uOttawa

L'Université canadienne
Canada's university

**Please print your name**

**CHM4155**

**FINAL EXAM (50%)** **Family name:** _____

**Dr. J.C. Scaiano** **First name:** _____

**April 18, 2009** **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 |
|---|---|---|---|---|---|---|---|---|
| Value | 30 | 15 | 15 | 10 | 10 | 10 | 10 | 10 |
| Mark | | | | | | | | |
| Notes | | | | | | | | |

| Total |
|---|
| 100 |
| |
| |

**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: no part marks.**

a) ***For the hypothetical reaction A + B → C + D, the activation energy is 26 kcal/mol. For the reverse reaction, the activation energy is 16 kcal/mol. What is the enthalpy change for the forward reaction ($\Delta H_{reaction}$)? _____**

b) ***For a first order reaction a straight line can be obtained by plotting (C=concentration)**
**1/C $C^2$ THE NATURAL LOGARITHM OF C as a function of time.**

c) ***The rate constant for a diffusion-controlled reaction will**
**INCREASE DECREASE STAY CONSTANT**
**with decreasing solvent viscosity.**

d) ***What is the driving force for cross metathesis?**

_____

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

f) ****A transition metal is said to be in "coordinative saturation" when it has**

_____ **ligands and**

**"electronically unsaturated" when it has less than _____**

**valence electrons.**

g) ****In the box, write one possible industrial synthesis of acrylonitrile. An important by-product of this synthesis is an organic solvent widely used by the pharmaceutical industry**

**The solvent formed as a by-product is: _____**

**h) *The complete combustion of methane yields water and carbon dioxide. Give a possible *final* product from the <u>incomplete</u> combustion of methane (apart from methane itself).**

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**i) *The chemist largely considered to be the "father" of industrial organic chemistry is**

**HOFMANN LIEBIG PERKIN LAVOISIER**

**j) *Surfactants with branched hydrophobic tails clean better than surfactants with linear hydrophobic chains. Why are linear surfactants used in practice? (choose <u>one</u>)**

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

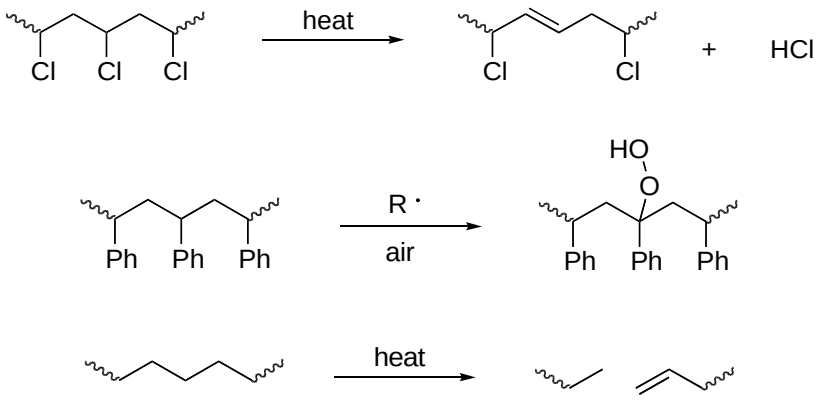
**k) *What is the effect of chain transfer?**

- θ **reduces chain length**
- θ **leads to an explosion**
- θ **increases chain length**
- θ **creates highly cross-linked polymers_**

**l) *Polyethylene can be made using many different synthetic methods. Associate each synthetic method (<u>use lines</u>) with the resulting polymer. (Hint: LLDPE stands for linear low density polyethylene)**

| | |
|---|---|
| **FREE RADICAL POLYMERIZATION** | **HDPE** |
| **ZIEGLER-NATTA POLYMERIZATION** | **LLDPE** |
| **CO-POLYMERIZED WITH A BRANCHED ALKENE** | **LDPE** |

**m) **Which of the following reactions would induce the <u>largest loss</u> in mechanical strength of the plastic? (choose one). In one line explain why.**

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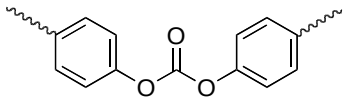
**n) **Below, draw a representative stress-strain curve for an elastomer, i.e., a rubber band (be precise, and include axis labels).**

**o) *The photodegradation of polycarbonates involves the photo-Fries reaction. Complete the reaction below with the final product :**




Functional group in polycarbonate

Product or the photo-Fries reaction

**p) *Polyacrylonitrile can be made via anionic polymerization. Which of the following should be rigorously removed from the reaction vessel?**

**$Li^+$ $Na^+$ WATER AIR MAGNETIC FIELDS**

**q) *What will be the average chain length of the resulting polymer if 1 mole of acrylonitrile is initiated by 0.001 mole of an anionic initiator?**

_____

**r) *In synthesizing a dendrimer, if you begin building the molecule from the periphery inwards, then you are using the _____ approach**

**s) *When a new car is introduced on the market, it is available in only a few colours. Explain why the industry shift from paints to resins for cars has limited the number of available colours for new cars.**

_____

_____

**t) **A radical polymerization is occurring at a rate of 0.05 mol/hr. If the concentration of the initiator is doubled, then the chain length will**

**INCREASE DECREASE by a factor of**

$\frac{1}{4}$ $\frac{1}{2}$ $\frac{1}{\sqrt{2}}$ $\sqrt{2}$ $\times 2$ $not\_change$

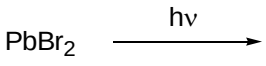
**u) *When you are looking outside through your window, you are exposed to:**

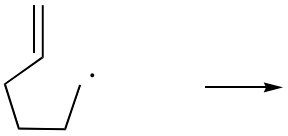
**UVA UVB UVC X-RAYS**

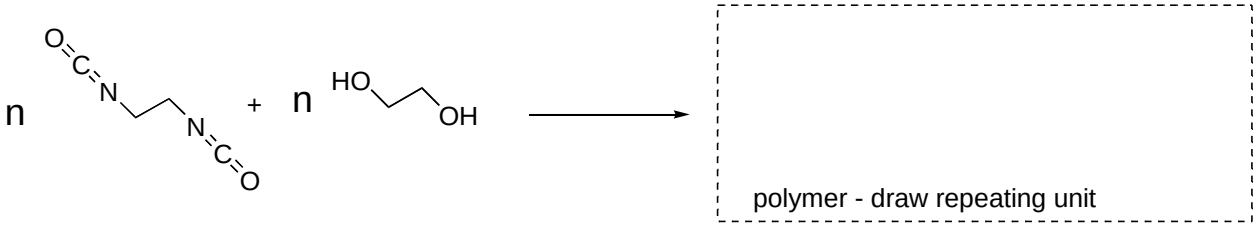
**v) *In microlithography, a photoresist film that becomes less soluble after exposure to light will give an image that is**

**POSITIVE NEUTRAL NEGATIVE REVERSE**

**w) ***Give the product of the following reactions** (no words, just the formulas!)






**BONUS QUESTIONS**

***Synthetic rubber has a higher $T_g$ than natural rubber. Try to rationalize this observation.**

_____

_____

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

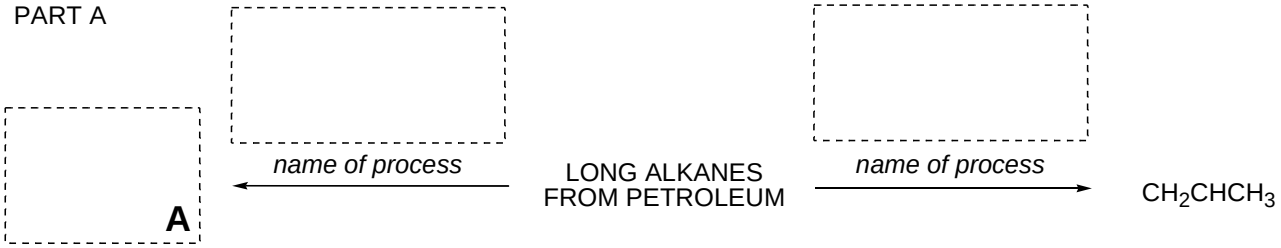
_____

_____

## 2. (15 MARKS) INDUSTRIAL ORGANIC CHEMISTRY

**Complete the following industrially relevant chemical reactions.**

PART A

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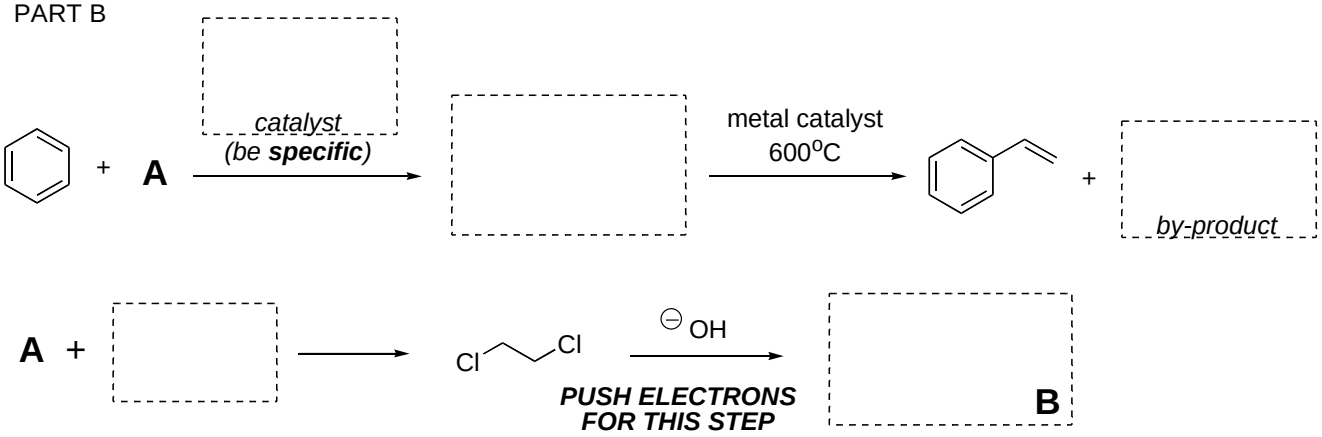
PART B

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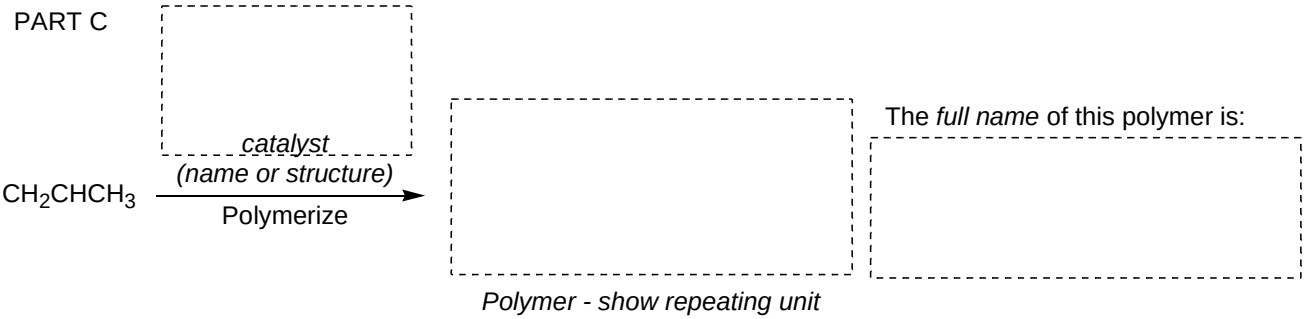
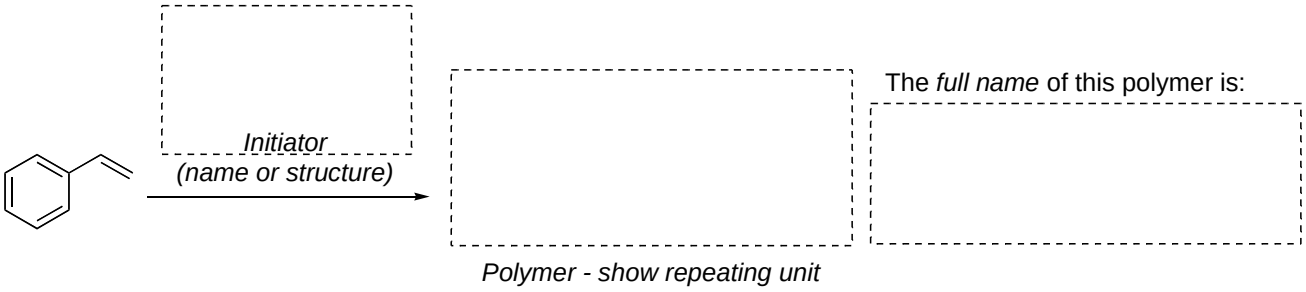
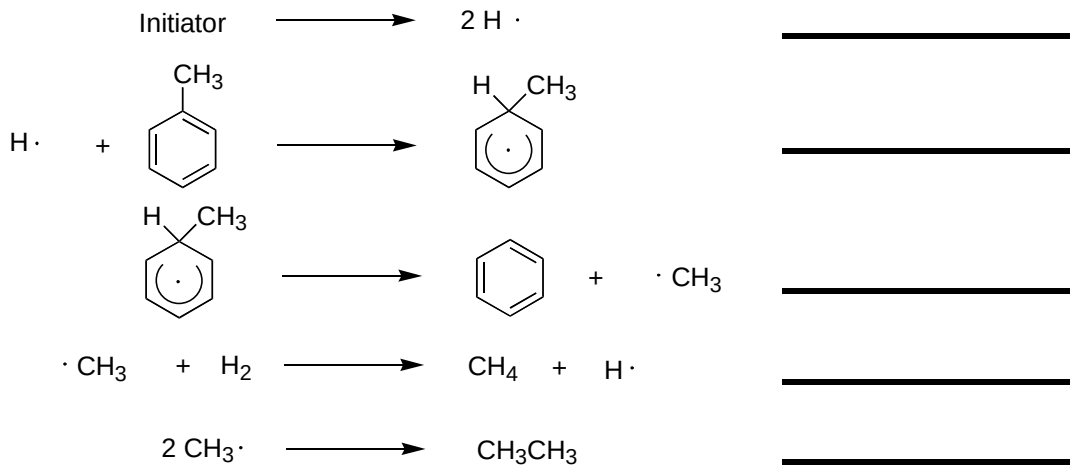
PART C



## 3. (15 MARKS) FREE RADICAL REACTIONS

**The following mechanism shows the hydrodealkylation of toluene at 700°C.**




**(a) Directly on the reaction scheme, identify all the steps in the mechanism.**

**(b) Write the overall reaction.**

**(c) Label the scheme with the appropriate rate constants and derive the rate expression for the chain reaction.**

**REMINDER: You must answer 4 questions only from questions 4 to 8**

## 4. (10 MARKS) POLYMER CHEMISTRY

**(a) (3 marks) 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. Match the r values in the column on the left with their corresponding polymer on the right using lines.**

| | |
|---|---|
| **$r_1$ and $r_2$ = 1.0** | **Alternating copolymer (almost perfect)** |
| **$r_1$ = 0.009, $r_2$ = 0.01** | **AAAAABAAAAAAABAAAA** |
| **$r_1$ = 20, $r_2$ = 0.015** | **Random copolymer** |

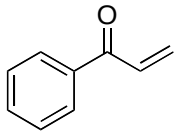
**(b) (5 marks) Describe in detail how polystyrene can be made via emulsion polymerization. List one advantage this method has over bulk polymerization. What is one possible problem with this polymerization technique?**

**(c) (2 marks) What is the tacticity of polymers formed by Ziegler-Natta polymerization and how does this affect their strength?**

## 5. (10 MARKS) POLYMER DEGRADATION AND THIN FILMS

**(a) (4 marks) Consider a <u>POLYMER</u> made from the monomer shown below. How would this polymer be affected upon exposure to UV light? Explain, using chemical reactions.**

*(Hint: Norrish)*

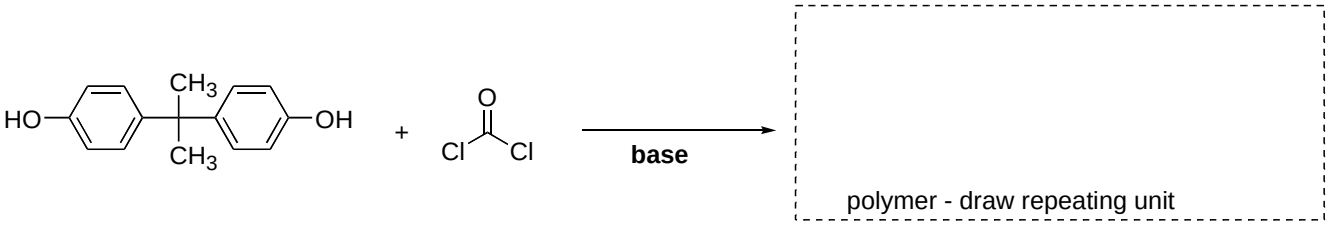



**(b) (2 marks) The degradation of the above polymer by UV light can be reduced by adding *ortho*-hydroxybenzophenone to the polymer. Explain how this additive reduces UV-induced degradation.**

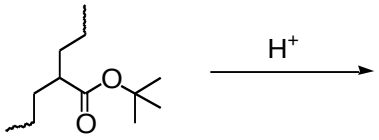
**---QUESTION CONTINUED ON NEXT PAGE---**

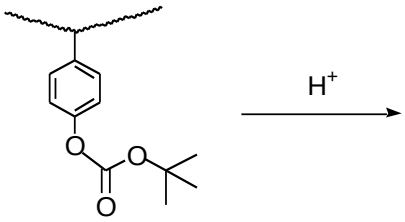
**5. CONTINUED…**

**(c) (2 marks) Draw the structure of the polymer that would result from these two monomers.**




(d) **2 marks) Complete the following two reactions:**



## 6. (10 MARKS) POLYMER AND SURFACTANT APPLICATIONS

**(a) (6 marks) Choose one of the following common polymers discussed in class (circle your selection):**

**NYLON-6** **PP**

**LDPE** **POLYACETYLENE**

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

**Monomer Formula:** **Polymer Formula:**

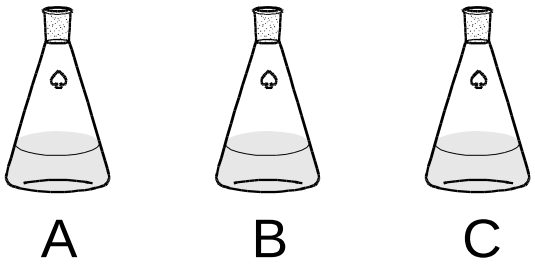
**Method of synthesis:**

**Polymer Properties (e.g., physical properties, applications, etc.)**

**---QUESTION CONTINUED ON NEXT PAGE---**

**6. CONTINUED…**

**(b) (4 marks) In three Erlenmeyer flasks, you are given three unknown samples of *dishwasher detergent, shampoo, and laundry detergent*. Use the observations below to determine which sample is which, and briefly explain your decision.**




A : makes foam, slightly acidic

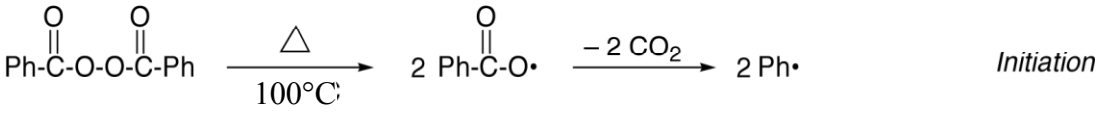
B : makes foam, slightly basic

C : no foam, strongly basic

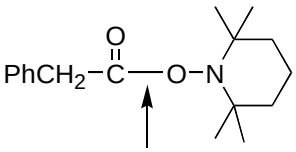
*(A few lines with the right answer will do, please do not fill the page)*

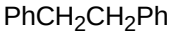
## 7. (10 MARKS) POLYMERIZATION METHODS

**(a) (3 marks) Polystyrene can be made *via* free radical vinyl polymerization. Show the mechanism for the polymerization, using benzoyl peroxide as the initiator.**

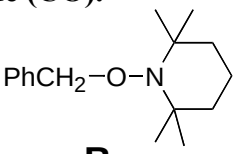



**(b) (4 marks) When irradiated with UV light, the molecule below cleaves homolytically at the position indicated by an arrow followed by rapid loss of carbon monoxide (CO).**




**A**




**B**

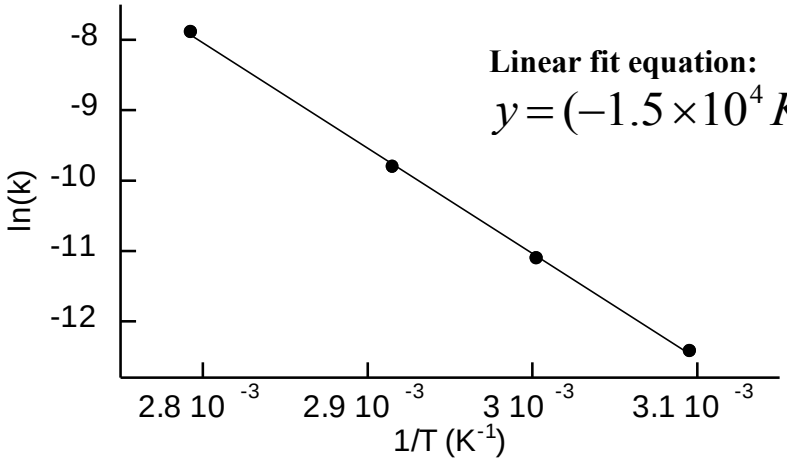
**During the irradiation, it was observed that in the first few seconds of the reaction, product A is the major product. However, at the end of the reaction, B was the overall dominant product (>90%). Why is A the product favoured early in the reaction but B is the overall major product?**

*Hint: Employ the concepts you learned while studying "living" free radical polymerization.*

## 8. (10 MARKS) ASSORTED QUESTIONS

**(a) (4 marks) The rate constant for the decomposition of lauryl peroxide ($C_{12}H_{25}OOC_{12}H_{25}$) was measured at different temperatures and an Arrhenius plot was constructed with the data. Estimate the activation energy and the pre-exponential factor for this reaction. What property of lauryl peroxide determines the value of the activation energy?**

**(Reminder: the Arrhenius expression is $k = Ae^{-E_a/RT}$ and R=8.31 J/mol.K )**




**Linear fit equation:**

$$y = (-1.5 \times 10^4\ K)x + 33.9$$

_____

*activation energy (show units!)*

_____ $s^{-1}$

*pre-exponential factor*

**---QUESTION CONTINUED ON NEXT PAGE---**

**8. CONTINUED…**

**(b) (2 marks) Diesel engines perform better when using <u>linear</u> alkanes while internal combustion engines perform better with <u>branched</u> alkanes. Briefly explain the reason for this observation.**

**(c) (4 marks) Aramid polymers are typically quite strong in part due to hydrogen bonding between chains. Explain two other factors that give this polymer class it's strength? Give an example of an aramid polymer?**