MATERIALS AND POLYMER CHEMISTRY

CHE-5350Y

Time allowed: 2 hours

Answer THREE questions.

You are advised to spend an equal amount of time on each question.

All questions carry an equal number of marks.

Answer EACH question in a SEPARATE answer book.

The breakdown of marks within each question is indicated by the percentage figures in brackets on the right.

Do not take this paper out of the examinations room.

Notes are not permitted in this examination.

Do not turn over until you are told to do so by the Invigilator.
1. Answer **ALL** parts (a) to (d).

(a) (i) Explain, with the use of diagrams, how tetrahedral and octahedral interstitial sites are formed by the close packing of spheres. [20%]

(ii) How many tetrahedral and octahedral sites are there per close packed sphere? [5%]

(b) (i) What is the difference between a point group and a space group? [10%]

(ii) Explain, with an example of each, what is meant by a glide plane and a screw axis. [10%]

(c) (i) Draw the unit cell for the perovskite structure. [10%]

(ii) Show that this structure is consistent with the stoichiometry ABO$_3$. [10%]

(iii) What are the co-ordination numbers of the A, B and O ions? [5%]

(d) Index the diffraction peaks, and determine the lattice parameter, $a$, for the cubic unit cell, if diffraction peaks are seen at $2\theta = 22.4^\circ$, $56.8^\circ$, $71.4^\circ$, $80.4^\circ$) for a cubic cell using Cu K$_\alpha$ X-rays of wavelength 0.154 nm. [30%]
2. Answer parts (a) and (b) and EITHER part (c) or part (d).

(a) Explain, using an appropriate sketch, the difference between atactic, syndiotactic, and isotactic side chains in a polyalkene. [20%]

(b) You are given a sample of polystyrene for analysis. Gel permeation chromatography (GPC) analysis suggests that the polymer mass distribution can be approximated by considering three fractions: 20 parts by number of mass $5.0 \times 10^5 \text{ g mol}^{-1}$, 40 parts by number of mass $6.5 \times 10^5 \text{ g mol}^{-1}$ and 40 parts by number of mass $8.5 \times 10^5 \text{ g mol}^{-1}$. Calculate the number-average molar mass ($M_n$), weight-average molar mass ($M_w$) and the dispersity ($D$) for this sample. Justify the accuracy of the values in your answer. [40%]

(c) Briefly outline how the GPC system in part (b) operates, including a sketch of the interior of a GPC column and detail of how absolute masses are determined. [40%]

(d) (i) Give a scheme for the formation of polycaprolactone from the monomer A, including any catalyst, intermediates and byproducts, and giving the structure of the final product. [20%]

(ii) Polycaprolactone has similar material properties to polyethylene: by comparing the molecular structures of the polymers, suggest an explanation for this. [15%]

(iii) Why might the use of polycaprolactone be favoured over polyethylene? [5%]
3. Answer **ALL** parts (a) to (c).

(a) (i) Write the equations describing the formation of a Schottky defect in NaCl and a Frenkel defect in AgCl. [20%]

(ii) Draw a plot of the variation in ionic conductivity with temperature for a material with a Schottky defect. [10%]

(iii) Explain the origin of the characteristic slopes of the plot. [10%]

(b) Explain, using band diagrams, why magnesium is a metal. [30%]

(c) Explain with reference to a plot of bulk magnetic susceptibility against temperature the difference between paramagnetic, ferromagnetic, anti-ferromagnetic and ferrimagnetic materials. [30%]
4. Answer **ALL** parts (a) to (f).

(a) Which of the following statements apply to a step polymerisation process?

(i) Monomer concentration decreases steadily;
(ii) Monomer, oligomers and polymers are present during the entire polymerisation reaction time;
(iii) Growing polymeryl chain adds one monomer at a time. [10%]

(b) Give a scheme for the reaction of B and C to give a linear polyamide (Nylon-66).

![Chemical structure](image)

[20%]

(c) Define the term *degree of polymerisation*. [10%]

(d) Reactions under step conditions require a high degree of polymerisation to yield high mass polymers. What feature of your scheme in part (b) mean that this is the case for the industrial formation of Nylon-66? [15%]

(e) Buta-1,3-diene can be polymerised using an anionic route using butyl lithium as an initiator. This process produces polymers of very narrow molar mass distribution as it follows a *living* mechanism.

(i) Explain what is meant by the term living polymerization. [15%]
(ii) Why does buta-1,3-diene polymerise under these conditions while ethene does not? [10%]

(f) A polymerisation of buta-1,3-diene is carried out under the living conditions described in part (e) with a monomer to initiator ratio of 5000 : 1. Assuming that the initiator mass can be ignored, what is the number-average molar mass of the resulting polymer? (Take the molar mass of hydrogen as 1.0 g mol⁻¹ and of carbon as 12.0 g mol⁻¹.) [20%]

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