Loughborough University

Further topics in Chemistry

22CMB107

Semester 2 22/23 In-Person Exam paper

This examination is to take place in-person at a central University venue under exam conditions. The standard length of time for this paper is **3 hours**.

You will not be able to leave the exam hall for the first 30 or final 15 minutes of your exam. Your invigilator will collect your exam paper when you have finished.

Help during the exam

Invigilators are not able to answer queries about the content of your exam paper. Instead, please make a note of your query in your answer script to be considered during the marking process.

If you feel unwell, please raise your hand so that an invigilator can assist you.

You may use a calculator for this exam. It must comply with the University's Calculator Policy for In-Person exams, in particular that it must not be able to transmit or receive information (e.g. mobile devices and smart watches are **not** allowed).

Relevant constants

Planck constant (h) = 6.626×10^{-34} J s

Gas constant (R) = 8.314 J K^{-1} mol^{-1}

Boltzmann constant (k) = 1.380×10^{-23} J K^{-1}

Speed of light (c) = 2.998×10^{8} m s^{-1}

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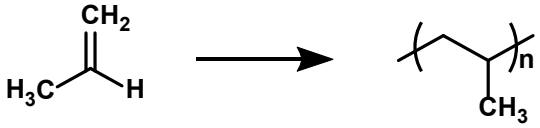
1. Answer **ALL** parts. Poly(propylene) is produced by the chain growth polymerisation of propene in the presence of a *Ziegler-Natta* catalyst in a fluidised bed reactor. *Ziegler-Natta* catalysts are a class of heterogeneous supported catalysts based on titanium compounds.



a. The choice of specific catalyst for the polymerisation will determine the tacticity of the final poly(propylene).

i. Define atactic, syndiotactic and isotactic monomer arrangements, and discuss how tacticity impacts polymer physical properties with respect to crystallinity and glass transition temperature.

[5 marks]

ii. A supported bis(salicylaldiminato)titanium catalyst was selected, which produced syndiotactic poly(propylene). This material was studied and shown to be of comparable stereoregularity and crystallinity to isotactic poly(propylene). However, it was more pliable at room temperature and had greater impact strength. Using your knowledge of all factors that influence polymer physical properties, explain this observation.

[4 marks]

b. Heterogenous Zeigler-Natta catalysts are predominantly used within industry although a number of homogeneous catalysts are available.

i. Explain the difference between homogeneous and heterogeneous catalysts.

[1 mark]

ii. Provide two possible reasons why a heterogeneous catalyst would be preferred in the discussed polymerisation reaction.

[2 marks]

iii. Explain how the catalyst influences the reaction, taking into account the tacticity of the poly(propylene).

[5 marks]

c. When conducting the polymerisation reaction described in 1a, some of the titanium catalyst (parts per million levels) will remain in the polymer. Specify an atomic spectroscopy method to determine the amount of titanium in the polymer. Your answer should give details on how the sample will be prepared and on how standardisation will be accomplished.

[8 marks]

Continued…

2. Answer **ALL** parts

a. Define the term chemisorption and explain its relevance to heterogeneous catalysis.

[5 marks]

b. The adsorption of a species onto a surface is in dynamic equilibrium with the associated gas. Using rate laws for adsorption and desorption, given below, obtain the Langmuir adsorption isotherm using surface coverage (θ), pressure (p) and the adsorption equilibrium constant (K).

$$v = k_a p(1 - \theta)$$

$$v = k_d \theta$$

[5 Marks]

c. Considering a bimolecular ($A_{(g)} + B_{(g)} \rightarrow C_{2(g)}$) reaction on a catalyst that follows a Langmuir-Hinshelwood mechanism.

i. Explain the defining concepts of the Langmuir-Hinshelwood mechanism.

[2 Marks]

ii. The reaction is performed at 1 bar pressure in a gas mixture of 5% A and 95% B. Given that K_A= 190 bar^{-1} and K_B =0.05 bar^{-1} provide a simplified rate law and the reasoning for your choice.

[4 marks]

iii. Given the information above draw a diagram showing the expected change in reaction rate when varying the composition of A in the gas mixture. Briefly discuss how the observed change in rate is related to surface coverage.

[4 marks]

iv. The adsorption equilibrium constant (K) of A and B was found to change when its morphology was altered from a cube to an octahedron. Explain why K would change and how it would impact on catalyst performance.

[5 marks]

Continued…

3. Answer **ALL** parts

a. Laser ablation (LA) can be used to perform sampling of a calcium phosphate coating on a titanium alloy, prior to analysis by ICP-MS or ICP-OES.

i. Sketch a labelled diagram of the apparatus required to perform laser ablation sampling.

[5 marks]

ii. Explain the advantages and disadvantages of sampling the coating by LA, compared to digesting the alloy and analysing it in liquid form.

[5 marks]

b. For the following analyses, select the most appropriate technique from FAAS, FAES, ICP-OES, ICP-MS or LIBS. Explain your choice of technique and give details and reasoning for any particular sample preparation, sample introduction or other instrumental details that are relevant.

i. Sorting of scrap metals and metal alloys as part of an industrial recycling process.

[5 marks]

ii. Determination of the size and particle number concentration of titanium dioxide nanoparticles in sunscreens.

[5 marks]

iii. Identification of the three MRI contrast agents shown in Figure 1 in wastewater.

[5 marks]

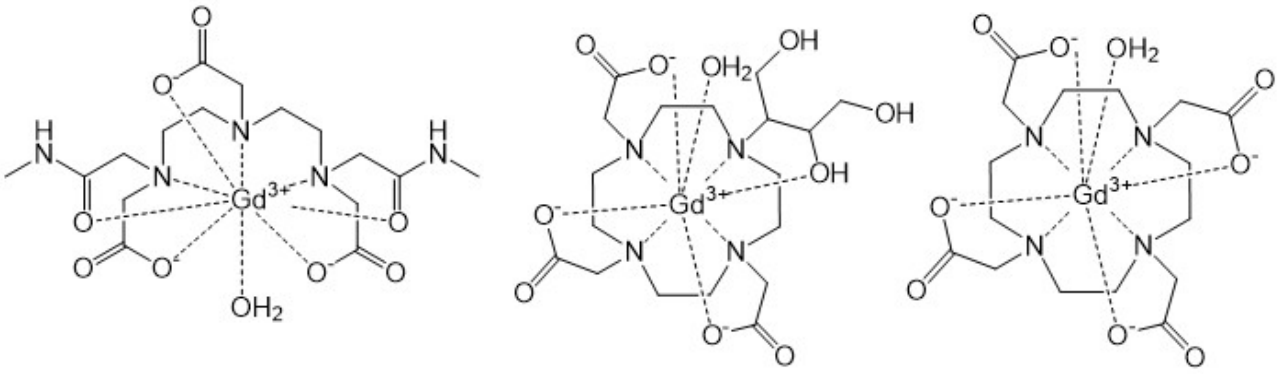


Figure 1. Structures of three MRI contrast agents. From left to right: Omniscan (Gd-DTPA-BMA), Gadovist (Gd-BT-DO3A), Dotarem (Gd-DOTA).

Continued…

4. Answer **ALL** parts

a. Define the following terms:

i. Number average molar mass
ii. Weight average molar mass
iii. Dispersity
iv. Degree of polymerisation

[2 marks]

b. Osmometry measurements carried out on a solution of poly(styrene) in toluene at the theta temperature at a concentration of 0.02 g/mL gave an osmotic pressure (π) of 74 Pa. The PDI of the sample is 2.32. Calculate, showing your working:

i. The number average molecular weight

$$\left(\frac{\pi}{c}\right) = \frac{RT}{M_n}$$

[3 marks]

ii. The weight average molecular weight

[2 marks]

iii. Explain why it is important to perform osmometry measurements in theta conditions?

[2 marks]

c. Chain growth and step growth polymerisations are the two main classes of polymerisation.

i. Explain the difference between each class with respect to polymer chain growth profile and consumption of monomer in the reaction.

[2 marks]

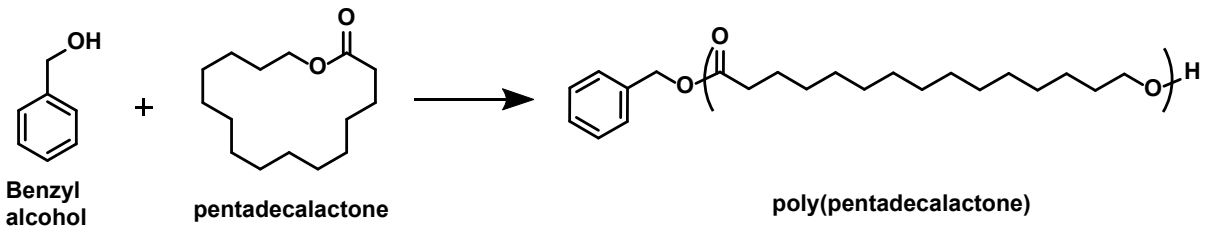
ii. Draw the expected profile for each class showing growth of chain molecular weight over reaction time. Justify your answer to this question.

[3 marks]

iii. Provide an example of a step growth polymerisation, using chemical structures.

[4 marks]

d. 100 g of ω-pentadecalactone (240.38 g/mol) was polymerised using ring-opening polymerisation to form poly(pentadecalactone), using 0.45 g of benzyl alcohol (108.14 g/mol) as initiator in the presence of an yttrium phosphasalen catalyst.



Benzyl alcohol + **pentadecalactone** → **poly(pentadecalactone)**

i. Calculate the average molar mass of the resultant polymer.

[5 marks]

ii. Poly(pentadecalactone) is often considered a possible environmentally friendly alternative to poly(ethylene). Explain this rationale.

[2 marks]

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