



uOttawa

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Please print

CHM4155

Family name: _____

FINAL EXAM (50%)

First name: _____

April-2008

Student #: _____

Time allowed: 180 minutes

NO BOOKS OR NOTES ALLOWED
NO MOLECULAR MODELS ALLOWED
CALCULATORS ALLOWED

Question	1	2	3	4	5	6	7	8	Total
Value	30	15	15	10	10	10	10	10	100
Mark									
Notes									

IMPORTANT: You must answer questions # 1, 2 and 3

You must answer 4 questions only from questions 4 to 8. Please indicate below which question you do NOT want marked. If you make no selection, question 8 will not be marked.

Please do NOT mark question: _____ 

1. (30 MARKS – stars show marks) Short Answer Questions.

a) *If you plot the natural logarithm of concentration ($\ln c$) as a function of time for a given chemical reaction and obtain a straight line, the reaction occurs through a **FIRST ORDER UNIMOLECULAR SECOND ORDER** process.

b) * The chain length of a chain reaction is directly proportional to (circle one):

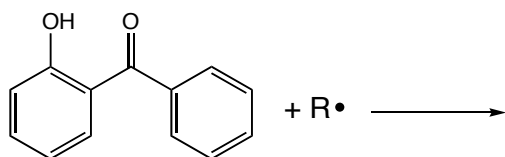
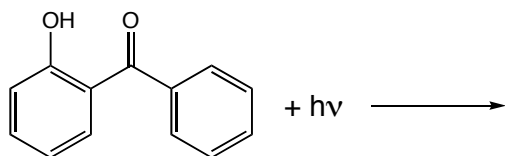
$\frac{\text{initiation}}{\text{termination}}$

$\frac{\text{termination}}{\text{propagation}}$

$\frac{\text{propagation}}{\text{initiation}}$

c) *One reason why *gasification* is the most favoured method for processing coal is _____.

d) **Show the 2 roles of *o*-hydroxybenzophenone in preventing polymer degradation:



e) *The blue luminescence of cool flames is due to emission from the excited state of **FORMALDEHYDE PEROXIDES SOOT**

f) *The average number of surfactant molecules needed to form a micelle is known as the _____.

g) *Surfactants with branched hydrophobic tails clean better than surfactants with linear hydrophobic chains. Why are linear surfactants used in practice? (choose one)

- BRANCHED SURFACTANTS DO NOT DISSOLVE EASILY
- LINEAR SURFACTANTS ARE CHEAPER
- BRANCHED SURFACTANTS ARE NOT BIODEGRADABLE
- LINEAR SURFACTANTS DO NOT CAUSE RASHES ON SKIN

h) ****A methyl radical is (circle one) PLANAR PYRAMIDAL LINEAR , reflecting that the hybridization at the carbon centre is: _____.**

i) ***For a given reaction, the plot of $\ln K_{eq}$ versus $1/T$ yields a slope of -22.0 and a y-intercept of -4.5 . Knowing this information, the reaction has**

$$E_a > 0$$

$$\Delta G < 0$$

$$E_a < 0$$

$$\Delta G > 0$$

j) ***The chemist largely considered to be the “father” of industrial organic chemistry is**

HOFMANN

LIEBIG

PERKIN

LAVOISIER

k) ***In synthesizing a dendrimer, if you begin building the molecule from the core outward, then you are using the _____ approach.**

l) ***A vinyl monomer is polymerized using free radical vinyl polymerization. It was observed that using cyclohexane as the solvent reduces the molecular weight of the polymer, where using benzene does not. Why?**

m) ***In olefin metathesis, the four-membered transition state is known as the _____ intermediate.**

n) ****The two inter-chain interactions responsible for Kevlar’s strength are _____ and _____.**

o) ***Polyethylene can be made using many different synthetic methods. Associate each synthetic method with the resulting polymer.**

FREE RADICAL POLYMERIZATION

UHMWPE

ZIEGLER-NATTA POLYMERIZATION

HDPE

METALLOCENE- CATALYZED POLYMERIZATION

LDPE

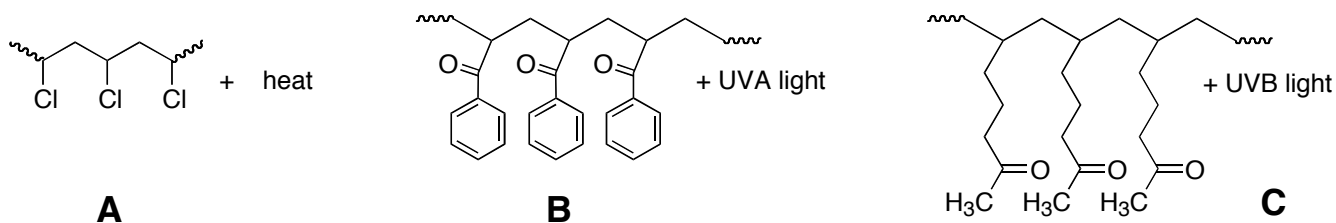
p) ***Trans-polyacetylene is treated with solid potassium metal. This is known as**

n-DOPING

NON-REDOX DOPING

p-DOPING

q) *Which of the following combinations would induce the largest loss in mechanical strength of the plastic? (choose one)



r) *Draw the possible monomer(s) used to make Novolac by acid-catalyzed polymerization.

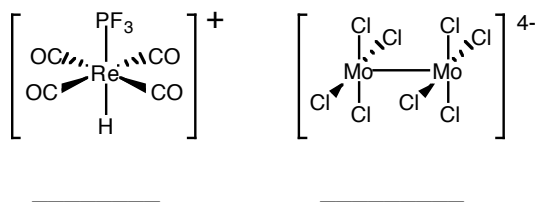


s) *Which of these additives would be the *most* efficient at preventing light-induced damage in a polymer?

PLACTICIZER SUNSCREEN RADICAL SCAVENGER WATER

t) *One advantage to using a powder coating instead of a wet paint is _____

u) **Label the oxidation state of the metal centre in each of the complexes below:

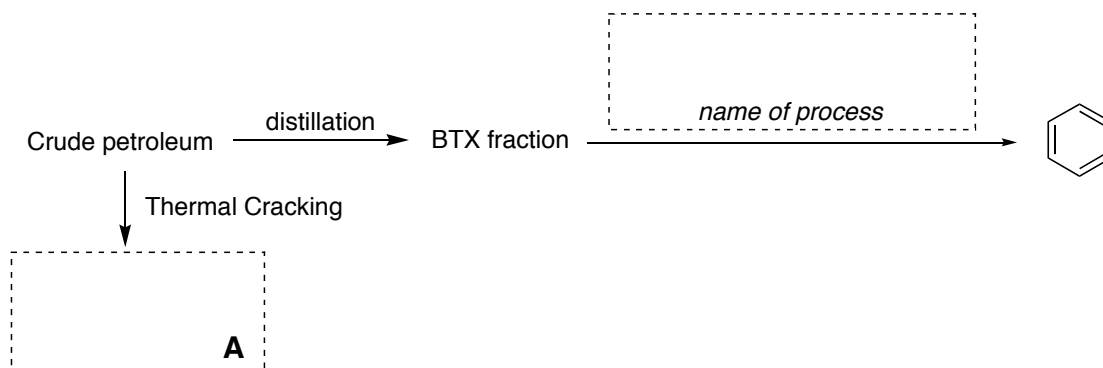


v) *In microlithography, a photoresist film that becomes more soluble after exposure to light will give an image that is

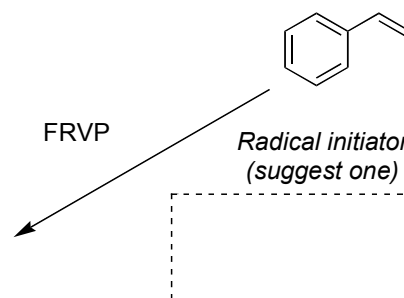
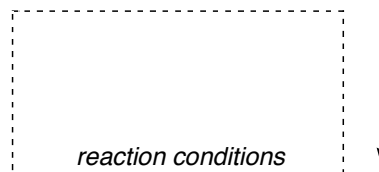
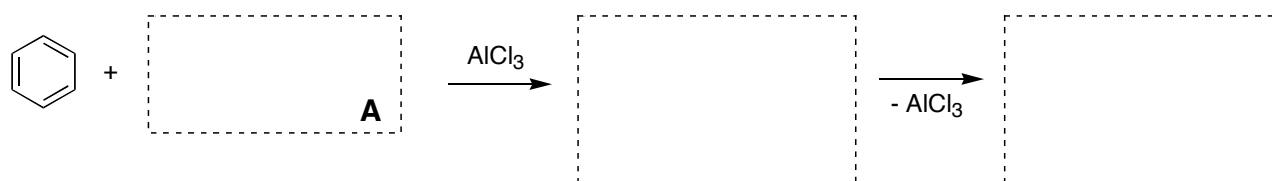
POSITIVE NEUTRAL NEGATIVE REVERSE

2. (15 MARKS) INDUSTRIAL ORGANIC CHEMISTRY

Complete the following reactions, showing the synthesis of a valuable product.



FOR THIS REACTION, INCLUDE ELECTRON-PUSHING ARROWS



Polymer - show repeating unit

The name of this polymer is:



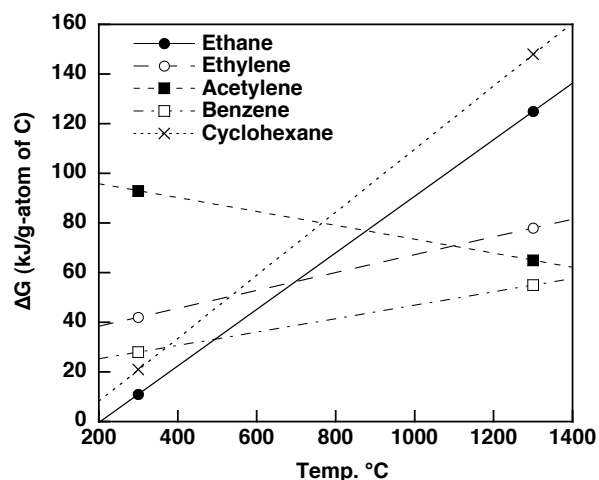
A major use of this polymer is:



3. (15 MARKS) PETROLEUM CHEMISTRY AND COMBUSTION

(a) (4 marks) What scale is used to measure gasoline quality? What type of chemical compounds are desirable for a high quality fuel?

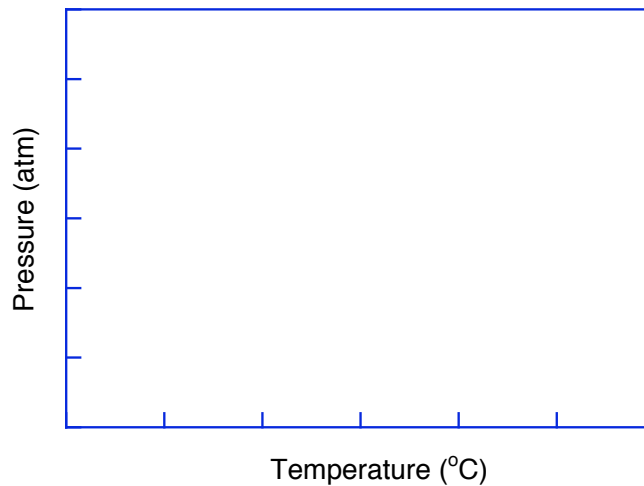
(b) (5 marks) From the molecules in the graph below, choose the most desirable compound for use in automobile fuel, and describe how this compound may be formed using a heavy petroleum fraction (e.g. C_{50} hydrocarbons) as your starting material. Don't forget to describe any necessary reaction conditions (T, P & catalyst).



---QUESTION CONTINUED ON NEXT PAGE---

(c) (3 marks) On the graph below, draw and label the following two temperature-pressure curves:

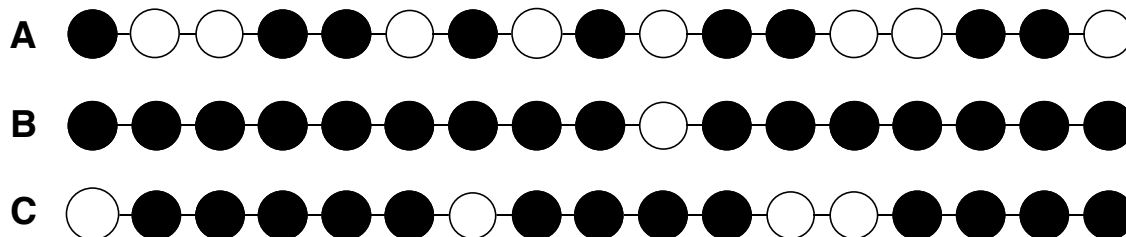
- (i) for the fuel described in part (c)**
- (ii) for the same fuel, but with MTBE added to it**



(d) (3 marks) Gasoline can be directly obtained from petroleum via fractional distillation. Why, then, is further refining of crude oil necessary?

4. (10 MARKS) POLYMER CHEMISTRY

In a copolymerization reaction, the parameters r_1 and r_2 describe the tendency of a polymer with a radical centre derived from one of the monomers to react with another monomer molecule of the same type, or with a different one. Polymers A, B, and C below have been prepared by free radical polymerization of monomers X (r_1) and Y (r_2). Identify which polymer corresponds to each case and explain your answer for polymers B and C.



Case 1

$r_1 = 0.1$

$r_2 = 5$

Case 2

$r_1 = 1.2$

$r_2 = 0.98$

Case 3

$r_1 = 0.001$

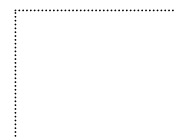
$r_2 = 14$

(a) (3 marks) The polymers are: _____
(insert letter A, B or C in each space)

(b) (3 marks) I have selected polymer A as case _____ for the following reasons:

(c) (3 marks) I have selected polymer C as case _____ for the following reasons:

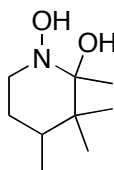
(d) (1 mark) In polymer A, the black monomer units correspond to X or Y?



5. (10 MARKS) POLYMER DEGRADATION AND THIN FILMS

(a) (3 marks) “Polymer degradation cannot be carried out exclusively via hydroperoxide chemistry or carbonyl photochemistry; the two processes are too intertwined to be distinguishable from each other”. Explain this statement, using chemical reactions to support your answer.

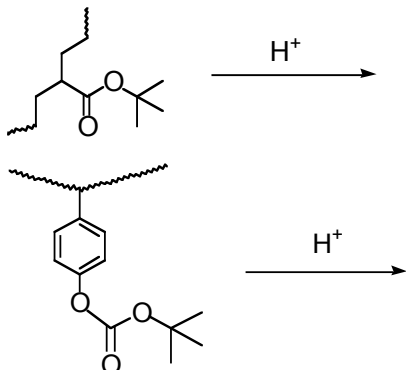
(b) (2 marks) The molecule shown below is often added to plastic and cosmetic formulations as an excited state quencher (ESQ). However, it can also protect against photodegradation via another mechanism. What is it? Demonstrate, using a chemical reaction.



---QUESTION CONTINUED ON NEXT PAGE---

5. CONTINUED...

(c) (2 marks) Complete the following two reactions:



(d) (2 marks) If these reactions are used in photoresist chemistry, do you expect positive or negative images? Briefly explain your answer.

(e) (1 mark) Does this chemistry correspond to an amplified or non-amplified resist?

AMPLIFIED

NON-AMPLIFIED

6. (10 MARKS) POLYMER AND SURFACTANT APPLICATIONS

(a) (5 marks) Choose one of the following common polymers discussed in class (circle your selection):

PVC

PMMA

LLDPE

POLYCARBONATE of BISPHENOL A

Fill in the spaces below with details about the polymer you've chosen.

Monomer Formula(s):

Polymer Formula:

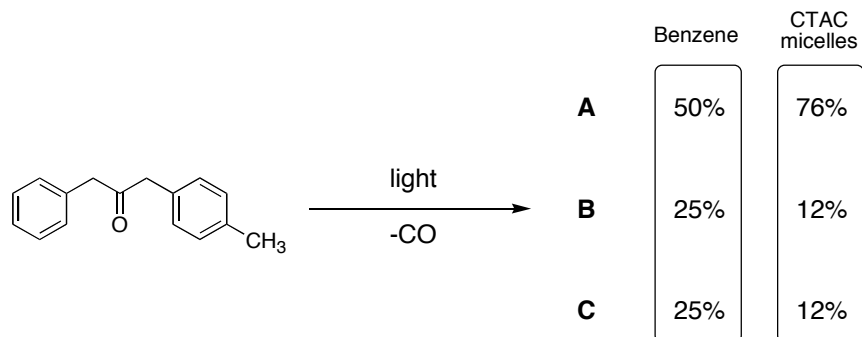
Method of synthesis:

Polymer Properties:

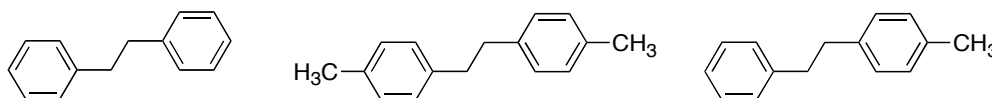
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6. CONTINUED...

(b) (2 marks) The following reaction, giving three products, A, B and C, is performed in benzene and then in micellar solution:



Below, circle the product molecule which corresponds to the dominant product A.



The yield of product A increases in micelles due to:

- A. THE PERSISTENT FREE RADICAL EFFECT
- B. THE CAGE EFFECT
- C. THE KINETIC SOLVENT EFFECT
- D. ORIENTATION EFFECTS

(c) (3 marks) You wish to perform the photo-dimerization of molecule A in micellar solution:



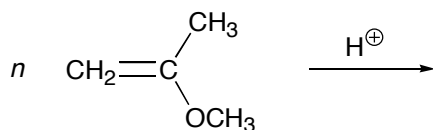
Assuming that the reaction is 100% efficient, and given the data below, what is the minimum amount of surfactant S you will need to do the reaction in 1 L of solution?

Mass of A = 10.0 g
 Molecular Mass of A = 100.0 g/mol
 Volume of solution = 1.000 L

Molecular Mass of S = 300 g/mol
 Aggregation Number for S = 50
 cmc of S = 0.01 mol/L

7. (10 MARKS) POLYMERIZATION METHODS

(a) (3 marks) Write the mechanism (with electron-pushing arrows) for the following ionic polymerization:

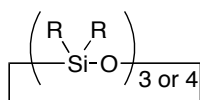


(b) (2 pts) In order to obtain high molecular weights, what must be carefully eliminated from the polymerization chamber? In your answer, show the corresponding reaction.

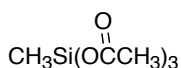
(c) (2 pts) Polyisobutene was prepared using the method shown in part (a): a 1000 L chamber was filled with 2.3×10^4 mol of isobutene along with exactly 1.50 mol of a strong acid (such as HCl). What would be the chain length of the reaction?

---QUESTION CONTINUED ON NEXT PAGE---

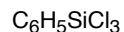
(c) (3 pts) The following ingredients are available to make various types of silicones:



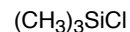
A



B



C



D

In order to prepare each of the following polymers, circle in the table the amounts of each component that would be desirable to achieve the correct properties:

(a) Silicone caulking, capable of conserving its shape and with extremely low solubility:

A	B	C	D
None	None	None	None
A small amount	A small amount	A small amount	A small amount
Main component	Main component	Main component	Main component
The only component	The only component	The only component	The only component

(b) A silicone light lubricating oil:

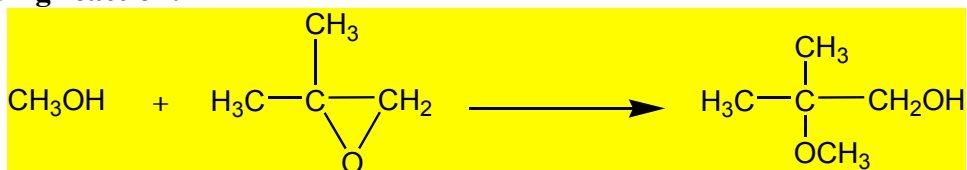
A	B	C	D
None	None	None	None
A small amount	A small amount	A small amount	A small amount
Main component	Main component	Main component	Main component
The only component	The only component	The only component	The only component

(c) A syndiotactic silicone ladder polymer

A	B	C	D
None	None	None	None
A small amount	A small amount	A small amount	A small amount
Main component	Main component	Main component	Main component
The only component	The only component	The only component	The only component

8. (10 MARKS) ASSORTED QUESTIONS

(a) (3 marks) Using the values (in kcal/mol) from the table below, calculate the enthalpy change for the following reaction:



C-(H) ₃ (C)	-10.20	O-(C)(H)	-37.90
C-(H) ₂ (C) ₂	-4.93	O-(H)(O)	-16.30
C-(H)(C) ₃	-1.90	O-(H)(CO)	-58.10
C-(C) ₄	0.50	O-(C) ₂	-23.20
C-(C) ₃ (O)	-6.6	C-(H)(O)(C) ₂	-7.20
CO-(H)(C)	-29.10	C-(H) ₃ (O)	-10.08
CO-(C) ₂	-31.40	C-(H) ₂ (O)(C)	-8.10
Epoxide ring correction 26.8		C-(H) ₂ (O) ₂	-10.10

Show the calculations, NOT just the answer

Answer: $\Delta H^\circ_{\text{rxn}} =$ _____

---QUESTION CONTINUED ON NEXT PAGE---

8. CONTINUED...

(b) (2 marks) In the cracking of 2,7-dimethyl-octane, the process is initiated by the reaction of CH_3^\bullet with the weakest C-H bond in the molecule. Write the mechanism for the reaction and show the relative yields of the products.

(c) (3 marks) A first order reaction is 30% complete in one hour. What is the value of the rate constant?

(d) (2 marks) Draw the mechanism and product for the following ROMP reaction:

