CHEMISTRY 363

Physical Chemistry

Class Test 12.00 noon, Wednesday 7 September, 2005

Instructions:

Answer **ALL** questions.

Write your answers in the provided booklet.

Total marks: 50 (marks per question are as indicated).

Time allowed: 50 minutes

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1. (25 marks)

   (a) Explain briefly the following terms:

   (i) Hamilton's equations of motion;
   (ii) variation principle,
   (iii) raising operator.

   (b) Show that $[L^2, L_z] = 0$.

   What is the significance of the result?

   (c) Use the system of a particle in a cubic box to explain the term "degeneracy".

   (d) Show that the energy levels in the Hückel approximation for the allyl radical ion, ($C_3H_5^+$), are $E = \alpha, \alpha \pm \sqrt{2}\,\beta$. What are the parameters α and β?

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2. (25 marks)

(a) In a particular polycondensation process, poly(butylene terephthalate), PBT, is made from reaction between 12.0 mol butylene glycol, 12.0 mol terephthalic acid and 0.1 mol acetic acid.

(i) After 3 hours of polymerization time, 75 % of the carboxylic acid groups in the system have reacted. Calculate the number-average degree of polymerization, $\overline{DP}_n$, of the PBT at this stage.

(ii) After 12 hours of polymerization time, the maximum possible conversion of functional groups has been attained. Calculate $\overline{DP}_n$ for the final PBT product that is obtained at this stage.

(iii) In this example, $\overline{DP}_n$ of the final polymer product is controlled through addition of a small amount of a monofunctional reagent. Briefly outline another strategy for controlling $\overline{DP}_n$ in step-growth polymerization.

(b) Benzoyl peroxide is dissolved to a concentration of 0.01 mol L^{-1} in acrylonitrile, and polymerization is allowed to take place at 60°C. Use the information given at the end of this part of the question to carry out the following tasks:

(i) Calculate the initial steady-state rate of polymerization.

(ii) Given that termination occurs exclusively by combination and that no chain transfer reactions occur, calculate the number-average degree of polymerization, $\overline{DP}_n$, of the polyacrylonitrile made during the initial stage of the polymerization.

(iii) Calculate the time it takes to produce a polymer chain of average length during the initial stage of the polymerization.

[Given information: For this system, rate coefficient for initiator decomposition $k_d = 3 \times 10^{-4}$ s^{-1}, initiator efficiency $f = 0.4$, monomer density = 0.8 g cm^{-3}, monomer molar mass = 53 g mol^{-1}, rate coefficient for propagation $k_p = 1960$ L mol^{-1} s^{-1}, and rate coefficient for termination $k_t = 7.8 \times 10^7$ L mol^{-1} s^{-1}.]

(c) One of the fundamental differences between step- and chain-growth polymerizations is in the way $\overline{DP}_n$ varies with conversion. Referring to your answers to parts (a) and (b), outline this difference.