

Materials Science and Engineering PhD Qualifying Exam

WRITTEN EXAM: Wednesday, May 12, 2021 9:00AM-1:00PM.
Upload responses by 1:30PM.
Via Zoom and Blackboard. Session will be recorded.

ORAL EXAM: Monday, May 17, 2021, **TBD** 10AM-5PM
Via Zoom (See No. 5, below, for schedule)

General Instructions:

- Calculators are allowed.
- Only the books indicated will be allowed.
- NO INTERNET (other than the Blackboard/Zoom connections)

1) Log into Blackboard, [Materials PhD Written Qual](#)

2) Log into Zoom and turn on your Video. This session will be recorded.

<https://bostonu.zoom.us/j/97370206054?pwd=eUJncHhXZVM4OGJHdjI0cCtmWlJmdz09>

Meeting ID: 973 7020 6054, Passcode: 364978

3) Questions will appear as Assignments automatically after 8:55AM. Sign the Honor Code at the top of each section (write "Honor Code" and sign).

See page 3 for General Guidance. **Include notes w/ exam response upload/email).**

4) Complete the topical sections as instructed.

Upload responses to the Blackboard between 1:00 and 1:30PM.

Section I: Answer MS 577 Problems

- **Problem 1:** Electrical, Optical, Magnetic Properties of Matls (MS 577 Swan) – Books and Notes permitted, no internet or people. Calculator permitted, no magnetism on the exam.

Section II: Answer 3 out of 4 Problems

- **Problems 1 and/or 2:** Thermodynamics and Statistical Mechanics (MS 505, Pal) – OPEN NOTES (1 pg, double sided), bring ruler to the exam, graphing calculator optional.
- **Problems 3 and/or 4:** Kinetic Proc. in Matls (MS 503, Basu) – Open Book/Open Notes

Section III: Answer 1 out of 2 Problems

- **Problem 1:** Materials Chemistry (CH 550, Grinstaff) CLOSED BOOK/NOTES.
- **Problem 2:** Physics of Semiconductor Materials (MS 574, Bellotti) – CLOSED BOOK. NOTES ALLOWED (one page, double-sided).

General Written Exam Guidance on Page 3

Oral Exam Schedule, Monday, May 17.

<https://bostonu.zoom.us/j/92134070878?pwd=N044TW9NZzdVbVFwNUFZeW1uRWFIUT09>

Meeting ID: 921 3407 0878

Passcode: 670890

Time	Breakout Rm	Last	First	Fac1	Fac2	Fac3	Fac4	Advisor
10:30AM	1	Morey	Madison	Swan 11:10- 11:30	Basu	Pal	Grinstaff	Ryan
11:30AM	2	Taylor	Matthew	Swan 12:10- 12:30	Basu	Pal	Grinstaff	(Grinstaff)
12:30PM	3	Resing	Anton	Swan 12:30- 12:50	Basu	Pal	Bellotti	Werner
1:30PM	Committee Meeting			Swan	Basu	Pal	Gopalan	Grinstaff Bellotti

General Written Exam Guidance

- **8:30AM, Wednesday, May 12.** This is the time recommended to enter the Zoom meeting and Blackboard so that you can ask the proctor questions and be ready for the questions which will be released automatically at 8:55AM and close at 1:00PM (will allow upload until 1:30PM).
- **Blackboard**
 - [Materials PhD Written Qual](#)
- **Zoom**
 - <https://bostonu.zoom.us/j/97370206054?pwd=eUJncHhXZVM4OGJHdjI0cCtmWlJmdz09>
 - Meeting ID: 973 7020 6054
 - Passcode: 364978
 - The Zoom session will be recorded.
 - Your camera should show your face and your work surface.
 - Virtual backgrounds are not permitted.
- **Exam timeframe:** 9:00AM-1:00PM
- **Exam Responses** must be uploaded to Blackboard by 1:30PM. (Use a cell phone app or scanner to pdf responses and upload or email to instructor for grading.)
- **General Guidelines**
 - Calculators are permitted.
 - Bathroom breaks are permitted.
 - No other smart devices are permitted (i.e., no cell phones except if used for Zoom connection)
 - Only books and notes permitted as indicated on exam cover sheet.
- **You must sign the honor code on each exam question.** Just write “Honor Code” at the top and sign. The honor code is:
 - Honor Code Statement: I have not received nor given any unauthorized aid during this exam in accordance with the indicated rules outlined above. I further certify that all work is entirely my own and does not violate the Boston University Academic Conduct Code.
Signature and UID:
- **Exam Responses**
 - Make sure your handwriting is clear and legible.
 - Only write on one side of each exam response sheet. You will need to upload to Blackboard no later than 1:30PM.
 - Number the pages by question.
- **Clarification Needed During the Exam?** Send a private chat to the Exam Proctor if clarification is needed on anything.
 - Please include your cell phone number in case the faculty member wants to call and talk to you rather than chat via Zoom.
 - The Exam Proctor will contact the faculty and the faculty will send clarification via the proctor, enter the Zoom and chat with you directly, or call you.

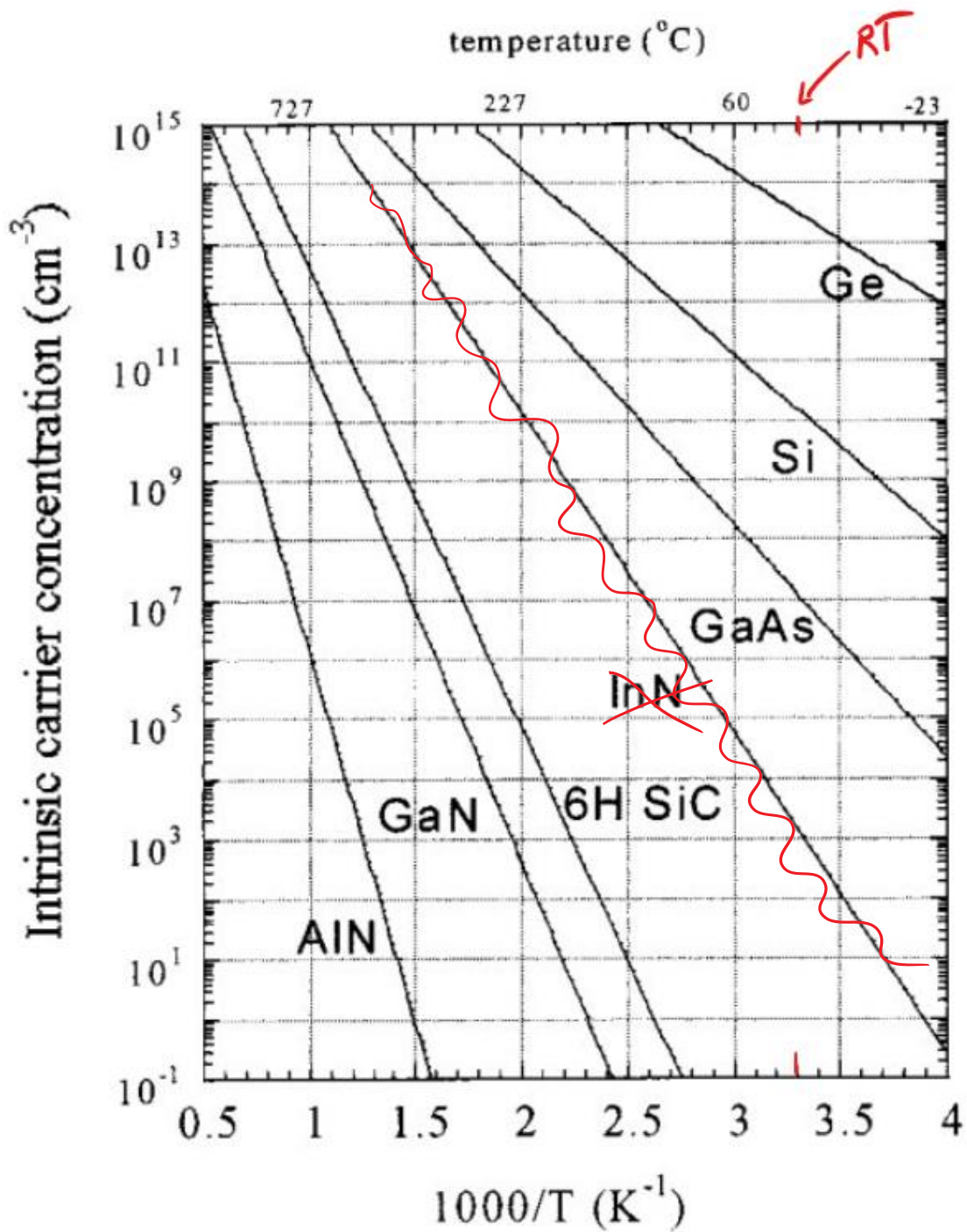
On the next page the temperature dependence of semiconductor intrinsic carrier concentration is shown according to a particular dataset. The materials measured were not perfect, but we will use it. However disregard the InN measurement completely (not from clean sample)

- a. Use the diagram to estimate the intrinsic carrier concentration at RT ($1000/T=3.3$) for the six different materials. (hint: use a ruler). Discuss the main reason for the variation.

- b. Use the diagram to find the bandgap $E_G = E_C - E_V$ in eV for 6H SiC. Note that this is a $\log n$ vs $1000/T$ plot. $k_B = 8.617 \cdot 10^{-5}$ eV/K.

- c. Consider making a photoconductor sensor that works on the principle that the electrical mobility changes with optical illumination. If you want the sensor to have the highest dynamic range between dark (no light) versus light on for green light (2.3 eV), which material (and why) would you choose of the ones shown if the different material mobility were similar? (Disregard InN)

- d. Consider instead making a doped semiconductor device for high temperature usage (up to $\sim 500\text{K}$) with doping level of $10^{15}/\text{cm}^3$. Discuss the usage of Ge, Si or GaAs.



$$n = N_c \exp\left(\frac{E_C - E_F}{kT}\right) \quad p = N_v \exp\left(\frac{E_F - E_V}{kT}\right)$$

$$n = n_i \exp((E_F - E_i)/kT) \quad \text{and} \quad p = n_i \exp((E_i - E_F)/kT) \quad pn = n_i^2$$

May 2021 MSE Qualifier Questions: MS 503

Closed book, NO additional notes

Some kinetics formulas that may or may not be relevant:

$$c(x,t) = \frac{S}{\sqrt{4\pi Dt}} \exp(-x^2/4Dt), \quad c(x,t) = A + \text{Berf}(x/2\sqrt{Dt}),$$

$$c(x,t) = \frac{4c^0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin\left(\frac{(2j+1)\pi x}{l}\right) \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$

$$\bar{c}(t) = \frac{8c^0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(-\left(\frac{(2j+1)}{l}\right)^2 Dt\right)$$

$$D(\text{vacancy mechanism}) = \gamma a^2 v_D p_v \exp\left(-\frac{\Delta G_m^v}{RT}\right),$$

$$D(\text{interstitial mechanism}) = \gamma a^2 v_D \exp\left(-\frac{\Delta G_m^i}{RT}\right),$$

$$D(\text{self interstitial mechanism}) = \gamma a^2 v_D \exp\left(-\frac{\Delta G_{si}}{RT}\right) \exp\left(-\frac{\Delta G_m^v}{RT}\right),$$

$$\frac{\partial \Delta G}{\partial p} = \Delta V; \Delta V_m = 0.15V_{molar}, \Delta V_v = 0.55V_{molar}, \Delta V_{si} = -0.3V_{molar}$$

$$pV = nRT$$

$$D(\text{vacancy mechanism}) = \gamma a^2 v_D p_v \exp(-\Delta G_m/RT)$$

For chemical reaction: $aA + bB = cC + dD$;

$$\frac{d[C]}{dt} = -\frac{c}{a} \frac{d[A]}{dt}$$

$$D_{gb} = D_{gb}^0 \exp\left(-\frac{\Delta G_m^{gb}}{RT}\right), D_l = D_l^0 \exp\left(-\frac{\Delta G_m^l}{RT}\right)$$

$$\frac{dr}{dt} = \frac{2DX_{\infty}\sigma\Omega}{kTr} \left(\frac{1}{\bar{r}} - \frac{1}{r}\right)$$

$$dX = (1-X)dX_e, \theta = Kp/(1+Kp), X_r = X_{\infty} \left(1 + \frac{2\sigma\Omega}{rkT}\right)$$

$$X = 1 - \exp\left(-\frac{\pi IU^3 t^4}{3}\right)$$

$$\exp(-\Delta G^0/RT) = (a_c)^c (a_d)^d / (a_A)^a (a_B)^b$$

$$\text{reaction rate} = K_f [A]^{\alpha} [B]^{\beta} - K_b [C]^{\gamma} [D]^{\delta}$$

$$D_{eff} = \eta D_{gb} + (1-\eta) D_l;$$

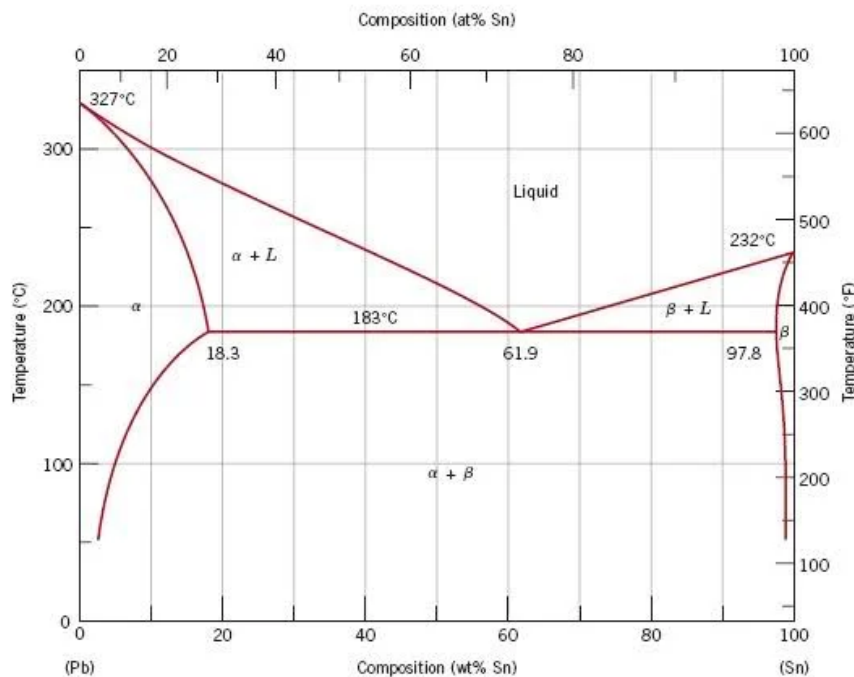
Problem 1.

Explain with figures and equations (whenever possible), why the following statements are TRUE or FALSE. If a statement is FALSE, provide an alternate statement that is TRUE.

1. A plot of $\ln D$ versus $1/T$ for a polycrystalline metal shows two different slopes, a steeper slope in the high temperature range and a lower slope in the lower temperature range.
2. Tracer diffusivity (D^*) is **always** less than self-diffusivity (D_{self}) in a given pure metal.
3. Vacancies **always** diffuse faster than interstitial atoms.
4. In an ideal solution, where bond energies are independent of atomic species forming the bond, atoms go from higher to lower concentration because they can 'sense' the local concentration gradient in the material.
5. Cation diffusivity in a non-stoichiometric oxygen deficient oxide increases with p_{O_2} .

Problem 2.

Sn-Pb alloys are important in soldering applications. The Sn-Pb eutectic phase diagram is shown below.



A 90wt%Pb-10wt%Sn alloy is heated to 200°C to achieve the equilibrium microstructure as predicted by the phase diagram. The alloy is then rapidly cooled to 100°C and held there for the microstructure to reach equilibrium as predicted by the phase diagram.

As predicted, α precipitates start to homogeneously nucleate and grow during the 100°C hold. Interestingly, initially, all α precipitates increase in size (we will term this 'behavior I'). However, after a certain time, the smaller α precipitates start to shrink while the larger α precipitates continue to grow (we will term this 'behavior II').

a) Explain behavior I. If the nucleation rate and growth rate of the α precipitates are I and U respectively, **derive** the time dependence of the volume fraction of α phase formed. Clearly state and justify all assumptions.

b) Can you predict (approximately) from the phase diagram, at what weight fraction of the α precipitates, will the behavior switch from I to II?

c) Explain behavior II, in terms of thermodynamic driving forces. Be as quantitative as possible. Assume that the kinetics of diffusion of Sn atoms in the Sn-Pb alloy is much slower than the jump across the α/β interface. Show the diffusion profile of Sn in β adjacent to a large and a small α precipitate. Pay attention to details.

May 2021 MSE PhD Qualifying Exam

Section 2, Problems 3 and 4

MS 505, Prof. Uday Pal

1. Derive a relationship starting from first law that describes the rate of change of temperature of an adiabatic dry parcel of air as it moves up or down in the atmosphere; assume that air behaves as an ideal gas. Given g (acceleration due to gravity) is 9.8 m/s^2 and C_p for dry air is $1,005 \text{ J/kg-K}$ what is temperature change of the parcel of air when it moves up 3 km ? Discuss the implications of the rate of change of temperature with height if the parcel of air is saturated with water vapor.

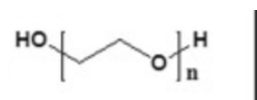
2. A calorimeter (adiabatic container) containing 3.2 kg of liquid lead at 400 C is used to determine the heat of mixing of two metals, A and B. By previous experiments it was determined that the heat capacity of the liquid lead bath at $400 \text{ }^\circ\text{C}$ is 130 J/kg-C . With the bath originally at 400 C , the following two experiments were performed.
 - A mechanical mixture of 1 g of A and 1 g of B (both at 25 C) is dropped into the calorimeter. When the two have dissolved, the temperature of the bath is found to have increased by 0.2 C .
 - 2 g of a $50/50$ (wt. percent) A-B alloy at 25 C is dropped similarly. The temperature decreases by 0.4 C .
 - a. What is the heat of mixing of the $50/50$ (wt percent) A-B alloy (per gram of alloy)?
 - b. To what temperature does it apply?
 - c. How will you change the experiment if you want to measure the heat of mixing of a $75/25$ (wt. percent) A-B alloy at 50 C ?

LAST NAME _____ FIRST NAME _____

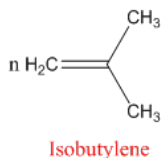
CHEMISTRY 550 (Closed Book/Notes)

1. Write out the polymerization reaction (monomer and product) for the following polymers (show stereochemistry where relevant on the polymer) and identify the repeat unit (18 Points):

a. Poly(ethylene oxide) (3 pts)



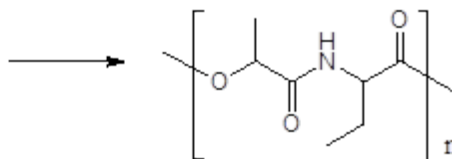
b. Poly(isobutylene) (3 pts)



c. *Cis*-1,4-Poly(1,3-butadiene) (3 pts)

d. Poly(lactide) (3 pts)

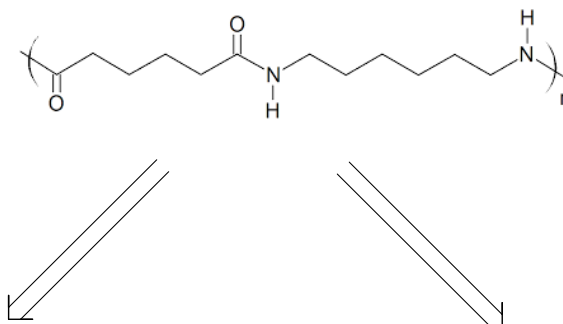
e. Poly..... (3 pts)



f. poly(10-decanoate) (3 pts)

2. Nylon 6,6 can be theoretically produced by either condensation, step-growth polymerization or by addition, chain-growth polymerization (16 pts).

a. Based on retrosynthetic analyses, provide the monomers that could be employed for each method below (4 pts).



Condensation, step-growth monomers

Addition, chain-growth monomers

b. For each polymerization mechanism, describe the characteristics below:

i. How does the polymerization proceed? (4 pts)

Chain-growth:

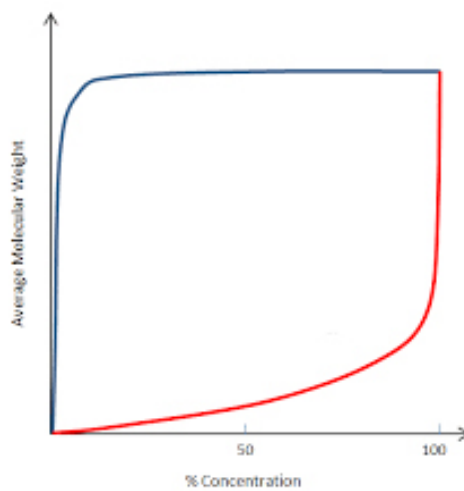
Step-growth:

ii. How are the typical polydispersity index? (PDI) (4 pts)

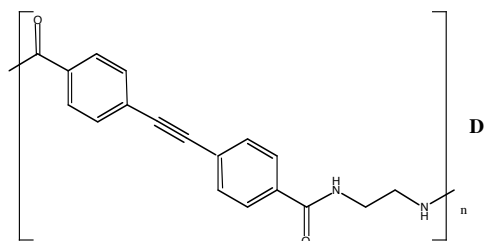
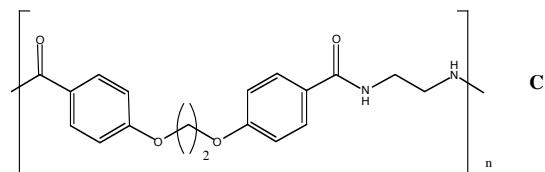
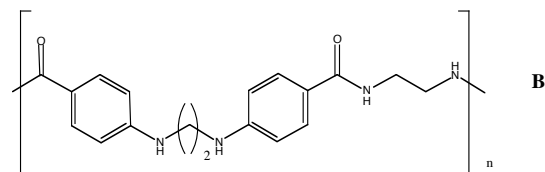
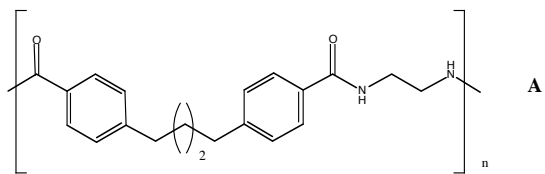
Chain-growth:

Step-growth:

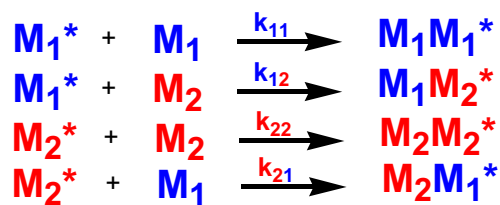
c. Identify the mechanism that corresponds to each curve below. (4pt)



3. Rank the following polymers in order of decreasing T_g and explain your answer (10 pts). Circle the polymer which has the highest T_m ?



4. For the copolymerization of styrene (M_1) with vinyl chloride (M_2), the reactivity ratio values are $r_1 = 17$ and $r_2 = 0.02$. (20 pts)

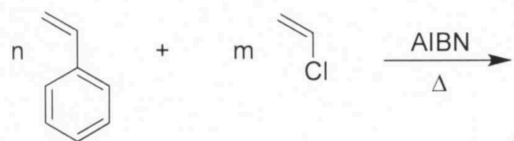


4a. Write the rate equations for the disappearance of M_1 and M_2 .

4b. Draw a line on the following plot that represents copolymer formation F , based on feed composition of the monomer, f , for the copolymerization above.

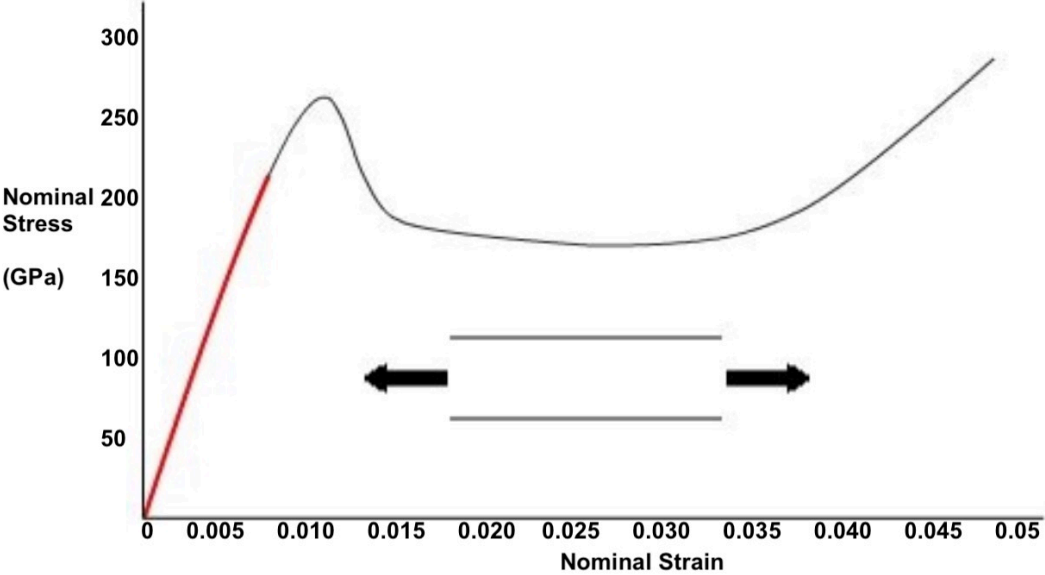


4c. Draw the polymer structure(s) for the expected sample, qualitatively, that would result from the following copolymerization conditions.



4d. Draw the polymer structure(s) for the expected sample, qualitatively, that would result if the reactivity ratio values for styrene (M_1) with vinyl chloride (M_2), are $r_1 = 0$ and $r_2 = 0$.

5a. For the following stress-strain curve for a polymer, label the FAILURE POINT, COLD DRAWING, ELASTIC REGION, NECKING REGION, YIELD POINT, and STRAIN HARDENING REGION. (20 pts)



5b. For the stress-strain curve above, estimate Young's Modulus (E).

- EC574 Problem

Consider a simple 3D cubic lattice with lattice constant a and one basis atoms at $\vec{b} = 0$.

- Sketch the Wigner-Seitz, compute the reciprocal lattice vectors, sketch the Brillouin zone.
- Using the tight binding method derive an expression for the energy bands as a function of k_x , k_y and k_z .
- Compute the effective masses along $[111]$ and $[100]$ directions.