PRINCE OF SONGKLA UNIVERSITY

FACULTY OF ENGINEERING

Midterm Examination : Semester I — Academic Year : 2005

Date : 31 July 2005 — Time : 09.00 — 12.00

Subject : 230 - 463 Polymer Technology — Room : A401

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

Number of questions : 4

Time : 3 hours

Total marks : 100

Notes are not allowed

Calculators are allowed

Question	Full Marks	Marks Received
1	20	
2	30	
3	20	
4	30	
Total	100	

ทุจริตในการสอบโทษขั้นต่ำคือ ปรับตกในรายวิชาที่ทุจริต และพักการเรียน 1 ภาคการศึกษา

1. a) For linear step polymers, the number distribution and the weight distribution of x-mers are given by:

$$N_x^* = p^{x-1}(1-p)$$

$$w_x = x(1-p)^2 p^{x-1}$$

where N_x^* = number fraction of x-mer

w_x = weight fraction of x-mer

Plot N_x^* and w_x against x for x values 0, 50, 100, 150 and 200 at p =0.97.

Explain the relationships between N_x^* and w_x with x at this extent of reaction.

(8 marks)

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b) Would the gel occur in the two cases of stepwise polymerizations below?

b.1). The initial mixture contains 2.5 moles of a dicarboxylic acid, 1.4 moles of glycerol (a triol) and 0.8 moles of methanol.

b.2). The initial mixture contains 1.8 moles of a dicarboxylic acid, 1.2 moles of glycerol (a triol) and 0.3 moles of ethylene glycol (a diol).

(12 marks)

Note that:

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

Answer to Q1.

Q1a)

Graph for plot of distribution curves

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2. a) Derive the expression for radical concentration [M•] in free radical chain polymerizatrion.

(5 marks)

b) Polyvinylacetate is produced by bulk polymerization in which no solvent is used. Only the monomer and initiator are added into the reactor. The density of liquid vinylacetate monomer is 0.9 g/cm^3 and its molecular weight is 86.1 g/mole. A peroxide initiator (mol.wt. = 250 g/mole, half life = 130 hours) is used at 0.5% by weight. Termination occurs mainly by disproportionation. The rate constants are:

k_p = 1000.0 L/(mol.sec)

k_t = 3.0 x 10^7 L/(mol.sec)

the initiator efficiency, f = 0.8

(Hint: Use basis 1 litre of reactor volume which contains 900 g of vinylacetate)

(b.1) Calculate the k_d in s^{-1}.

(b.2) Calculate the rate of polymerization in mol/ L.s

(b.3) Calculate the time required for 70% conversion.

(b.4) Calculate $\bar{M}_n$ 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)

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3) a) Why is polystyrene a clear plastic?

(2 marks)

b) At room temperature polystyrene is hard and brittle while silicone rubber is very flexible. Please explain why?

(2 marks)

c) Why do HDPE and LDPE have different densities?

(2 marks)

d) What is the branching coefficient in step polymerization?

(2 marks)

e) Please write a reaction for preparation of polyurethane.

(2 marks)

f) What is kinetic chain length in chain polymerization?

(2 marks)

g) What are homogeneous and heterogeneous Ziegler-Natta catalysts?

(2 marks)

h) Please write reaction steps for preparation of a polymer by cationic polymerization?

(2 marks)

i) Comment on the molecular weight distribution of polymers prepared from anionic polymerization.

(2 marks)

j) Please explain the meaning of stereospecific polymerization.

(2 marks)

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4. a) Explain the conditions for formation of a block copolymer by free radical reaction. What type of polymerization reaction is usually used in the production of a block copolymer?

(5 marks)

b) Butadiene (monomer 1) at 3 mol/L and styrene (monomer 2) at 4 mol/L concentration are copolymerized in the reactor. Reactivity ratios are $r_1 = 1.40$ and $r_2 = 0.80$.

(b.1) Calculate the copolymer composition (in mole percent) formed at an early stage of the reaction.

(b.2) Plot F_1 vs. f_1 on the provided graph on page 12. What is the copolymer structure?

(b.3) Does the copolymer have the azeotropic composition? Why?

(b.4) If it is required to produce this copolymer with constant composition F_1 of 0.75 how would you control the reactor?

Note that :

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

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

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

(20 marks)

c) Please describe how the values of reactivity ratios for a pair of monomers are obtained from the experiment.

(5 marks)

End of Question

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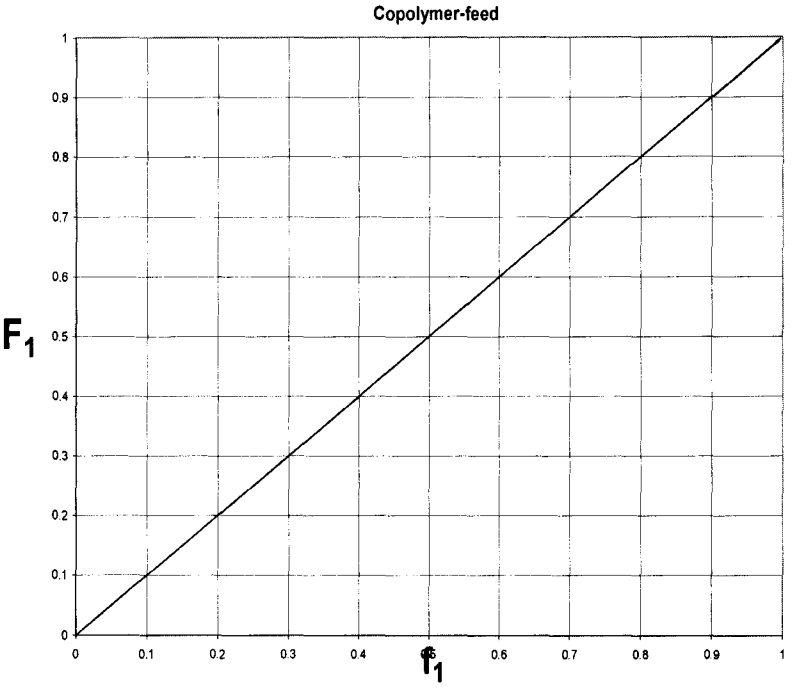
Answer to Q4.(continued)

Graph paper for Question 4(b.2)



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