
UNIVERSITI SAINS MALAYSIA

First Semester Examination
2015/2016 Academic Session

December 2015 / January 2016

EBP 201/3 – Polymer Synthesis *[Sintesis Polimer]*

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains TWELVE printed pages before you begin the examination.

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

This paper consists of SEVEN questions. ONE question from PART A, THREE questions from PART B and THREE questions from PART C.

[Kertas soalan ini mengandungi TUJUH soalan. SATU soalan dari BAHAGIAN A, TIGA soalan dari BAHAGIAN B dan TIGA soalan dari BAHAGIAN C.]

Instruction: Answer FIVE questions. Answer ALL questions from PART A, TWO questions from PART B and TWO questions from PART C. If a candidate answers more than five questions only the first five questions answered in the answer script would be examined.

Arahan: Jawab LIMA soalan. Jawab SEMUA soalan dari BAHAGIAN A, DUA soalan dari BAHAGIAN B dan DUA soalan dari BAHAGIAN C. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.]

The answers to all questions must start on a new page.

[Mulakan jawapan anda untuk semua soalan pada muka surat yang baru.]

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

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

In the event of any discrepancies in the examination questions, the English version shall be used.

[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah digunapakai.]

PART A / BAHAGIAN A

1. [a] Consider a hypothetical polymer sample composed of chains of four distinct molecular weights, 100 000, 200 000, 500 000 and 1 000 000 g/mol in the ratio 1:5:3:1. Calculate M_n , M_w and polydispersity of the polymer sample.

Pertimbangkan sampel polimer hipotesis yang mengandungi rantai dengan empat berat molekul yang berbeza, 100 000, 200 000, 500 000 dan 1 000 000 pada nisbah 1:5:3:1. Kirakan M_n , M_w dan polisebaran bagi sampel polimer tersebut.

(30 marks/markah)

- [b] List 5 important requirements for the successful synthesis of a high molecular weight polymer via step-growth polymerization.

Senaraikan 5 keperluan utama bagi memastikan sintesis polimer berberat molekul tinggi berjaya dihasilkan melalui pempolimeran pertumbuhan berlangkah.

(20 marks/markah)

[c] Refer to Table 1:

Table 1 / *Jadual 1*

	Q	e
Acrylonitrile / (<i>Akrilonitril</i>)	0.48	1.23
Butadiene / (<i>Butadiena</i>)	1.70	-0.50
Maleic Anhydride / (<i>Maleik Anhirida</i>)	0.86	3.69
Styrene / (<i>Stirena</i>)	1.00	-0.80
Methyl Methacrylate / (<i>Metil Metakrilat</i>)	0.74	0.40
Vinyl acetate / (<i>Vinil asetat</i>)	0.026	-0.88

Answer the followings:

- (i) Why is the Q value of butadiene and styrene higher than that of vinyl acetate?
- (ii) Suggest which monomer pairs will form a random copolymer and block copolymer. Show your suggestion based on Q and e values.

Rujuk Jadual 1:

Jawab yang berikut:

- (i) *Mengapa nilai Q bagi butadiena dan stirena adalah lebih tinggi dari vinil asetat?*
- (ii) *Cadangkan pasangan monomer yang akan membentuk kopolimer rawak dan kopolimer blok. Tunjukkan cadangan ini berdasarkan nilai Q dan e.*

(50 marks/markah)

PART B / BAHAGIAN B

2. [a] Derive the following expression for the number average molecular weight (M_n).

X_i is the mole fraction of polymers with molecular weight (or molar mass) M_i .

Terbitkan ungkapan yang berikut; bagi nombor purata berat molekul (M_n). X_i ialah pecahan mol bagi polimer dengan berat molekul (atau berat molar) M_i .

$$M_n = \sum_{i=1}^{\infty} X_i M_i$$

(30 marks/markah)

- [b] Calculate the maximum number average molecular weight (M_n) for poly(butylene terephthalate) prepared under optimum conditions to 97.5% conversion.

Kirakan nombor purata maksimum berat molekul (M_n) bagi poli(butilena tereftalat) yang disediakan di bawah keadaan optima kepada penukaran 97.5%.

(15 marks/markah)

- [c] Karl Ziegler and Giulio Natta are jointly contributed to the discovery of transition metal catalysts which polymerize hydrocarbon monomers such as ethylene and propylene.

Karl Ziegler dan Giulio Natta secara bersama telah menyumbang kepada penemuan mangkin logam peralihan yang boleh mempolimerkan monomer hidrokarbon seperti etilena dan propilena.

- (i) Provide an example of a Ziegler-Natta catalyst system.

Berikan satu contoh sistem mangkin Ziegler-Natta.

(5 marks/markah)

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- ii) Using chemical equations, describe the general mechanism for Ziegler-Natta catalyzed polymerization.

Menggunakan persamaan kimia, terangkan mekanisme am bagi pempolimeran dengan mangkin Ziegler-Natta.

(50 marks/markah)

3. [a] Calculate the number average degree of polymerization and number average molecular weight of an equimolar mixture of adipic acid and hexamethylene diamine for extents of reactions 0.900, 0.980 and 0.999.

Kirakan purata nombor darjah pempolimeran dan nombor purata berat molekul bagi campuran sama molar asid adipik dan heksametilena diamina untuk mencapai darjah tindak balas 0.900, 0.980 dan 0.999.

(50 marks/markah)

- [b] For a homogeneous polymerization of pure styrene with AIBN as initiator at 60 °C, the following data is available:

$$k_d = 0.96 \times 10^{-5} \text{ s}^{-1}$$

$$k_p^2/k_t = 1.18 \times 10^{-3} \text{ L/mol}$$

$$\text{assume } f = 1$$

- (i) Assuming the molar concentration of AIBN is a constant at the initial concentration of 0.05 mol/L, calculate the time needed to reach 10% and 20% monomer conversions.
- (ii) If you double the molar concentration of AIBN, calculate the time needed to reach 10% and 20% monomer conversions.

Bagi pempolimeran homogen stirena tulen menggunakan AIBN sebagai pemula pada suhu 60 °C, maklumat berikut sedia ada:

$$k_d = 0.96 \times 10^{-5} \text{ s}^{-1}$$

$$k_p^2/k_t = 1.18 \times 10^{-3} \text{ L/mol}$$

$$\text{anggap } f = 1$$

- (i) *Anggapkan kepekatan molar bagi AIBN kekal malar pada kepekatan mula iaitu 0.05 mol/L, kirakan masa yang diperlukan untuk mencapai 10% dan 20% penukaran monomer.*
- (ii) *Andainya anda menggandakan kepekatan molar bagi AIBN sebanyak 2 kali ganda, kirakan masa yang diperlukan untuk mencapai 10% dan 20% penukaran monomer.*

(50 marks/markah)

4. [a] Derive the following expression for the number average molecular weight (M_n).

ω_i is weight fraction of polymers with molecular weight (or molar mass) M_i .

Terbitkan ungkapan yang berikut; bagi nombor purata berat molekul (M_n).

ω_i ialah pecahan berat bagi polimer dengan berat molekul (atau berat molar) M_i .

$$M_n = \frac{1}{\sum_{i=1}^{\infty} \frac{\omega_i}{M_i}}$$

(30 marks/markah)

- [b] For the melt reaction of 1.0 mol $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ and 1 mol $\text{HOOC}-\text{CH}_2-\text{COOH}$
- (i) What is the repeat unit of the polymer?
 - (ii) What is the common "nylon" nomenclature?
 - (iii) What extent of reaction would be required to yield 80 number average degree of polymerization (X_n)?
 - (iv) What distribution of end groups would you expect?
 - (v) Suppose you wanted to control the molecular weight of the polymer. To achieve an X_n of 130, what options (at least two) would you have? Show calculations.

Bagi tindak balas leburan 1.0 mol $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ dan 1 mol $\text{HOOC}-\text{CH}_2-\text{COOH}$

- (i) *Apakah unit ulangan bagi polimer tersebut?*
- (ii) *Apakah katanama biasa bagi nilon tersebut?*
- (iii) *Apakah darjah tindak balas yang diperlukan untuk mencapai nombor purata darjah pempolimeran (X_n) bersamaan 80?*
- (iv) *Apakah taburan kumpulan hujung yang anda jangkakan?*
- (v) *Andaikan anda ingin mengawal berat molekul polimer. Bagi mencapai X_n bersamaan 130, apakah pilihan (sekurang-kurangnya 2) yang anda ada? Tunjukkan jalan pengiraan.*

(70 marks/markah)

PART C / BAHAGIAN C

5. [a] Explain the followings regarding emulsion polymerization:
- (i) Compare the use of surfactant in emulsion polymerization to that of stabilizer in suspension polymerization.
 - (ii) There is a slight increase in temperature of reaction medium towards the end of second stage of polymerization.
 - (iii) How does the degree of polymerization is not affected by the increase in rate of reaction in emulsion polymerization.

Bincangkan yang berikut berdasarkan pempolimeran emulsi:

- (i) *Bandungkan penggunaan surfaktan dalam pempolimeran emulsi dengan penstabil dalam pempolimeran ampaian.*
- (ii) *Terdapat sedikit peningkatan pada suhu medium tindakbalas pada pengakhiran langkah kedua pempolimeran.*
- (iii) *Bagaimana darjah pempolimeran tidak dipengaruhi oleh peningkatan kadar tindakbalas dalam pempolimeran emulsi.*

(60 marks/markah)

- [b] Verify that the rate of propagation in emulsion polymerization is half to that in non-emulsion system.

Jelaskan kadar perambatan dalam pempolimeran emulsi adalah separuh berbanding dengan pempolimeran bukan emulsi.

(40 marks/markah)

6. [a] Discuss why copolymerization reaction is seldom performed beyond 30% conversion rate.

Bincangkan mengapa tindakbalas pengkopolimeran jarang dibuat melebihi 30% darjah pempolimeran.

(30 marks/markah)

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- [b] Consider copolymerization of vinyl acetate (reactivity ratio r_2) with the following monomers (reactivity ratio r_1). Answer the followings based on the given Table 2:
- (i) Vinyl acetate radical is regarded as reactive intermediate while styrene radical is inactive intermediate. Explain.
 - (ii) Which monomer will copolymerize with vinyl acetate to form azeotropic condition and calculate the azeotropic copolymer composition
 - (iii) From the above azeotropic pair, what is the comonomer feed ratio composition which will give copolymer with 50% vinyl acetate units

Pertimbangkan pengkopolimeran vinil asetat (nisbah reaktiviti r_2) dengan monomer-monomer berikut (nisbah reaktiviti r_1). Jawab yang berikut berdasarkan Jadual 2 yang diberi:

- (i) *Radikal vinil asetat dianggap sebagai bahan perantara reaktif sementara radikal stirena dianggap bahan perantara tak-reaktif. Jelaskan.*
- (ii) *Monomer yang mana akan kopolimer dengan vinil asetat untuk membentuk keadaan azeotropik dan hitung komposisi azeotropik kopolimer ini.*
- (iii) *Dari pasangan azeotropik di atas apakah komposisi nisbah awalan komonomer bagi menghasilkan kopolimer dengan 50% unit vinil asetat.*

Table 2 / Jadual 2

	r_1	r_2
Acrylonitrile / <i>Akrlonitril</i>	4.05	0.61
Styrene / <i>Stirena</i>	55	0.01
Trichloroethylene / <i>Trikloroetilena</i>	0.01	0.66

(70 marks/markah)

7. [a] Consider the reaction between epichlorohydrin with bisphenol A in preparation of epoxy resin as shown below:

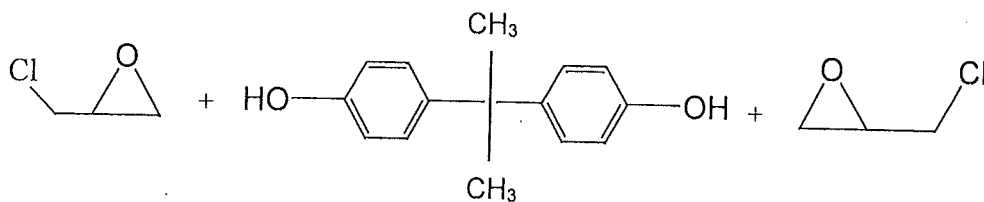
Answer the followings:

- (i) Discuss the role of NaOH as the catalyst in this reaction
- (ii) State the nucleophilic and electrophilic centres in this reaction and show the mechanism of reaction

Pertimbangkan tindakbalas antara epiklorohidrin dengan bisfenol A dalam penyediaan resin epoksi seperti berikut:

Jawab yang berikut:

- (i) *Bincangkan peranan NaOH sebagai pemangkin dalam tindakbalas ini.*
- (ii) *Nyatakan pusat nukleofil dan elektrofil dalam tindakbalas ini dan tunjukkan mekanisme tindakbalas.*

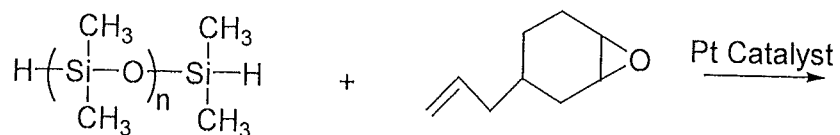


(40 marks/markah)

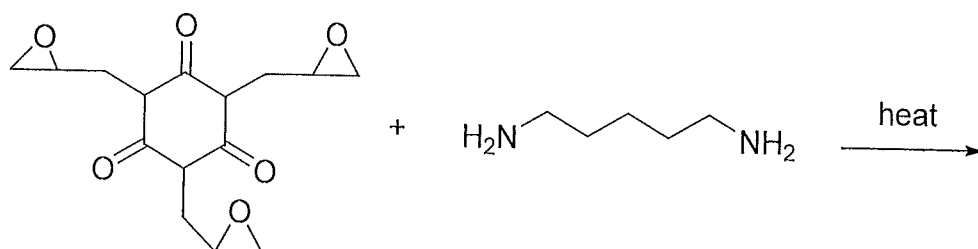
[b] State the product of the followings:

Nyatakan hasil tindakbalas yang berikut:

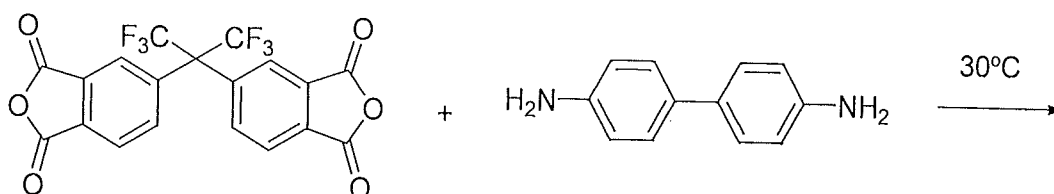
(i)



(ii)



(iii)



(60 marks/markah)