

PRINCE OF SONGKLA UNIVERSITY
FACULTY OF ENGINEERING

Midterm Examination : Semester II

Academic Year : 2009

Date : 21 December 2009

Time : 09.00 – 12.00

Subject : 230 - 463 Polymer Technology

Room : S201

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	20	
2	20	
3	30	
4	30	
Total	100	

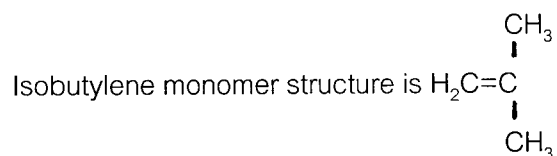
All notations used on this examination paper have their usual meanings.

ทุจริตในการสอบโทษขั้นต่ำคือ ปรับตกในรายวิชาที่ทุจริต และพักการเรียน 1 ภาคการศึกษา

Student Name: ID no. :

Question 1

- (a) Give two properties of a polymer which will be suitable for use as flexible oil pipe or hose in cold climate at -20°C .
- (b) Compare number-average degree of polymerization in step and chain polymerizations.
- (c) Write polymerization reaction for the cationic polymerization of isobutylene using BF_3 initiator and water co-catalyst. Comment on the reaction conditions and molecular weight of the polymer formed.



- (d) Explain chain transfer in free radical polymerization and its effect on the polymer molecular weight. How is the chain transfer constant determined?
- (e) What is Zeigler-Natta catalyst? How is it used in the production of polypropylene?

(20 marks)

Student Name: ID no. :

Question 2

- 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 = 0.98.

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

(8 marks)

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

b.1) The initial mixture contains 3.5 moles of a dicarboxylic acid, 2.0 moles of glycerol (a triol) and 1.0 moles of methanol.

b.2) The initial mixture contains 2.2 moles of a dicarboxylic acid, 1.4 moles of glycerol (a triol) and 0.5 moles of ethylene glycol (a diol).

(12 marks)

Note:

When reactants are present in equivalent reactant mixture:

$$\bar{X}_n = \frac{1}{1-p}$$

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

Student Name: ID no. :

Answer to Q2

Q2a)

Graph for plot of distribution curves

Student Name: ID no. :

Question 3

One hundred litres of methyl methacrylate is polymerized at 40°C with 300 g of dibenzoyl peroxide initiator. No solvent is used in the reaction. The density of liquid methyl methacrylate monomer is 0.87 g/cm³ and its molecular weight is 100 g/mole. The molecular weight of dibenzoyl peroxide is 242 g/mole.

Termination occurs only by disproportionation. The rate constants are:

$$\begin{aligned}k_d &= 3.0 \times 10^{-6} && \text{s}^{-1} \\k_p &= 513 && \text{L mol}^{-1} \text{s}^{-1} \\k_t &= 47 \times 10^6 && \text{L mol}^{-1} \text{s}^{-1}\end{aligned}$$

initiator efficiency, $f = 0.5$

- Calculate the steady-state concentration of free radicals.
- Calculate the per cent conversion of polymer formed in the first 3 hours of reaction.
- Calculate kinetic chain length, ν , of the polymer formed in (b)
- Calculate \overline{M}_n of the polymer formed in (b)

Note that:

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

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

$$-\ln \frac{[M]}{[M]_0} = \frac{k_p}{k_t^{1/2}} (f \cdot k_d [I])^{1/2} \cdot t$$

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

All notations have their usual meanings.

(30 marks)

Student Name: ID no. :

Question 4

- (a) Describe how the reactivity ratios are determined in a free radical copolymerization.
- (b) The copolymer equation in terms of concentrations is given by:

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

It can also be written in mole fractions as shown below.

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

All notations have their usual meanings.

In a free radical copolymerization of styrene (M_1) and methyl methacrylate (M_2) at 60°C using AIBN as free radical initiator, $r_1 = 0.585$ and $r_2 = 0.478$, calculate F_1 at different values of f_1 .

- (b.1) Show f_1 and the corresponding F_1 in table form.
- (b.2) Plot F_1 versus f_1 .
- (b.3) Comment on the structure of the copolymer formed.
- (b.4) Comment on feed composition for this monomer pair.
- (b.5) Derive the equation for azeotropic copolymer composition.

(30 marks)

Student Name: ID no. :

Answer to Q4

