
UNIVERSITI SAINS MALAYSIA

First Semester Examination
2014/2015 Academic Session

December 2014 / January 2015

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

Duration : 3 hours
[Masa : 3 jam]

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

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

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

[Kertas soalan ini mengandungi TUJUH soalan. SATU soalan di BAHAGIAN A, TIGA soalan di BAHAGIAN B dan TIGA soalan di 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 suatu sampel polimer hipotetik 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] Consider the values of cross-propagation rate constant k_{12} for radical centre-monomer reaction during radical copolymerization as given in the Table 1 below:

Pertimbangkan nilai pemalar kadar perambatan-silang k_{12} bagi tindakbalas pusat radikal-monomer semasa pengkopolimeran radikal yang diberi dalam Jadual 1 di bawah.

Table 1 - Cross-propagation rate constant k_{12}
Jadual 1 - Pemalar kadar perambatan silang k_{12}

Monomers	Polymer radicals			
	Butadiene	Styrene	Methyl methacrylate	Vinyl acetate
Butadiene	100	280	2060	
Styrene	70	165	1130	230000
Methyl methacrylate	130	314	515	154000
Vinyl acetate		3.4	26	2300

...3/-

- (i) Why do the k_{12} values of butadiene and styrene polymer radicals are mostly lower compared to that of methyl methacrylate and vinyl acetate.

Mengapakah nilai k_{12} bagi polimer radikal butadiena dan stirena lebih rendah berbanding radikal metil metakrilat dan vinil asetat.

- (ii) Based on the k_{12} values above, explain why styrene will form ideal copolymer with butadiene.

Berdasarkan nilai k_{12} di atas, jelaskan mengapa stirena membentuk kopolimer unggul dengan butadiena.

- (iii) Choose a polymer radicals-monomer pair which would give a block copolymer. Explain your choice.

Padankan pasangan radikal polimer-monomer yang akan membentuk kopolimer blok. Jelaskan jawapan anda.

(50 marks/markah)

PART B / BAHAGIAN B

2. [a] Define each of the following terms:

- (i) Polymer
- (ii) Monomer
- (iii) Degree of polymerization
- (iv) Homopolymer
- (v) Copolymer
- (vi) Functionality

Takrifkan setiap istilah yang berikut:

- (i) *Polimer*
- (ii) *Monomer*
- (iii) *Darjah pempolimeran*
- (iv) *Homopolimer*
- (v) *Kopolimer*
- (vi) *Kebolehan berfungsi*

(30 marks/markah)

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

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

(15 marks/markah)

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

Karl Ziegler dan Giulio Natta bersama-sama telah menyumbang kepada penemuan pemangkin 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 pemangkin Ziegler-Natta.

(5 marks/markah)

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

Menggunakan persamaan kimia, terangkan secara umum mekanisme bagi pemolimeran dengan pemangkin Ziegler-Natta.

(50 marks/markah)

3. [a] What is the meaning of each of the following terms?

- (i) Head-to-head addition
- (ii) Head-to-tail addition
- (iii) Tail-to-head addition

Apakah yang dimaksudkan oleh setiap istilah yang berikut?

- (i) *Penambahan kepala-ke-kepala*
- (ii) *Penambahan kepala-ke-ekor*
- (iii) *Penambahan ekor-ke-kepala*

(15 marks/markah)

[b] 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 nombor purata darjah pempolimeran dan nombor purata berat molekul bagi campuran sama molar asid adipik dan heksametilena untuk mencapai darjah tindakbalas 0.900, 0.980 dan 0.999.

(35 marks/markah)

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

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

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

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

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

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

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 dua kepekatan molar bagi AIBN, kirakan masa yang diperlukan untuk mencapai 10% dan 20% penukaran monomer.*

(50 marks/markah)

4. [a] Define each of the following terms:

- (i) Repeat unit
- (ii) Homochain polymer
- (iii) Heterochain polymer
- (iv) Thermoplastic
- (v) Thermoset
- (vi) Functional groups

Takrifkan setiap istilah yang berikut:

- (i) *Unit ulangan*
- (ii) *Polimer homorantai*
- (iii) *Polimer heterorantai*
- (iv) *Termoplastik*
- (v) *Termoset*
- (vi) *Kumpulan berfungsi*

(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 $H_2N-CH_2-CH_2-NH_2$ dan 1 mol $HOOC-CH_2-COOH$

- (i) Apakah unit ulangan bagi polimer tersebut?
- (ii) Apakah tatanama biasa bagi nilon tersebut?
- (iii) Apakah darjah tindakbalas yang diperlukan untuk mencapai nombor purata darjah pemolimeran (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 pengiraan.

(70 marks/markah)

PART C / BAHAGIAN C

5. [a] State the differences between the type of initiator, solvents used and the site of polymerization that occur between solution and emulsion polymerization.

Nyatakan perbezaan antara pemula, pelarut yang digunakan serta tapak berlaku pempolimeran antara pempolimeran larutan dan emulsi.

(30 marks/markah)

- [b] During the course of emulsion polymerization, the changes in polymerization rate is shown as in the Figure 1. Answer the followings based on this Figure 1.

Semasa pempolimeran emulsi, perubahan kadar pempolimeran ditunjukkan seperti dalam Rajah 1. Jawab soalan berdasarkan Rajah 1:

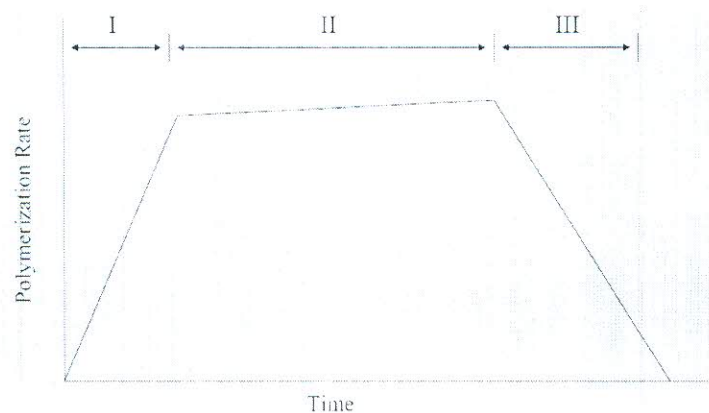


Figure 1

Rajah 1

- (i) In emulsion polymerization, what is meant by critical micelle concentration (CMC).

Dalam pempolimeran emulsi, apa yang dimaksudkan kepekatan kritikal misel.

- (ii) Describe the changes in size and number of micelles that is found during all the three stages during emulsion polymerization.

Perihalkan perubahan saiz dan bilangan misel yang terdapat dalam ketiga-tiga tahap pempolimeran emulsi ini.

- (iii) Describe the changes in size and number of polymer particles that is found during all the three stages during emulsion polymerization.

Perihalkan perubahan saiz dan bilangan partikel polimer yang terdapat dalam ketiga-tiga tahap pempolimeran emulsi ini.

- (iv) How does the surfactant that is added in emulsion polymerization affect the rate and molecular weight of polymer product?

Bagaimana surfaktan yang dicampurkan dalam pempolimeran emulsi mempengaruhi kadar dan berat molekul hasil polimer?

(70 marks/markah)

6. [a] During synthesis of polyimide, there remains some unreacted amine monomers in the reaction mixture. Describe the use of soxhlet extraction to separate this monomer from synthesised polyimide given that this monomer is highly non-polar with melting point of 80°C. Decide which is the appropriate solvent for the extraction from the solvent listed in Table 2:

Semasa sintesis poliimida, terdapat kelebihan monomer amina yang tak bertindakbalas dalam campuran tindakbalas. Jelaskan penggunaan ekstraksi soklet untuk mengasingkan monomer ini daripada hasil poliimida sekiranya monomer ini sangat tak-berkutub dengan takat lebur 80°C. Pilih pelarut yang sesuai untuk ekstraksi ini daripada jadual pelarut di dalam Jadual 2:

Table 2

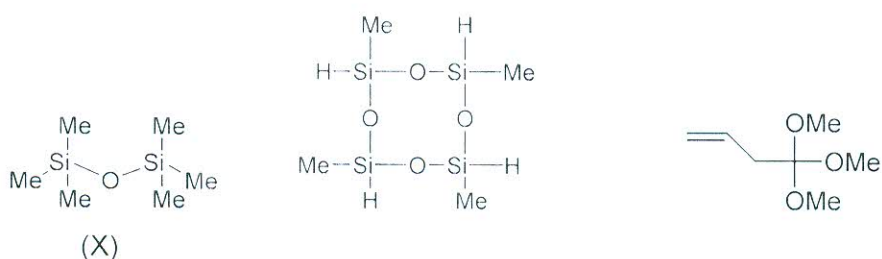
Jadual 2

Solvent <i>Pelarut</i>	Boiling point(°C) <i>Takat didih (°C)</i>
n-butanol	117
Hexane <i>Heksana</i>	69
Toluene <i>Toluena</i>	111

(50 marks/markah)

- [b] A crosslink network for a polysiloxane was synthesised using the following monomers. Catalyst used include HCl (aqueous) and Platinum. Answer the following questions:

Suatu rangkaian sambung-silang polisiloksana telah dihasilkan menggunakan monomer yang berikut. Pemangkin yang digunakan melibatkan HCl (akues) dan Platinum. Jawab soalan yang berikut:



- (i) Draw the crosslinked network structure.

Lukiskan struktur rangkaian sambung-silang ini.

- (ii) Name the two reactions that are involved in this synthesis.
(Note: At least 3 steps are involved)

Namakan dua tindakbalas yang terlibat dalam sintesis ini.

(Nota: Sekurangnya ada 3 langkah yang terlibat)

- (iii) What is the function of hexamethyldisiloxane monomer (X) during this synthesis.

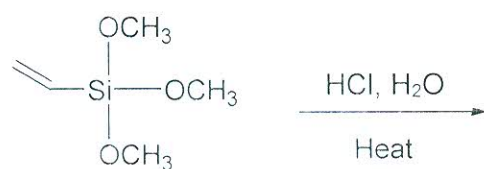
Apakah fungsi monomer heksametildisiloksana (X) dalam sintesis ini.

(50 marks/markah)

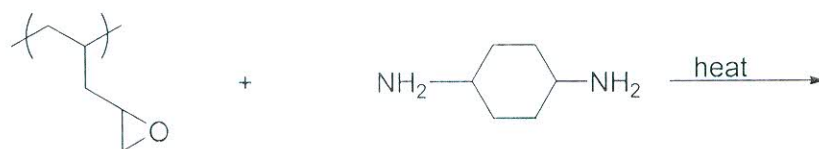
7 [a] Determine the product of the followings:

Nyatakan hasil bagi yang berikut:

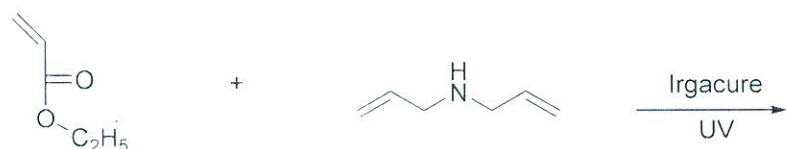
(i)



(ii)



(iii)

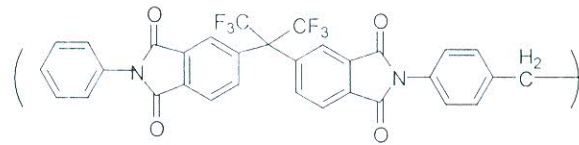


(60 marks/markah)

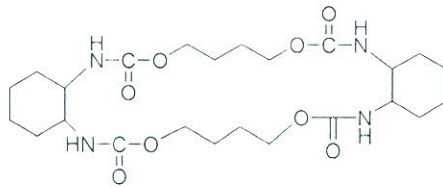
[b] Determine the starting monomer to produce the followings:

Nyatakan monomer pemula bagi menghasilkan yang berikut:

(i)



(ii)



(40 marks/markah)