
UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2006/2007
Peperiksaan Semester Pertama
Sidang Akademik 2006/2007

Oktober/November 2006

EBP 201/3 - Polymer Synthesis ***EBP 201/3 - Sintesis Polimer***

Time : 3 hours
Masa : 3 jam

Please ensure that this paper consists of TEN printed pages before you proceed with the examination.

This paper contains SEVEN questions.

Answer any FIVE questions. If a candidate answers more than five questions, only the first five answers will be examined and awarded marks.

Answer to any question must start on a new page.

All questions could be answered in Bahasa Malaysia or English.

Sila pastikan bahawa kertas peperiksaan ini mengandungi SEPULUH muka surat yang bercetak sebelum anda memulakan peperiksaan.

Kertas soalan ini mengandungi TUJUH soalan.

Jawab LIMA soalan. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Mulakan jawapan anda untuk setiap soalan pada muka surat yang baru.

Semua soalan boleh dijawab samada dalam Bahasa Malaysia atau Bahasa Inggeris.

1. [a] Describe, using mathematical expression, what is meant by \bar{M}_w .
 (20 marks)
- [b] Size exclusion chromatographic data of a new polymer shows the following molecular weight distribution:

Number of molecules	Mass of each molecules
5	10000
3	30000
2	60000

Determine the \bar{M}_n and \bar{M}_w of this polymer hence its polydispersity.

(40 marks)

- [c] Describe a procedure to measure the molecular weight of polymer using Mark-Houwink equation as shown below:

$$[\eta] = KM^a$$

(40 marks)

1. [a] Jelaskan, dengan menggunakan persamaan matematik, maksud \bar{M}_w .
 (20 markah)
- [b] Data dari Kromatografi Penyingkiran Saiz bagi suatu polimer baru menunjukkan taburan berat molekul seperti berikut:

Jumlah molekul	Jisim setiap molekul
5	10000
3	30000
2	60000

Tentukan nilai \bar{M}_n dan \bar{M}_w seterusnya polidispersiti.

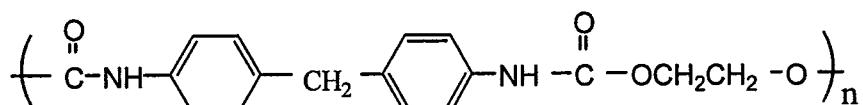
(40 markah)

- [c] Jelaskan suatu kaedah bagi menentukan jisim molekul polimer dengan menggunakan persamaan Mark-Houwink seperti dibawah:

$$[\eta] = KM^a$$

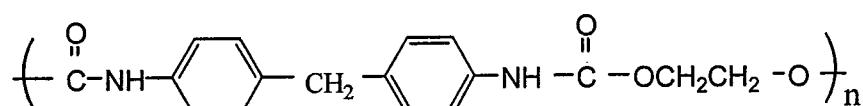
(40 markah)

2. A repeat unit of polyurethane is shown below:



- [a] Show the reaction scheme for the synthesis of the above through step-growth polymerization.
(30 marks)
- [b] What is the effect of an increase of methylene group (-CH₂-) unit in the chain backbone on the thermal property of the above polymer? Verify your suggestion.
(30 marks)
- [c] Calculate the average number molecular weight, M_n, for the above polymer at the extent of reaction of 35%, 67%, 90% and 99%.
(40 marks)

2. Unit berulang bagi poliuretana adalah seperti berikut:



- [a] Tunjukkan skema tindakbalas langkah tumbuhan bagi polimer ini.
(30 markah)
- [b] Apakah kesan penambahan unit kumpulan metilena (-CH₂-) pada rangka tulang belakang ke atas sifat termal bagi polimer dalam bahagian (a) di atas?
(30 markah)
- [c] Hitung nombor purata berat molekul, M_n, bagi polimer dalam bahagian (a) di atas pada tahap tindakbalas 35%, 67%, 90% dan 99%.
(40 markah)

3. [a] What is the function of a sensitizer during a radical polymerization.
(10 marks)
- [b] Derive an expression showing that rate of radical polymerization is proportional to the monomer concentration and square root of initiator concentration.
(40 marks)
- [c] A data for rate of disappearing of monomer concentration during a radical polymerization was determine spectroscopically as follows:

Time/min	Concentration/M	Time/min	Concentration/M
0	3.06	60	1.76
10	2.62	70	1.63
20	2.43	80	1.51
30	2.24	90	1.40
40	2.07	100	1.29
50	1.91		

Show that the reaction is first order with respect to the monomer concentration hence determine the first order rate constant. What does this constant signify on the kinetic of the reaction mechanism.

(50 marks)

3. [a] Apakah fungsi "sensitizer" dalam pempolimeran radikal?
(10 markah)

[b] Terbitkan persamaan yang menunjukkan kadar pempolimeran radikal adalah berkadar terus dengan kepekatan monomer dan punca ganda dua dengan kepekatan pemula.

(40 markah)

[c] Suatu data bagi kadar pengurangan kepekatan monomer dalam satu tindakbalas pempolimeran radikal telah diperolehi melalui kaedah spektroskopi seperti berikut:

masa/min	kepekatan/M	masa/min	kepekatan/M
0	3.06	60	1.76
10	2.62	70	1.63
20	2.43	80	1.51
30	2.24	90	1.40
40	2.07	100	1.29
50	1.91		

Tunjukkan bahawa tindakbalas ini berlaku secara tertib pertama bersandarkan kepekatan monomer seterusnya tentukan pemalar kadar bagi tertib pertama ini. Apakah signifikasi pemalar ini merujuk kepada kinetik mekanisme tindakbalas?

(50 markah)

4. Answer any 3 of the followings:

- [a] Aromatic polyketone is highly crystalline and thus induced a premature precipitation in most reaction solvent during its synthesis. Suggest a synthetic route in order to circumvent this problem so as to produce a high molecular weight polymer.
- [b] Preparation of styrene-methyl methacrylate block copolymer is possible by the addition of methyl methacrylate to a living polystyrene but not in the reverse sequence. Explain.
- [c] Radical polymerization of 1,3-butadiene produces a predominantly 1,4-addition rather than 1,2- and 3,4-addition. Explain.
- [d] During emulsion polymerisation, the rate of polymerization is dependent on monomer concentration but is independent on initiator concentration.

(100 marks)

4. Jawab 3 daripada yang berikut:

- [a] Poliketon aromatik adalah sangat berhablur mengakibatkannya senang termendak dalam pelarut tindakbalas. Cadangkan suatu kaedah sintesis bagi mengatasi masalah ini bagi menghasilkan polimer yang berjisim tinggi.
- [b] Penyediaan kopolimer blok stirena-metil metakrilat adalah mungkin dengan mencampurkan metil metakrilat kepada polistirena hidup tapi tidak pada urutan sebaliknya. Jelaskan.
- [c] Pempolimeran radikal bagi 1,3-butadiena menghasilkan hasil utama penambahan-1,4 berbanding hasil penambahan-1,2 dan -3,4. Jelaskan.
- [d] Dalam kaedah pempolimeran emulsi, kadar pempolimeran bergantung kepada kepekatan monomer sahaja tidak kepada kepekatan pemula.

(100 markah)

5. High molecular weight polymer and chain tacticity have been two strategies in synthetic trends for optimizing end properties of polymer. Describe synthetic methods for:

[a] controlling molecular mass of polymer in radical polymerization.
(50 marks)

[b] controlling chain tacticity in coordination polymerization.
(50 marks)

5. Berat molekul yang tinggi serta taktisiti rantai merupakan 2 strategi dalam sintesis polimer bagi menghasilkan ciri-ciri yang optimum. Bincangkan kaedah yang digunakan untuk:

[a] mengawal jisim molekul polimer dalam pempolimeran radikal.
(50 markah)

[b] mengawal taktisiti rantai dalam pempolimeran koordinat.
(50 markah)

6. [a] In copolymerization synthesis, what is meant by reactivity ratio hence describe a method for its determination.

(40 marks)

- [b] How does "compositional drift" occur during copolymerization between two different monomers?

(30 marks)

- [c] The following is the value of Q-e scheme for the given monomers during copolymerization process:

Monomer	Q	e
Styrene	1.00	-0.80
Acrylamide	1.18	1.30
Propylene	0.002	-0.78

Predict the type of copolymer that will be form during copolymerization between styrene and acrylamide as well as styrene and propylene. Explain your answer.

(30 marks)

6. [a] *Dalam sintesis kopolimer, apakah yang dimaksudkan dengan nisbah kereaktifan serta bagaimana nilai ini ditentukan.*

(40 markah)

- [b] *Bagaimanakah 'anjakan komposisi' terjadi dalam pempolimeran kopolimer antara dua monomer berbeza.*

(30 markah)

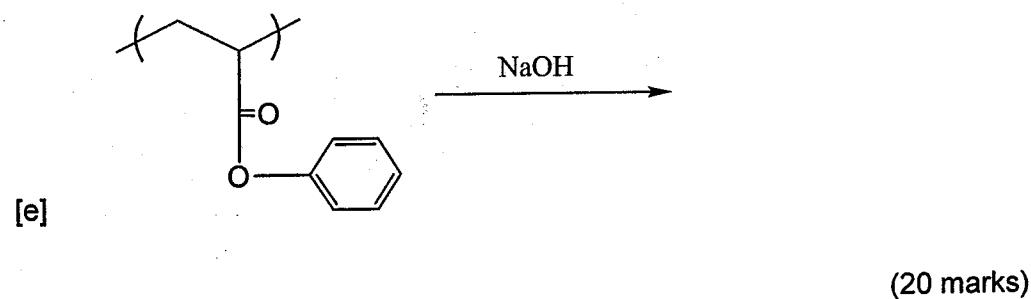
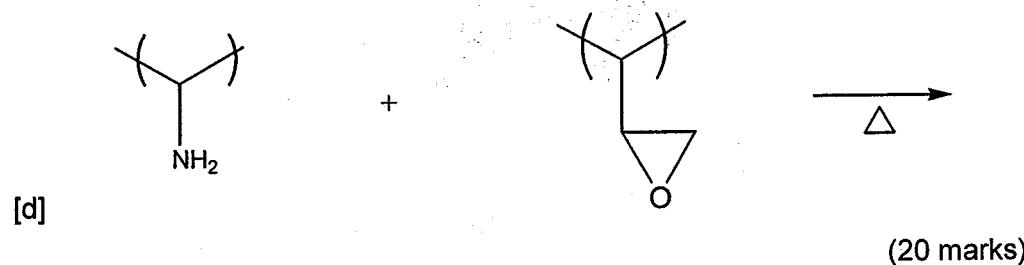
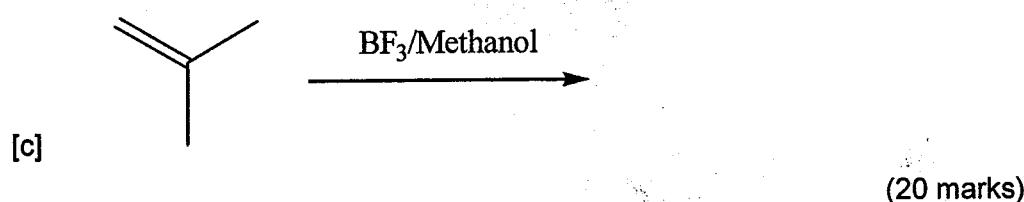
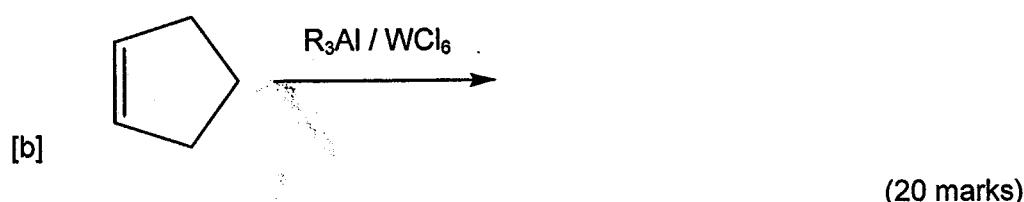
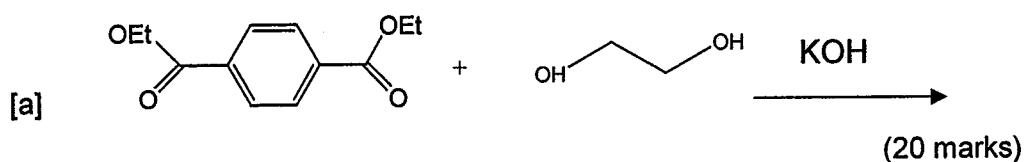
- [c] *Berikut adalah nilai skema Q-e bagi beberapa monomer untuk proses pengkopolimeran:*

Monomer	Q	e
Stirena	1.00	-0.80
Akrilamida	1.18	1.30
Propilena	0.002	-0.78

Jangkakan jenis kopolimer yang terhasil bagi pengkopolimeran stirena dan akrilamida serta stirena dan propilena. Jelaskan jawapan anda.

(30 markah)

7. Predict the reaction products of the following and indicate their repeat unit:



7. Ramalkan hasil dari tindakbalas berikut serta tentukan unit berulang polimer yang terhasil.

