UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

EKC 107 – Organic Chemistry
[Kimia Organik]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of TWELVE pages of printed material before you begin the examination.

[Sila pastikan bahawa kertas peperiksaan ini mengandungi DUA BELAS muka surat yang bercetak sebelum anda memulakan peperiksaan ini.]

Instructions: Answer **FOUR** (4) questions. Answer **TWO** (2) questions from Section A. Answer **TWO** (2) questions from Section B.

*[**Arahan:** Jawab **EMPAT** (4) soalan. Jawab **DUA** (2) soalan dari Bahagian A. Jawab **DUA** (2) soalan dari Bahagian B.]*

You may answer the question either in Bahasa Malaysia or in English.

[Anda dibenarkan menjawab soalan sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.]

Section A : Answer any TWO questions.
Bahagian A : Jawab mana-mana DUA soalan.

1. [a] Draw the structure of each of the following compounds:-
Lukiskan struktur setiap sebatian berikut:

[i] 4-isopropyl-2,4,5-trimethylheptane
4-isopropil-2,4,5-trimetilheptana

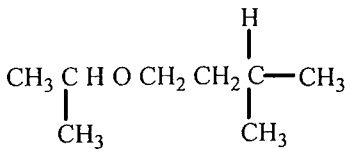
[ii] *ter*-butyl isobutyl ether
ter-*butil isobutil eter*

[iii] 2-ethyl-N-propylcyclohexanamine
2-etil- N-propilsikloheksanamina

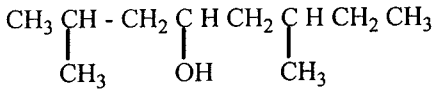
[6 marks/markah]

[b] Give the systematic (IUPAC) name for each of the followings:
Berikan nama sistematik (IUPAC) bagi setiap yang berikut:

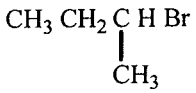
[i]



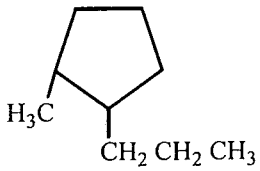
[ii]



[iii]



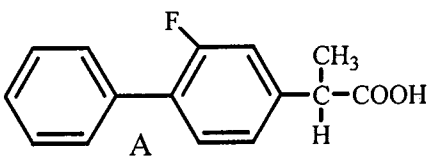
[iv]



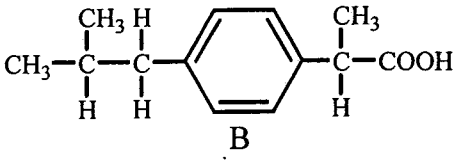
[6 marks/markah]

[c] A and B belong to the group of drugs known as non-steroidal anti-inflammatory drugs (NSAIDs). Both are only slightly soluble in water, but one is a little more soluble than the other. Explain which of the drugs has greater solubility in water.

A dan B tergolong dalam kumpulan dadah yang dikenali sebagai dadah anti radang bukan steroid (NSAIDs). Kedua-duanya larut sedikit sahaja di dalam air, tetapi yang satu adalah lebih larut daripada yang lain. Terangkan dadah manakah yang lebih larut di dalam air.



A



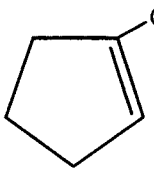
B

[3 marks/markah]

...3/-

[d] Give the products of each of the following reactions, ignoring stereoisomers:
Berikan produk bagi setiap tindakbalas berikut, dengan mengabaikan stereoisomer.

[i] $CH_2 = CHCH_2CH_2CH_3 + Br_2 \xrightarrow{hv}$

[ii]  + NBS $\xrightarrow[\text{peroxide}]{\Delta}$

[4 marks/markah]

[e] Catalytic cracking of $C_{18}H_{38}$ was carried out using a zeolite catalyst.
Pemecahan bermangkin $C_{18}H_{38}$ telah dijalankan dengan menggunakan mangkin zeolit.

[i] State two methods which will generate $^+C_{18}H_{37}$ carbocations.
Nyatakan dua kaedah yang akan menghasilkan 'carbocations' $^+C_{18}H_{37}$.

[ii] Give the corresponding equations associated with the production of $^+C_{18}H_{37}$.
Berikan persamaan-persamaan yang berkaitan dengan penghasilan $^+C_{18}H_{37}$.

[6 marks/markah]

2. [a] [i] Dichlorocarbene can be generated by heating chloroform with HO^-. Propose a mechanism for the reaction.
Diklorokarbena boleh dihasilkan dengan memanas klorofom bersama HO^-. Cadangkan mekanisma bagi tindakbalas ini.

$$\underset{\text{Chloroform}}{CHCl_3} + HO^- \xrightarrow{\Delta} \underset{\text{dichlorocarbene}}{Cl_2C:} + H_2O + Cl^-$$

[ii] Dichlorocarbene can also be generated by heating sodium trichloroacetate. Propose a mechanism for the reaction.
Diklorokarbena boleh dihasilkan dengan memanas natrium trikloroasetat. Cadangkan mekanisma bagi tindakbalas ini.

$$ClCCO^-Na^+ \longrightarrow Cl_2C: + CO_2 + Na^+Cl^-$$

[6 marks/markah]

[b] What product would be obtained from hydroboration-oxidation of the following alkenes?
Apakah produk yang boleh diperolehi daripada hidroborasi-pengoksidaan bagi alkena berikut?

[i] 2-methyl-2-butene
2-metil-2-butana

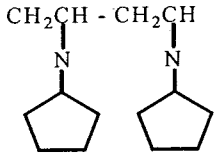
[ii] 1-methylcyclohexene
1-metilsikloheksana

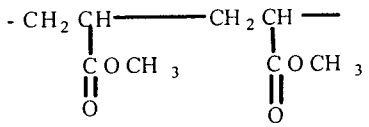
[4 marks/markah]

...4/-

[c] Which monomer and which type of initiator would you use to synthesize each of the following polymers?
Monomer mana dan jenis pemula manakah yang boleh digunakan untuk mensintesis setiap daripada polimer berikut?

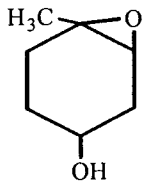
[i] $-CH_2CH_2OCH_2CH_2O-$

[ii] 

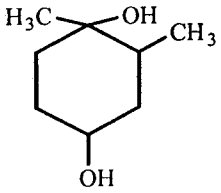
[iii] 

[6 marks/markah]

[d] Ahmad added 3,4-epoxy-4-methyl-cyclohexanol to an ether solution of methyl magnesium bromide and then added dilute HCl. He expected that the product would be a diol. He did not get any of the expected products. What product did he get?
Ahmad mencampurkan 3,4-epoksi-4-metil-sikloheksanol ke larutan eter metil magnesium bromida dan kemudiannya menambahkan larutan HCl cair. Beliau menjangka yang produknya ialah diol. Beliau tidak dapat produk yang dijangkakan. Produk apakah yang beliau diperolehi?



(3,4-epoxy-4-methyl-cyclohexanol)
(3,4-epoksi-4-metil-sikloheksanol)



(1,2-dimethyl-1, 4-cyclohexanediol)
(1,2-dimetil-1, 4-sikloheksanadiol)

[3 marks/markah]

[e] [i] Polyethylene can be used for the manufacture of beach chairs and beach balls. Which of these items is made from highly branched polyethylene?
Polietilina boleh diguna untuk menghasilkan kerusi dan bola pantai. Benda yang manakah diperbuat daripada polietilina yang mempunyai banyak cabang.

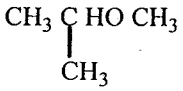
[2 marks/markah]

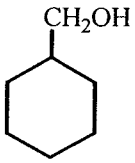
[ii] When propylene oxide undergoes anionic polymerization, nucleophilic attack occurs at the less substituted carbon of the epoxide, but when it undergoes cationic polymerization, nucleophilic attack occurs at the more substituted carbon. Explain.
Semasa propilina oksida melalui pempolimeran anion, serangan nukleofilik berlaku pada karbon epoksida yang kurang terganti. Tetapi bila ia melalui pempolimeran berkation, serangan nukleofilik berlaku pada karbon yang lebih terganti. Terangkan.

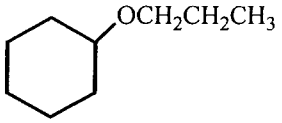
[4 marks/markah]

...5/-

3. [a] Starting from alkene, indicate how each of the following compounds can be synthesized.
Bermula dari alkena, jelaskan bagaimana setiap daripada sebatian berikut boleh disintesiskan.

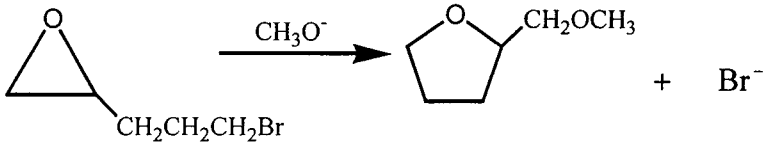
[i] 

[ii] 

[iii] 

[6 marks/markah]

[b] [i] Propose a mechanism for the following reaction:
Cadangkan mekanisma bagi tindakbalas berikut:

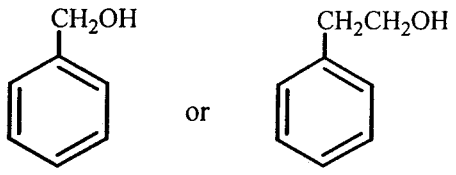


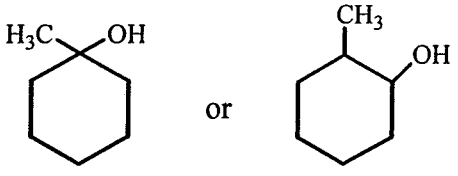
[ii] A small amount of a product containing a six-membered ring is also formed from the above mechanism. Give the structure of that product.
Sejumlah kecil produk yang mengandungi gelang 6-ahli juga terbentuk daripada mekanisma di atas. Berikan struktur bagi produk itu.

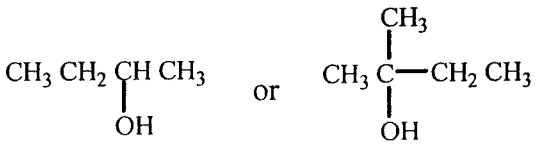
[iii] Why is little six-membered ring product formed?
Mengapakah hanya sedikit produk gelang 6-ahli terbentuk?

[7 marks/markah]

[c] Indicate which alcohol will undergo dehydration more rapidly when heated with H_2SO_4 and why?
Nyatakan alkohol manakah yang akan menjalani penyahhidratan lebih cepat bila dipanaskan dengan H_2SO_4 dan apakah sebabnya?

[i] 

[ii] 

[iii]  or

[6 marks/markah]

[d] [i] When heated with H_2SO_4, 3,3-dimethyl-2-butanol and 2,3-dimethyl-2-butanol are dehydrated to form 2,3-dimethyl-2-butene. Which alcohol dehydrates more rapidly and why?
Bila dipanaskan dengan H_2SO_4, 3,3-dimetil-2-butanol dan 2,3-dimetil-2-butanol dinyahhidratkan untuk membentuk 2,3-dimetil-2-butena. Alkohol manakah yang dinyahhidratkan dengan lebih cepat dan kenapa?

[ii] When 3-methyl-2-butanol is heated with concentrated HBr, a rearranged product is obtained. When 2-methyl-1-propanol reacts under the same conditions, a rearranged product is not obtained. Explain.
Bila 3-metil-2-butanol dipanaskan dengan HBr pekat, produk teratur semula telah diperolehi. Bila 2-metil-1-propanol bertindakbalas dalam keadaan yang sama, produk teratur semula tidak diperolehi. Terangkan.

[6 marks/markah]

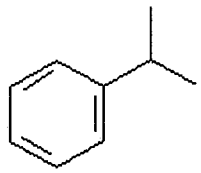
Section B : Answer any TWO questions.
Bahagian B : Jawab mana-mana DUA soalan.

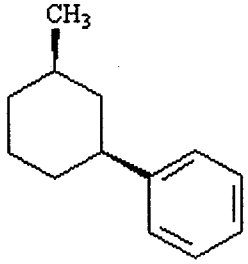
4. [a] Draw structures for compounds [i] to [iii] and provide IUPAC names to the structures [iv] to [vii].
Lukiskan struktur bagi sebatian-sebatian [i] hingga [iii] dan berikan nama IUPAC untuk struktur-struktur [iv] hingga [vii].

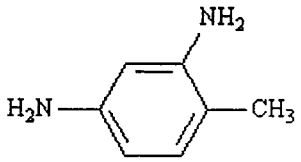
[i] *m*-fluoronitrobenzene
m-fluoronitrobenzena

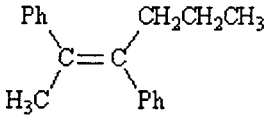
[ii] *o*-chlorophenol
o-kloropenol

[iii] 3,5-dimethylbenzoic acid
asid 3,5 dimetilbenzoik

[iv] 

[v] 

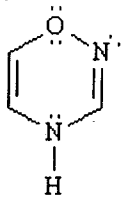
[vi] 

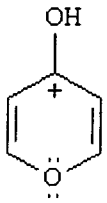
[vii] 

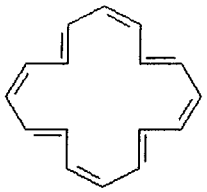
[7 marks/markah]

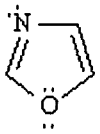
[b] For each molecule below, predict whether the molecule would be expected to show aromatic character or not. Explain your answer in each case.

Bagi setiap molekul di bawah, ramalkan sama ada molekul tersebut akan menunjukkan ciri-ciri aromatik atau tidak. Terangkan jawapan anda untuk setiap kes.

[i] 

[ii] 

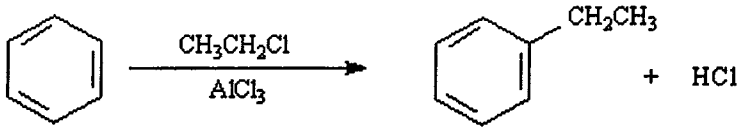
[iii] 

[iv] 

[8 marks/markah]

[c] Consider the Friedel-Crafts alkylation reaction below to answer the following question(s):

Pertimbangkan tindakbalas pengalkilan Friedel-Crafts di bawah ini untuk menjawab setiap kes:



[i] Draw the structure of the electrophilic intermediate in this reaction.
Lukiskan struktur perantara elektrofilik dalam tindakbalas ini.

[ii] What is the role of the $AlCl_3$ in the reaction?
Apakah peranan $AlCl_3$ dalam tindakbalas ini?

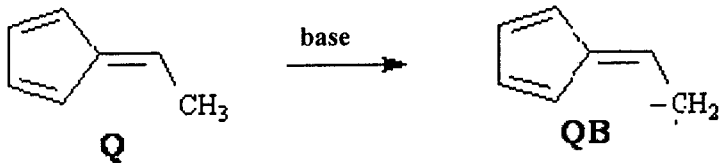
[iii] Write the complete stepwise mechanism for this reaction. Show all electron flows with arrows and include all intermediate structures.
Tuliskan mekanisma berlangkah yang lengkap bagi tindakbalas ini. Tunjukkan semua aliran elektron dengan anak panah dan lukiskan semua struktur perantara.

[7 marks/markah]

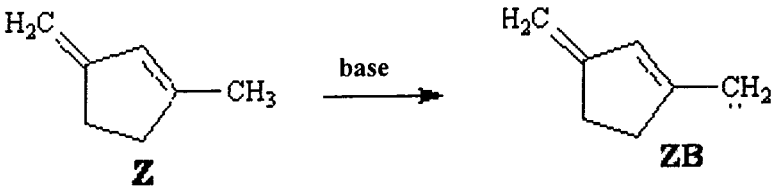
[d] What is thermosetting resin? Give an example.
Apakah resin termoset? Berikan satu contoh.

[3 marks/markah]

5. [a] Consider the data below to answer the following question(s).
Pertimbangkan data di bawah untuk menjawab soalan-soalan berikut.

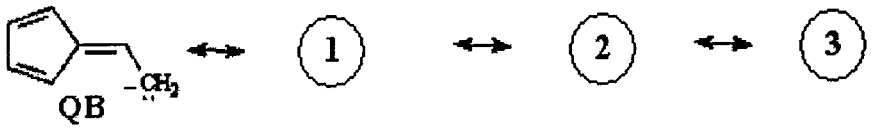


and



Conjugate bases **QB** and **ZB** are both resonance stabilized. Fill in all resonance forms (1 → 5) for **QB** and **ZB**.

Kedua-dua bes konjugat QB dan ZB adalah terstabil secara salunan. Isikan semua bentuk salunan (1 → 5) untuk QB dan ZB.



[5 marks/markah]

[b] Select the most appropriate answer from the following list (a – h) for each description [i] – [v] below.

Berdasarkan senarai (a – h) yang berikut, pilih jawapan yang paling sesuai bagi setiap huraian [i] – [v] di bawah.

a. Benzyne
Benzyne
b. $^{+}NO_2$
c. R_3C^{+}
d. electron-donating
pendermaan elektron
e. ^{+}NO
f. Meisenheimer complex
Kompleks Meisenheimer
g. $R-C\equiv O^{+}$
h. electron-withdrawing
Penyingkiran elektron

[i] _____ The reactive electrophile in Friedel-Crafts acylation reactions.
Elektrofil reaktif dalam tindakbalas pengasilan Friedel-Crafts.

[ii] _____ The electrophile in aromatic nitration.
Elektrofil dalam penitratan aromatik.

[iii] _____ Groups which activate aromatic rings towards electrophilic substitution.
Kumpulan-kumpulan yang mengaktifkan gelang-gelang aromatik terhadap penggantian elektrofilik.

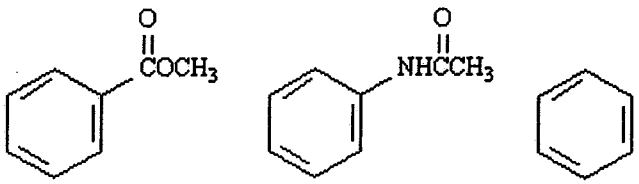
[iv] _____ Groups which deactivate aromatic rings.
Kumpulan-kumpulan yang menyahaktifkan gelang-gelang aromatik.

[v] _____ Intermediate in the elimination-addition mechanism of nucleophilic aromatic substitution.
Perantaraan dalam mekanisme penyingkiran-penambahan penggantian aromatik nukleofilik.

[5 marks/markah]

[c] Rank the compounds below according to their reactivity toward electrophilic aromatic substitution (most reactive = 1; least reactive = 3). Place the number corresponding to the compounds' relative reactivity in the blank below the compound.

Aturkan sebatian-sebatian di bawah menurut ketindakbalasan mereka terhadap penggantian aromatik elektrofilik (paling banyak bertindakbalas = 1, paling kurang bertindakbalas = 3). Tuliskan angka yang sepadan dengan kereaktifan relatif sebatian di ruang-ruang kosong di bawah sebatian tersebut.



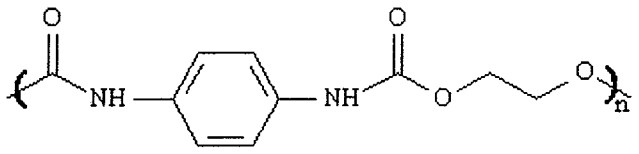
____ ____ ____

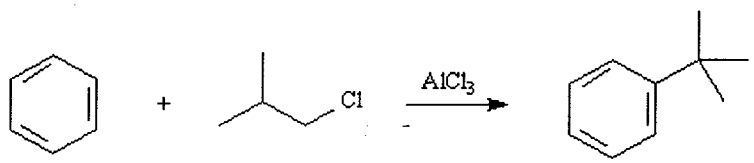
[3 marks/markah]

...10/-

[d] Attempts to prepare isobutylbenzene by direct Friedel-Crafts alkylation of benzene result in *tert*-butylbenzene as the major product. Write the complete stepwise mechanism for this reaction, showing all electron flows with arrows and showing all intermediate structures.

Percubaan untuk menyediakan isobutilbenzena melalui pengalkilan langsung Friedel-Crafts telah menghasilkan tert-butilbenzena sebagai produk utama. Tuliskan mekanisma berlangkah yang lengkap bagi tindakbals ini. Tunjukkan semua aliran elektron dengan anak panah dan semua struktur perantaraan.



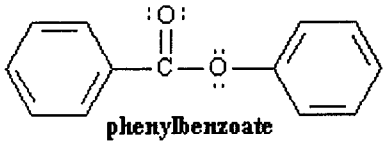


[5 marks/markah]

[e] What is a plasticizer?
Apakah bahan pemplastik?

[4 marks/markah]

[f] At what position, and on which ring, is bromination of phenyl benzoate expected to occur? Explain your answer.
Di kedudukan dan pada gelang yang manakah pembrominan fenil benzoat dijangka berlaku? Terangkan jawapan anda.



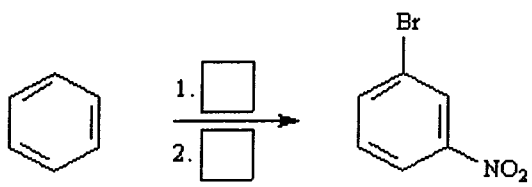
phenylbenzoate

[3 marks/markah]

6. [a] Choose the best reagent/catalyst from the list provided below for carrying out the following conversions.
Dari senarai yang diberikan di bawah, pilih reagen/mangkin yang terbaik bagi menjalankan penukaran-penukaan yang berikut:

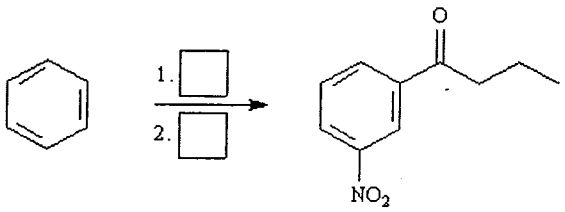
a. $KMnO_4$, H_3O^+
b. Br_2, $FeBr_3$
c. Cl_2, $FeCl_3$
d. CH_3Cl, $AlCl_3$
e. HNO_3, H_2SO_4
f. $ClCO(CH_2)_2CH_3$, $AlCl_3$
g. $CH_3CH_2CH_2CH_2Cl$, $AlCl_3$
h. Zn(Hg); aq. HCl
i. NBS, peroxides
NBS, peroksida
j H_2/ Zn(Hg)

[i]

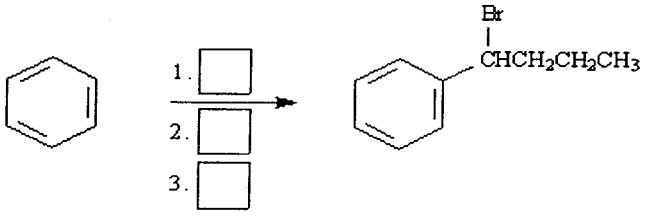


...11/-

[ii]



[iii]



[5 marks]

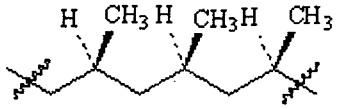
[b] Match a term or structure from the list below to each of the following definitions or names. Place the letter of the term or structure in the blank to the left of the definition or name which it describes.

Padankan istilah atau struktur dari senarai di bawah kepada setiap takrifan atau nama yang berikut. Letakkan abjad bagi istilah atau struktur tersebut di ruang kosong sebelah kiri takrifan atau nama yang berkaitan.

a. Elastomer

b. $Al(CH_2CH_3)_3 + TiCl_4$

c.



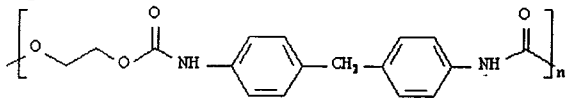
d. Plasticizers
Bahan pemplastik

e. thermosetting resins
resin termoset

f. Copolymers
kopolimer

g. step-growth polymer
polimer pertumbuhan-langkah

h.



Definitions
Takrifan

[i] ____ Produced by reactions in which each bond in the polymer is formed independently of the others.
Dihasilkan melalui tindakbalas di mana setiap ikatan dalam polimer terbentuk secara tak bersandar.

[ii] ____ Isotactic propylene.
Propilena isotatik.

[iii] ____ Polymers obtained when two or more different monomers are allowed to polymerize together.
Polimer yang diperolehi apabila dua atau lebih monomer yang berbeza dibenarkan untuk membentuk polimer.

[iv] ____ A polyurethane.
Poliuretana.

[v] ____ Small organic molecules that act as lubricants between polymer chains.
Molekul-molekul organik kecil yang bertindak sebagai pelincir antara rantaian polimer.

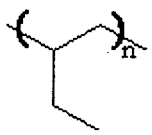
[vi] ____ Amorphous polymers that have the ability to stretch out and spring back to their original shape.
Polimer amorfus yang mempunyai keupayaan untuk meregang dan membidas kepada bentuk asal.

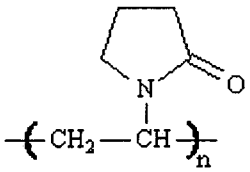
[vii] ____ Bakelite is this type of polymer.
Bakelit adalah jenis polimer ini.

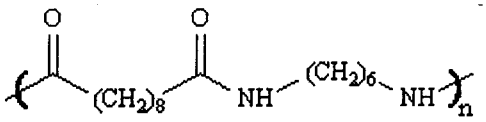
[viii] ____ A Ziegler-Natta catalyst.
Mangkin Ziegler-Natta.

[8 marks/markah]

[c] Classify each polymer below as step-growth or chain-growth.
Kelaskan setiap polimer di bawah sebagai pertumbuhan-langkah atau pertumbuhan-rantai.







[4 marks/markah]

[d] Write the main steps for the preparation of Aspirin commercially.
Tuliskan langkah-langkah utama bagi penyediaan aspirin secara komersil.

[4 marks/markah]

[e] What are the major limitations of Friedel-Crafts alkylations? Give an example.
Apakah had-had utama pengalkilan Friedel-Crafts: Berikan satu contoh.

[4 marks/markah]

- ooo O ooo -