightarrow$ Foaming

e) You form a poly urea



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

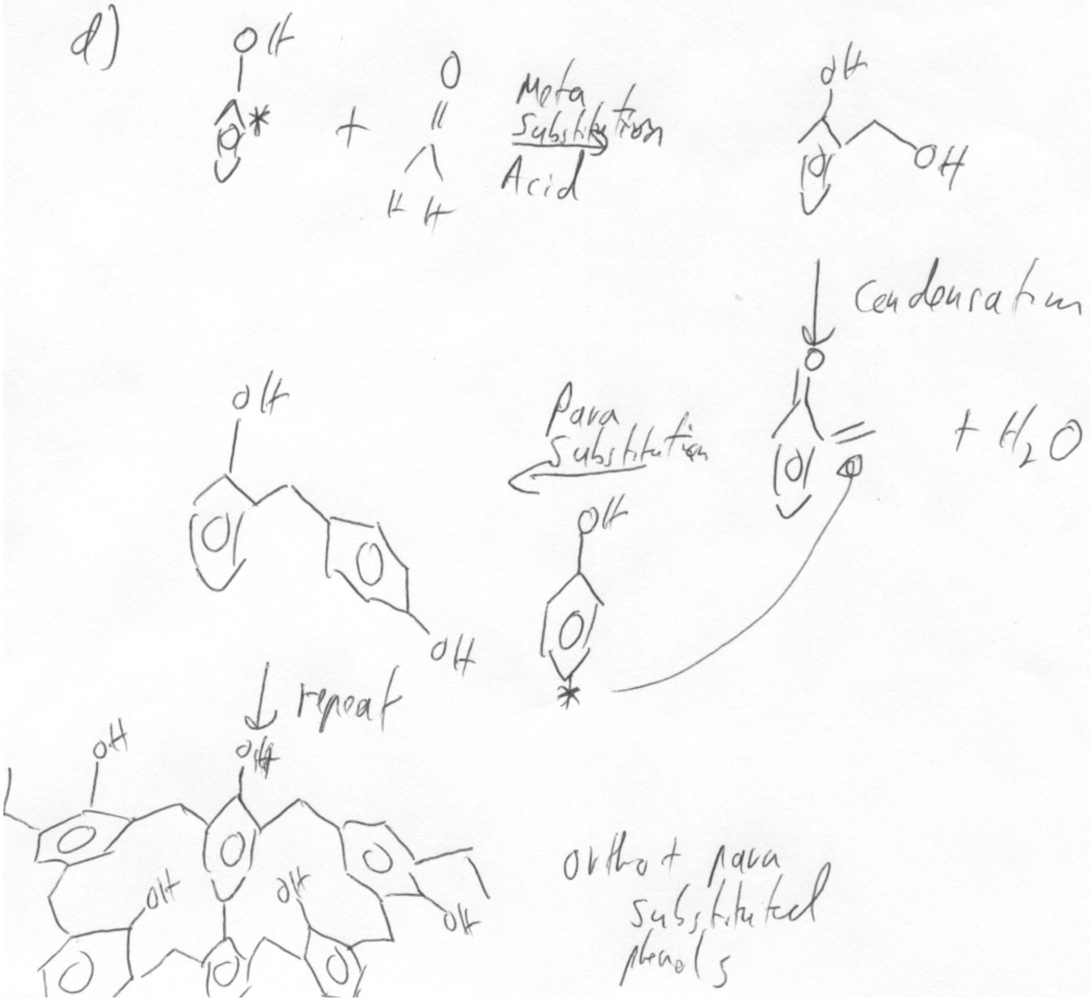
2) a) Phenol & Formaldehyde



b) Same reactants for a resole

c) Acid we used Acetic acid + HCl

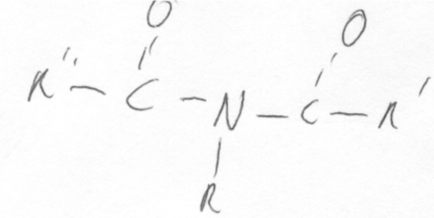
d)



ortho + para substituted phenols

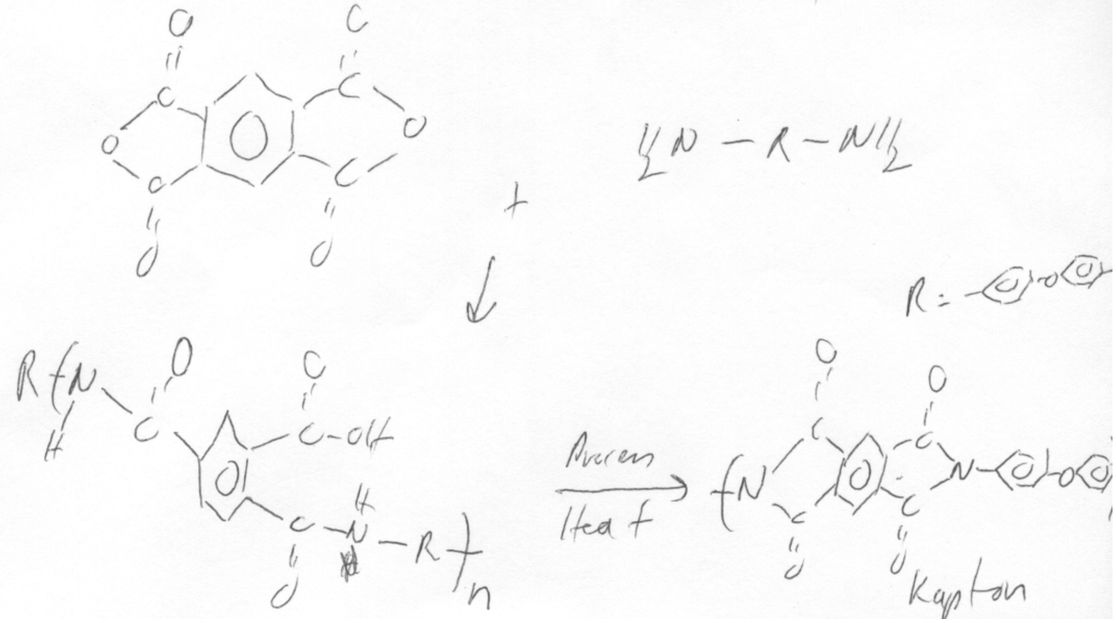
e) Resole requires heating to a boil for the last step. Novolac only requires addition of acid to fully form the polymer (pink precipitate on the stir rod).

3) a)



b) pyromellitic anhydride diamide

c)



Introduction to Polymers Quiz 7 090225

This week we discussed chain growth polymerization using free radical initiators. We performed two synthesizes for Polystyrene involving bulk polymerization and emulsion polymerization.

1) a) What are the three main stages of chain growth polymerization?
b) Is an initiator a catalyst?
c) Write an expression for the rate of propagation for chain growth polymerization in terms of the monomer concentration and the initiator concentration.
d) Obtain an exponential expression for the monomer concentration from part c and show that this is linear for early stages of the reaction.
e) Obtain an expression for the kinetic chain length for chain growth polymerization in terms of the monomer concentration and the initiator concentration.

2) a) List and draw the monomer, initiator, reaction temperature, and solvent for bulk polymerization of styrene.
b) 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.

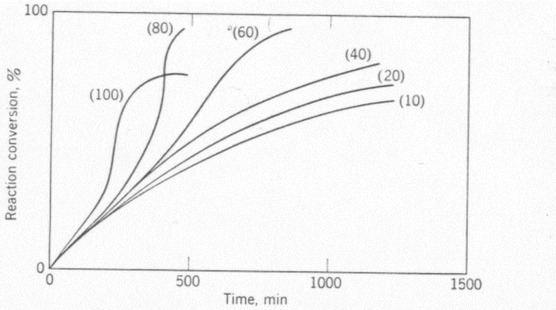


Figure 11-4. Effect of dilution on rate of polymerization of methyl methacrylate at 50°C. Curves are labeled for per cent concentration of monomer in solvent.[174] From R. W. Lenz's book.

c) 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).
d) How was polystyrene purified after the bulk polymerization?
e) What are the disadvantages of bulk polymerization?

3) a) List and draw the monomer, initiator, reaction temperature, solvent for emulsion polymerization of styrene.
b) Describe other materials needed for emulsion polymerization and why they are needed.
c) Obtain an expression for the rate of polymerization and the kinetic chain length for emulsion polymerization.
d) How does emulsion polymerization overcome the disadvantages of bulk polymerization (see question 2e).

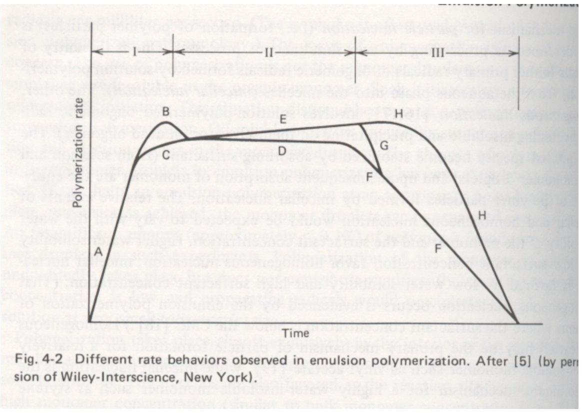
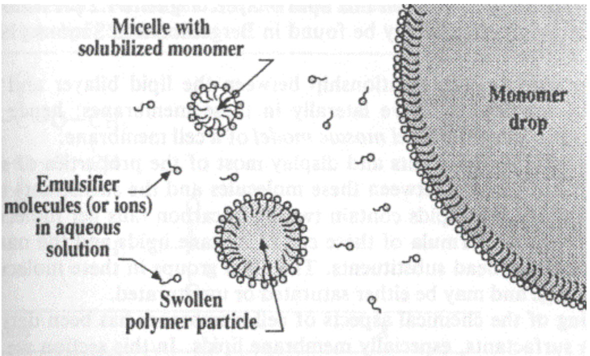


Fig. 4-2 Different rate behaviors observed in emulsion polymerization. After [5] (by per
sion of Wiley-Interscience, New York).



Figures from Heimenz *Colloid Science.*

e) The figure above (left) 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 from what you know from class. (Explain the polymerization.)

ANSWERS: Introduction to Polymers Quiz 7 090225

1) a) Initiation, propogation and termination.

b) A catalyst is not consumed in a reaction but plays a part in facilitating the reaction. Initiators are consumed and generally lead to one end group of the chain polymerized polymer. So an initiator is not a catalyst even though it is used in a small amount to facilitate a reaction.

c) $R_p = -\frac{d[M]}{dt} = k_p\sqrt{\frac{fk_d}{k_t}}\sqrt{[I]}[M] = K\sqrt{[I]}[M]$

$$\int_{[M]_0}^{[M]} \frac{d[M]}{[M]} = -K\sqrt{[I]}\int_0^t dt$$

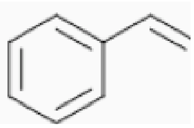
d) $\ln\left(\frac{[M]}{[M]_0}\right) = -K\sqrt{[I]}t$

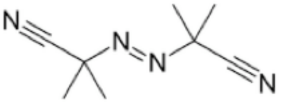
$$[M] = [M]_0 \exp\left(-K\sqrt{[I]}t\right)$$

The exponential can be expanded, $\exp -x = 1 - \frac{x}{1!} + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \ldots$

For short times we can consider only the first two terms so, $[M] \approx [M]_0\left(1 - K\sqrt{[I]}t\right)$

e) $\bar{\upsilon} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p\sqrt{\frac{fk_d}{k_t}}\sqrt{[I]}[M]}{fk_d[I]} = \frac{k_p[M]}{k_t\sqrt{fk_d[I]}}$

2) a) monomer: Styrene 



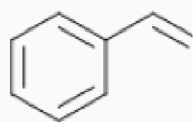
initiator: AIBN Azobisisobutyronitrile
Temperature: 80C (degradation of AIBN at 60C)
Solvent: Bulk polymerization i.e. no solvent

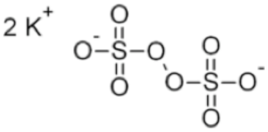
b) $R_p = K\sqrt{[I]}[M]$ and $[M] = [M]_0 \exp\left(-K\sqrt{[I]}t\right)$

c) This is a manifestation of the Trommsdorf (gel) effect. The increase in rate occurs because termination is primarily by combination and two chains cannot reach each other when the system gels so that termination stops. Propagation continues since monmers can still diffuse to the growing chain. The system is viscous so the heat generated by propagation increases the temperature rapidly.

d) The bulk polymerization product was dissolved in a small amount of toluene and this solution was precipitated by adding to an excess of propanol while stirring. The polymer was washed several times with propanol.

e) The disadvantages of bulk polymerization are poor heat transfer from the reaction that leads to overheating of the polymerizing system and the Trommsdorf effect. Polydispersity is high due to backbiting of the radical on the chain. Chain transfer is prominent due to the high density of chains. Reducing [I] increases molecular weight but only at the epense of lowering the rate of polymerization. You can not get high molecular weight and high rate of polymerization.

3) a) monomer: Styrene 

initiator: Potassium persulfate 

Temperature: ~80C (degradation of Potassium persulfate at ~60C)
Solvent: There is no solvent. The reaction occurs in the bulk within micelles that are suspended in water.

b) Micelles are made from sodium dodecyl sulfate 

Water is used to suspend the micelles and as a medium to form free radicals with potassium persulfate.
The micelles are broken with NaCl after the reaction is complete.
c) The micelles are active (growing free radical) half of the time and are dormant (no growing free radical) half of the time. The rate of polymerization depends on the number of micelles, N and the monomer concentration [M].

$$R_p = \frac{k_p[M]N}{2}$$

The micelles grow half of the time. The rate of the micelles being turned on and off is given by the rate of initiation, R_i, divided by the number of micelles, N, $\rho = \frac{R_i}{N} = \frac{2fk_d[I]}{N}$. The kinetic chain length is the rate of propagation divided by this rate of switching on and off, $\bar{\upsilon} = \frac{k_p[M]N}{2fk_d[I]}$.

d) By increasing N both the degree of polymerization and the rate can be increased. This can be achieved by adding more SDS. Decreasing [I] will only effect the degree of polymerization. This overcomes the problem with bulk polymerization that for high molecular weight products you need to slow the reaction rate.

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 that 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.

090304 Quiz 8 Introduction to Polymers (Chemistry)

This week we ran a suspension polymerization to make polystyrene, a solution polymerization to make polyacrylamide and we discussed Ziegler-Natta polymerization to make polypropylene.

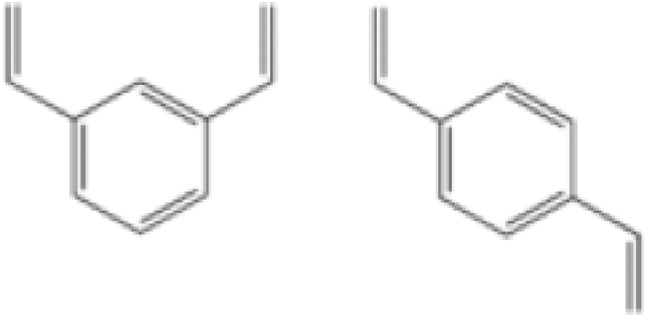
1) Suspension polymerization is similar to emulsion polymerization.
   a) Describe the importance of water to emulsion and suspension polymerization. Does water play an identical role in these two polymerizations? Is water a solvent?
   b) Describe the initiator that we used in suspension polymerization. What condition is needed to initiate this reaction? Why was a different initiator used in the emulsion polymerization?
   c) What is divinyl benzene and why is it included in this reaction?
   d) What controls the size of the polymer beads (droplet size) that result from suspension polymerization?
   e) What was the advantage of emulsion polymerization (over suspension polymerization) that lead to its development by Goodyear Tire and Rubber in the 1920's?

2) Polyacrylamide is soluble in water as is the monomer acrylamide therefore this is a solution polymerization.
   a) Use the words *ferric* and *ferrous* to describe the initiator system for this polymerization. Why is this called a *redox system*?
   b) When hydrogen peroxide was added to the reaction mixture it turned from a faint bluish green to red (rust color). Later the color seemed to fade. Why did it change color?
   c) What temperature was needed to perform this polymerization? Why?
   d) How was polymer separated from the viscous reaction mixture after polymerization?
   e) Explain the disadvantage of solution polymerization compared to emulsion or suspension polymerization.

3) We looked at Ziegler-Natta polymerization briefly.
   a) What two compounds would you mix to make a Ziegler-Natta catalyst system?
   b) Why does one of these include a transition metal?
   c) Is Ziegler-Natta polymerization carried out in the bulk or in solution? (You may need to guess an answer to this, ethylene monomer is a gas at STP.)
   d) Why was there a problem with polymerization of propylene by free radical mechanisms?
   e) Why does Ziegler-Natta polymerization result in isotactic polypropylene?

ANSWERS: **090304 Quiz 8 Introduction to Polymers (Chemistry)**

1) a) Bulk polymerization heats up to much so the idea in both emulsion and suspension polymerization is to disperse the bulk polymerization into small droplets where heat transfer is fast to a water phase. In emulsion polymerization the initiator is in the water phase and the water phase also contains reservoirs of monomer that feed the micellar reacting nano-droplets. In suspension polymerization the initiator is in the monomer phase so multiple initiated chains exist in each droplet. The kinetics of polymerization are the same for suspension and for bulk.
b) Benzoyl peroxide was used. It is initiated by heat at about 80C. BP goes into the monomer phase. In emulsion polymerization potassium persulfate was used as the initiator and it was in the water phase so it initiated the micelles only at the interface.
c) Divinyl benzene (below) acts as a tetrafunctional crosslinking agent making a network in the suspension particles.



d) The droplet size is controlled by the rate of mixing, the amount of polymer and the presence of polyvinylalcohol. The size is a balance between coalescence and breakup of the monomer/polymer droplets.
e) Emulsion polymerization allowed the production of sticky polymers such as polybutadiene and polyisoprene rubber.

2) a,b) 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). The rust color fades later due to reduction of Fe+3 by –OH species in the aqueous solution.
c) The reaction occurred at room temperature. Heating was not an issue for this redox catalyst system.
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. The polymerization rate is much slower in solution polymerization of high molecular weight polymers.

3) a) $TiCl_3$ and $Al(C_2H_5)_2Cl$ or $TiCl_4$ $Al(C_2H_5)_3$ or VCl_4 and $Al(C_2H_5)_2Cl$.
b) 6 bonding orbitals with only 5 filled leaves one for coordination with a vinyl bond. Transition metals have multiple oxidation states, this is why they are used as catalysts.
c) It is carried out in solution as described by the UBC web page, http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/UBCWassellExperiment%209.htm, although they do not give the solvent used. This is either p-xylene or dichlorobenzene at high temperature (135C).
d) Polypropylene can not propogate with a free radical mechanism because the methyl side group can hold a free radical more easily than the vinyl group.
e) The Cossee-Arlman mechanism is highly sterically restricted. The monmer only fits into the catalyst site in one orientation with respect to the growing chain.

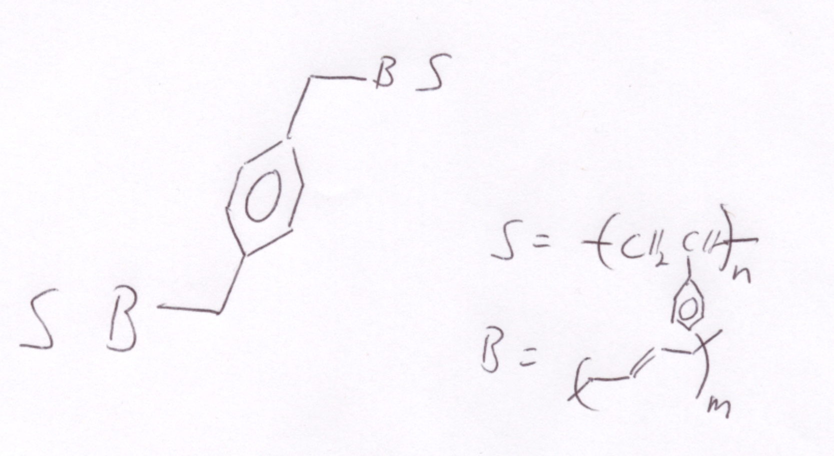
090313 Quiz 9 Introduction to Polymers (Chemistry)

This week we ran an ATRP polymerization and discussed anionic and cationic polymerization as well as the nomenclature for stereochemistry of polymers.

1) a) Name and draw the structure of the monomers used for ATRP polymerization in class.
b,c) Explain how ATRP is a living polymerization, that is, give the mechanism for the extension of the lifetime of the free radical including chemical species involve in the synthesis done in class.
d) In the ATRP reaction the reaction mixture turned first blue, then green then back to blue. Explain these color changes.
e) Why was vitamin C added to the reaction mixture? Is this always necessary for an ATRP polymerization?

2) a) Describe the basic unit of stereochemistry in polymers and the possible states that this basic unit can display.
b) What is the smallest stereochemical unit that can be measured and explain why this is the smallest measurable stereochemical unit.
c) Describe the states that the stereochemical unit of part b can display.
d) PVME (polyvinylmethylether) polymerized cationically at very low temperatures is predominantly isotactic. Polyisobutylene polymerized under identical conditions is not. Explain why.
e) Describe an atactic polymer and describe a stereochemically random polymer.

3) a) Why is there no real termination for ionic polymerizations (i.e. no coupling or disproportionation)?
b) Briefly outline how you would produce Kraton Rubber which is a block copolymer with the structure:

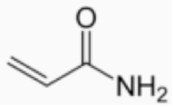


c) How would you make a 4-arm star polymer of polystyrene using a similar polymerization to part *e*?
d) Name a typical initiator for anionic polymerization.
e) Why are the number of monomers that can possibly be polymerized by anionic and cationic polymerization extremely limited? Give examples of monomers that can be polymerized by these two mechanisms and show the propagating species.

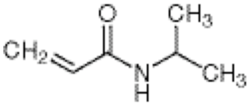
Answers: 090313 Quiz 9 Introduction to Polymers (Chemistry)

1) a)

Monomer 1 Acrylamide

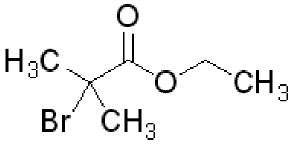


Monomer 2 n-isopropylacrylamide



b,c) In ATRP an organohalide (RX) and a transition metal (Mt)/ligand complex (Lm) are in equilibrium with a radical R•. The radical initiator reacts with a monomer to produce a propagating polymeric species. The halide/radical equilibrium serves to protect the radical from recombination since the radical is only present a small amount of the time in an unprotected, propagating form and spends most of the time protected by the organohalide group.

In class the organohalide was

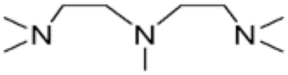


Ethyl Bromo isobutyrate

The transition metal came from

Cupric Bromide Cu(II)Br

The ligand was



PMDETA N,n,n',n',n-Pentamethyldiethylenetriamine

d) When PMDTA is added the solution turns blue because the Cu(II) ligand complex is formed. With addition of ascorbic acid the solution turned dark blue/black/ or green depending on the amount of reducing agent. This is conversion of Cu^{+2} to Cu^{+} with formation of the protected free radical in the activated state. The color is determined by the equilibrium between activated and deactivated state. Oxygen in air gradually dissolves in the solution from the air and oxidizes Cu^{+} to Cu^{+2} causing the color to return towards blue.

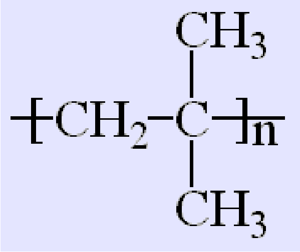
e) Vitamin C is ascorbic acid see question d. It is a reducing agent and it removes dissolved oxygen from the water. It would not have been necessary if the water was degassed and if the reaction were run under an inert gas (dry Nitrogen).

2) a) The basic unit is a diad and it can be meso (same orientation of substitution) or racemic (mixed state of substitution).

b) NMR measures only triads since it measures the perturbation of nuclear spin at a particular substitutent group by neighboring mer units (substitutent groups). Since a given substitutent group is equal distance to two other groups it can only measure a group of 3 at the smallest size. Larger groups can be measured. A group of 3 mer units is called a triad.

c) isotactic mm, syndiotactic rr, heterotactic mr or rm.

d) Polyisobutylene is symmetrically substituted so it does not display tacticity.

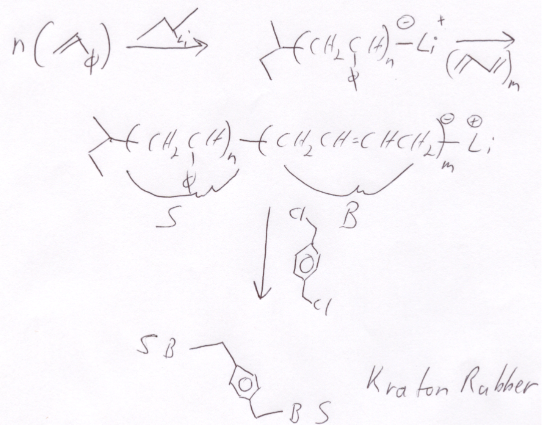


$$\left[CH_2 - \underset{CH_3}{\overset{CH_3}{C}} \right]_n$$

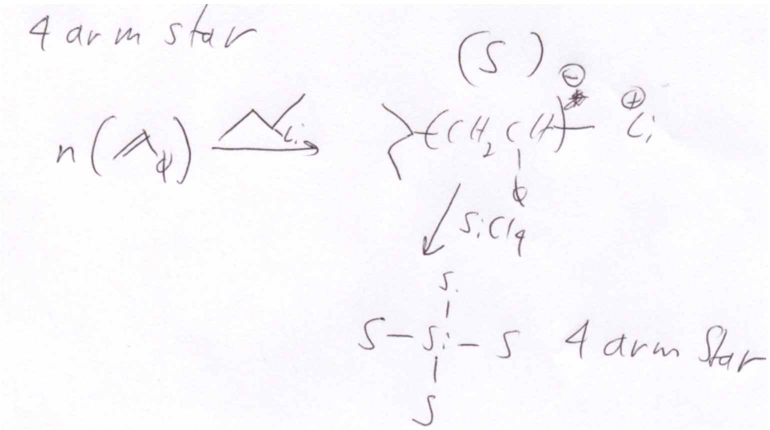
e) A stereochemically random polymer contains 50% racemic and 50% meso diads; 25% isotactic, syndiotactic and 50% heterotactic triads; etc for higher order tacticities. An atactic polymer doesn't crytallize but there isn't a fixed tacticity value.

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

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

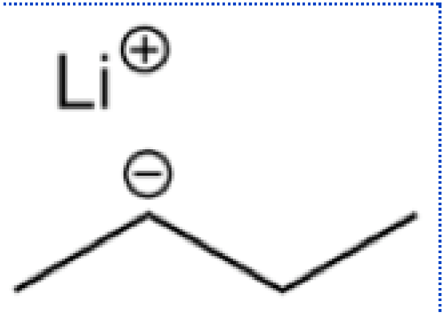


c)



d) sec-butyl lithium or tert-butyl lithium (t-butyl lithium).

***sec*-Butyllithium**



***tert*-Butyllithium**