IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2013, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

ADVANCED CHEMISTRY THEORY IIIA

Paper 1

Monday 07th January 2013, 09:30-12:30

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

3.I2 – Advanced Main Group Chemistry

Answer part a) **AND** any **TWO** parts from b), c) and d) of this question.

a) Answer **BOTH** parts of this question.

i) Outline a synthetic route to a disilyne that is stable towards self-reaction. Similarly, outline a route to a stable diplumbene using $PbBr_2$ as a starting material. In each case, describe the most important structural features of the unsaturated compounds. What types of reactions they might undergo? Give examples.

(11 marks)

ii) In what ways does a disilyne differ from an alkyne, and how does a diplumbene differ from an alkene?

(4 marks)

b) Draw the structure of BrF_4^+ and use a simple molecular orbital diagram to account for any differences in bond lengths present in the structure.

(5 marks)

c) Give two reasons to account for the difficulty in preparing a three-coordinate silyl cation, R_3Si^+. Give a synthetic route to a stable R_3Si^+ species that enables these difficulties to be overcome.

(5 marks)

d) What is meant by the term "weakly coordinating anion"? Give an example of such an anion, show how it can be made, and give an example of its use in main group chemistry.

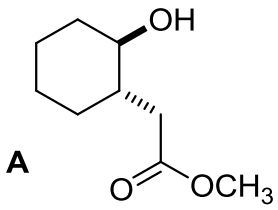
(5 marks)

3.O11 – Synthesis Part 2

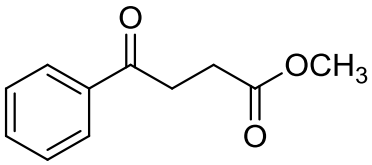
Answer **ALL** parts of this question.

a) For each of the compounds **A** and **B** shown below, show a simplifying C–C bond disconnection. Identify the synthons implied by your disconnections, and write down the synthetic equivalents of the synthons.

(2 x 5 marks)



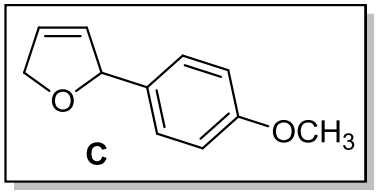
A



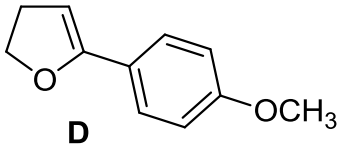
B

b) Explain how compound **C** below may be disconnected using a Heck reaction, identifying the reactants you would use in the forward reaction. Explain why the Heck reaction you have proposed gives **C** as the product, rather than the isomeric compound **D**.

(5 marks)



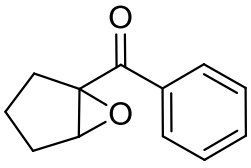
C



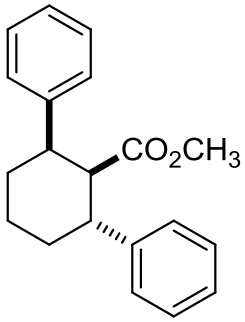
D

c) Devise a synthesis of **EITHER** compound **E OR** compound **F** shown below. Show clearly your retrosynthetic analysis, identifying synthons and synthetic equivalents where necessary. Propose reagents for your forward synthesis.

(10 marks)



E



F

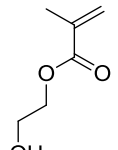
3.O3 – Polymers – The Essential Guide

Answer **ALL** parts of this question.

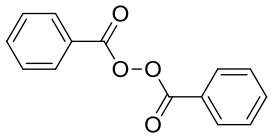
a) Answer **ALL** parts of this question.

i) Define "chain transfer" and provide mechanistic details for one of the possible chain transfer process in the polymerisation of 2-hydroxyethyl methacrylate (**A**) thermally initiated with benzoyl peroxide (**B**) in the bulk.

(6 marks)



A



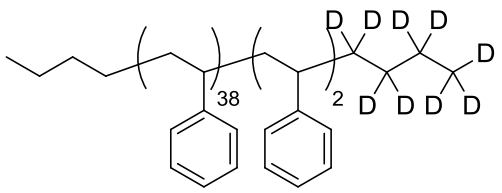
B

ii) Draw out the exact molecular structure of poly(2-hydroxyethyl methacrylate) for a degree of polymerisation of 98, prepared as described in part i) assuming comproportionation as the only termination reaction.

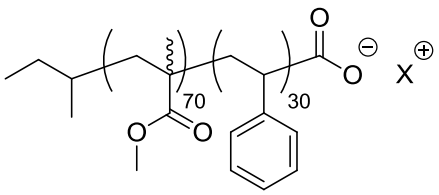
(4 marks)

b) Answer any **FIVE** of the EIGHT parts i) – viii) of this question.

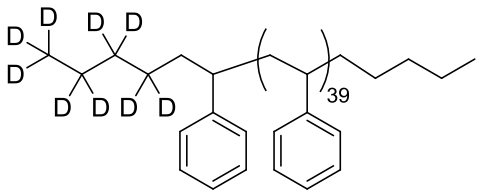
Polymers **C**-**F** have been synthesised by living anionic polymerisation. Each polymerisation was terminated with an appropriately chosen electrophile.
Note: You only have access to fully hydrogenous and fully deuterated chemicals.



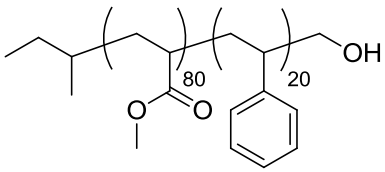
C



E



D



F

QUESTION CONTINUED OVERLEAF

i) Identify the necessary reagents, specify their stoichiometry and provide mechanistic details for the initiation, propagation and termination reaction in the synthesis of **C**.

(3 marks)

ii) Identify the necessary reagents, specify their stoichiometry and provide mechanistic details for the initiation, propagation and termination reaction in the synthesis of **E**.

(3 marks)

iii) Suggest a suitable termination agent for the synthesis of **F**, requiring the smallest number of synthetic steps.

(3 marks)

iv) Identify the cation "**X**" in polymer **E** and the reagents for the synthesis of **D**.

(3 marks)

v) Which polymer in pairs **C**/**D** and **E**/**F** possesses the lower T_g? Explain.

(3 marks)

vi) Suggest a chain transfer agent for a living anionic polymerisation process and provide mechanistic details for the chain transfer step.

(3 marks)

vii) Suggest the synthesis of a triblock copolymer by selecting from **C**-**F**. Include all necessary reagents.

(3 marks)

viii) Specify the monomer to initiator ratios used in the synthesis of **C**-**F**.

(3 marks)

3.P3 – Molecular Reaction Dynamics

Answer any **TWO** of the three parts a), b) and c) of this question.

There is an attached sheet of equations that you may find useful.

a) Answer **BOTH** parts of this question.

i) Draw and label the key components of a femtosecond transient absorption experimental set up. Briefly explain each component, and outline the key properties of the laser beams that are required.

(5 marks)

ii) Discuss, in terms of classical mechanics, the observation that the reaction $F + HCl \rightarrow Cl + HF$ is approximately five times as efficient when HCl is in the first vibrationally excited state than when it is in its ground vibrational state, although HCl has the same total energy (kinetic + vibrational). Assuming that the interaction is collinear, draw two-dimensional potential energy surfaces to explain this observation.

(7.5 marks)

b) Answer **BOTH** parts of this question.

i) An electron can cross a 40 Å thick biological membrane in less than 10 ms via electron transfer reactions using three molecular species. Explain why the membrane is too broad to be bridged by a single donor-acceptor electron relay pair.

Be as quantitative as possible in your discussion, stating clearly what assumptions are made in any calculation (you may take the electron tunnelling coefficient to have a value of 1.4 $Å^{-1}$). Ensure that you define every term used in your calculation and explain the meaning of any equations that you use.

(6.5 marks)

ii) To study the dynamics of a chemical reaction it is necessary to employ a triggering mechanism to initiate the reaction. Briefly discuss three triggering techniques, highlighting their advantages and limitations.

(6 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **BOTH** parts of this question

i) Demonstrate that an observable calculated from an eigenstate does not vary with time even when the time-dependent part of the wavefunction is taken into account. Define each symbol that you use in your derivation.

(5 marks)

ii) Demonstrate that an observable calculated from a linear superposition of two eigenstates does show oscillations in its value as a function of time. Define each symbol that you use in your derivation.

(7.5 marks)