PRINCE OF SONGKLA UNIVERSITY

FACULTY OF ENGINEERING

Midterm Examination : Semester I | Academic Year : 2007

Date : 4 August 2007 | Time : 09.00 — 12.00

Subject : 230 - 463 Polymer Technology | Room : R 300

Student Name: ..... ID no. : .....

Number of questions : 4

Time : 3 hours

Total marks : 100

Books and notes are not allowed

Calculators are allowed

Writing in pencil is allowed

Question	Full Marks	Marks Received
1	24	
2	25	
3	25	
4	26	
Total	100	

ทุจริตในการสอบโทษขั้นต่ำคือ ปรับตกในรายวิชาที่ทุจริต และพักการเรียน 1 ภาคการศึกษา

Student Name: ..... ID no. : .....

1. a) Compare the characteristics of step and chain polymerizations.

   b) Write the repeating units of the following polymers: polyester, natural rubber, polystyrene and polyacrylonitrile

   c) Write a polymerization reaction when hexamethylene diamine, $H_2N(CH_2)_6NH_2$ reacts with adipic acid, $HOOC(CH_2)_4COOH$. What is the name of polymer formed?

   d) Why is chain transfer to initiator relatively unimportant in free radical chain reaction, even when the initiator's chain transfer constant is large?

   e) In a free radical chain polymerization, what would be the effect upon $\bar{x}_n$ when $[M_0]$ is increased 2 times at constant $[I_0]$?

   f) In a free radical chain polymerization of styrene, what would be the effect upon molecular weight and molecular weight distribution if the solvent used is changed from benzene to carbon tetrachloride?

   g) Write initiation and termination reactions for polystyrene using Lewis catalyst, BF_3 by cationic polymerization.

   h) Explain the catalyst systems used in co-ordination polymerization.

(24 marks)

Answer to Q1

Student Name: ..... ID no. : .....

2. a) In the stepwise polymerization of two monomers adipic acid, HOOC-$(CH_2)_4$-COOH and ethylene glycol, HO-$(CH_2)_2$-OH it was planned to add both reactants in stoichiometric amount. If ethylene glycol contains 1% methanol CH_3OH, calculate the $\bar{x}_n$ and $\bar{M}_n$ of the polymer formed when p =0.999.

Note that:

In the reaction of monomer types A-A and B-B with an excess of functional group type B the number-average degree of polymerization is given by

$$\bar{x}_n = \frac{1+r}{1+r-2rp}$$

where r = ratio of the functional group types in which $r \leq 1$

p = extent of reaction of the functional group type A

(5 marks)

b) Suggest how you would derive the equation given in question 2a).

(5 marks)

c) A polymerization system contains of 1.2 moles of a dicarboxylic acid (diacid), 0.4 moles of glycerol (triol) and 0.6 moles of ethylene glycol (diol).

2c.1 Would the gelation occur and at what extent of reaction?. Note that:

$$p = \frac{2}{f_{av}} - \frac{2}{\bar{X}_n f_{av}}$$

2c.2 Calculate p_c by statistics and branching coefficient, α_C.

Note that:

f = functionality of the branch unit

$$\alpha_c = \frac{1}{(f-1)} = \frac{rp_c^2\rho}{1-rp_c^2(1-\rho)}$$

$$r = \frac{\text{All number of F.G. type A}}{\text{All number of F.G. type B}} = \frac{N_A}{N_B}$$

$$\rho = \frac{\text{Number of F.G. type A in branch unit}}{\text{Number of F.G. type A in reaction mixture}}$$

(15 marks)

Student Name: ..... ID no. : .....

3. One hundred liters of methyl methacrylate, MMA is reacted with 5.0 moles of an initiator at 60 °C. No solvent is used. Initiator concentration can be assumed constant during the first 10 hours of reaction.

mol. wt. of MMA monomer is 100.1 g/mol

density of MMA monomer is 0.94 g/cm^3

k_p = 5.5 x 10^2 L/ (mol.s), k_t = 25.5 x 10^6 L/ (mol.s)

initiator half-life = 50 hours

initiator efficiency, f = 0.7

3a) Calculate the kinetic chain length.

3b) How much polymer has been made in the first 3 hours of the reaction?

3c) If termination occurs 80% by combination and 20% by disproportionation, estimate the $\bar{x}_n$ and molecular weight $\overline{M}_n$ of the polymer formed.

Note that:

$$\text{initiator half life} = \frac{\ln 2}{k_d}$$

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} (f k_d [I])^{1/2} [M]$$

$$-\ln \frac{[M]}{[M]_o} = \frac{k_p}{k_t^{1/2}} (f.k_d [I])^{1/2}. t$$

$$\nu = \frac{k_p [M]}{2 (f k_d k_t [I])^{1/2}}$$

(25 marks)

Student Name: ..... ID no. : .....

4. Styrene (monomer 1) at 4 mol. L^{-1} and methyl methacrylate (monomer 2) at 12 mol. L^{-1} concentration are copolymerized in the reactor at 60°C in benzene solution. The free radical reaction is initiated by adding 0.15 mol. L^{-1} of azobisisobutyronitrile. The reactivity ratios are $r_1 = 0.52$ and $r_2 = 0.46$.

   4.1 Plot F_1 vs. f_1 on the provided graph on page 12. What is the copolymer structure?

   4.2 Calculate the copolymer composition (in mole percent) formed at an early stage of the reaction.

   4.3 Will a composition drift occur? Why?

   4.4 Show how to derive an equation for azeotropic feed composition, f_c.

   4.5 Would the azeotropic composition occur in this system?

   What feed composition gives constant product composition?

   Note that:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\,(r_1[M_1] + [M_2])}{[M_2]\,([M_1] + r_2[M_2])}$$

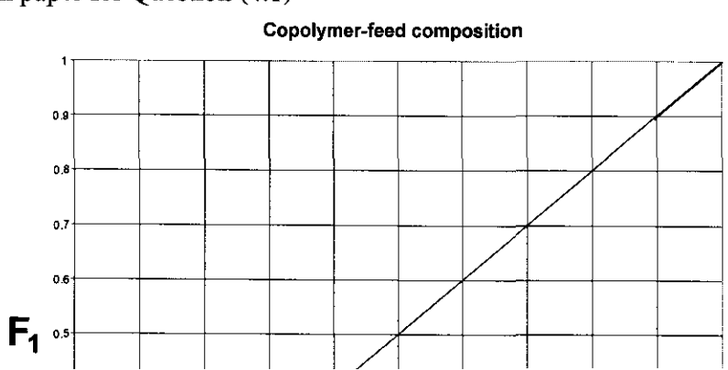
$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

$$(f_1)_c = \frac{1 - r_2}{2 - r_1 - r_2}$$

(26 marks)

End of Question

Graph paper for Question (4.1)



Student Name: ..... ID no. : .....

Answer to Q4.

Graph paper for Question (4.1)