
UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2009/2010 Academic Session

April/May 2010

KIT 254 – POLIMER
[POLIMER]

Duration : 2 hours
[Masa : 2 jam]

Please check that this examination paper consists of NINE pages of printed material before you begin the examination.

Instructions:

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

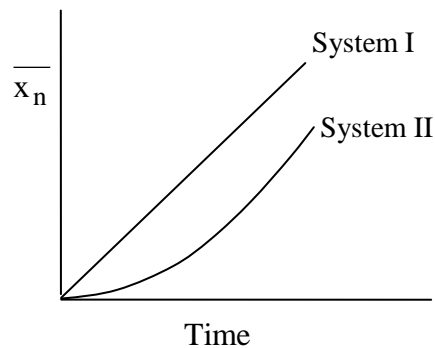
You may answer the questions either in Bahasa Malaysia or in English.

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

In the event of any discrepancies, the English version shall be used.

Answer **FOUR (4)** questions.

1. (a) Differentiate between the terms *glass transition* and *melting*. What is the significance of glass transition temperature of a polymer to consumers? Give examples. (8 marks)
 - (b) An equimolar mixture of phenylene-1,4-diisocyanate and ethylene glycol (2.00 M) was polymerised to 99.8 % extent in the presence of 3×10^{-3} M ethanol as impurity. Calculate the molecular weight of the polymer obtained with and without the presence of the impurity. From the answer, conclude the effect of impurity on molecular weight. (10 marks)
 - (c) Draw two structural variations that are possible for polypropylene but not for polyethylene. Discuss how the structure of the polymers influences their physical properties. (7 marks)
2. (a) Give **three** differences between chain-reaction and step-reaction polymerizations. Suggest one experimental test for making this distinction. (8 marks)
 - (b) The following diagram shows the kinetics of two step-polymerization systems in which stoichiometric amounts of diol and diacid are used. Identify the two systems and explain the diagram briefly. (6 marks)



(6 marks)

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- (c) In a solution polymerization experiment, methyl methacrylate (MMA, 1.80 M) and AIBN (0.35 M) were dissolved in toluene and heated to 60 °C for two hours. The product, PMMA, was filtered, washed and dried.
- (i) If there is no side reaction occurs and the chain termination takes place solely by disproportionation, calculate the expected number-average molecular weight of the polymer.
[Given: $f = 0.35$; $k_d = 1.1 \times 10^{-3} \text{ s}^{-1}$; $k_p^2/k_t = 16.0 \text{ L mol}^{-1} \text{ s}^{-1}$]
- (ii) In the actual experiment, the molecular weight of PMMA obtained was $2.7 \times 10^4 \text{ g mol}^{-1}$, indicating that chain transfer reactions did happen. Assuming that only chain transfer to solvent has occurred, find the concentration ratio of toluene to MMA if known that the chain transfer constant, C_s is 1.5.
- (11 marks)
3. (a) Draw the structure of the copolymer produced from a mixture of 1,4-divinyl benzene, $\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2)_2$, and styrene having a 1 to 5 ratio.
- (i) What is the effect of increasing the proportion of divinyl benzene on the dimensional stability of this copolymer?
- (ii) Suppose you have two beads of this material, one having 1 % divinyl benzene and the other having 10 % divinyl benzene. How could you distinguish them using just a beaker of toluene? Give the reason for the observed effect.
- (6 marks)
- (b) Describe the morphology of polymers. Outline **one** factor that has influence on the polymer morphology.
- (6 marks)
- (c) You are provided with three polymers: *cis*-1,4-polyisoprene, polystyrene and polyacrylonitrile.
- (i) Draw the structure of the repeating unit of each polymer.
- (ii) Explain how they could be distinguished by means of the following three analytical methods: Infrared (IR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy and Differential Scanning Calorimetry (DSC) or any other method that you know.
- (13 marks)

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4. (a) Free radical initiators may be classified into four general types: peroxides (or hydroperoxides), azo compounds, redox initiators and photoinitiators.
- (i) Write the name and structure for each type.
 (ii) What is the major advantage of photoinitiation?

(8 marks)

- (b) List the differences between free radical polymerization and ionic polymerization.

(7 marks)

- (c) Normally a monomer can be polymerized either via anionic or cationic polymerization. Nonetheless, polystyrene can be formed from styrene using both anionic and cationic as well as free radical polymerization. Explain.

(10 marks)

5. (a) Write a concise definition for each of the following terms:

- (i) Polydispersity index.
 (ii) Hydrodynamic radius.
 (iii) Syndiotactic.
 (iv) Thermoplastic elastomer.

(10 marks)

- (b) The flow times in a capillary viscometer for poly(isobutene) solutions in toluene at 25 °C are as follows:

Concentration/g cm ⁻³	0.004	0.008	0.012	0.016
Time/second	200	246	298	357

The flow time for pure solvent is 160 seconds.

- (i) Evaluate the intrinsic viscosity of the polymer in toluene at 25 °C.
 (ii) Calculate the viscosity-average molecular weight for poly(isobutene), given the Mark-Houwink parameters in toluene at 25 °C as $K = 8.7 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ and $a = 0.56$.

(15 marks)

TERJEMAHAN

Arahan:

Jawab **EMPAT** (4) soalan.

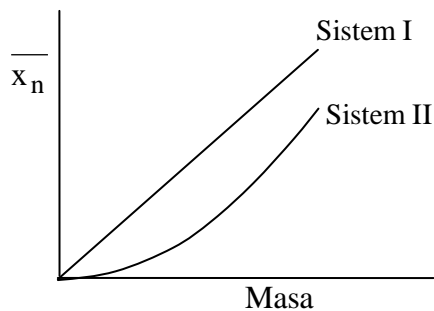
Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

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

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

Jawab **Empat (4)** soal.

1. (a) Bezakan antara istilah peralihan kaca dan peleburan. Apakah kepentingan suhu peralihan kaca bagi suatu polimer kepada pengguna? Beri contoh. (8 markah)
 - (b) Suatu campuran ekuimolar fenilen-1,4-diisosiyanat dan etilena glikol (2.00 M) telah dipolimerkan sehingga 99.8 % dalam kehadiran 3×10^{-3} M etanol sebagai bendasing. Hitung berat molekul polimer yang diperoleh dengan dan tanpa kehadiran bendasing. Daripada jawapan itu, simpulkan kesan bendasing ke atas berat molekul polimer. (10 markah)
 - (c) Lukiskan dua variasi struktur yang mungkin bagi polipropilena tetapi tidak bagi polietilena. Bincangkan bagaimana struktur polimer-polimer tersebut mempengaruhi sifat fiziknya. (7 markah)
2. (a) Berikan **tiga** perbezaan antara pempolimeran tindak balas-rantai dan tindak balas-berperingkat. Cadangkan satu ujian eksperimen bagi membuat perbandingan ini. (8 markah)
 - (b) Gambarajah berikut menunjukkan kinetik bagi dua sistem pempolimeran berperingkat yang mana diol dan diasid digunakan dalam amaun yang stoikiometrik. Kenalpastikan dua sistem tersebut dan terangkan gambarajah ini secara ringkas.



(6 markah)

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- (c) Dalam suatu eksperimen pempolimeran larutan, metil metakrilat (MMA, 1.80 M) dan AIBN (0.35 M) telah dilarutkan dalam toluena dan dipanaskan ke 60 °C selama 2 jam. Hasilnya, PMMA, telah dituras, dibasuh dan dikeringkan.
- (i) Sekiranya tiada tindak balas sampingan berlaku dan penamatan rantai berlangsung hanya secara disproporsinasi, hitung berat molekul purata-bilangan yang dijangkakan bagi polimer tersebut. [Diberi: $f = 0.35$; $k_d = 1.1 \times 10^{-3} \text{ s}^{-1}$; $k_p^2/k_t = 16.0 \text{ L mol}^{-1} \text{ s}^{-1}$]
- (ii) Dalam eksperimen yang sebenar, berat molekul PMMA yang diperoleh ialah $2.7 \times 10^4 \text{ g mol}^{-1}$, menunjukkan tindak balas pemindahan rantai telah terjadi. Andaikan pemindahan rantai ke pelarut sahaja berlaku, cari nisbah kepekatan toluena terhadap MMA jika diketahui bahawa pemalar pemindahan rantai, C_s ialah 1.5.

(11 markah)

3. (a) Lukiskan struktur kopolimer yang terhasil daripada suatu campuran 1,4-divinil benzena, $\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2)_2$, dan stirena dengan nisbah 1:5.
- (i) Apakah kesan menambahkan nisbah divinil benzena ke atas kestabilan dimensi kopolimer ini?
- (ii) Katakan anda mempunyai dua butir manik bahan ini, satu mengandungi 1 % divinil benzena dan yang satu lagi 10 % divinil benzena. Bagaimanakah anda dapat membezakan kedua-duanya hanya dengan menggunakan sebikar toluena? Beri sebab bagi kesan yang dilihat itu.
- (6 markah)
- (b) Huraikan mengenai morfologi polimer. Beri garis kasar **satu** faktor yang mempunyai pengaruh ke atas morfologi polimer.
- (6 markah)
- (c) Anda diberikan tiga polimer: *cis*-1,4-poliisoprena, polistirena dan poliakrilonitril.
- (i) Lukiskan struktur unit ulangan bagi setiap polimer.

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- (ii) Jelaskan bagaimana polimer-polimer tersebut dapat dibezakan dengan menggunakan tiga kaedah analisis berikut: Spektroskopi Inframerah (IR), spektroskopi Resonans Magnetik Nukleus (NMR) dan Kalorimetri Pengimbasan Pembezaan (DSC) atau sebarang kaedah lain yang anda tahu.
(13 markah)
4. (a) Pemula radikal bebas boleh dikelaskan kepada empat jenis umum: peroksida (atau hidroperoksida), sebatian azo, pemula redoks dan pemulafoto.
- (i) Tuliskan nama dan struktur bagi setiap jenis.
(ii) Apakah kelebihan utama pemfotomulaan?
(8 markah)
- (b) Senaraikan perbezaan antara pempolimeran radikal bebas dan pempolimeran ionik.
(7 markah)
- (c) Lazimnya suatu monomer boleh dipolimerkan sama ada melalui pempolimeran anionik atau kationik. Namun, polistirena boleh dibentuk daripada stirena melalui pempolimeran anionik dan kationik serta radikal bebas. Jelaskan.
(10 markah)
5. (a) Tuliskan satu takrifan yang jitu bagi setiap istilah berikut:
- (i) Indeks kepolisebaran.
(ii) Jejari hidrodinamik.
(iii) Sindiotaktik.
(iv) Elastomer termoplastik.
(10 markah)

- (b) Masa pengaliran di dalam kapilari viskometer bagi larutan poli(isobutena) di dalam toluena pada 25 °C adalah seperti berikut:

Kepekatan/g cm ⁻³	0.008	0.008	0.012	0.016
Masa/saat	200	246	298	357

Masa pengaliran bagi pelarut tulen adalah 160 saat.

- (i) Tentukan kelikatan intrinsik bagi polimer ini dalam toluena pada 25 °C.
- (ii) Kirakan berat molekul purata-kelikatan bagi poli(isobutena).
Diberikan parameter Mark-Houwink bagi poli(isobutena) di dalam toluena pada 25 °C sebagai $K = 8.7 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$ dan $a = 0.56$.

(15 markah)