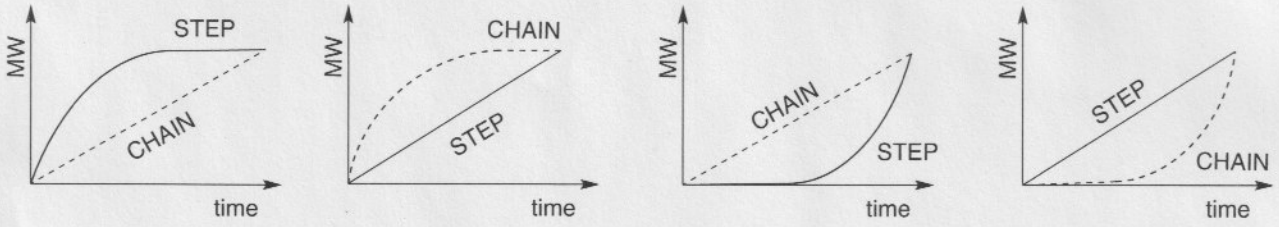
1. (30 pts) Short Answers – one or two points each.

a) Which graph best represents the rate of polymer molecular weight growth for chain and step reactions?



A B C D

b) The reaction A → products is second order in [A]. To find the rate constant, we must draw the graph of 1/[A] **as a function of** time**. The unit(s) of k is/are** $M^{-1}s^{-1}$ OR $L\,mol^{-1}s^{-1}$**.**

c) In a class demonstration, we showed that polystyrene packing chips (Styrofoam) dissolve very easily in acetone. One packing chip, however, did not. Name the polymer that was used to make that particular packing chip and explain why it did not dissolve.

Polyurethane – it is cross-linked and is thus a THERMOSET polymer

d) The blue luminescence of cool flames is due to emission from

FORMALDEHYDE CO_2 PEROXIDES SOOT

e) In the gasification process, coal is transformed into syn gas ($CO + H_2$)**.**

f) The C8 component that equilibrates rather sluggishly with the other isomers is

p-XYLENE *m*-XYLENE *o*-XYLENE ETHYLBENZENE

g) The average number of surfactant molecules that assemble into a micelle is known as the aggregation number**.**

h) Norrish photochemistry occurs from the

S_0 S_1 T_0 T_1

state of a carbonyl compound.

i) The methyl radical is (PLANAR) PYRIMIDAL LINEAR which indicates that the hybridization of the C atom is sp^2.

j) For a hypothetical reaction, the graph of ln k versus 1/T gives a straight lime with a slope of –150 and a y-intercept of +98.0. This means that :

($E_a > 0$) $\Delta H < 0$ $E_a < 0$ $\Delta H > 0$

k) One way to promote the photochemical degradation of a polymer is :

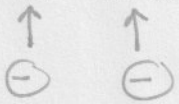
add carbonyl groups (or other chromophores), increase conjugation (to shift absorption to longer wavelengths), have γC-H's for NTII...

l) In the Monsanto Process, methanol is converted to CH_3COOH.

m) After a few generations, dendrimers adopt a globular conformation due to hydrogen-bonding in the branches. TRUE (FALSE)

n) According to the Gibbs' Free Energy Equation ($\Delta G = \Delta H - T\Delta S$), polymerization will be (thermodynamically):

- ☐ always spontaneous
- ☐ never spontaneous
- ☒ spontaneous at low T
- ☐ spontaneous at high T



o) In LFRP, low polydispersity polymers are obtained because the recombination of 2 transient polymer radicals ($P\cdot + P\cdot$) is suppressed.

p) As the degree of isotacticity of a polymer increases, we would expect the value of the material's T_g to correspondingly increase.

q) A catalyst lowers the activation energy barrier by 1.3 kcal/mol. The reaction rate will:

- ☐ NOT CHANGE
- ☒ ACCELERATE x 10
- ☐ DECELERATE x 10
- ☐ ACCELERATE x 1.3
- ☐ DECELERATE x 1.3

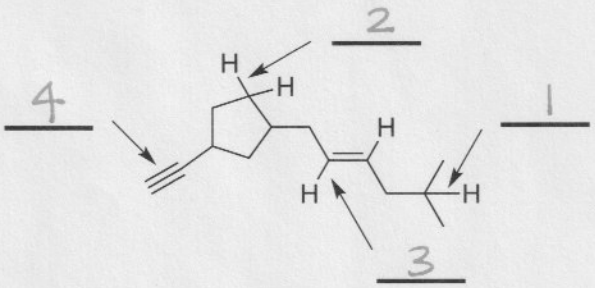
r) What are the two interchain interactions responsible for Kevlar's strength?

H-bonding ____ π-stacking

s) Match the polyethylene to its method of polymeriation:

FREE RADICAL POLYMERIZATION	UHMWPE
ZIEGLER-NATTA POLYMERIZATION	HDPE
METALLOCENE CATALYZED POLYMERIZATION	LDPE

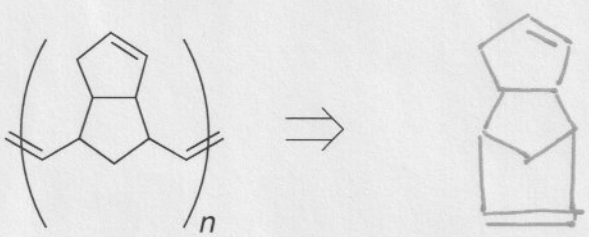
t) Place the following bonds in order of increasing BDE:



u) Give reasonable values of r_1 (●) and r_2 (○) for the following copolymer:

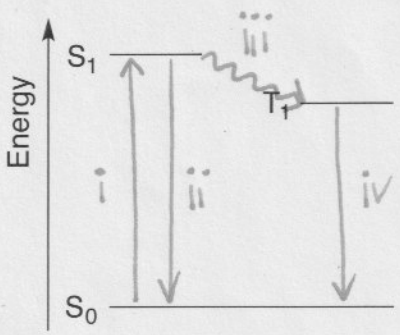
r_1 = 1 r_2 = 5 or 6

v) The following polymer was generated by ROMP. Draw the structure of the original monomer that produced this polymer.



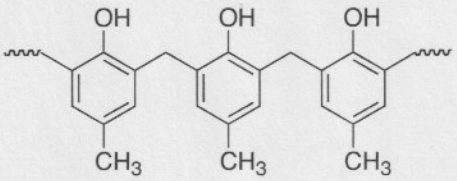
w) On the provided Jablonski diagram template, draw and label (i to iv) the appropriate arrows showing the following processes for a diamagnetic starting material:

i. absorption of a photon
ii. fluorescence
iii. spin flip to the triplet state
iv. phosphorescence

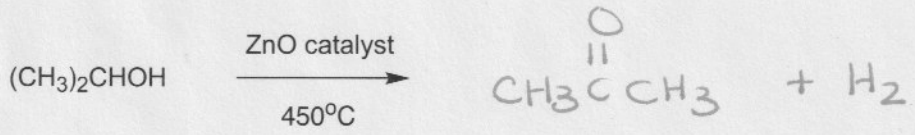


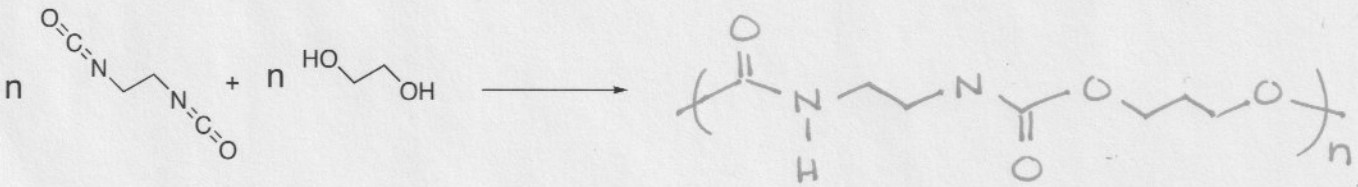
x) **In FRVP, if the concentration of initiator is doubled, the expected molecular weight of the resulting polymer will also double.** **TRUE** **FALSE**

y) **Novolac is a possible polymer made from phenol-formaldehyde polymerization. What is the purpose of the *para*-methyl group?** decrease functionality from 3 to 2 → polymer is linear and not crosslinked



z) **Give the final products of the following reactions (no mechanisms):**





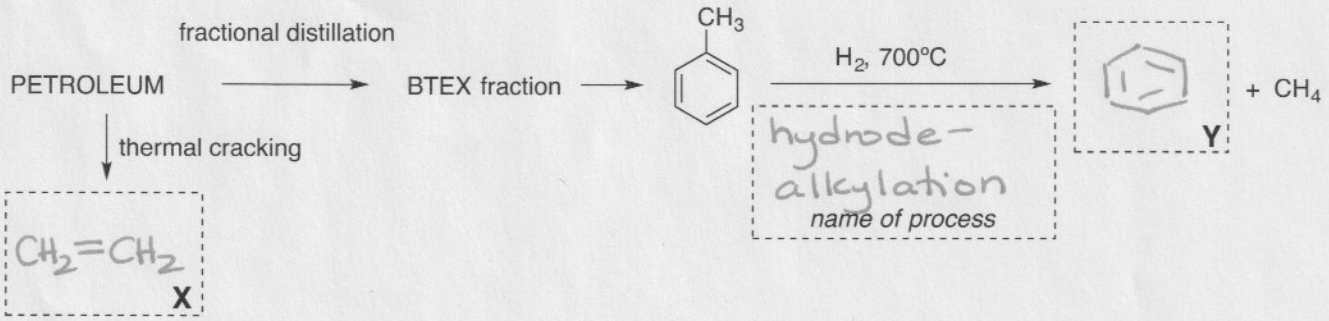
BONUS – 2 pts

In a Youtube video, we saw someone smash a rubber ducky into small pieces with a single tap from a hammer. Explain what was observed.

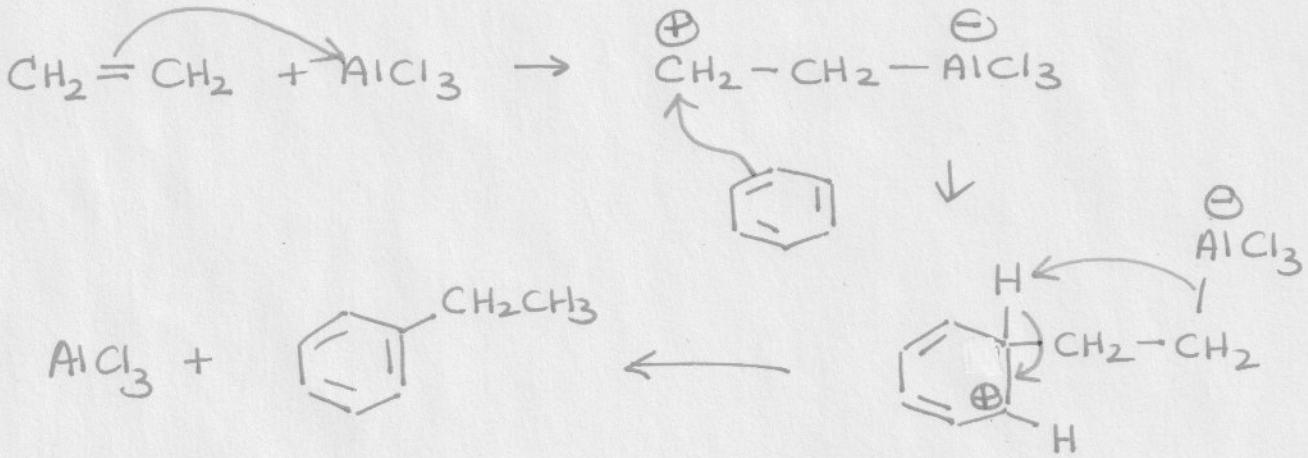
The rubber ducky was cooled to below its Tg in liquid nitrogen. As a result the plastic became extremely brittle and easy to shatter.

2. (15 pts) CUMULATIVE QUESTION 1

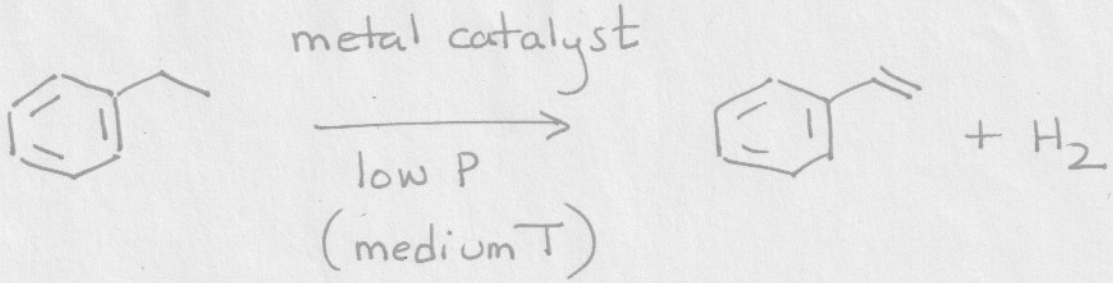
a) (1.5 pts) Complete the following reactions.



b) (4 pts) In the space below, draw the mechanism for the reaction of X and Y (from part a), catalyzed by $AlCl_3$.

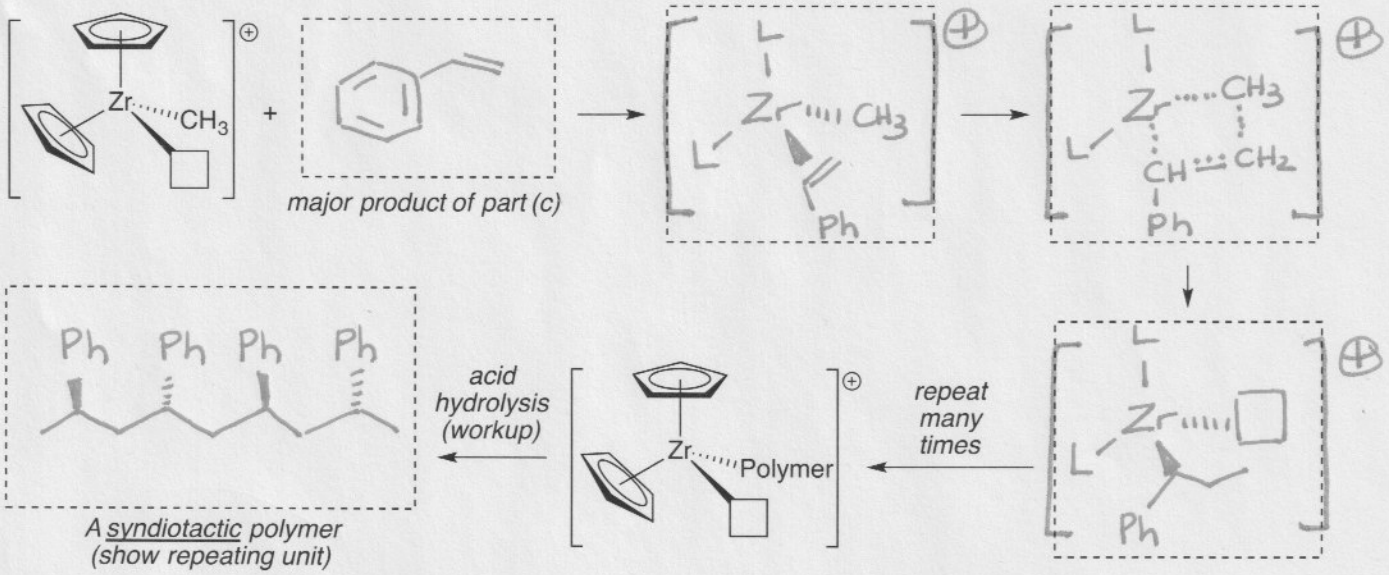


c) (1.5 pts) How is the product of part (b) converted into styrene? Make sure to include the relevant reaction conditions.



-- QUESTION CONTINUED ON THE NEXT PAGE -

d) (4.5 pts) Complete the following metallocene-catalyzed polymerization, where the monomer is the product of part (c).



e) (1.5 pts) Give the name and abbreviation for this polymer, and the oxidation state of the Zr atom in the initial metallocene catalyst.

polystyrene, PS.

Zr^{+4}

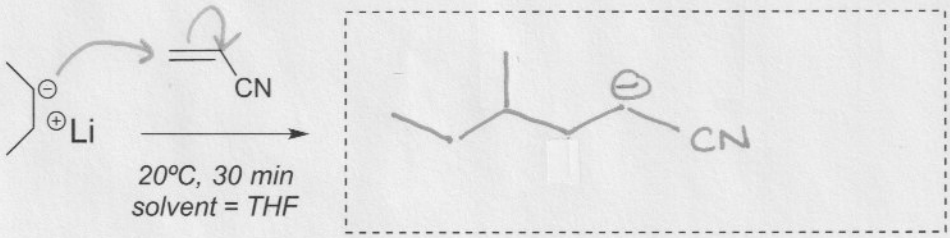
f) (2 pts) This polymer can also be synthesized by FRVP. How would the structure of the resulting polymer differ if this method was used? Why?

In FRVP, the growing polymer radical can undergo BACK-BITING reactions, where the resulting polymer will end up being highly BRANCHED, with no TACTICITY CONTROL and thus a much lower CRYSTALLINITY (more amorphous).

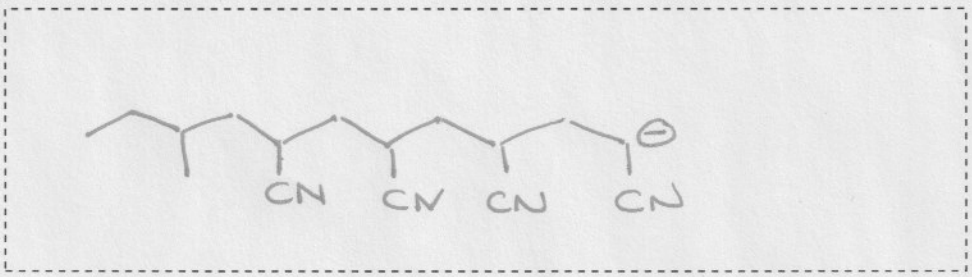
3. (15 pts) CUMULATIVE QUESTION 2

Complete the following steps for the sequential anionic block copolymerization of acrylonitrile and vinyl chloride under the provided conditions.

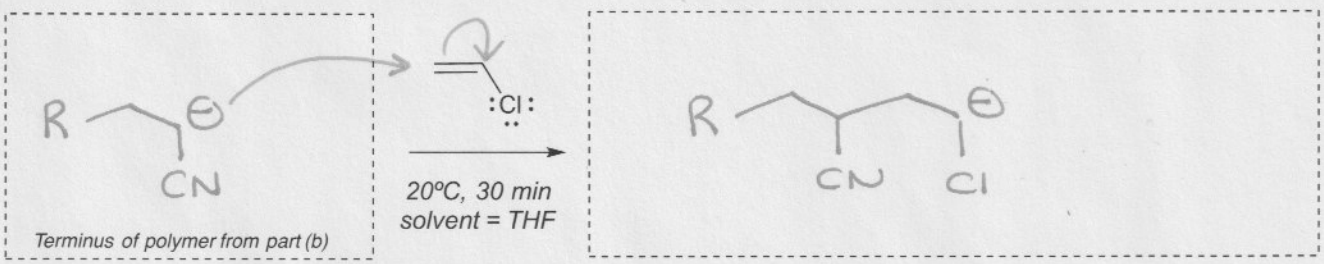
a) (2 pts) Draw the mechanism for the initiation step and its product:



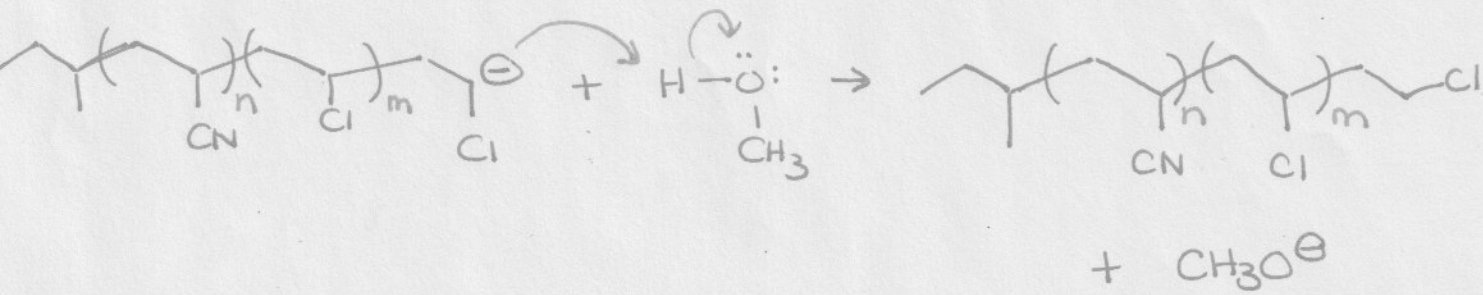
b) (1 pt) Draw a structure corresponding to the addition of 4 acrylonitrile monomer units:



c) (2 pts) Draw a mechanism for the reaction between the polymer terminus from part b above and vinyl chloride and draw the resulting product:



d) (2 pts) Draw a mechanism for the termination of the polymer (containing *n* acrylonitrile monomers and *m* vinyl chloride monomers) by addition of excess methanol:



– QUESTION CONTINUED ON THE NEXT PAGE –

e) (3 pts) Given the enthalpy and entropy of polymerization for acrylonitrile and vinyl chloride below, determine the temperature range under which polymerization of each will be spontaneous.

$\Delta G = \Delta H - T\Delta S < 0$

$\therefore T < \frac{\Delta H}{\Delta S}$

	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
(A) acrylonitrile	-73	-104
(B) vinyl chloride	-35	-104

(A) $T < \frac{-73\,000\ J/mol}{-104\ J/mol\,K} = 702\ K = 429°C$

(B) $T < \frac{-35\,000\ J/mol}{-104\ J/mol\,K} = 336\ K = 63°C$

f) (3 pts) Imagine that the temperature for polymerization was misread and the reaction was carried out at as 70°C rather than 20°C. What would be the final products of the polymerization? Explain.

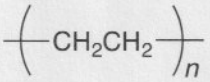
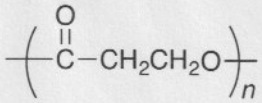
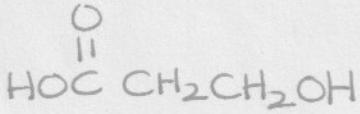
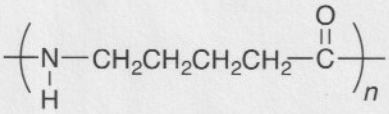
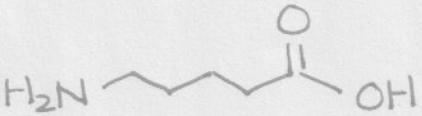
70°C is greater than 63°C but lower than 429°C. Therefore, the acrylonitrile will polymerize spontaneously but vinyl chloride will not. (A HOMOPOLYMER of polyacrylonitrile will be obtained).

g) (2 pts) What is the degree of polymerization in part (a) if the acrylonitrile concentration was 0.100 M and the n-butyl lithium concentration was 0.28 mM?

$DP = \frac{[M]}{[In]} = \frac{0.100\,M}{0.00028\,M} = 357$

4. POLYMER PROPERTIES

a) (3 pts) Complete the following table by adding the missing monomers.

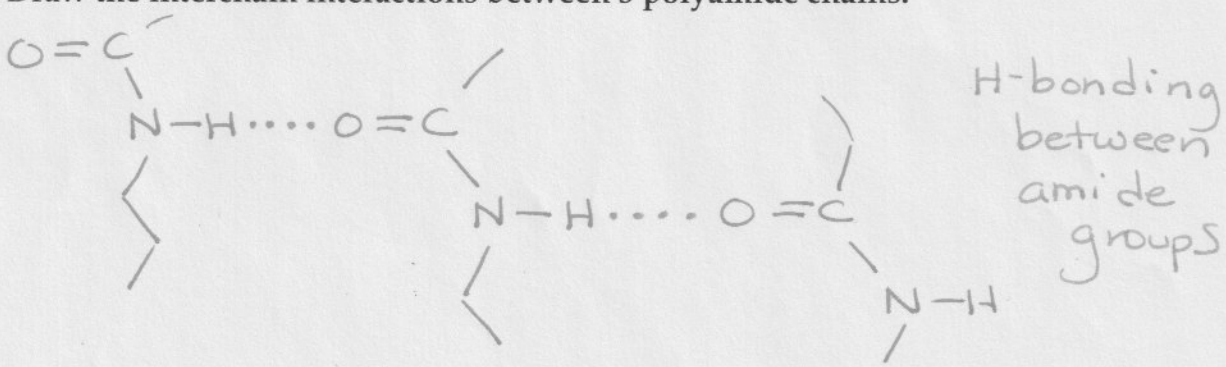
Polymer	Melting point, T_m	Monomer(s)
	170°C	$CH_2=CH_2$
	240°C	
	280°C	

b) (3 pts) Explain the observed trend in melting points.

As the intermolecular forces between polymer chains increase, crystallinity increases. More energy is needed to disrupt these forces and T_m ↑

(FORCES: van der Waals < dipole-dipole < H-bonding)

c) (3 pts) Draw the interchain interactions between 3 polyamide chains.



d) (1 pt) Name the third polymer in the table.

Nylon-5

5. POLYMER APPLICATIONS

a) (5 pts) Choose one of the following common polymers discussed in class (circle your selection) and fill in the spaces below with details about the polymer you've chosen.

POLYBUTADIENE **PETE** **LLDPE** **PMMA**

Monomer Structure(s): **Polymer Structure:**

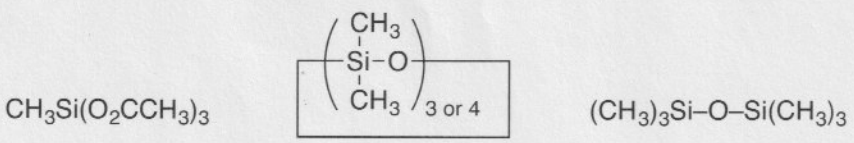
Polymerization Method Used: * marked based on selection *

Give a physical property and application of the polymer you've chosen:

b) (3 pts) Gases such as air or N_2 can't be used as blowing agents for rigid foams. Why?

$d_{plastic} = 1\ g/mL$] factor of 1000x
$d_{foam} = 1\ g/L$ ↵ $P_1V_1 = P_2V_2$

If foams are expanding against external atmospheric pressure ($P_2 \sim 1$ atm) that means $P_1 \approx 1000$ atm, which is extremely difficult/dangerous to achieve!



A B C

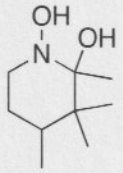
c) (2 pts) From the above list, which ingredients (and in what relative amounts) would you need to produce:

i. **a light silicone oil?** mostly B and a bit of C

ii. **RTV (silicone caulking)** mostly B and a bit of A

6. POLYMER DEGRADATION

The molecule at right is a common plastic additive because it acts as an excited state quencher.



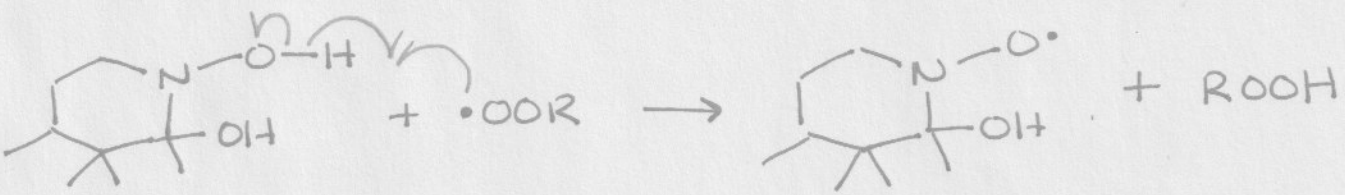
a) (4 pts) What are the two criteria for an excited state quencher?

(1) Follow the conservation of energy: the excited-state energy of the quencher must be equal to or lower than that of the polymer.

(2). The excited state quencher returns harmlessly to the ground state without creating any new radicals (eg. emits heat)

b) (3 pts) This compound can also protect polymers from photodegradation by another mechanism. What is this process? Illustrate your answer with a chemical reaction.

It's also an ANTIOXIDANT, as it has a weak O-H bond and forms a radical that does not react with O_2:



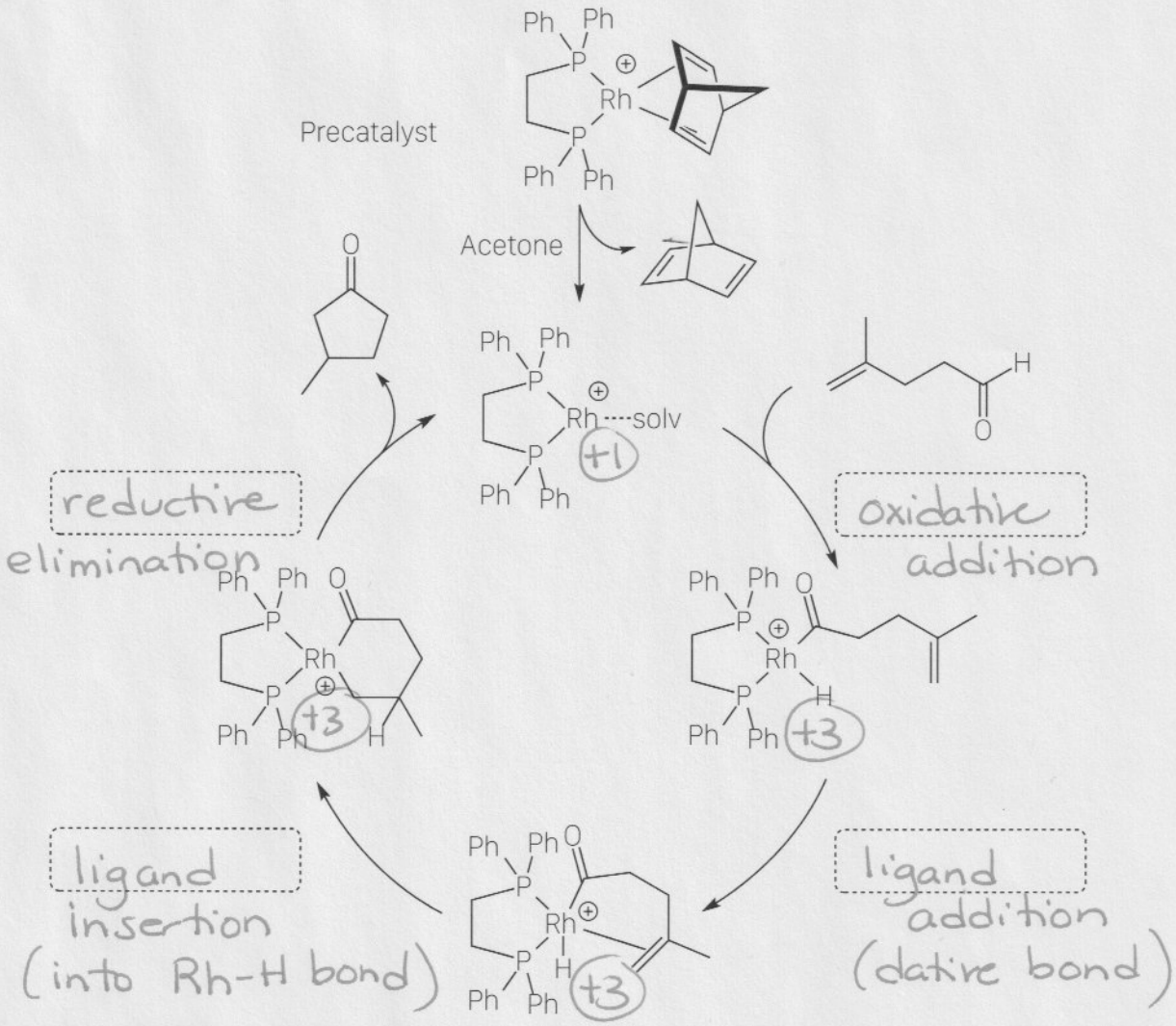
c) (3 pts) You are provided with two apparently identical pieces of polyethylene. One is brand new, but the other has been left to age naturally for 6 months. How would you be able to distinguish between the two samples? Explain.

The easiest way is to test the plastic's mechanical properties. For example, we could measure the tensile strength of each sample. The degraded polymer will be weakened and is expected to reach its breaking point first.

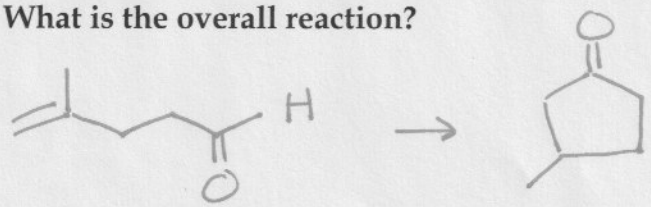
7. INDUSTRIAL CATALYTIC CYCLES

Shown below is the catalytic cycle for a process called intramolecular hydroacylation.

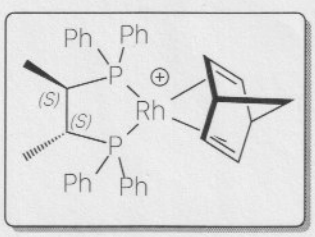
a) (6 pts) In the boxes, write the name of each type of reaction step, and write the oxidation state of the rhodium centre below each intermediate.



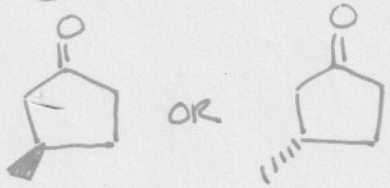
b) (2 pts) What is the overall reaction?



c) (2 pts) Suppose we changed the precatalyst to the one shown in the box at right. How might it affect the product of the reaction?



This might control the stereochemistry of the insertion step, leading to one of the 2 enantiomers, eg.



8. ASSORTED QUESTIONS

a) (3 pts) The main component of most commercial detergents is NOT the surfactant, but another compound. What are these molecules? Why are they added to detergents?

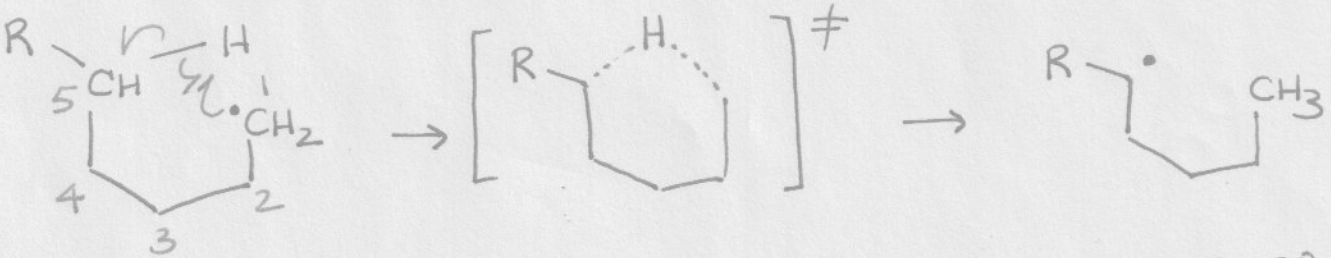
They are BUILDERS (water softeners).
Their job is to prevent the formation of SOAP SCUM by chelating the hard water ions (Ca^{2+}/Mg^{2+}) responsible.

b) (3 pts) A bimolecular reaction is 50% complete in 25 min. What is the rate constant? How long will it take for the reaction to be 75% complete?

$t'_{1/2} = \frac{\ln 2}{k} = 25\,\text{min} \quad \therefore k = 0.028\ \text{min}^{-1}$

$75\% = 2 \times t'_{1/2} = 50\,\text{min}$

c) (4 pts) Draw an example of the back-biting reaction. Why is this reaction always exothermic? Explain why it occurs at the C5 position instead of other sites.



It's exothermic because BDE 1° C-H > BDE 2° C-H
It occurs at the C5 position because a 6-membered transition has NO RING STRAIN.