UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2009/2010

November 2009

EBP 201/3 - Polymer Synthesis
[Sintesis Polimer]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains NINE printed pages before you begin the examination.
[Sila pastikan bahawa kertas peperiksaan ini mengandungi SEMBILAN muka surat yang bercetak sebelum anda memulakan peperiksaan ini.]

This paper consists of SEVEN questions.
[Kertas soalan ini mengandungi TUJUH soalan.

Instruction: Answer **FIVE** questions. If candidate answers more than five questions only the first five questions answered in the answer script would be examined.
*[**Arahan**: Jawab **LIMA** soalan. 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.]

…2/-

1. [a] Show that the rate of radical polymerization is proportional to $[I]^{1/2}$.

Tunjukkan bahawa kadar pempolimeran radikal adalah berkadaran dengan $[I]^{1/2}$.

(40 marks/*markah*)

[b] The rate of polymerization for styrene [M] using benzoyl peroxide (BP) as the initiator was taken at sufficiently low conversion such that $[M] = [M]_o$. Given initiation rate constant, $k_i = 1.0 \times 10^{-5}\ s^{-1}$, termination rate constant, $k_t = 6.0 \times 10^{7}\ M^{-1}s^{-1}$, efficiency factor, $f = 0.8$ and initial monomer concentration, $[M]_o = 0.5M$. Calculate k_p, propagation rate constant for this reaction.

Kadar pempolimeran stirena (M) menggunakan benzoil peroksida (BP) sebagai pemula telah diambil pada tahap pertukaran yang agak rendah di mana $[M] = [M]_o$. *Diberi pemalar kadar permulaan,* $k_i = 1.0 \times 10^{-5}\ s^{-1}$, *pemalar kadar penamatan,* $k_t = 6.0 \times 10^{7}\ M^{-1}s^{-1}$, *faktor kecekapan,* $f = 0.8$ *dan kepekatan awal monomer,* $[M]_o = 0.5M$. *Kirakan pemalar kadar perambatan,* k_p *bagi tindakbalas ini.*

Table 1

Jadual 1

Benzoyl peroxide (M) ***Benzoil peroksida(M)***	**Rate of polymerization, R_p ($Ms^{-1} \times 10^{-4}$)** ***Kadar pempolimeran,*** R_p ($Ms^{-1} \times 10^{-4}$)
0.089	2.32
0.211	4.96
0.350	6.04
0.454	7.24
0.510	7.86
0.704	7.63

(60 marks/*markah*)

2. [a] The rate of emulsion polymerization proceeds through three stages as depicted in Figure 1. Describe what happens during each of these stages.

Kadar pempolimeran ampaian berlaku dalam 3 peringkat seperti ditunjukkan dalam Rajah 1. Perihalkan apa yang berlaku dalam setiap peringkat ini.

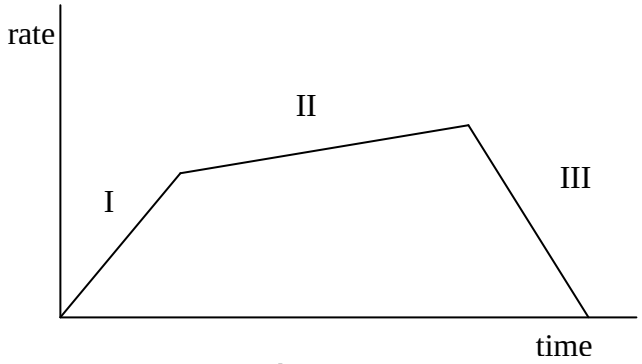


Figure 1

Rajah 1

(50 marks/*markah*)

[b] Sketch a graph of product % conversion against time when using potassium laurate as surfactant at 0.035M, 0.070M and 0.0140M during an emulsion polymerization and hence discuss your result.

Lakarkan graf % pertukaran hasil melawan masa apabila menggunakan potassium laurat sebagai surfaktan pada kepekatan 0.035M, 0.070M dan 0.0140M semasa pempolimeran ampaian dan seterusnya bincangkan bentuk lakaran ini.

(50 marks/*markah*)

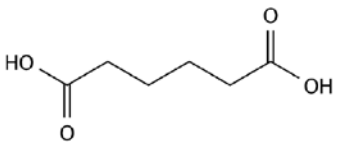
3. [a] Discuss the observation that monomer disappears at early stage during step growth polymerization as compared to addition polymerization.

Bincangkan pemerhatian bahawa berlaku kehilangan monomer pada peringkat awal dalam pempolimeran tumbuh berbanding pempolimeran penambahan.

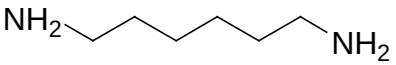
(30 marks/*markah*)

[b] Consider performing condensation polymerization between adipic acid and hexamethylene diamine. Calculate the feed ratio of adipic acid and hexamethyl diamine (Figure 2) that should be employed to obtain a polyamide of approximately 500, 700, 1000 molecular weight at 90% conversion.
(Given atomic mass C = 12.0, H = 1.0, O = 16.0, N = 14.0)

Pertimbangkan pempolimeran kondensasi antara asid adipik dengan heksametil diamina. Hitungkan nisbah asal asid adipik dan heksametil diamina (Rajah 2) bagi menghasilkan poliamida dengan berat molekul lebih kurang 500, 700 dan 1000 pada pertukaran 90%.
(Diberi jisim atom C = 12.0, H = 1.0, O = 16.0, N = 14.0)



Adipic acid



hexamethyl diamine

Figure 2

Rajah 2

(70 marks/*markah*)

4. [a] 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 2

Jadual 2

	Polymer radicals Radikal Polimer			
Monomers *Monomer*	Butadiene *Butadiena*	Styrene *Stirena*	Methyl methacrylate *Metil metakrilat*	Acrylonitrile *Akrilonitril*
Butadiene *Butadiena*	100	280	2060	98000
Styrene *Stirena*	70	165	1130	49000
Methyl methacrylate *Metil metakrilat*	130	314	515	13100
Acrylonitrile *Akrilonitril*	330	413	422	1960

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

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

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

(i) Mengapakah nilai k_{12} bagi polimer radikal butadiena dan stirena lebih rendah berbanding polimer radikal metil metakrilat dan akrilonitril.

(ii) Berdasarkan nilai k_{12} di atas, jelaskan mengapa stirena membentuk kopolimer selang-seli dengan butadiena.

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

(42 marks/*markah*)

[b] Determine the monomer A and B feeding ratio having reactivity ratio r_A = 20 and r_B = 0.015 so as to give the mole ratio of monomer A in copolymer composition at 0.25, 0.5 and 0.75.

Tentukan nisbah asal monomer A dan B dengan nisbah reaktiviti r_A = 20 dan r_B = 0.015 bagi menghasilkan kopolimer dengan komposisi monomer A sebagai 0.25, 0.5, 0.75.

(58 marks/*markah*)

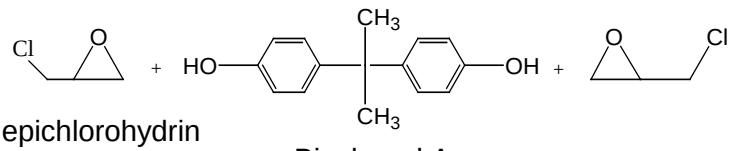
5. [a] Describe the use of soxhlet extraction during polymer synthesis.

Perihalkan penggunaan ekstraksi 'soxhlet' semasa sintesis polimer.

(30 marks/*markah*)

[b] Consider the preparation of dietherglycidyl bisphenol A (DEGBA) resin as shown below:

Pertimbangkan penyediaan resin dietilglisidil bisphenol A (DEGBA) seperti ditunjukkan di bawah:



epichlorohydrin Bisphenol A

Figure 3

Rajah 3

(i) Describe the effect of using NaOH as catalyst.

(ii) What happen to the final product when the mole ratio of the epichlorohydrin to bisphenol A is reduced.

(iii) The crude epoxy product was obtained using water as solvent followed by refluxing at a temperature below for 2h. Elaborate this procedure further.

(i) Terangkan kesan penggunaan NaOH sebagai mangkin.

(ii) Apakah kesannya terhadap hasil akhir apabila nisbah antara epiklorohidrin terhadap bifenol A dikurangkan.

(iii) Hasil kasar epoksi diperolehi dengan menggunakan air dan direfluk dibawah suhu 95^{o}C selama 2 jam. Huraikan dengan lebih lanjut tatacara ini.

(70 marks/*markah*)

6. [a] Previously known radical polymerization of α-alkenes produced atactic polymers but tacticity can be controlled using Ziegler-Natta or metallocene catalyst. Comment on this statement.

Pempolimeran radikal bagi α-alkena sebelum ini menghasilkan polimer ataktik tetapi sifat taktik ini boleh dikawal menggunakan mangkin Ziegler-Natta atau metallocene. Berikan komen anda tentang keterangan ini.

(20 marks/*markah*)

[b] Discuss the catalytic features in Ziegler-Natta catalyst which is responsible in controlling tacticity during α-alkenes polymerisation. Your answer should include metal component of the catalysts, type of monomers and the role of vacant orbital of the metal atom.

Bincangkan ciri-ciri pemangkinan dalam mangkin Ziegler-Natta yang bertanggungjawab dalam mengawal sifat taktik semasa pemangkinan α-alkenes. Jawapan perlulah menyentuh tentang komponen logam, jenis monomer serta peranan orbital kosong pada atom logam itu.

(40 marks/*markah*)

[c] Discuss the catalytic feature of a metallocene catalyst which is responsible in controlling the tacticity during α-alkenes polymerization. Your answer should include the chirality, rigidity and stereo-structure at the catalytic site.

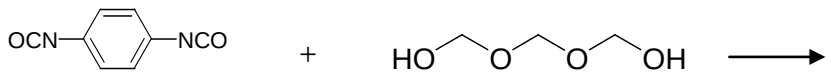
Bincangkan ciri-ciri pemangkinan dalam mangkin 'metallocene' yang bertanggungjawab mengawal sifat taktik semasa pempolimeran α-alkena. Jawapan perlulah menyentuh sifat kiral, kekakuan dan struktur-stereo pada pusat pemangkinan.

(40 marks/*markah*)

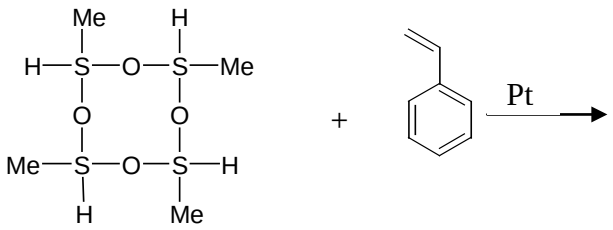
7. [a] Predict the products of the following reactions:

Berikan hasil bagi tindakbalas yang berikut:

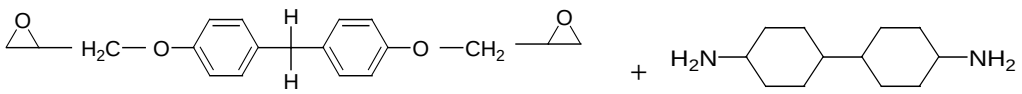
(i)



(ii)



(iii)

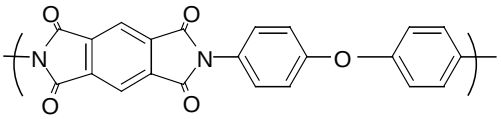


(60 marks/*markah*)

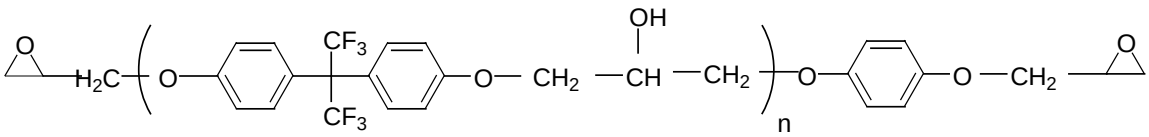
[b] Determine the monomers used to produce the followings:

Tentukan monomer yang digunakan untuk menghasilkan yang berikut:

(i)



(ii)



(40 marks/*markah*)

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