IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES –MAY 2016, 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 IIIB

Paper 1

Thursday 05th May 2016, 09:30-12:30 (maximum)

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 any **FIVE** of the following six parts of this question

a) Give an example of the synthesis of a stable distannyne using a tin halide precursor. How might such a distannyne be used to effect the industrially important separation of propane from propene? Comment on the likely viability of such a process on a large scale.

(5 marks)

b) Sketch the HOMO and the LUMO for a simple silylene. Comment on the donor/acceptor nature of such a species. What are the likely products from the reaction of a silylene with:

i) Et_3SiH

ii) Ethene

(5 marks)

c) Give two properties for a molecule to be a useful MOCVD precursor. Give a precursor both for In and for P, for making InP by CVD processes. Give a balanced equation to show the reaction taking place in the formation of the InP using your precursors.

(5 marks)

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

The stannylium cation $(Mes)_3Sn^+$ was synthesized *via* the following route:

Identify **R** and **A**. Draw a plausible curly arrow mechanism for this reaction via intermediate **B**.

(3 marks)

e) Describe the expected structure of the stannylium cation and what experimental data would confirm it.

(2 marks)

QUESTION CONTINUED OVERLEAF

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

Group II complexes have good catalytic activity in a variety of useful transformations.

i) Write the equation for a hydroamination reaction and identify a suitable Ca catalyst for this reaction.

(2 marks)

ii) Draw a plausible catalytic cycle for the reaction in fi).

(3 marks)

g) Give an example of reversible H_2 activation by a Frustrated Lewis Pair *via* the electron transfer mechanism. Contrast this reactivity to the reaction of a digermyne with H_2 and comment on their relative utility in catalysis.

(5 marks)

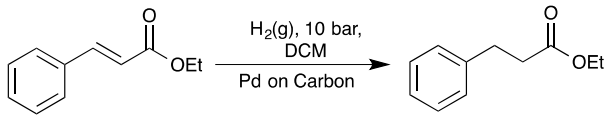
3.I12 – Flow Chemistry

Answer part a**)** and **EITHER** part b**) OR** part c**)** of this question.

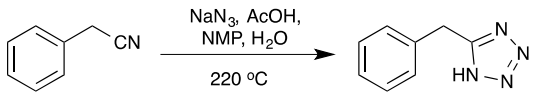
a) Answer **ALL** parts of this question.

Discuss the possible advantages of conducting the reactions shown below under flow conditions.

- Reaction 1

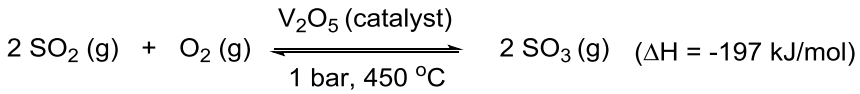


- Reaction 2

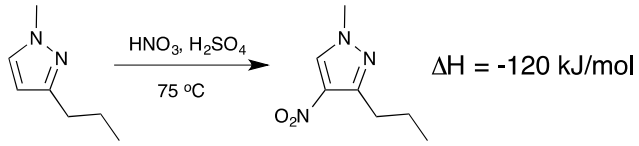


NMP = N-Methyl-2-pyrrolidone, high boiling point solvent

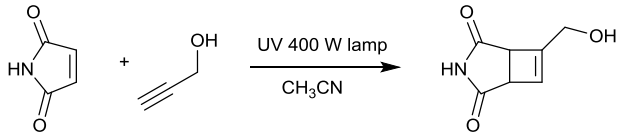
- Reaction 3



- Reaction 4



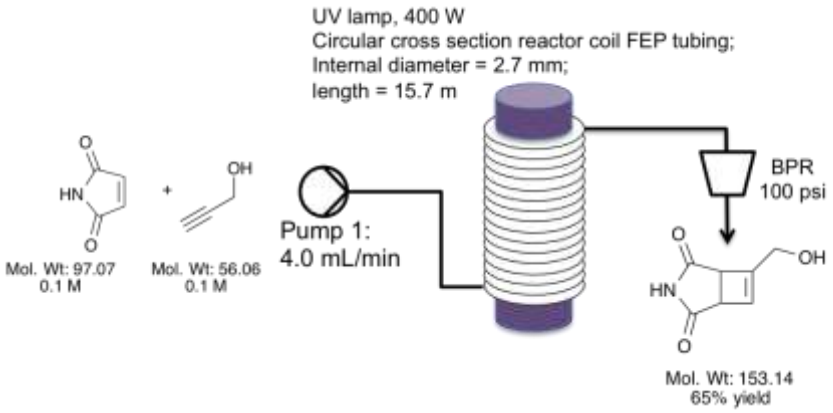
- Reaction 5



(5 x 3 marks)

QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts using the information in the scheme below.



i) Calculate the volume of the reactor coil.

(1 mark)

ii) Calculate the amount of product produced if the reaction system is left running in continuous flow for 24 hrs.

(4 marks)

iii) Suggest a method for scaling-up this reaction in flow.

(1 mark)

iv) Determine if the reaction is operating under a laminar flow regime. The density and viscosity of the reaction mixture are: 0.8 g cm^{-3} and 8.9 x10^{-4} kg m^{-1} s^{-1} respectively.

(4 marks)

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

i) Define 'laminar flow' and discuss the advantages and disadvantages of this flow regime.

(4 marks)

ii) Explain how the following techniques can be used to enhance mixing under laminar flow regimes; use a diagram if necessary:

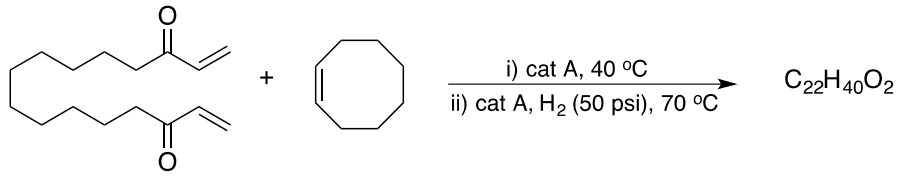
- Droplet based microfluidics
- Chaotic advection
- Hydrodynamic focusing

(6 marks)

3.O1 – Organometallic Complexes in Organic Synthesis

Answer any **FIVE** of the six parts a)-f) of this question.

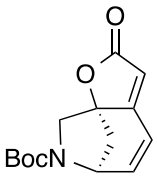
a) Predict the product of the following transformation involving tandem catalysis. Explain the use of the term tandem catalysis in this example.



cat A = a ruthenium carbene complex

(5 marks)

b) The butenolide shown below was generated by a transformation described as a hetero-Pauson-Khand reaction. Write down the structure of the monocyclic substrate and assign the stereogenic centre in the substrate as *R* or *S* giving your reasoning. [Boc = C(O)OBu^t]

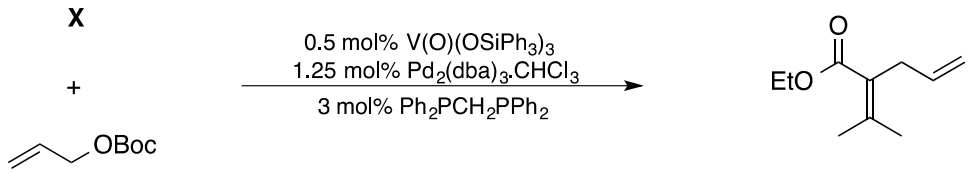


(5 marks)

c) Propose a catalytic cycle to represent the transition metal catalysed trimerisation of an alkyne and suggest a catalyst for the reaction.

(5 marks)

d) Write down the structure of the missing substrate **X**. The ratio of [Pd]:[V] is high (5:1). Suggest a by-product that might be generated if this ratio is lowered. [Boc = C(O)OBu^t; dba = dibenzylideneacetone]



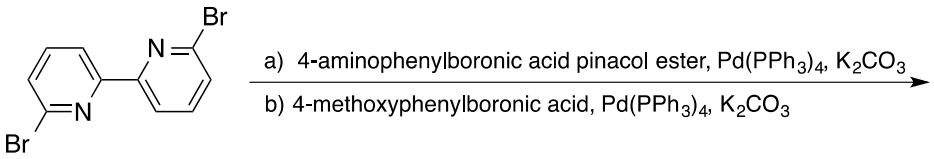
(5 marks)

QUESTION CONTINUED OVERLEAF

e) Propose a catalyst for the reaction depicted below and suggest two roles for the *N*-oxide functional group (detail not required).

(5 marks)

f) Consider the reaction below and then write down the structure of the two boron-containing reagents and the structure of the unsymmetrical product.



(5 marks)

3.O7 – Polymers

Answer part a) and **EITHER** part b) **OR** part c) of this question.

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

Give a brief definition of the following terms:

i) freely jointed chain, crystallite, annealing

(3 marks)

ii) The refractive index of an amorphous polymer changes abruptly with temperature. Explain this phenomena.

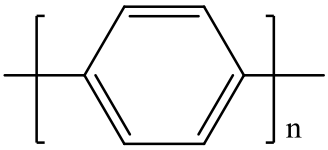
(3 marks)

iii) Explain the fundamental differences between x-ray scattering and neutron scattering with respect to the structural determination of polymers.

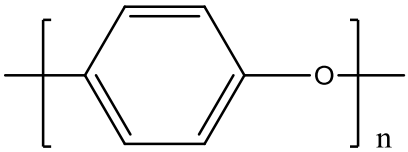
(2 marks)

iv) Which of the two polymers below **A** or **B** will have a higher Tg? Explain why.

(3 marks)



A



B

v) Explain the concept of Scherrer line broadening. How might this be overcome?

(2 marks)

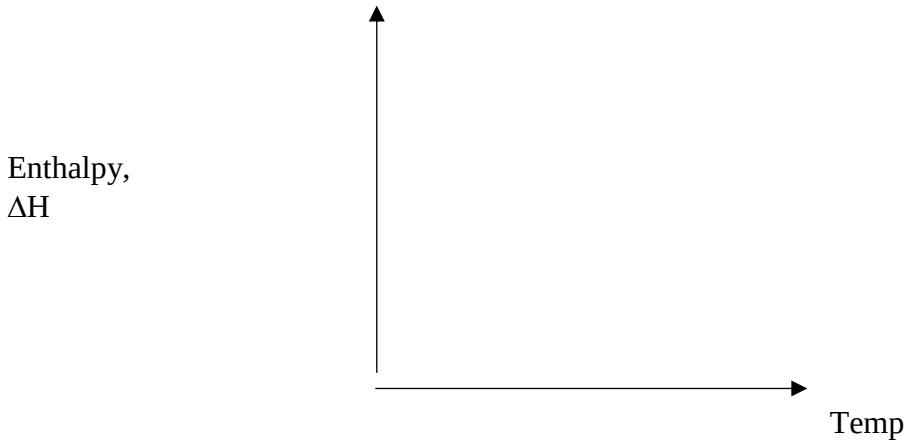
vi) Explain what sources of line broadening are present in solid state NMR. How are these effects minimised?

(3 marks)

vii) On page 8 is a series of DSC curves (on heating) for a series of different polymers, explain the shape of the curves. What conclusions can be drawn about the structure of the polymers from this data?

(4 marks)

QUESTION CONTINUED OVERLEAF



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

i) Explain how T_1 ^1H relaxation times in NMR spectroscopy can be used to determine the degree of crystallinity in a polymer.

(2 marks)

ii) Phenol (C_6H_5OH) and formaldehyde (methanal) $H_2C=O$ are reacted together in a ratio of 1:3, in presence of an acid catalyst. Using your knowledge of organic chemistry predict a structure for this. Name two methods that might be used to characterise the final product.

(3 marks)

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

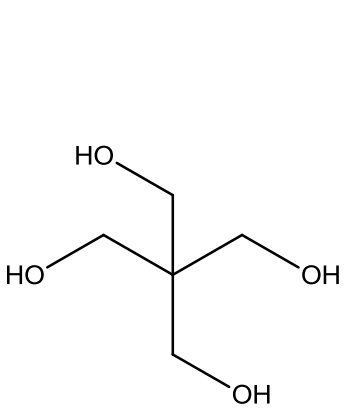
i) Sulphur, readily polymerises upon heating. Sketch a DSC curve (on heating) for the sulphur polymer that has been rapidly quenched in water from the melt and then partially heated **below** Tg.

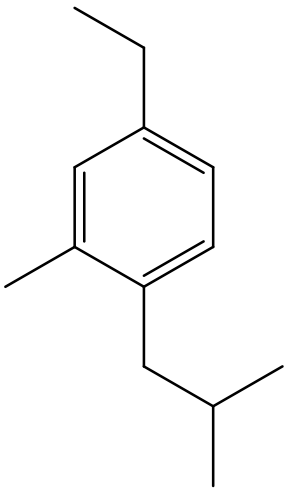
(2 marks)

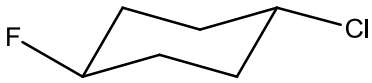
QUESTION CONTINUED OVERLEAF

ii) Define plasticisation and anti-plasticisation for a polypropylene polymer. For the following molecules below choose which is the best one for plasticisation and justify your choice?

(3 marks)







3.P10 – Soft Condensed Matter

Answer part a) and **EITHER** part b) **OR** part c) of this question.

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

i) With the help of appropriate diagrams explain the physical origin of the hydrophobic interaction in terms of enthalpy and entropy terms.

How does the hydrophobic interaction vary with temperature?

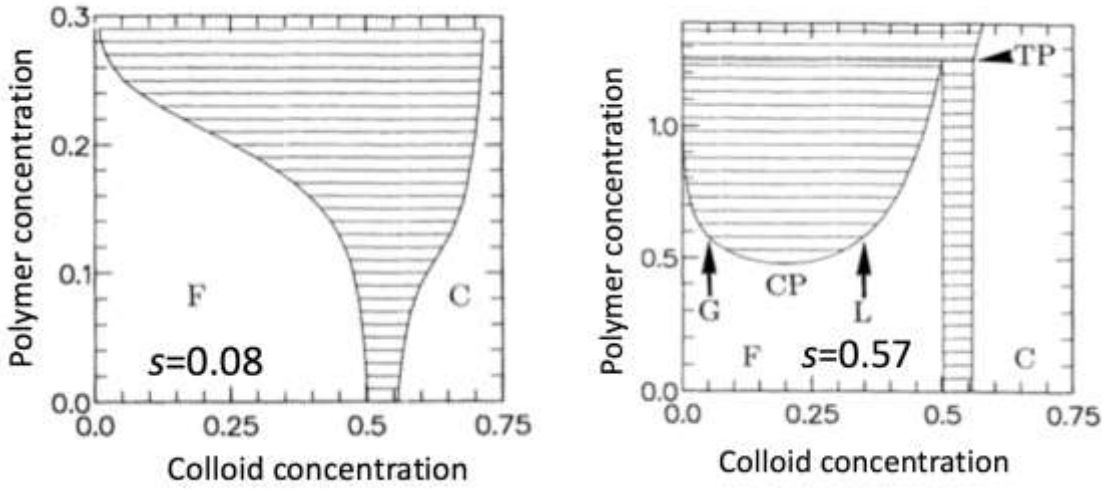
(3 marks)

ii) The phase diagram of colloid-polymer mixture changes significantly upon modifying the ratio, *s*, of the diameters of the polymers and colloids.

Explain this experimental observation.

Note: F, C, L and G, indicate fluid, crystal, liquid and gas phases.

(2 marks)



iii) A binary mixture demixes by forming primarily spherical nuclei.

Show that the nuclei are formed at a rate, *k*, given by:

$$k \propto \exp(-\frac{\Delta F^*}{k_B T}) \text{ where, } \Delta F^* = 16\pi\gamma^3/(3\Delta F_v^2).$$

In what region of the phase diagram does the demixing take place?

(6 marks)

QUESTION CONTINUED OVERLEAF

iv) Calculate the work needed to stretch a polymer chain in solution, from its ideal size, 1 μm, to 3 μm.

You may assume the polymer chain can be modelled using the Freely Jointed Chain theory.

(5 marks)

b) Answer **ALL** parts of this question

i) Show that the mean field energy of mixing for a binary mixture is given by:

$$\Delta U_{mix} = \frac{Nz}{2}\left[2\varepsilon_{ab} - \varepsilon_{aa} - \varepsilon_{bb}\right] x_a x_b$$

Explain "all" your working.

(7 marks)

ii) Sketch the phase diagram of a binary mixture. Your answer should show the spinodal and binodal lines and how these are defined in terms of the Helmholtz free energy of the mixture.

(2 marks)

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

i) The mean square displacement of a colloid in the ballistic regime varies as t^n, where n is an integer. Derive an equation for the mean square displacement and find the value of the exponent n.

(6 marks)

ii) Estimate the relaxation time required to observe viscoelastic behaviour in a suspension consisting of colloids with diameter 1 μm and diffusion coefficient $D_{colloid} = 10^{-13}$ m^2/s.

(3 marks)

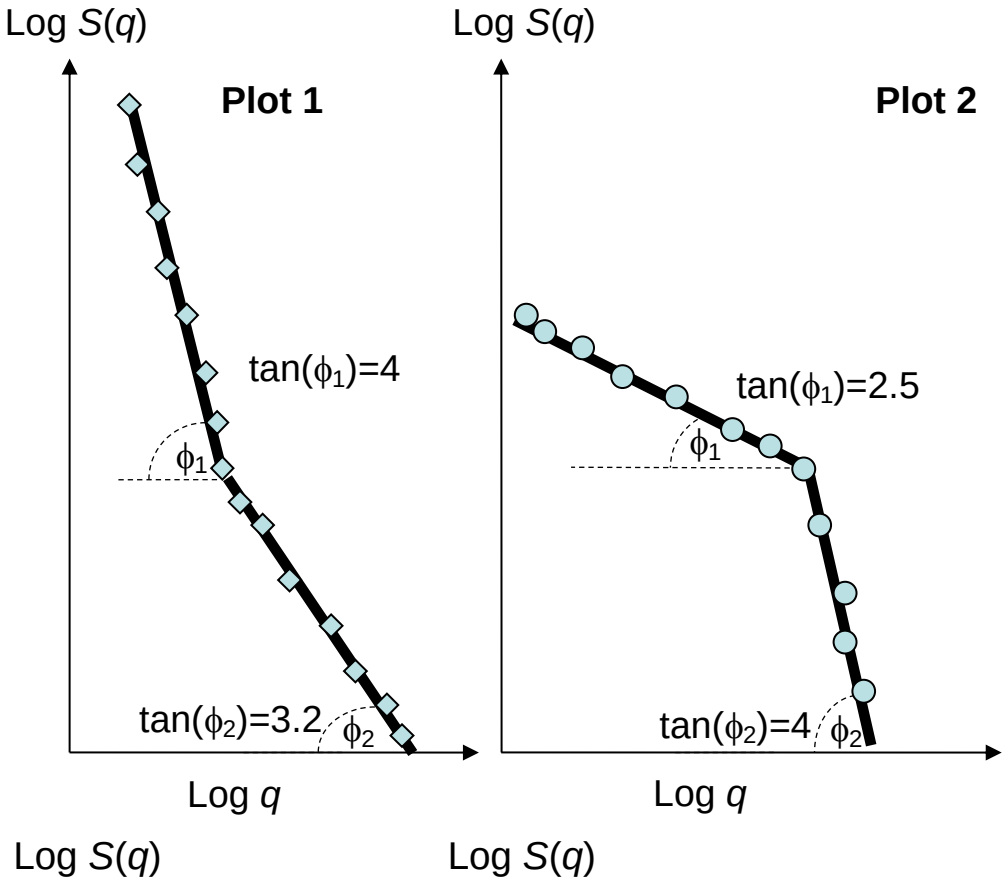
CH3.CMP8 – Complexity

Answer part a) **AND** either b) **OR** c) or d) of this question.

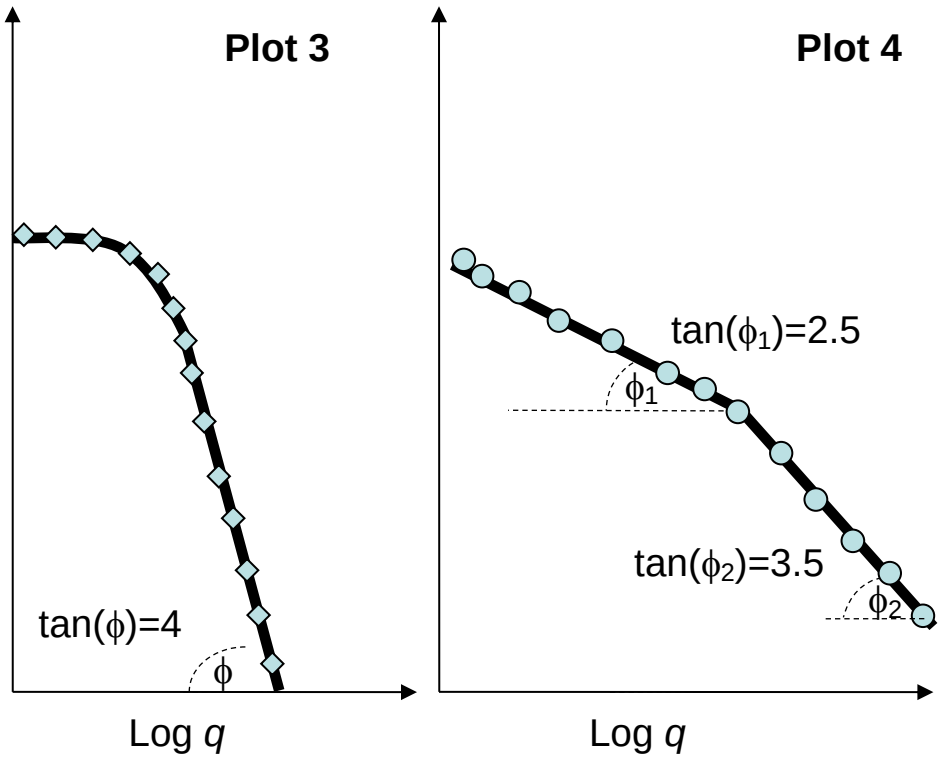
a) Answer all parts of this question.

(12 marks)

Small angle X-ray scattering intensities from four powder catalysts are shown below as functions of momentum-transfer. What can you deduce about the ***morphology and mechanisms of growth*** of each sample, looking at these graphs? Explain the principles of interpretation of these kinds of data (3 marks) and interpret each graph (2.5 marks per graph).



QUESTION CONTINUED OVERLEAF

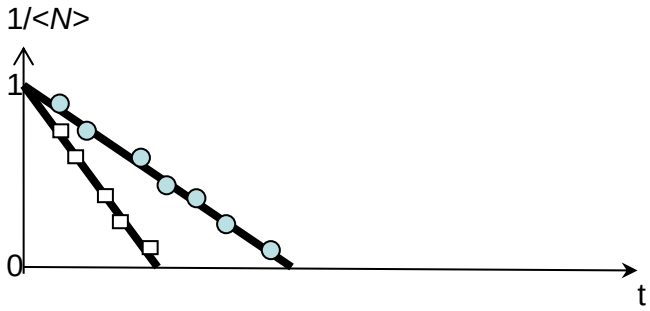


b) Answer all parts of this question:

The time evolution of average mass, <*N*>, of ***growing colloidal clusters*** was studied in solutions with two different starting concentrations of single particles, see two data sets:

○ □

in the graph below.



i) Which aggregation mechanisms could one assign to these two systems? Base your answer on the extended Smoluchowski theory of aggregation kinetics.

(4 marks)

QUESTION CONTINUED OVERLEAF

ii) Put down the system of Smoluchovski equations and specify the kernel for this mode of growth. Give physical interpretation to this kernel.

(4 marks)

iii) Explain the meaning of the slopes of these curves and the point at which theses straight lines reach zero.

(2.5 marks)

iv) Which of the data sets correspond to higher initial concentration?

(2.5 marks)

c) Answer **ALL** parts of this question:

i) Consider a ***random site percolation*** on a one dimensional grid. What will be the ratio of the averages sizes of the clusters, if the probability *p* of site occupation is 30% and if it is only 45%?

(2.5 marks)

ii) Check how will the same ratio change for percolation on a Bethe lattice with Z=3?

(2.5 marks)

iii) Compare the results for (i) and (iii) and explain the difference qualitatively

(3 marks)

iv) A forest was planted on a square grid. If the probability of ignition of each tree at extreme drought condition is 60%, what will be the ratio of the number of trees on fire after time t_1 and time t_2 if $t_2 / t_1 = 2$ under unchanged conditions?

(5 marks)

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

Analysis of the spectral density *S*(*f*) of the noise patterns

 (a)  (b)

shows that $S(f) \propto 1/f^{\beta}$ where $\beta = 1.2$ (a) and $\beta = 2.9$

i) What is the Hurst exponent of these random processes and what kind of processes are these?

(5 marks)

QUESTION CONTINUED OVERLEAF

ii) What are the fractal dimensions of the lines generated by these “noises”?

(5 marks)

iii) If the same processes span in X and Y directions, what will be the fractal dimensions of the correspondingly generated surfaces?

(3 marks)