UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2008/2009

April/May 2009

KIT 254 – Polimer
[Polimer]

Duration : 2 hours
[Masa : 2 jam]

Please check that this examination paper consists of **TEN** printed pages before you begin the examination.

Instructions:

Answer any **FOUR** (4) questions.

You may answer the questions either in Bahasa Malaysia or in English.

If a candidate answers more than four questions, only the answers to the first four questions in the answer sheet will be graded.

...2/-

Answer **Four (4)** questions.

1. (a) Nine samples of polyethylene with different molar masses were used to calibrate Gel Permeation Chromatography Column. The following results were obtained.

M /g mol^{-1}	V_{pk}/ cm^3
2.0×10^6	21.0
1.2×10^6	21.1
7.8×10^5	22.1
5.0×10^5	23.7
3.1×10^5	25.5
1.6×10^5	27.9
1.0×10^5	29.4
5.0×10^4	29.9
1.0×10^4	30.0

   (i) Use the data to construct a calibration curve.

   (ii) Explain the shape of the curve.

(15 marks)

   (b) The molar masses of two monodispersed samples of polymer are given below.

Sample	M / g mol^{-1}
X	10.0×10^5
Y	25.0×10^5

Suppose a blend was made by mixing together one part of sample Y and three parts of sample X by weight. Calculate the number-average and weight-average molar masses of the blend.

(10 marks)

2. (a) Derive an expression for the volume fraction, ϕ_c, and mass fraction of crystals, χ_c, of crystal for a semicrystalline polymer in terms of the density of the sample, ρ, the density of the crystals phase, ρ_c, and the density of the amorphous phase, ρ_a.

(12 marks)

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(b) A polymer of 2 mm thickness and 6 mm width was subjected to tensile test and the following results were obtained. The original thickness of this polymer is 75 mm.

Force/kN	3.50	6.25	10.00	12.75	14.50	18.25	24.00
Extension/mm	0.1	0.7	1.9	2.6	4.1	7.6	9.0

(i) Discuss the information that can be obtained from this data.

(ii) Explain how you can estimate the Young's modulus of this polymer.

(13 marks)

3. (a) Discuss the factors which govern the rate of polymerization of styrene monomer initiated by butyl-lithium in dioxane.

(12 marks)

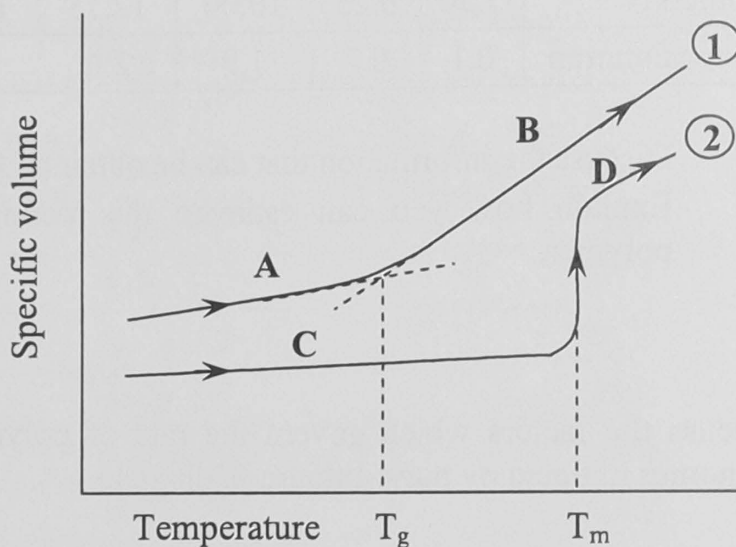(b) Suggest a suitable class of polymer and an example for each of the following applications. Give reasons.

(i) Used to make car bumpers.

(ii) Suitable as textile threads.

(iii) Used to make car tyres.

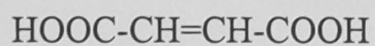(iv) Commonly used as food containers.

(13 marks)

4.   (a)   The following figure shows the behaviour of two types of polymers, 1 and 2, during heating.

For each type of the polymers, provide its physical states at A and B, or C and D. Describe the transitions shown.

(10 marks)

   (b)   A chemist is preparing a polyester using maleic acid (250 g) and diethylene glycol (230 g) as the monomers. The polyester should have the molecular weight 15,000 g mol^{-1}.

HOOC-CH=CH-COOH   HOCH$_2$CH$_2$OCH$_2$CH$_2$OH

        Maleic acid   Diethylene glycol

The reaction is carried out in toluene with a mineral acid as catalyst. After 1 hour reaction, the chemist measures the acidity of the mixture and finds that 2.0 % of the acid groups remain unreacted.

   (i)   Draw the structure of the polyester and calculate the formula weight of the repeating unit.

   (ii)   Calculate the molecular weight of the polymer obtained after 1 hour. Will he get the polymer he wants? If yes, give your reason. If no, explain why and suggest how he could rectify the problem.

(15 marks)

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5. (a) An engineer has prepared polyacrylonitrile as follows:

An amount of 107 g L^{-1} acrylonitrile (CH_2=CH-CN) in methanol was left to react at 25 °C. Isobutyril peroxide (0.4 M) was used as an initiator with 45 % efficiency. It was known that this polymerisation was terminated by combination mode only, $k_p^2/k_t = 25$ L (mol s)$^{-1}$ and $k_d = 1.32$ x 10^{-3} mol $L^{-1}s^{-1}$ at 25 °C.

(i) Calculate the average molecular weight of the polyacrylonitrile.

(ii) How do you determine whether the termination step occurs by combination or disproportionation from the polymer structure?

(15 marks)

(b) Briefly explain the followings:

(i) Steady state condition in radical chain polymerization.

(ii) Low density polyethylene, LDPE.

(iiii) Carothers' equation.

(10 marks)

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TERJEMAHAN

Arahan:

Jawab **EMPAT (4)** soalan.

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

Jika calon menjawab lebih daripada empat soalan, hanya empat soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Jawab **Empat (4)** soalan.

1. (a) Sembilan sample polietilena dengan jisim molar yang berlainan telah digunakan menentukur Kolum Kromatografi Penelapan Gel. Keputusan berikut diperoleh.

M /g mol^{-1}	V$_{pk}$/ cm^3
2.0×10^6	21.0
1.2×10^6	21.1
7.8×10^5	22.1
5.0×10^5	23.7
3.1×10^5	25.5
1.6×10^5	27.9
1.0×10^5	29.4
5.0×10^4	29.9
1.0×10^4	30.0

(i) Dengan menggunakan data-data ini, lakarkan keluk tentukuran tersebut.

(ii) Terangkan keluk yang anda peroleh.

(15 markah)

(b) Jisim molar bagi dua sampel polimer monosebaran diberikan seperti berikut.

Sample	M / g mol^{-1}
X	10.0×10^5
Y	25.0×10^5

Bahan tersebut dicampurkan bersama-sama pada kadar satu bahagian sampel Y dan tiga bahagian sampel X berdasarkan pada berat. Kirakan purata-nombor dan purata-berat jisim molar bagi campuran tersebut.

(10 markah)

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2. (a) Terbitkan persamaan-persamaan bagi pecahan isipadu hablur, ϕ_c, dan pecahan jisim isipadu hablur, χ_c, bagi satu polimer separa hablur dalam hubungan dengan ketumpatan sampel polimer, ρ, ketumpatan fasa hablur didalam polimer, ρ_c, dan ketumpatan fasa amorfous didalam polimer, ρ_a.

(12 markah)

(b) Satu polimer yang mempunyai ketebalan 2 mm dan lebar 6 mm dikenakan ujian tensil. Keputusan berikut diperoleh. Panjang asal polimer ini adalah 75 mm.

Daya/kN	3.50	6.25	10.00	12.75	14.50	18.25	24.00
Pertambahan panjang/mm	0.1	0.7	1.9	2.6	4.1	7.6	9.0

(i) Bincangkan maklumat yang dapat diperoleh daripada data ini.
(ii) Terangkan bagaimanakah anda dapat menanggarkan modulus young bagi polimer ini.

(13 markah)

3. (a) Bincangkan faktor-faktor yang mengawal kadar pempolimeran monomer stirena dengan pemula butil-litium dalam pelarut dioxana.
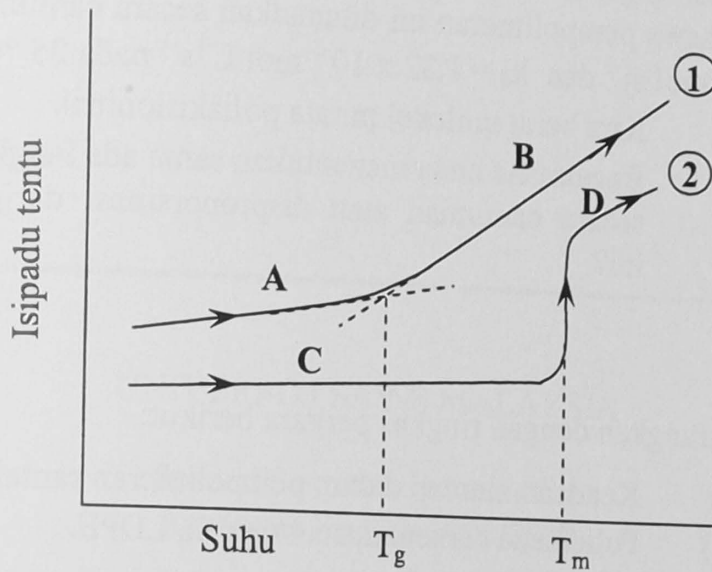
(12 markah)

(b) Cadangkan kelas polimer dan satu contoh yang sesuai bagi setiap aplikasi berikut. Berikan sebab.
(i) Digunakan untuk membuat bumper kereta.
(ii) Sesuai sebagai benang tekstil.
(iii) Digunakan untuk membuat tayar kereta.
(iv) Biasanya digunakan sebagai bekas makanan.
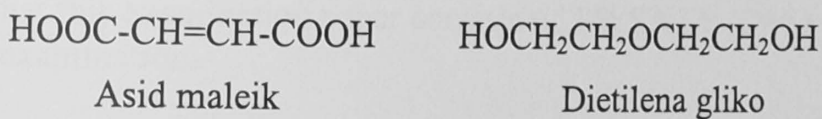
(13 markah)

4. (a) Rajah berikut menunjukkan kelakuan dua jenis polimer, 1 and 2, semasa pemanasan.

Bagi setiap jenis polimer itu, berikan keadaan fiziknya di A dan B, atau C dan D. Perihalkan peralihan yang ditunjukkan.

(10 markah)

(b) Seorang ahli kimia sedang menyediakan suatu poliester menggunakan asid maleik (250 g) dan dietilena glikol (230 g) sebagai monomer. Poliester itu harus mempunyai berat molekul 15,000 g mol^{-1}.

HOOC-CH=CH-COOH   HOCH$_2$CH$_2$OCH$_2$CH$_2$OH

Asid maleik   Dietilena gliko

Tindak balas ini dijalankan di dalam toluena dengan asid mineral sebagai mangkin. Selepas 1 jam bertindak balas, ahli kimia itu mengukur keasidan campuran itu dan mendapati bahawa 2.0 % kumpulan asid belum bertindak balas.

(i) Lukiskan struktur poliester tersebut dan hitung berat formula unit ulangannya.

(ii) Hitung berat molekul polimer yang diperolehi selepas 1 jam. Berjayakah dia mendapatkan polimer itu? Jika ya, berikan alasan anda. Jika tidak, terangkan mengapa dan cadangkan bagaimana dia dapat memperbaiki masalah ini.

(15 markah)

...10/-

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5. (a) Seorang jurutera telah menyediakan poliakrilonitril seperti berikut:

Sebanyak 107 g L^{-1} akrilonitril ($CH_2=CH-CN$) dalam metanol telah dibiarkan bertindakbalas pada suhu 25 °C. Isobutiril peroksida (0.4 M) telah digunakan sebagai pemula dengan kecekapan 45 %. Diketahui bahawa pempolimeran ini ditamatkan secara cantuman sahaja, $k_p^2/kt = 25$ L (mol s)$^{-1}$ dan $k_d = 1.32 \times 10^{-3}$ mol $L^{-1}s^{-1}$ pada 25 °C.

(i) Kira berat molekul purata poliakrilonitril.

(ii) Bagaimana anda menentukan sama ada langkah penamatan berlaku secara cantuman atau disproporsinasi daripada struktur polimer itu?

(15 markah)

(b) Terangkan dengan ringkas perkara berikut:

(i) Keadaan mantap dalam pempolimeran rantai radikal.

(ii) Polietilena berketumpatan rendah, LDPE.

(iii) Persamaan Carothers.

(10 markah)

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