PRINCE OF SONGKLA UNIVERSITY

FACULTY OF ENGINEERING

Midterm Examination : Semester I — Academic Year : 2004

Date : 2 August 2004 — Time : 09.00 — 12.00

Subject : 230 - 463 Polymer Technology — Room : A201, A203

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

Number of questions : 4

Time : 3 hours

Total marks : 115

Notes are not allowed

Calculators are allowed

Question	Full Marks	Marks Received
1	25	
2	30	
3	30	
4	30	
Total	115	

ทุจริตในการสอบโทษขั้นต่ำคือ ปรับตกในรายวิชาที่ทุจริต และพักการเรียน 1 ภาคการศึกษา

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1 a) In a linear step polymerization, the weight fraction w_x of x-mers is given by

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

Plot and comment on the distribution of w_x at p = 0.97 and p = 0.99.

Explain the relationships between w_x and x at any extent of reaction.

(8 marks)

b) For the following polycondensation reactant mixture, calculate the extent of reaction at the gel point.

Monomer	Moles	
Ethylene glycol (bifunctional diol)	0.8	mole
Glycerol (trifunctional triol)	0.4	mole
Adipic acid (bifunctional)	1.4	mole

Note that:

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

(8 marks)

c) If 0.8 mole of methanol, (CH_3OH) was added by error instead of ethylene glycol in problem (1b) will the gelation occur?

(9 marks)

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2. In the bulk polymerization of polystyrene no solvent is used. The density of liquid styrene monomer is 0.8 g/cm^3 and its molecular weight is 104.14 g/mole. Benzoyl peroxide initiator (mol.wt. = 242 g/mole, half life = 44 hours) is used at 1% by weight. Termination occurs mainly by combination. The rate constants are:

k_p = 145.0 L/(mole.sec)

k_t = 0.13×10^7 L/(mole.sec)

the initiator efficiency, f = 0.5

(Hint: Use basis 1 litre of reactor volume which contains 800 g of styrene)

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

(b) Calculate [M] and [I] in mol/L

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

(d) Calculate the time required for 60% conversion.

(e) Calculate $\bar{M}_n$ of the polymer formed.

Note that:

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

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

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

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

(30 marks)

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3) a) Define the following terms: $\bar{x}_n$, $\overline{DP}$, tacticity, polydispersity index, amorphous polymer and Ziegler-Natta catalysts.

(6 marks)

b) In a free radical reaction k_t is faster than k_p but polymerization rate continues and the polymer with high molecular weight is formed. Please explain why?

(6 marks)

c) Write chain transfer in free radical reactions and explain the effects of chain transfer on R_p and $\bar{x}_n$ for the following cases.

(c.1) $k_p >> k_{tr}$ and $k_r < k_p$

(c.2) $k_p >> k_{tr}$ and $k_r = k_p$

(6 marks)

d) Styrene can be polymerized by free radical, anionic and cationic mechanisms. Acrylonitrile can be polymerized by free radical and anionic mechanisms and not cationic mechanism. Please explain why?

(6 marks)

e) Write initiation and termination reactions for the following reactions. Choose your own initiators or catalysts.

(e.1) anionic polymerization of styrene

(e.2) cationic polymerization of isobutylene, $CH_2=C(CH_3)_2$

(6 marks)

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4. a) From the copolymer equations show that the critical or azeotropic feed composition is given by:

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

(5 marks)

b) Acrylonitrile (monomer 1) at 1 mol/L and styrene (monomer 2) at 3 mol/L concentration are copolymerized in the reactor. Reactivity ratios are $r_1 = 0.01$ and $r_2 = 0.40$.

(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. What is the copolymer structure?

(b.3) What molar ratio of monomers in the feed produces a copolymer composition which is the same as the feed composition ?

Note that :

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

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

(20 marks)

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

(5 marks)

_____ End of Question