100608 Final Exam Introduction to Polymers (each part, a,b,c,…, is worth 2.2 points)

1) Polymers are different than low-molecular weight oligomers. For example an oligomeric polyethylene is wax, oligomeric polystyrene is similar to naphthalene (moth balls), oligomeric rubber is oil or grease. One way to quantify the difference between an oligomer and a polymer is through rheology.

a) Give Newton's law for viscosity.
b) Define the shear stress.
c) Define the rate of strain.
d) Define the velocity gradient.
e) The tensile (or extensional) viscosity is used to describe the ability of a fluid to form a fiber. Explain how the tensile (or extensional) viscosity is defined.
f) Sketch the behavior of viscosity as a function of velocity gradient showing how the zero-shear-rate viscosity or Newtonian-plateau viscosity are obtained.
g) Sketch the dependence of the zero-shear-rate viscosity on molecular weight.
h) How can your plot of part "b" be used to define a polymer?

2) GPC is a common technique to determine the molecular weight of a polymer.

a) What does GPC stand for? Give two other names for this instrument and explain what each of these names has to do with the functioning of this instrument.
b) How is the polydispersity index, PDI, obtained from a GPC curve? (Explain how moments are calculated from the GPC curve in your answer.)
c) How is the PDI related to the standard deviation for the distribution curve?

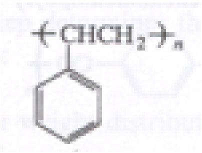
3) Molecular weight can be obtained by a number of methods.

a) What molecular weight average is obtained with light scattering? Relate this molecular weight average to the moments of the distribution curve, M1, M2, M3.
b) Explain the function of a membrane osmometer in determining the molecular weight of a polymer by comparing with the ideal gas law. What molecular weight average is obtained from a membrane osmometer?
c) Explain how molecular weight can be obtained using a capillary viscometer.
d) What moment of molecular weight is obtained in a capillary viscometer? Define this molecular weight using the Mark-Houwink equation, $\eta = kM^a$.

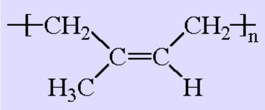
4) Draw the structure or give the name of the following polymers and indicate which of the two types of polymerization could be responsible for this polymer. Indicate, where appropriate, the polyester, polyamide or polyurethane linkages.

a) polyethylene terephthalate

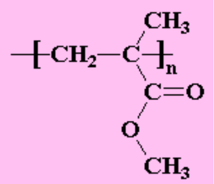
b)



c)



d)



e) Poly vinyl alcohol

f) List the 4 types of polyethylene that are commonly used in industry and indicate the difference in chain structure between these types.

g) Describe the difference between atactic and isotactic polymers.

5) The synthesis of glyptal involves a trifunctional and a difunctional reactant in a condensation reaction.

a) Give the monomers involved in glyptal synthesis in a stoichiometrically balanced chemical reaction equation.

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 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.

6) a) What are the three main stages of chain growth polymerization?

b) Write an expression for the rate of propagation for chain growth polymerization in terms of the monomer concentration and the initiator concentration.

c) Obtain an exponential expression for the monomer concentration from part c and show that this is linear for early stages of the reaction.

d) Obtain an expression for the kinetic chain length for chain growth polymerization in terms of the monomer concentration and the initiator concentration.

7) 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?

8) a) Give the Flory-Huggins equation for polymer blends and explain which part corresponds to entropy and which to enthalpy of mixing.

b) Sketch this function for χ below the critical point, at the critical point and above the critical point.

c) Show where the binodal and spinodal points are determined in the plot of b.

d) Show how the plot of part c can be used to construct a phase diagram.

e) Explain what an LCST and UCST phase diagram is and how they can be obtained from an interaction parameter of the form A + B/T. Why does PVME/water display an LCST phase diagram?

9) a) 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 $p_c = 2/f_{avg}$.

b) Give the structure of TEOS

c) Show the reaction scheme (including stoichiometry) for hydrolysis of TEOS.

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.

Answers: ***100406 Quiz 1. Introduction to Polymers***

1)

a) Give Newton’s law for viscosity.

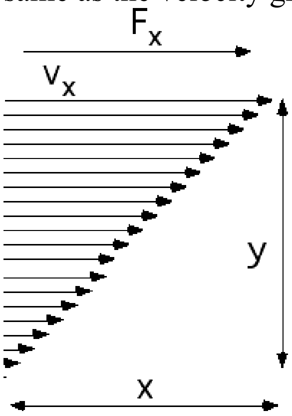
Shear stress is proportional to the shear strain rate with the viscosity as the scaling coefficient $\tau = \eta\dot{\gamma}$.

b) Define the shear stress.

c) Define the rate of strain.

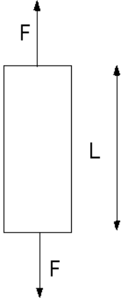
d) Define the velocity gradient.

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.



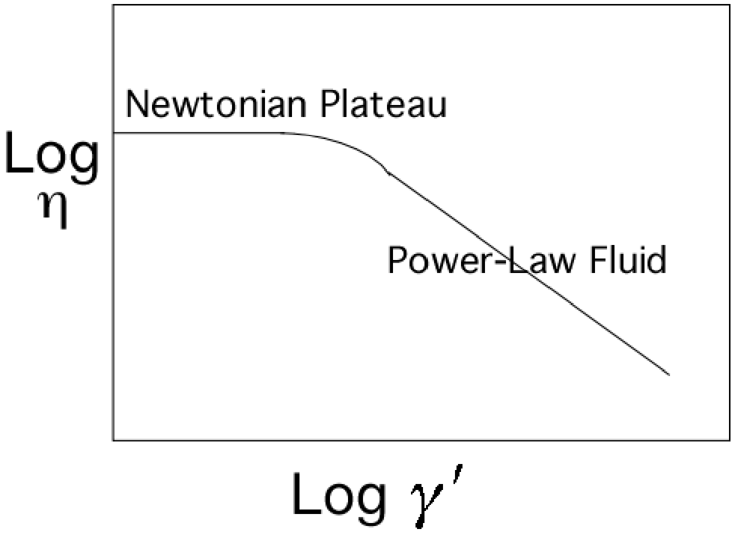
e) The tensile (or extensional) viscosity is used to describe the ability of a fluid to form a fiber. Explain how the tensile (or extensional) viscosity might be defined.

A force is applied to the surface normal to the force. The length changes in the same direction as the force. $\sigma = F_x/A_x$ and $\varepsilon_{xx} = \Delta L_x/L_x$, the elongational rate of strain is the velocity of the vertical strain so you need to pull the fluid like pulling taffy except with a continuous rate of strain.

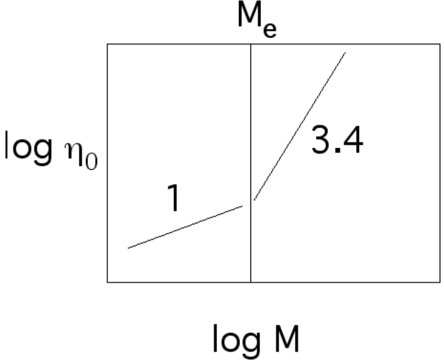


The extensional viscosity is defined as $\eta_{\dagger} = \sigma_{xx} / \dot{\varepsilon}_{xx}$. A special experimental design is necessary to measure the extensional viscosity.

2) a) Sketch the behavior of viscosity as a function of velocity gradient showing how the zero-shear-rate viscosity or Newtonian-plateau viscosity are obtained.



b) Sketch the dependence of the zero-shear-rate viscosity on molecular weight.



c) How can your plot of part "b" be used to define a polymer?

Above the entanglement molecular weight the material behaves like a polymer since it displays melt strength, shear thinning and other features normally associated with polymers.

1) a) Gel permeation chromatography, Size Exclusion Chromatography (SEC) and High Pressure Liquid Chromatography (HPLC).

b) The instrument involves pumping a dilute **liquid** solution of a polymer under **high pressure** through a **gel** and observing the concentration of polymer in the effluent stream. The polymer **permeates** the gel following pathways that are large enough through the gel molecular structure to allow for passage. The molecular weights of the polymer are separated by the process of **size exclusion**. That is, large polymers are excluded from small pores in the gel so that these large molecules pass through the large pores quickly and elute first. Small polymers are not excluded from the gel pores and have a higher residence time in the gel structure, eluting at a later time.

c) PDI is the ratio of the weight average molecular weight, M_w, to the number average molecular weight, M_n. Mw is obtained from the ratio of the second to the first moments, $M_2/M_1 = M_w$. The moments are obtained by integration of the GPC curve, P(M) times the power of the molecular weight of interest, $M_P = \frac{\int_0^\infty M^P P(M)\,dM}{\int_0^\infty P(M)\,dM}$. $M_n = M_1$.

d)

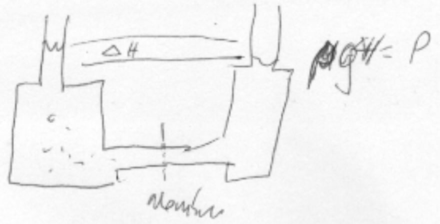
$$\sigma = \frac{\int_0^\infty (M - M_1)^2 P(M)dM}{\int_0^\infty P(M)dM} = \frac{\int_0^\infty M^2 P(M)dM - 2\int_0^\infty M M_1 P(M)dM + M_1^2 \int_0^\infty P(M)dM}{\int_0^\infty P(M)dM}$$

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

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

2) a) Light scattering yields the weight average molecular weight. $M_2/M_1 = M_w$.

b)



$$P = \frac{n}{V}RT$$

n = # of polymer molecules

$$M_1 = \frac{\text{Total Mass of Polymers}}{n}$$

c) $M_1 = M_n$ is obtained.

d), e) The intrinsic viscosity is obtained from the flow time for the solvent, t_{solv}, and the flow time of the solution $t_{solution}$ using the Poiseuille equation.

$$\frac{t_{solution}}{t_{solv}} = 1 + \phi[\eta]$$

$$[\eta] = kM_v^a$$

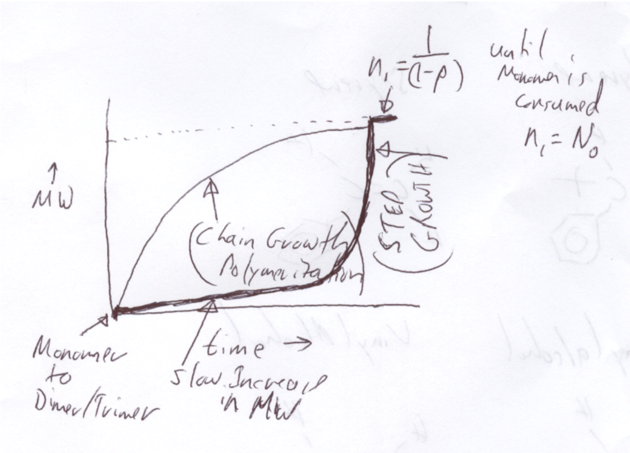
where the second equation is the Mark-Houwink equation and the molecular weight M_v is the viscosity average which is between the weight and the z average in magnitude.

3) 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)



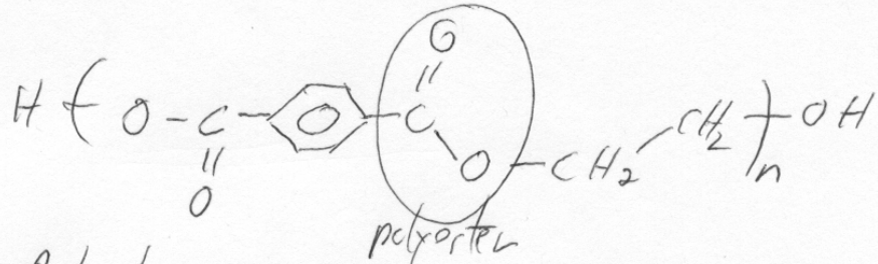
d) $n_1 = n_n = 1/(1-p)$; $n_w = (1+p)/(1-p)$

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

1)

②

a) PET is a polyester made by step growth

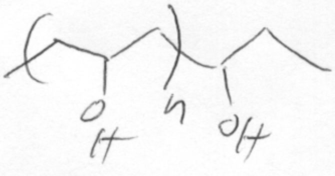


b) Polystyrene is a vinyl polymer made by chain growth

c) Polyisoprene is a diene polymer made by chain growth

d) Polymethylmethacrylate is an acrylic made by chain growth

e)



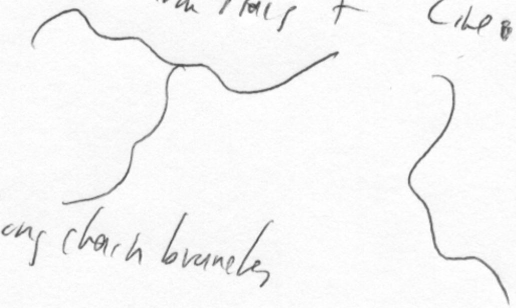
a vinyl polymer made by chain growth

LDPE Low density

short + Long chain branches

HDPE High density

3-arm stars + Linear

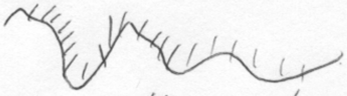


Long chain branches

LLDPE Linear Low Density Polyethylene

Short chain branches

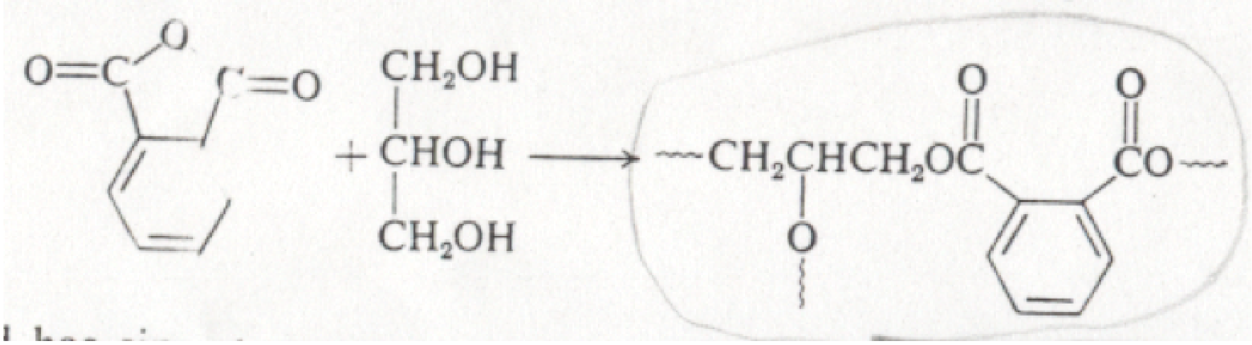
Metallocene PE



Many short chain branches
Very low density
elastomeric PE

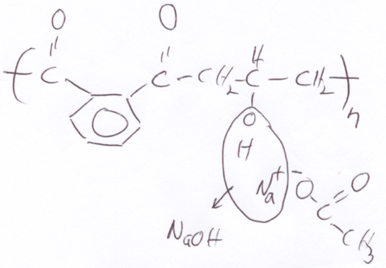
h) Isotactic polymers are composed of all meso diads, mm triads (all the same sterochemical arrangement). Atactic are composed of a random distribution of triads so 50% m and 50% r and 25% mm, 25% rr (syndiotactic) and 50% mr (heterotactic). Atactic generally refers to a polymer that will not crystallize.

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



b) The reaction is run 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)

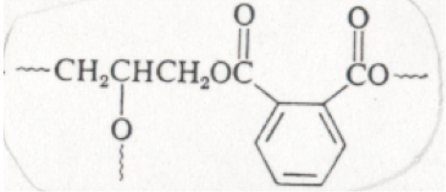
Ⓐ First Stage of Rxn
Pthalic Anhydride Melts (131°C)
+
Mixes with Glycerin

Ⓑ Rxn ① & ② Occur
Water is produced that vaporizes

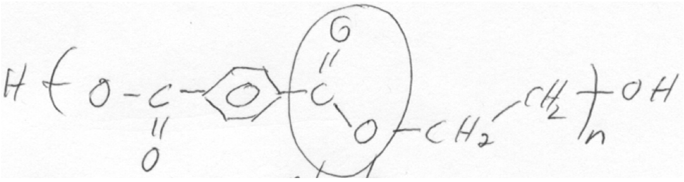
Ⓒ Some water reacts ⓦ phthalic anhydride
by ③ to make vapors acidic

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

d)

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

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

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

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

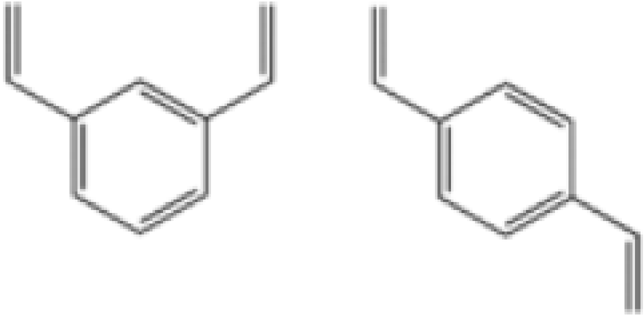
For short times we can consider only the first two terms so, $[M] \approx [M]_0\left(1 - K\sqrt{[I]}t\right)$

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

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.



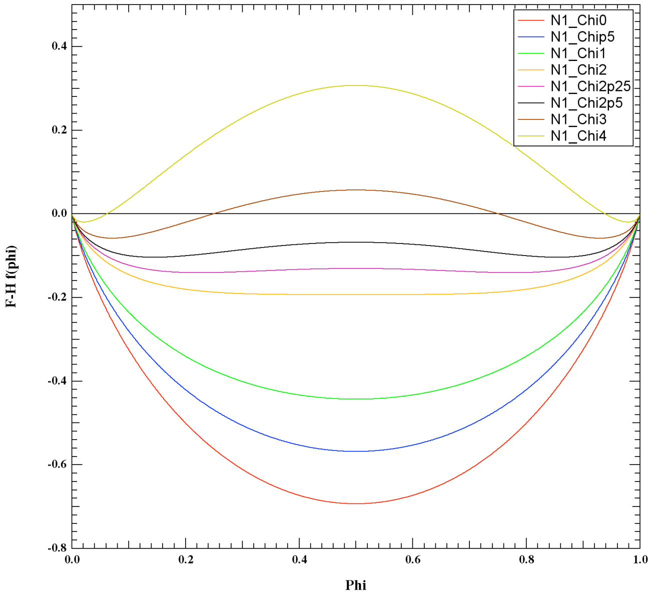
d) The droplet size is controlled by the rate of mixing, the amount of polymer and the presence of polyvinylalcohol. The size is a balance between coalescence and breakup of the monomer/polymer droplets.

e) Emulsion polymerization allowed the production of sticky polymers such as polybutadiene and polyisoprene rubber.

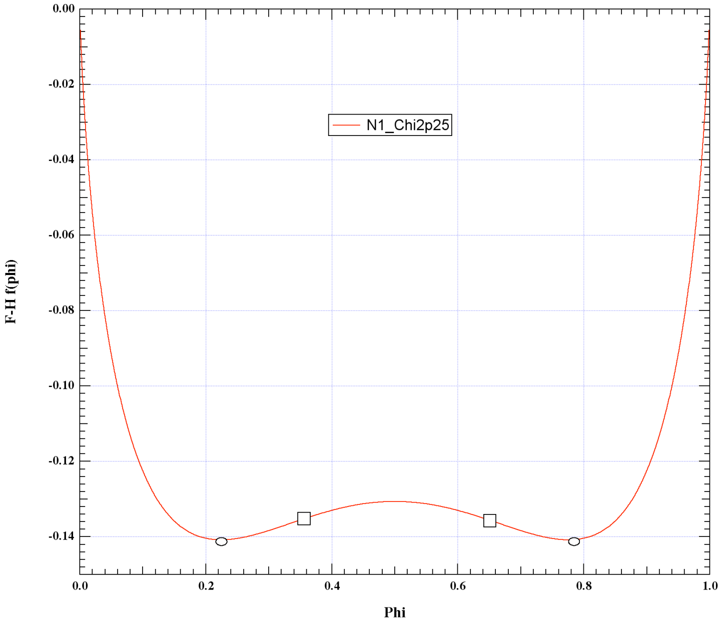
3) a) $$\frac{\Delta G}{RT} = \frac{\phi_A}{x_A}\ln\phi_A + \frac{\phi_B}{x_B}\ln\phi_B + \phi_A\phi_B\chi_{AB}$$

x_i is the degree of polymerization of component i.

b) Critical point is chi = 2



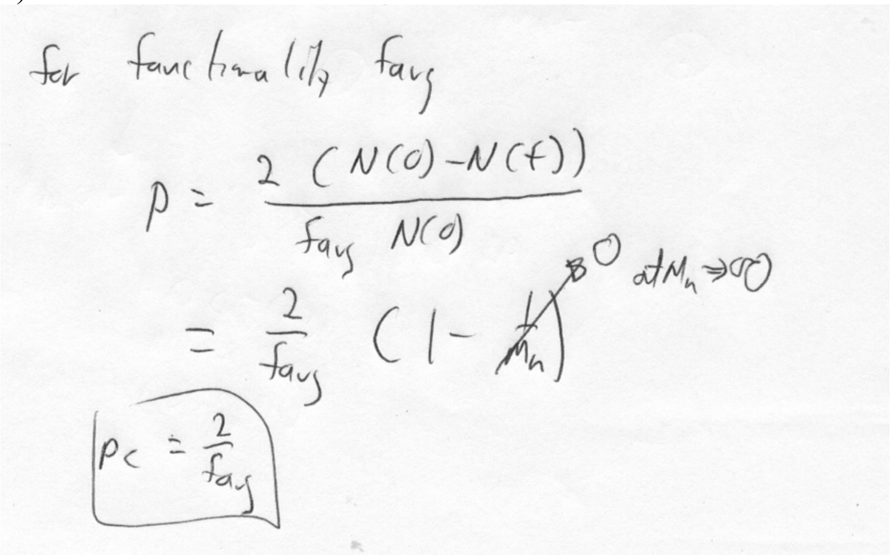
c) Binodal is where the first derivative is equal for two points (circles), this is the miscibility limit. Spinodal is where the second derivative is zero (squares). This defines the metastable region between binodal and spinodal. The critical point is where the third derivative is zero (central maximum).



d) The points of part c are plotted on a temperature versus composition plot as shown in the notes and in class. You should sketch out how to do this in your answer to this question.

e) Gone over in class.

1)



for functionality f_{avg}

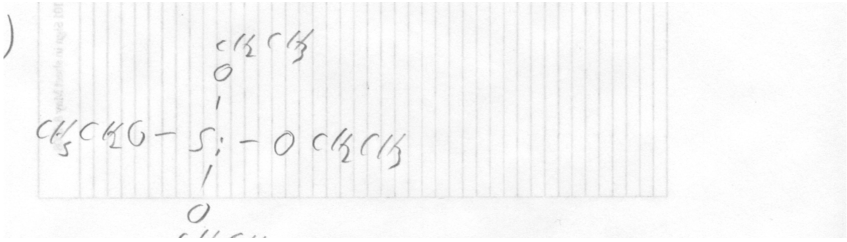
$$p = \frac{2\,(N(0)-N(f))}{f_{avg}\,N(0)}$$

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

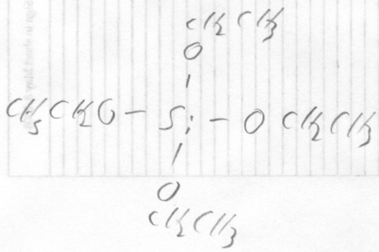
$$\boxed{p_c = \frac{2}{f_{avg}}}$$

2)

a)

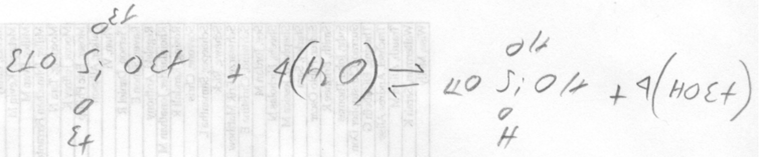


$$\begin{array}{c} OCH_2CH_3 \\ | \\ CH_3CH_2O - Si - OCH_2CH_3 \\ | \\ O \end{array}$$



$$\mathrm{CH_3CH_2O-\underset{\underset{\displaystyle OCH_2CH_3}{|}}{\overset{\overset{\displaystyle OCH_2CH_3}{|}}{Si}}-OCH_2CH_3}$$

b)



$$\mathrm{EtO\underset{\underset{\displaystyle Et}{O}}{\overset{OEt}{Si}}OEt + 4(H_2O) \rightleftharpoons HO\underset{\underset{\displaystyle H}{O}}{\overset{OH}{Si}}OH + 4(HOEt)}$$

c)

$$\mathrm{Si(OH)_4 \rightleftarrows \underset{Silica(s)}{SiO_2} + 2(H_2O)}$$

d)

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.