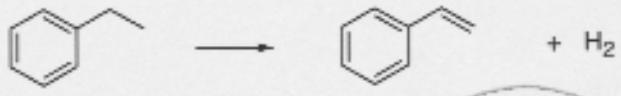
1. (18 pts) Short answers – one or two points each.

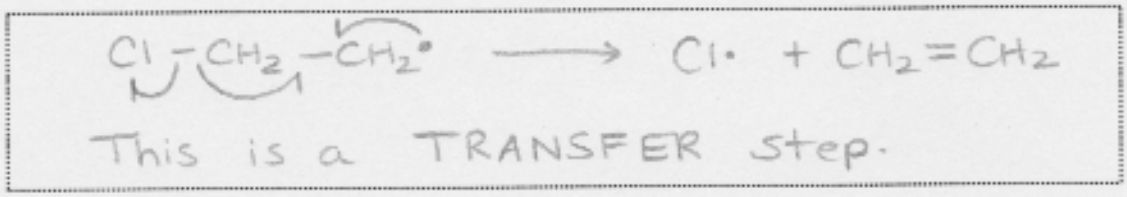
a) The following reaction is a direct route to styrene:



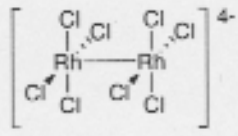
As written, this route will require a(n) ACID (METAL) BASE catalyst and a (LOW) HIGH IRRELEVANT hydrogen pressure.

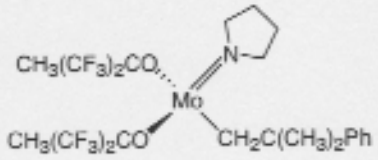
b) Below is the mechanism for the thermal decomposition of 1,2-dichloroethane. What does the $ClCH_2CH_2\bullet$ do? Draw a mechanism. How does this step fit in to the overall reaction?

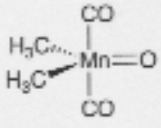
$$ClCH_2CH_2Cl \longrightarrow Cl\bullet + ClCH_2CH_2\bullet$$
$$Cl\bullet + ClCH_2CH_2Cl \longrightarrow HCl + ClCH_2\dot{C}HCl$$
$$ClCH_2\dot{C}HCl \longrightarrow Cl\bullet + CH_2{=}CHCl$$
$$Cl\bullet + ClCH_2\dot{C}HCl \longrightarrow HCl + ClCH{=}CHCl$$

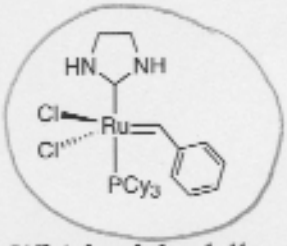


c) Which of these structures is a possible olefin metathesis catalyst?

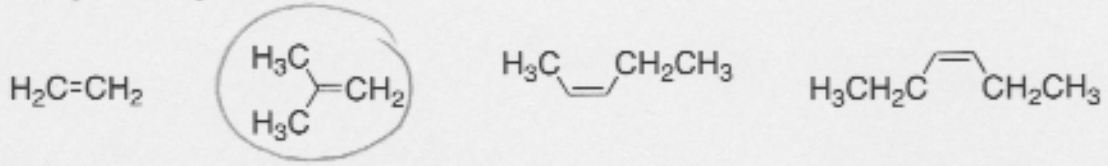




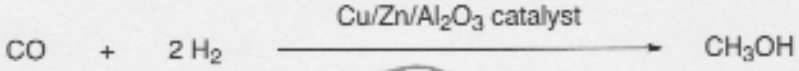




d) A 1:1 mixture of propene and 1-butene undergo olefin metathesis. Which of the following is NOT a possible product of the reaction?



e) Circle the most appropriate temperature and pressure for the conversion of syn gas to methanol.



TEMPERATURE = (250°C) 25°C 1000°C

PRESSURE = < 1 atm 2 atm (50 atm)

f) The cmc of a hypothetical surfactant is 1 mM and its aggregation number is 100. If the concentration of the surfactant in water is 10 mM, what is the micelle molarity?

$$\text{Molarity} = \frac{10\text{mM} - 1\text{mM}}{100} = 0.090\text{mM}$$

g) Which is the major ingredient of a typical laundry detergent formulation?

SURFACTANT (BUILDER) COLOUR ADDITIVES FRAGRANCES

h) Shown below is the Dow process, a possible route to phenol:

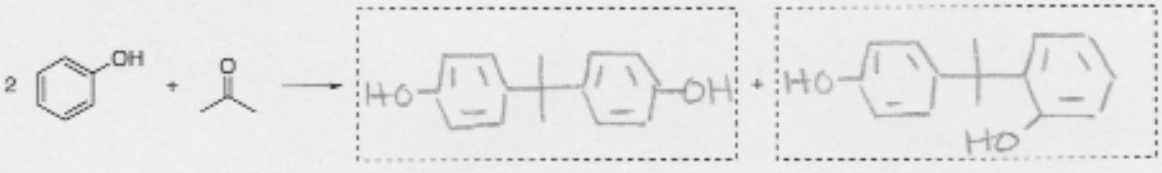
Name one reason why this process is NOT widely used:

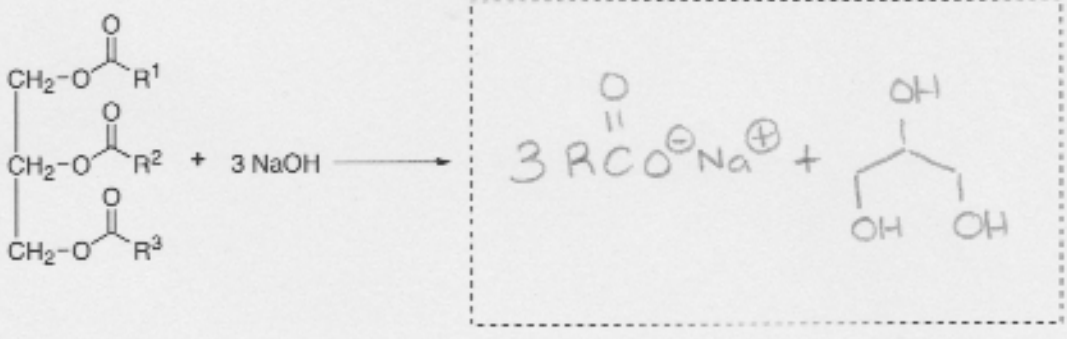
Many possible answers : most likely = WASTE of Cl_2!

i) Which of the following is the most likely T_g for the rubber hoses used by firefighters?

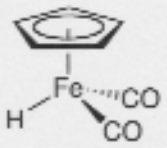
+137°C (-55°C) 0°C 25°C

j) Complete the following reactions (no mechanisms):

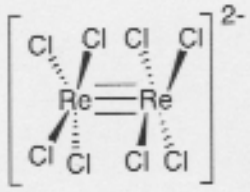




k) Determine the oxidation state at the metal centre.

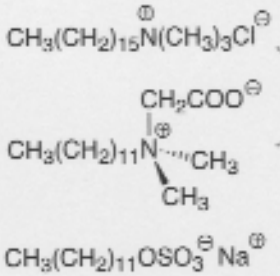


+2



+3

l) Draw lines matching the surfactant structure to its description.



amphoteric surfactant

main ingredient in shampoo

main ingredient in conditioner

m) When all the chains in a polymer sample are of exactly the same size, the polydispersity index has a value of $\overline{M_w}/\overline{M_n}$ = 1.

n) Of the four polymerization processes (bulk, solution, suspension, emulsion), choose one and list one advantage and one disadvantage.

* from Table 9.2 *

Method: _____

Advantage: _____

Disadvantage: _____

BONUS

Formaldehyde is obtained by thermal dehydrogenation of methanol. In practice, however, oxygen is allowed in the reaction mixture. Briefly explain the role of oxygen.

O_2 combusts the released H_2, making the overall process EXOTHERMIC (coupled process).

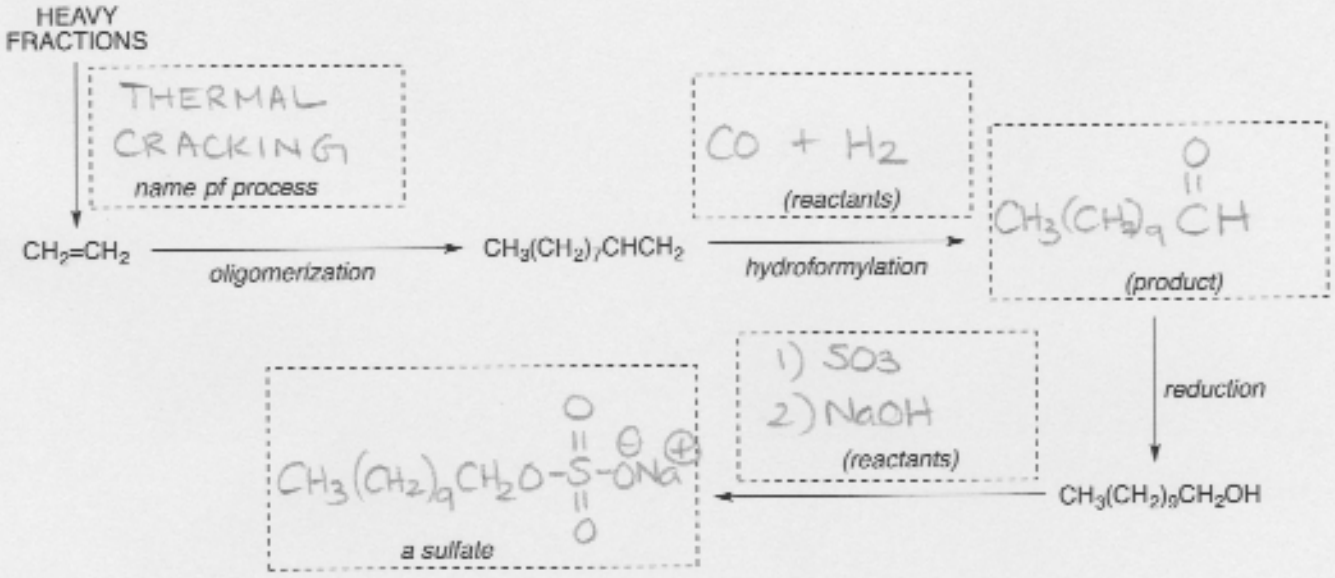
$$H_2 + \tfrac{1}{2} O_2 \longrightarrow H_2O \quad \Delta H^\ominus$$

When adding very small amounts of sodium dodecyl sulfate (SDS) surfactant in water, where might the first surfactant molecules be located?

At the air/water & water/container INTERFACES (forming MONOLAYERS)

2. (10 pts) CUMULATIVE QUESTION

a) (5 pts) Complete the following reaction scheme for the formation of a surfactant – add reactants, products, or process names as needed.



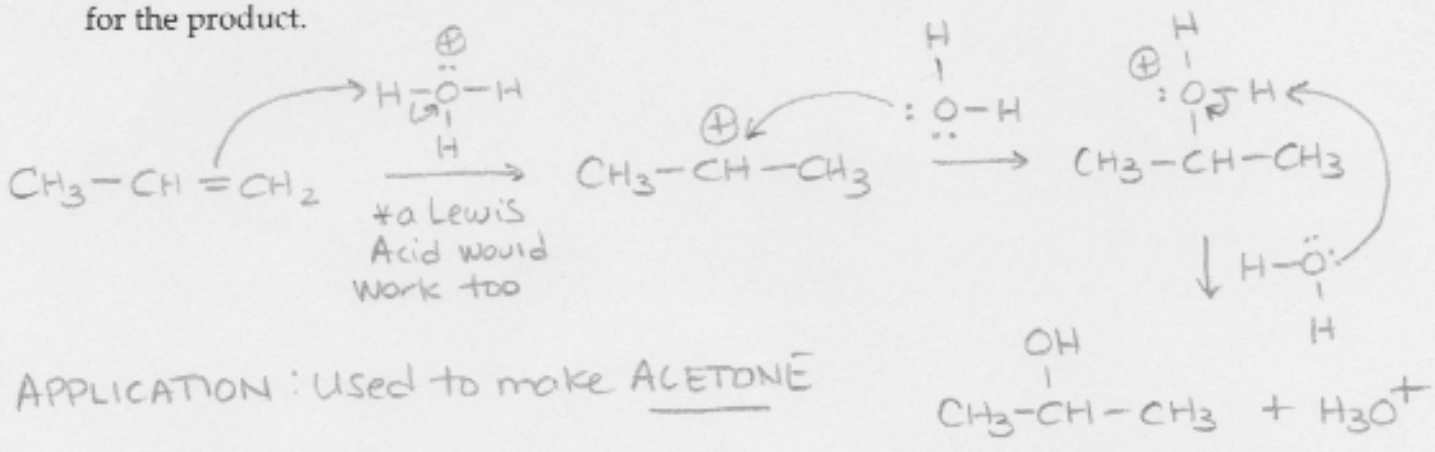
a) (3 pts) Is the final product a biohard or biosoft surfactant? What do these two terms mean? Briefly explain.

It is a bio soft surfactant.

BIOHARD = highly branched surfactant with high solubility but low biodegradability (it persists in the environment.

BIOSOFT = mostly linear surfactant, with lower solubility but much improved biodegradability (better for the environment)

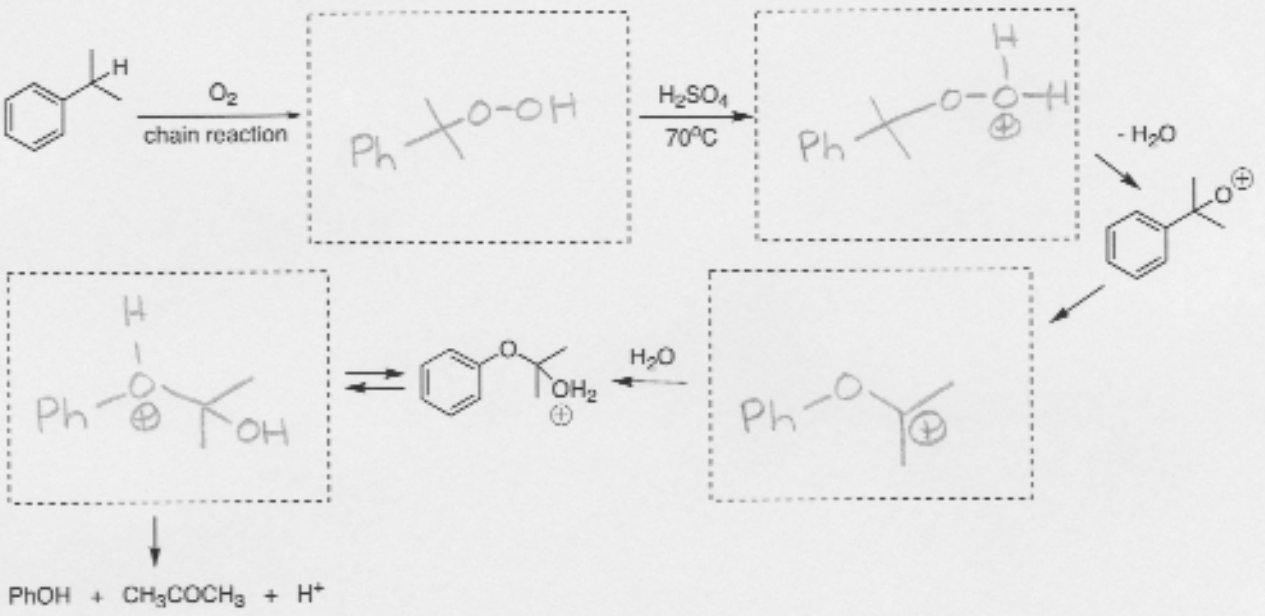
b) (2 pts) Draw the mechanism for the hydration of propylene. Give one possible application for the product.



APPLICATION: used to make ACETONE

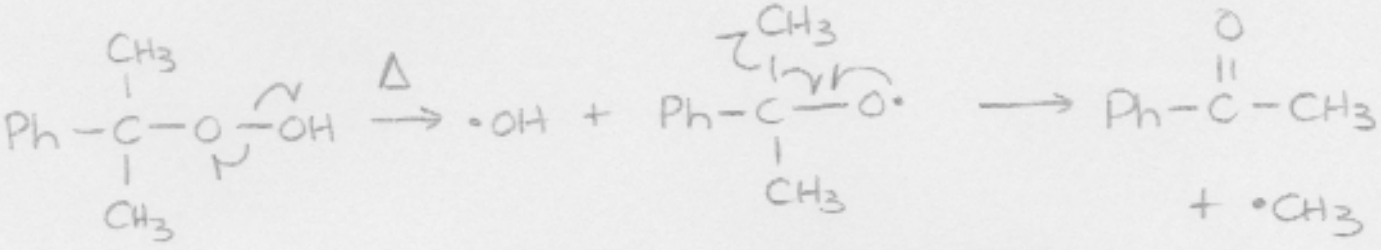
3. (8 pts) ORGANIC DERIVATIVES

a) (4 pts) Complete the following mechanism for the production of phenol and acetone from cumene (no arrows, just intermediates).

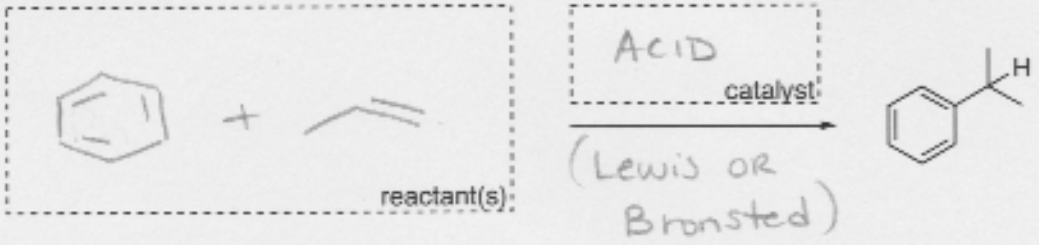


b) (2.5 pts) During the above synthesis it was noted that on one particular occasion in which the mixture in the chain reaction step overheated, a considerable amount of acetophenone (CH_3COPh) was produced. Explain how it was produced, using chemical equations.

The product of the reaction is a HYDROPEROXIDE, with a weak O-O bond. If the reaction overheats, this bond will break first:

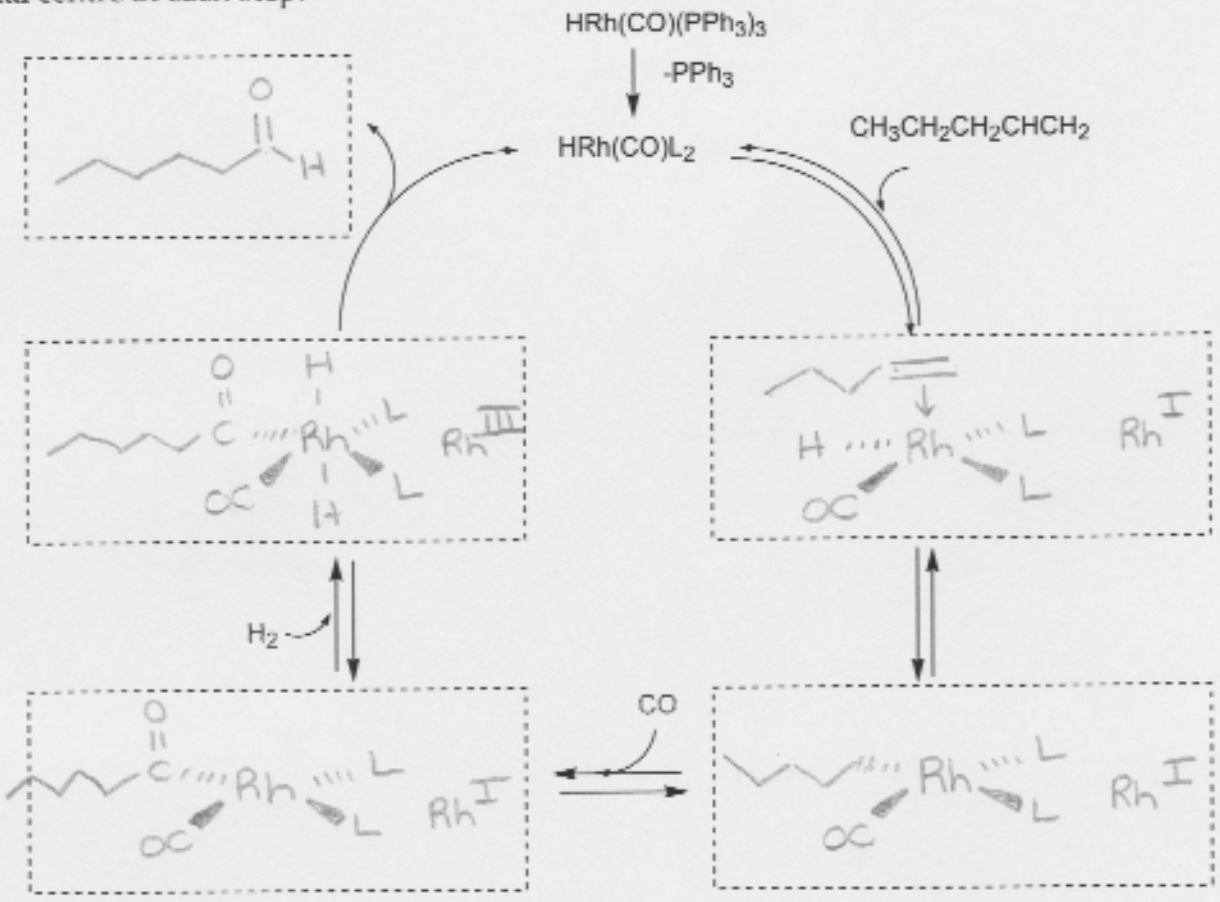


c) (1.5 pts) What chemical reaction is used to make cumene industrially?

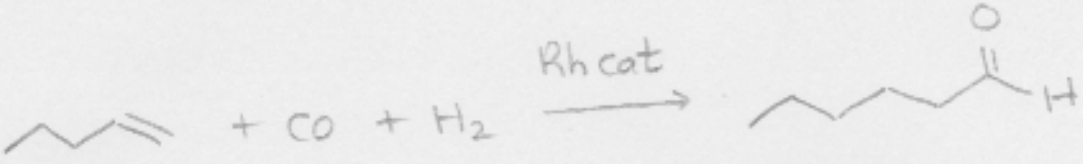


4. (8 pts) INDUSTRIAL CATALYTIC CYCLES

a) (5 pts) In the template below, the olefin hydroformylation of 1-pentene, fill in the boxes with the appropriate intermediates/major products AND include the oxidation state of the metal centre at each step.

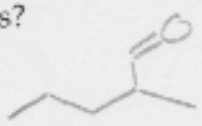


b) (1 pt) Write the overall reaction below.



c) (2 pts) During the reaction, a minor product is observed. What is this product and why is it formed in smaller amounts?

Product =



It is formed in minor amounts due to STERIC HINDRANCE impeding addition to C2 in the alkene insertion step.

5. (8 pts) SURFACTANT CHEMISTRY

The following figure illustrates three droplets of an oil-based liquid dirt on different surfaces immersed in a surfactant solution.

a) (3 pts) Estimate the contact angles for drops A and C. What does the contact angle reflect in terms of interactions between different materials?

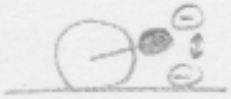
A ~ 180°
B ~ 90°
C ~ 45°

θ decreases as the intermolecular forces b/n the drop + the surface increases (affinity ↑)

b) (1 pt) Which of these surfaces is possibly Teflon? (A) B C

c) (3 pts) If you had to choose a surfactant to remove this dirt, what type would you use? Describe what happens when the surfactant is added and how it facilitates dirt removal.

An ANIONIC surfactant would work best, since negative charges are needed to facilitate the ROLL-UP mechanism of dirt removal. Repulsion between the negative surfactant heads and the negatively charged surface leads to separation of the dirt from the surface.



d) (1 pt) In the case of drop B, will the dirt be spontaneously released? If not, what else is required?

NO → mechanical work (scrubbing/agitation) is required.

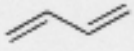
6. (8 pts) POLYMER CHEMISTRY

a) (3 pts) What is the main structural difference between thermoplastic and thermoset polymers? What are the effects on the solubility and thermal stability of the polymer?

THERMOPLASTIC = mostly linear polymer. These materials DISSOLVE in appropriate solvents and MELT when heated.

THERMOSET = highly crosslinked network polymer. These materials do NOT DISSOLVE and do NOT MELT when heated.

b) (2 pts) Rubber septa made from the monomer below display unusual behaviour, but only in certain solvents. What is this characteristic, and why is it observed? What type of solvents would produce this effect?

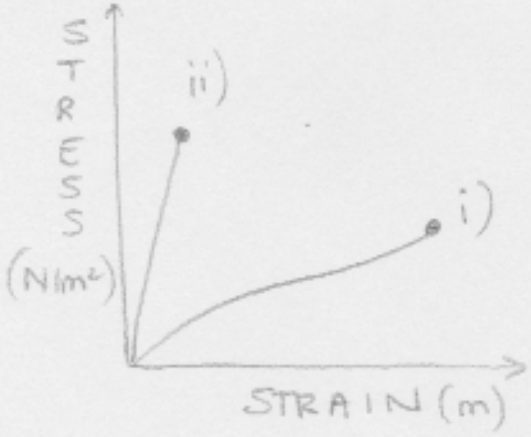


butadiene

The rubber septa SWELL in certain solvents because the polymer is SLIGHTLY CROSS-LINKED.

Since butadiene is non-polar, poly butadiene swells in non-polar solvents (LIKE DISSOLVES LIKE).

c) (3 pts) Draw two representative stress-strain curves for i) a thermoplastic polymer and ii) a thermoset polymer. Try to be as accurate as possible, and label your graphs. In one or two sentences, explain the differences between your two curves.



Thermoplastic polymer is much more AMORPHOUS, allowing for a lower YOUNG'S MODULUS (E). It takes little effort to stretch the material. A thermoset polymer however, is highly cross-linked, meaning the chains are covalently bonded together. As a result, much more stress is required, leading to a much higher E.