THE CANADIAN CHEMISTRY CONTEST 2021

for high school and CEGEP students

PART C: CANADIAN CHEMISTRY OLYMPIAD
Final Selection Examination 2021

(120 minutes)

This segment has five (5) questions. While students are expected to attempt **all** questions for a complete examination in 2 hours, it is recognized that backgrounds will vary and **students will not be eliminated from further competition because they have missed parts of the paper.**

Your answers are to be written in the spaces provided on this paper. All of the paper, is to be returned **immediately** by email or upload.

— PLEASE READ —

1. BE SURE TO COMPLETE THE INFORMATION REQUESTED AT THE BOTTOM OF THIS PAGE BEFORE BEGINNING PART C OF THE EXAMINATION.
2. STUDENTS ARE EXPECTED TO ATTEMPT ALL QUESTIONS OF **PART A** AND **PART C**. CREDITABLE WORK ON A LIMITED NUMBER OF THE QUESTIONS MAY BE SUFFICIENT TO EARN AN INVITATION TO THE NEXT LEVEL OF THE SELECTION PROCESS.
3. IN QUESTIONS WHICH REQUIRE NUMERICAL CALCULATIONS, BE SURE TO SHOW YOUR REASONING AND YOUR WORK.
4. ONLY NON-PROGRAMMABLE CALCULATORS MAY BE USED ON THIS EXAMINATION.
5. NOTE THAT A PERIODIC TABLE AND A LIST OF SOME PHYSICAL CONSTANTS WHICH MAY BE USEFUL CAN BE FOUND ON A DATA SHEET PROVIDED AT THE END OF THIS EXAMINATION.

PART A ( ) Correct Answers

25 x 1.6 = ... /040

PART C

1. .... /012
2. .... /012
3. .... /012
4. .... /012
5. .... /012

TOTAL .... /100

Name ______________________________ School ______________________________
(LAST NAME, Given Name; Print Clearly)

City & Province ______________________________ Date of Birth __________________

E-Mail ______________________________ Home Telephone ( ) - _________________

Years at a Canadian high school ___ No. of chemistry courses at a Québec CÉGEP ___

Male ☐ Canadian Citizen ☐ Landed Immigrant ☐ Visa Student ☐

Female ☐ Passport valid until February 2022 ☐ Nationality of Passport ___________

Teacher __________________________ Teacher E-Mail________________________

1. PHYSICAL CHEMISTRY

Physical Chemistry of Carbon Monoxide.

Methanol (CH_3OH) is widely used in polymer and fuel production, as well as in organic synthesis. Methanol is produced industrially from syngas, a mixture of CO and H_2, in accordance with the following reaction:

$$CO(g) + 2H_2(g) \overset{K_p}{\rightleftharpoons} CH_3OH(g)$$

The following thermodynamic data at 298 K are available for the reaction above:

	CO (g)	H_2(g)	CH_3OH (g)
$\Delta_f H^o$ (kJ/mol)	-110.5	0	-220.7
S^o ($J \cdot K^{-1} mol^{-1}$)	197.5	131.0	239.7

a) Calculate the equilibrium constant (K_p) for the reaction above under standard conditions at 298 K and when T = 398 K, assuming enthalpic and entropic independence from temperature. Based on your result, is the forward or reverse reaction thermodynamically favorable under standard conditions? ***3 marks***

$K_{p,\ 298K}$ = $K_{p,\ 398K}$ =

Favorable at 298K? (Yes/No)

b) Write down an expression for the equilibrium constant (K_p) that includes partial pressures of CO, H_2, and CH_3OH. ***1 mark***

c) In a given system, the initial pressure values of CO, H_2, and CH_3OH are 1 bar, 2 bar, and 0.5 bar, respectively at T = 450 K. Given the final equilibrium pressure of the system is 2 bar, calculate K_p^{450K}, the equilibrium constant for the reaction above at T=450K. ***3 marks***

d) In industry, CO is converted into CH_3OH in the presence of a heterogeneous catalyst, typically a metal oxide, such as CuO or ZnO. In general, the adsorption of gases onto metal catalysts (e.g. CO adsorption to the surface of a metal oxide) may be described by the Langmuir adsorption model:

$$CO(g) + S \rightleftharpoons CO(ad)$$

$r_1 = k_1 P_{CO}[S]$
$r_{-1} = k_{-1}[CO(ad)]$
$[S_{tot}] = [S] + [CO(ad)]$

where [S] is the concentration of unoccupied binding sites, $[S_{tot}]$ is the total concentration of binding sites, P_{CO} is the partial pressure of CO, [CO(ad)] is the surface concentration of CO, and k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively.

At equilibrium, knowing that the rates of the forward and reverse reactions are equal and using the equations above, show that:

$$\theta_{CO} = \frac{K_{eq}P_{CO}}{1 + K_{eq}P_{CO}}$$

where K_{eq} is the equilibrium constant for the reaction above and θ_{CO} is defined as the number of occupied binding sites divided by the total number of sites. i.e:

$$\theta_{CO} = \frac{[CO(ad)]}{[S_{tot}]}$$

2 marks

e) When P_{CO} is sufficiently large ($P_{CO} >> 1$), all adsorption sites are occupied. What does this suggest for the value of θ? Show that the equation for the Langmuir adsorption isotherm accounts for this. ***1 mark***

f) An analogous version of the Langmuir equation is often used to describe protein-ligand binding interactions. For a certain protein, carbon monoxide is a ligand, and the binding process may be modelled using the following equation, where P is free protein, CO is carbon monoxide, and PCO is the protein-carbon monoxide complex.

$$P + CO \rightleftharpoons PCO$$

The associated equation is:

$$\frac{[PCO]}{[CO]} = -\frac{1}{K_d}[PCO] + \frac{[P]_{tot}}{K_d}$$

Where K_d is the equilibrium constant for the reverse reaction and $[P_{tot}] = [P] + [PCO]$:

i) What would the x-intercept of a graph plotting [PCO]/[CO] against [PCO] represent? What would the slope represent? ***1 mark***

ii) Suppose that the complex PCO is coloured and its concentration in solution can be measured with a spectrophotometer. The absorbance of a 4.0 mL sample of PCO in a cuvette with a length of 1.00 cm was measured at an unspecified wavelength and a reading of A = 0.30 was recorded. Addition of 0.001 mol of PCO to the sample changed the absorbance to 0.37. Calculate the concentration of PCO in the original 4 mL sample. Assume that P and CO don't absorb at the wavelength used for this experiment. ***1 mark***

2. ANALYTICAL CHEMISTRY

A white solid **A** is insoluble in water or aqueous sodium hydroxide. **A** dissolves in diluted hydrochloric acid to form a colorless solution **B** and a colorless, foul odor gas **C**. When aqueous ammonia is added to **B,** a white precipitate **D** is formed, however, **D** dissolves in excess amount of aqueous ammonia to form a colorless solution **E**. When gas **C** is introduced to aqueous $CdSO_4$, a yellow precipitate **F** is formed. When gas **C** is introduced to solution **E,** solid **A** is reformed. Electrolysis of molten **A** produces a metal which is diamagnetic.

a) Identify compound **A, B, C, D, E** and **F** and write appropriate balanced reaction equation for the formation of **<u>B and C</u>**, **D, E, F** and **A** (electrolysis is NOT required). ***7 marks***

A:	B:	C:
D:	E:	F:

Reactions *(0.8 mark each for a total of 4.0 marks)*:

1.

2.

3.

4.

5.

An unknown compound containing iron in the form of Fe^{2+} is to be analyzed to determine the iron content. A sample of 12.000g of the compound is completely dissolved into an acid and the solution is then diluted by deionized water to 1.000L. A 50.00mL of the sample is then titrated by a 0.100M solution of Ce^{4+}. When 10.00mL of Ce^{4+} is added, the reading of the potentiometer is 745mV. (assume in the unknown compound only Fe^{2+} participates in the reaction and all reactions go to completion at $25^{0}C$)

$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ $\quad E^{0} = 0.771V$
$Ce^{4+} + e^{-} \rightarrow Ce^{3+}$ $\quad E^{0} = 1.72V$

b) What is the volume of Ce^{4+} solution needed to reach the equivalence point?
2.5 marks

c) What would be the potential reading at equivalence point? ***1 mark***

d) What would be the potential reading when 50.00mL of Ce^{4+} solution is added?
1 mark

e) What is the percent composition of iron in the sample? ***0.5 mark***

3. INORGANIC CHEMISTRY

Iron is a metal that is both essential to and dangerous for life. The redox properties of iron are essential to biochemical catalysis; however, iron overload facilitates the production of toxic reactive oxygen species (ROS). In this section, you will apply your knowledge of many areas of chemistry to explore the importance of organic iron and the complex balance that exists between iron deficiency and overload in a living organism.

Part 1: Hemoglobin and Iron Coordination

Hemoglobin (Hgb) is the main oxygen transporter in humans. Its oxygen carrying capacity is facilitated by its *heme* group, which contains a N_5 coordinated Fe(II) atom in its deoxygenated state. The sixth empty coordination site is thus free for oxygen binding. For the purposes of this question, the coordination structure of iron in deoxy-Hgb may be thought of as containing two bidentate ligands binding through nitrogen atoms in the *x-y* plane, as well as a single monodentate nitrogen occupying the fifth coordination site along the *z* axis.

a) Draw the coordination structure of an iron atom in deoxy-Hgb. ***0.5 mark***

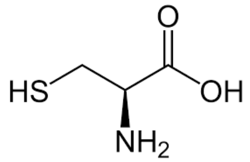
b) According to a recent publication by Sánchez et al. (2017), the bond Fe—N coordination distances in the x-y plane are 2Å whereas the Fe-N coordination distance along the z axis is 2.2Å. Draw the crystal field splitting diagram, but do not fill in the electrons, for an iron atom in deoxyhemoglobin. Be sure to label the d orbitals. ***1 mark***

c) Upon oxidation by molecular O_2, oxy-Hgb undergoes a conformational change, achieving a typical octahedral geometry. Draw the corresponding splitting diagram **and** fill in the electrons, assuming that oxy-Hgb adopts a low spin configuration. ***1 mark***

In biological systems, iron does not exclusively exist in octahedral coordination complexes. Several classes of proteins include structures called iron-sulfur clusters that are biologically and electrochemically interesting.

d) One class of iron-sulfur clusters contain cores with 4 Fe and 4 S atoms [4Fe-4S]. Each iron atom in the cluster achieves tetravalent coordination. Draw the structure of the iron sulfur cluster, which has the formula $Fe_4S_4Cys_4$, where Cys = cysteine (structure below). You may use Cys as an abbreviation instead of drawing the actual structure. **However, circle the atom on cysteine that is bonded to the iron-sulfur cluster core**. ***3 marks***

Hint: There are no Fe-Fe bonds.



e) Under oxidative conditions, the following reaction occurs (cysteine are ignored):

$$[4Fe - 4S]^{2+} + O_2 \rightarrow Fe^{3+} + Fe^{2+} + S_2^{2-} + D + E$$

D is a charged, toxic molecule and contains only one type of atom. All atoms in **D** are sp^3 hybridized. Draw the structures of **D** and **E.** ***2 marks***

Part 2: Fenton Catalysis

Iron also participates in a catalytic redox cycle (the Fenton/Haber-Weiss reactions), producing the ROS hydroxyl (OH•). Hydroxyl is highly reactive and irreversibly cross-links biomolecules, leading to cell damage, cell death, and potential cancerous transformation. Fenton catalysis takes place in two steps:

Reaction 1: Iron (State 1) reacts with superoxide (O_2^-) to produce molecular oxygen.

Reaction 2: Iron (State 2) reacts with hydrogen peroxide under acidic conditions to produce water and hydroxyl.

f) Write out the balanced chemical reactions 1 and 2, as well as the net reaction for Fenton catalysis. Clearly indicate the oxidation states of iron. ***1.5 marks***

g) In a particular biological system, the following redox potentials are provided (unbalanced):

$H_2O_2 + H^+ \rightarrow H_2O + OH\bullet$ E = 400 mV

$O_2 \rightarrow O_2^-$ E = -150 mV

For which range(s) of potentials for the Fe^{3+}/Fe^{2+} redox couple will Fenton activity be spontaneous? ***0.5 mark***

Part 3: The Deferiprone Controversy - Putting it Together

Thalassemias are a class of blood disorders characterized by hemoglobin deficiency. Affected patients must undergo frequent blood transfusions, which leads to the unfortunate outcome of systemic iron overload. This is managed through iron chelation therapy.

Deferiprone was one such (bidentate) chelator investigated in the 1990s at the Hospital for Sick Children in Toronto. This trial raised many controversial questions regarding the legal and ethical roles of both researchers and pharmaceutical companies. Interested students are encouraged to explore the topic further after the contest.

In this problem, you will calculate the redox potentials for another (imaginary) bidentate chelator CCO-2021 (abbreviated XH) and comment on its safety. A similar, albeit more elegant, approach was taken by El-Jammal & Templeton (1996) to evaluate the Fenton activity of deferiprone.

h) Iron reacts with this chelator in buffer solution (HA/A^-) according to the following equation:

$$Fe^{3+} + nHX + nA^- \rightarrow FeX_n^{3-n} + nHA$$

Write the expression for the complexation (equilibrium) constant for this reaction, β'.
0.5 mark

i) The reduction potential of ferric iron (Fe^{3+}/Fe^{2+}) in the above reaction is given by the Nernst Equation:

$$E = E° - 0.0615 \log (\beta')$$

Given pKa(HA) = 6.7, pKa(XH) = 8.9, $\beta = 2.79 \times 10^{10}$, and E° = 548 mV, where β is the equilibrium constant for the reaction below:

$$Fe^{3+} + nX^- \rightarrow FeX_n^{3-n}$$

Calculate E(Fe^{3+}/Fe^{2+}) for the fully-coordinated (n = 3) iron atom. Based on your answer to question g), is this form of the chelator safe in terms of Fenton chemistry?
2 marks

4. ORGANIC CHEMISTRY

HSAB can be used to predict reactivities of Lewis bases and acids (also called nucleophiles and electrophiles).

Hard acid/bases are smaller, less polarizable, more electronegative, and have higher charge density than soft acid/bases. Hard bases prefer to attack hard acids, soft bases prefer to attack soft acids.

With this information, answer questions a) – e):

A) NH_3

B) OH^-

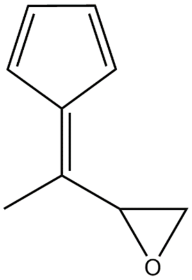
C) CH_3MgBr

D) CH_3Li

E) $:CH_2$

F) $(CH_3)_2CuLi$

G)



Workup with water is assumed to happen after each step if necessary. All the products formed by questions b), c) and d) are unique.

a) Rank the Lewis bases A, B, C, D, E from softest to hardest. ***0.5 mark***

b) Draw the product of the reaction of B) with G). ***0.5 mark***

The reaction is: SN1 SN2 E1 E2

(circle the right answer)

c) Draw the product of the reaction of two equivalents of E) with G) and write the mechanism. ***1 mark***

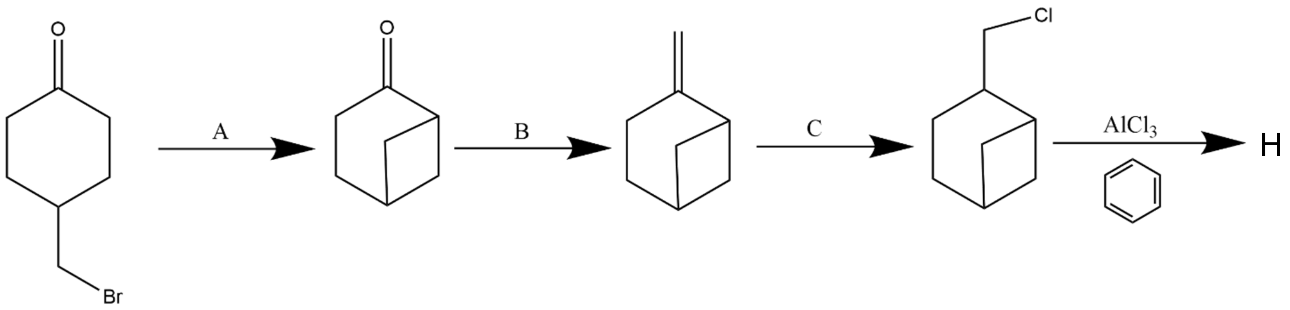
d) D) is reacted with G), forming two products R_1 and R_2. Both contain alcohols and have two rings. ***4 marks***

Draw the charged, aromatic intermediate that occurs in the formation of both products.

Draw the two products (R_1 and R_2). Circle which product is favored at lower temperatures and explain.

Draw the mechanism for the formation of the kinetically favored product.

Consider the following reaction scheme:



e) Which of the following conditions causes reaction A *(circle the right answer).* ***0.5 mark***

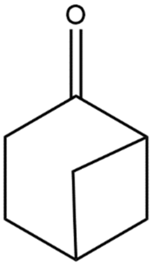
CH₂Cl₂, Zn/Cu NAH Radical initiator heat

f) Write down the reagent that can be used for reactions B and C. ***2 marks***

g) Write down the reagent that can be used to reverse reactions B and C. ***1 mark***

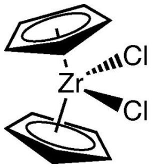
h) Draw the structure of H. ***1 mark***

i) The compound below can only form one enol tautomer. Draw the tautomer and explain why the other tautomer cannot form. ***1.5 marks***



5. POLYMER CHEMISTRY

Olefin polymerization is a common class of reactions where alkenes are polymerized. Ziegler and Natta won the 1963 Nobel Prize in Chemistry for developing a catalyst that makes this reaction possible.



Zirconocene dichloride ($ZrCp_2Cl_2$, structure above) is a complex that can be used in olefin polymerization, and the polymerization mechanism is shown below:

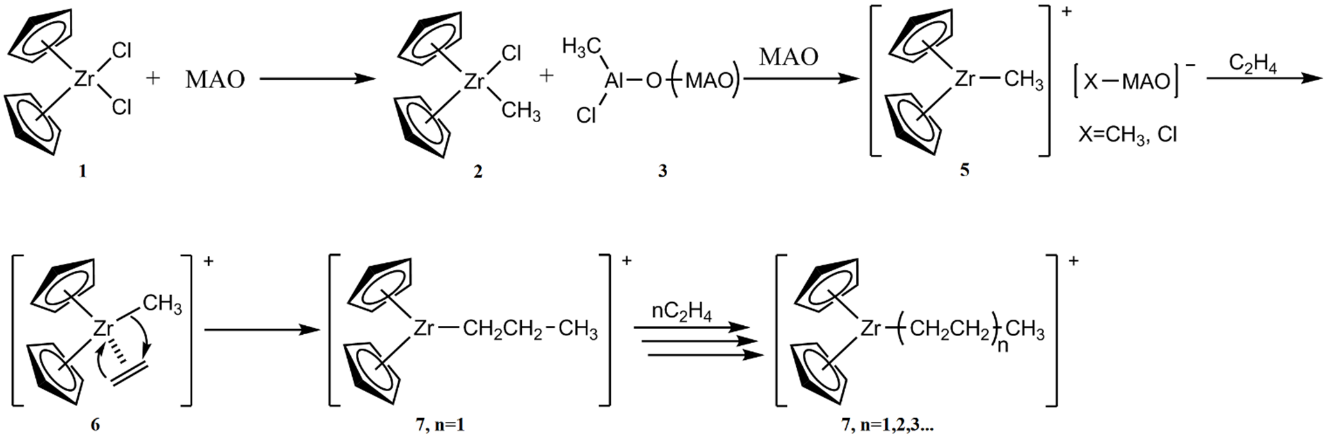


Figure 1

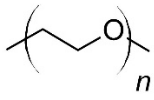
Cp = cyclopentadienyl

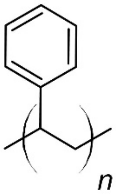
Note about intermediate **6**: in the case of substituted alkenes such as propene, the alkyl group will migrate towards the more substituted carbon atom.

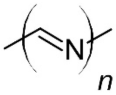
a) Determine the oxidation state of the metal centre in zirconocene dichloride. ***0.5 marks***

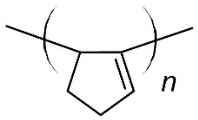
b) Draw the structure of the intermediate akin to **7** when 3 molecules of 2-butene polymerize with $ZrCp_2Cl_2$ and MAO via the mechanism described above. Specifying stereochemistry is not required. ***0.5 marks***

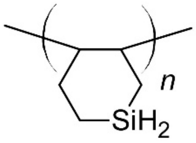
c) Which of the following polymers can be synthesized from alkene monomers via a Ziegler Natta catalyst? Circle all that apply. ***1 mark***

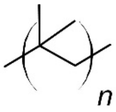


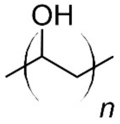


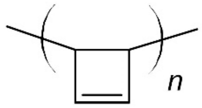






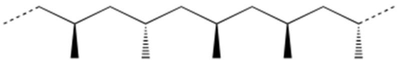






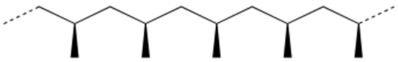
When zirconocene dichloride is used to polymerize propene, the resulting polymer is atactic (no control of stereochemistry of adjacent monomers). However, the tacticity can be controlled by altering zironocene dichloride into the C_2 variant or the C_s variant, which do have stereochemical control:

$ZrCp_2Cl_2$



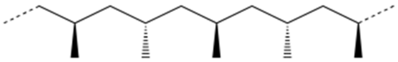
atactic

C_2 variant



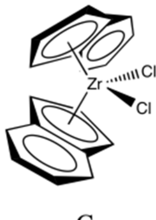
isotactic

C_s variant

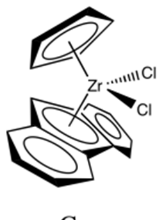


syndiotactic

The structures of the altered catalysts are shown below:



C_2



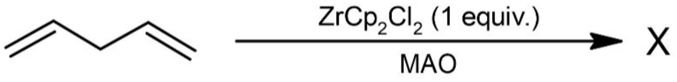
C_s

d) Indicate which of these catalysts is/are chiral. ***0.5 marks***

e) Explain the difference in the resulting polymer tacticity. You may use drawings to aid your explanation. ***2 marks***

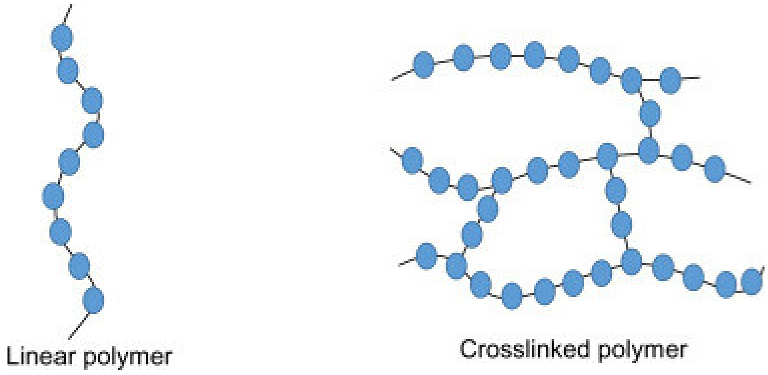
f) The extent of a polymerization reaction is defined by p, which takes values between 0 and 1. So when the reaction reaches completion, p = 1 and when p = 0.5, the polymerization is halfway complete. Derive an expression for the average number of x-mers (polymers consisting of x monomers) for polypropylene in terms of x, p and N, where N is the total number of polymer molecules. You may do this by considering that p can also represent the probability that an alkene functional group has reacted, then counting the number of reacted and unreacted alkene groups for a given x-mer. ***1.5 marks***

Now consider this reaction:



g) Draw the major organic product X of this reaction, knowing that $[Cp_2ZrH]^+$ is formed as a byproduct and product X has molecular formula C_6H_{10}. ***2 marks***

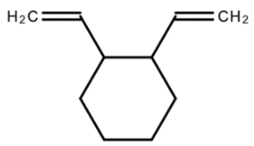
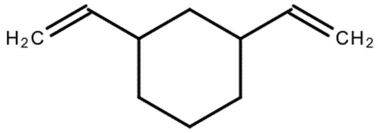
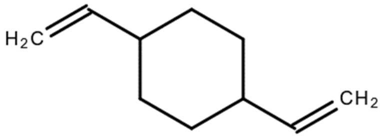
Polymers can grow in a linear manner, with each monomer unit bonding to the end of an existing chain in a linear fashion. However, some polymers can do crosslinking, where monomer units from different polymer chains bond. This can happen when a monomer can bond with more than two other monomers. The following questions deal with cross linked polymers using the mechanism described in Figure 1.



h) Is it possible for propene to form cross linked polymers? *Circle your answer* ***0.5 mark***

Yes No

i) Which polymer type, linear or cross linked, is more flexible? Which is stronger? Briefly answer and explain both questions. ***1 mark***

		
A	B	C

j) Only one of the monomers above can properly undergo cross linking. Choose which and briefly explain why the rest cannot do cross linking. ***0.5 marks***

k) The monomer chosen in the previous question is studied for cross linking. When cross linking occurs, one of the alkene groups serves as the attachment point for another monomer.

i) What is the maximum number of bonds that each monomer unit can make to other monomer units/methyl groups? ***0.5 marks***

ii) A 10-mer (10 monomer units combine to form a polymer) has eight double bonds. What is the average number of bonds that each monomer unit forms with other monomer units/methyl groups? ***0.5 marks***

iii) Derive an equation relating the average number of bonds each monomer forms, to the number of double bonds a in the polymer and the number of monomers b. ***1 mark***

-END OF PART C-