UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2011/2012

January 2012

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 a 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.]

In the event of any discrepancies, the English version shall be used.
[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.]

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1. [a] Given that the rate of a radical polymerization as

$$= \frac{k_p k_i^{1/2}}{k_t^{1/2}} [M][I]^{1/2}$$

Prove that the overall activation energy is

$E_a = ½E_i + E_p - ½E_t$

where E_i is initiation, E_p is propagation and E_t is termination activation energies respectively.

Diberi kadar pempolimeran radikal sebagai

$$= \frac{k_p k_i^{1/2}}{k_t^{1/2}} [M][I]^{1/2}$$

Buktikan keseluruhan tenaga pengaktifan adalah

$E_a = ½E_i + E_p - ½E_t$

di mana E_i ialah tenaga pengaktifan permulaan, E_p tenaga pengaktifan perambatan dan E_t tenaga pengaktifan penamatan.

(30 marks/*markah*)

[b] Describe in detail how would you determine the activation energy of a polymerization process.

Jelaskan bagaimana anda menentukan tenaga pengaktifan sesuatu proses pempolimeran.

(40 marks/*markah*)

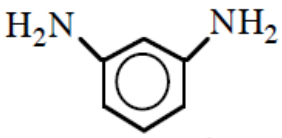
[c] The activation energy of propagation E_p for styrene monomer is 30 kJ/mol but for vinyl chloride monomer is only 15 kJ/mol. Justify your reasons.

Tenaga pengaktifan perambatan E_p bagi monomer stirena ialah 30 kJ/mol tapi bagi vinil klorida ialah 15 kJ/mol. Berikan beberapa penjelasan.

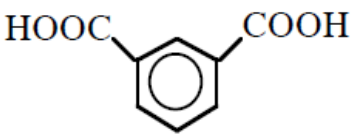
(30 marks/*markah*)

2. Consider bulk polymerization between m-aminoaniline (0.1586 moles) and isophthalic acid (0.1598 moles) whose structures are shown below:

Pertimbangkan pempolimeran pukal bagi m-amino anilina (0.1586 mol) dan asid isoftalik (0.1598 mol) dengan struktur seperti ditunjukkan di bawah:



m-aminoaniline



isophthalic acid

(a) Based on given information, derived

(i) extent of reaction, p

(ii) feeding ratio, r

(iii) degree of polymerization, $\overline{D}p$

Berdasarkan kenyataan yang diberi, tentukan

(i) jangkauan tindakbalas, p

(ii) nisbah suapan, r

(iii) darjah pempolimeran, $\overline{D}p$

(60 marks/*markah*)

(b) Calculate the average molecular weight, M_n, of this polymerization at extent of reaction of 0.98 and 0.99.

Hitung berat purata, M_n, bagi pempolimeran ini pada jangkauan tindakbalas 0.98 dan 0.99.

(40 marks/*markah*)

3. Explain the followings:

(a) The presence of small amount of nitrobenzene will reduce the rate of polymerization of styrene but the presence of small amount of hydroquinone will completely stop this polymerization.

(b) During step growth polymerization, high product conversion is achieved towards the later stage of polymerization but in chain growth polymerization this is achieved at earlier stage of polymerization.

(c) Emulsion polymerization provide a system for a high molecular weight polymer production while maintaining the rate of polymerization.

(d) The copolymerization of styrene with methyl methacrylate preferably performed under radical condition compared to ionic condition.

Jelaskan yang berikut:

(a) Kehadiran sedikit nitrobenzena akan mengurangkan kadar pempolimeran stirena tetapi kehadiran sedikit hidrokuinon akan menghentikan terus pempolimeran ini.

(b) Semasa pempolimeran pertumbuhan berperingkat, penukaran hasil yang tinggi berlaku pada penghujung proses tindakbalas tapi dalam pempolimeran pertumbuhan rantai, ini berlaku pada permulaan proses tindakbalas.

(c) Pempolimeran ampaian menyediakan sistem penghasilan berat polimer yang tinggi pada masa yang sama mengekalkan kadar pempolimeran.

(d) Pengkopolimeran stirena dengan metil metakrilat lebih sesuai dijalankan dalam keadaan sistem radikal berbanding sistem ionik.

(100 marks/*markah*)

4. [a] What is meant by 'compositional drift' during copolymerisation between two monomers.

Apakah yang dimaksudkan dengan 'anjakan komposisi' semasa pengkopolimeran antara dua monomer.

(20 marks/*markah*)

[b] Describe the effect of resonance and electronic properties on the rate constant of copolymerization between monomer A and monomer B.

Perihalkan kesan resonans dan sifat-sifat elektronik ke atas pemalar kadar pengkopolimeran antara monomer A dan B.

(30 marks/*markah*)

[c] k_{AB} refer to the copolymerization rate constant of propagating radical A with monomer B. Given the following data:

k_{AB} merujuk kepada pemalar kadar pengkopolimeran bagi perambatan radikal A terhadap monomer B. Diberi data yang berikut:

Monomer	Q	e
Styrene / *Stirena*	1.00	-0.80
Butadiene / *Butadiena*	1.70	-0.50
Vinyl chloride / *Vinil klorida*	0.056	0.6
Vinyl acetate / *Vinil asetat*	0.026	-0.88

(i) Why copolymerization rate constant for butadiene propagating radical with styrene monomer (k_{AB}= 80) very much lower than that of vinyl chloride propagating radical with styrene monomer (k_{AB}=550000)?

Kenapakah pemalar kadar pengkopolimeran bagi perambatan radikal butadiena dengan monomer stirena (k_{AB} = 80) sangat kecil berbanding pemalar kadar pengkopolimeran bagi perambatan radikal vinil klorida dengan monomer stirena (k_{AB} = 550000)?

(30 marks/*markah*)

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(ii) Predict which pair would give a higher k_{AB} value between butadiene propagating radical with vinyl chloride monomer or vinyl acetate propagating radical with vinyl chloride monomer.

Nyatakan pasangan mana akan memberikan nilai k_{AB} yang tinggi antara perambatan radikal butadiena dengan monomer vinil klorida atau perambatan radikal vinil asetat dengan monomer vinil klorida.

(20 marks/*markah*)

5. [a] Explain the followings regarding the Ziegler–Natta catalyst:

(i) Crystallinity of a polymeric product increased when using Ziegler-Natta catalyst compared to a normal radical initiator during polymerization of polyalkenes.

(ii) The monomer in the form of α-alkene is required when using this catalyst.

(iii) Transition metal is required as the central active site for this catalyst.

Jelaskan yang berikut berkenaan dengan mangkin Ziegler-Natta:

(i) Penghabluran suatu hasil polimer meningkat dengan menggunakan mangkin Ziegler-Natta berbanding dengan penggunaan pemula radikal biasa bagi proses pempolimeran polialkena.

(ii) Monomer dalam bentuk α-alkena adalah diperlukan semasa penggunaan mangkin ini.

(iii) Logam peralihan digunakan sebagai ruang pusat aktif bagi mangkin ini.

(60 marks/*markah*)

[b] Discuss the following regarding the metallocene catalyst:

(i) The active site of this catalyst is chiral

(ii) Narrow molecular weight distribution of final product is achieved.

Bincangkan yang berikut berkaitan dengan mangkin metallosena:

(i) Ruang aktif mangkin ini adalah bersifat kiral

(ii) Hasil akhir diperolehi yang mempunyai taburan berat molekul yang sempit.

(40 marks/*markah*)

6. [a] Filtration and distillation are two techniques for product purification. Compare between these two techniques.

Penurasan dan penyulingan adalah dua teknik penulenan produk. Bezakan di antara kedua-dua teknik ini.

(40 marks/*markah*)

[b] During synthesis of polyimide, the crude product obtained was in the dissolved form in the NMP solvent. Suggest with explaination, a method of obtaining the pure product from this crude sample.

Semasa sintesis poliimida, hasil kasar adalah dalam bentuk larutan dalam pelarut NMP. Cadangkan dengan penjelasan, satu kaedah bagi mendapatkan produk tulen dari sampel asal tadi.

(30 marks/*markah*)

[c] NaOH is used as catalyst during production of dietherglycidyl bisphenol A epoxy resin. How is the pure product recovered without contamination of this catalyst?

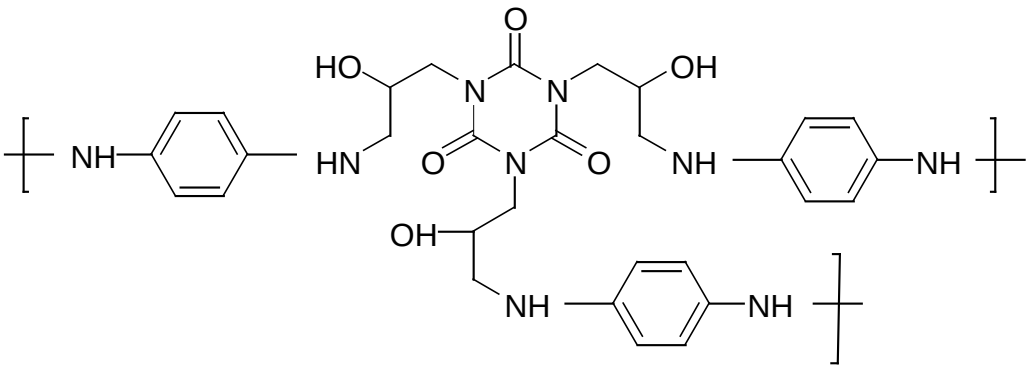
NaOH digunakan sebagai mangkin semasa penghasilan resin epoksi dieterglisidil bisfenol A. Bagaimanakah hasil tulen diperolehi bebas dari pencemaran bahan mangkin?

(30 marks/*markah*)

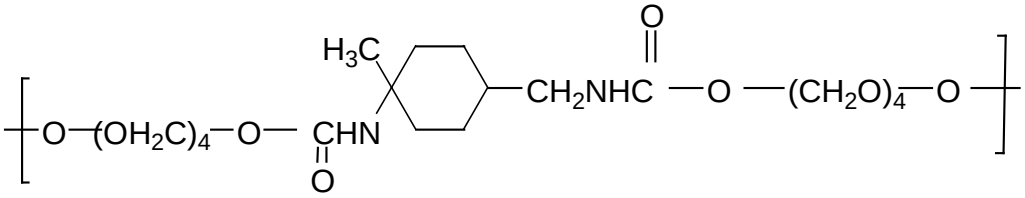
7. [a] Determine the monomers used to produce the followings:

Tentukan monomer yang diperlukan bagi menghasilkan yang berikut:

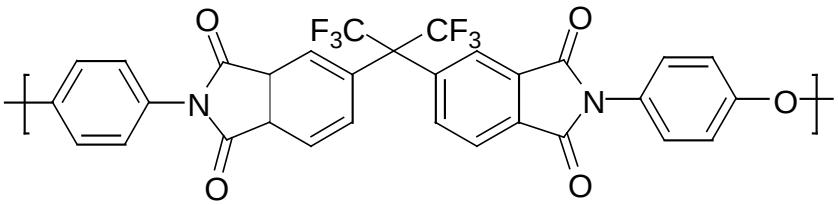
(i)



(ii)



(iii)

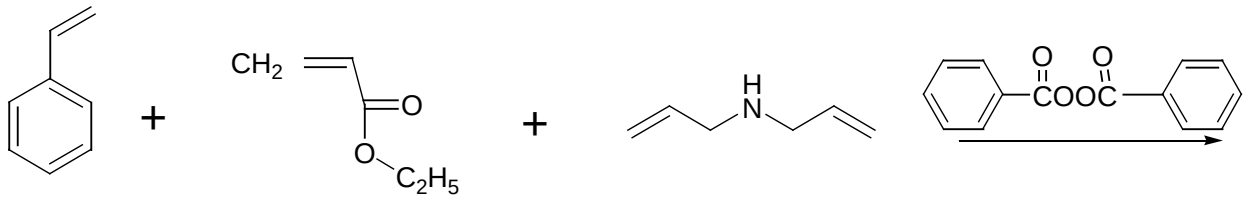


(60 marks/*markah*)

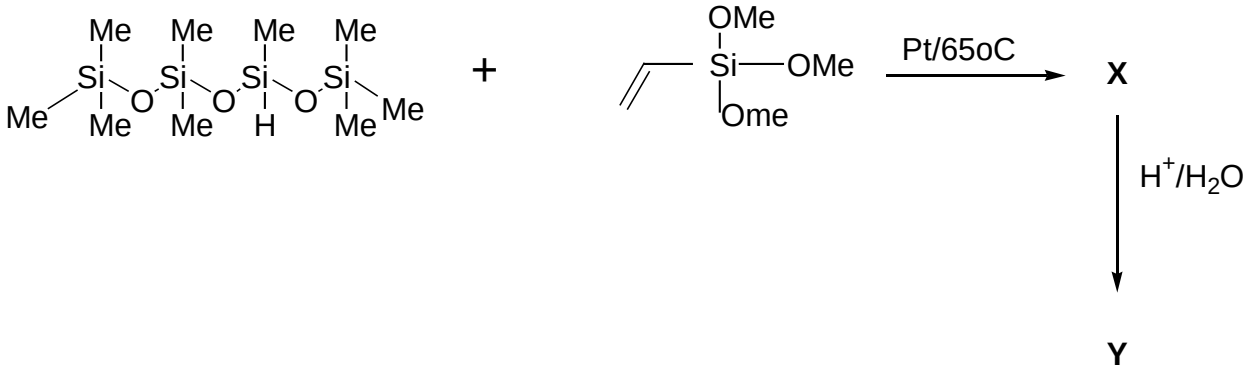
[b] Determine the products of the followings:

Tentukan hasil bagi yang berikut:

(i)



(ii)



(40 marks/*markah*)

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