National Exams

04-Chem-B8 Polymer Engineering

Three Hours Duration

NOTES:

1. If doubt exists as to the interpretation of any question, you are urged to submit with the answer paper, a clear statement of any assumptions made.
2. Property data required to solve a given problem are provided in the problem statement or are available in the recommended texts. If you are unable to locate the required data, do not let this prevent you from solving the rest of the problem. Even in the absence of property data, you still have the opportunity to provide a solution methodology.
3. This is an open-book exam.
4. Any non-communicating calculator is permitted.
5. The examination is in four parts – Part A (Questions 1 – 2), Part B (Questions 3 – 4), Part C (Questions 5 – 6), and Part D (Question 7). Answer **ONE** question from Part A, **ONE** question from Part B, **ONE** question from Part C, and the **ONE** question in Part D. **FOUR** questions constitute a complete paper.
6. Questions in Part A are worth **20 marks**, questions in Part B are worth **30 marks**, questions in Part C are worth **30 marks**, and the question in Part D is worth **20 marks**..

PART A: ANSWER ONE OF QUESTIONS 1 – 2 (20 marks)

Note: Four questions constitute a complete paper

(with one from Part A, one from Part B, one from Part C, and one from Part D).

Question #1

Solution viscosity measurements were carried out on a series of dilute solutions of polystyrene in toluene at 30°C, yielding the following results:

Concentration [g/dL]	Flow time [s]
0.000	67.04
0.402	107.70
0.505	121.05
0.595	132.77
0.804	161.39
1.207	227.84

For polystyrene in toluene the Mark-Houwink constants are $K = 1.2 \times 10^{-4}$ cm^3/g and $\alpha = 0.71$. Calculate the viscosity-average molecular weight for the polymer. The Mark-Houwink equation is $[\eta] = KM_V^{\alpha}$.

Question #2

The following data were obtained for the osmotic pressure of dilute solutions of polystyrene in toluene at 378 K:

Concentration [g/L]	1.35	2.00	2.70	3.71	4.52	5.94
Osmotic pressure [cm of toluene]	1.46	2.24	3.16	4.52	5.74	8.10

Given that R = 8.3143 J/mole·K and the density of toluene is 785 kg/m^3, calculate the number average molecular weight for the polystyrene.

PART B: ANSWER ONE OF QUESTIONS 3 – 4 (30 marks)

Note: Four questions constitute a complete paper

(with one from Part A, one from Part B, one from Part C, and one from Part D).

Question #3

In one process for the batch polymerization of styrene in solution, the concentration of the initiator is kept constant throughout the reaction by the continuous addition of initiator to make up for the amount consumed in the reaction. The polymer formed at the instant when monomer concentration is equal to 20% of initial monomer concentration has a number average molecular weight of 200,000. Estimate the number average molecular weight of the polymer formed at the instant when monomer concentration is equal to 10% of initial monomer concentration. Assume that:

a) termination occurs only by coupling
b) all kinetic parameters remain constant throughout the reaction
c) the polydispersities for the polymer formed at the two different monomer concentrations are the same.

Question #4

Consider the possibility of obtaining the polymer Nylon-12 by step-growth polymerization of the monomer $NH_2(CH_2)_{11}COOH$ in the presence of a catalyst. Write the appropriate equations and derive the relationships for the dependence of conversion and number average molecular weight on reaction time. Define all parameters clearly and write down all steps of the derivation. State all assumptions.

Compare the equations obtained for the dependence of conversion and number average molecular weight on time with those that would apply for the production of Nylon-6,6, which is obtained from the reaction involving two monomers: $NH_2(CH_2)_6NH_2$ and $HOOC(CH_2)_4COOH$. Moreover, write the formulas depicting the final polymer composition in each case.

PART C: ANSWER ONE OF QUESTIONS 5 – 6 (30 marks)

Note: Four questions constitute a complete paper

(with one from Part A, one from Part B, one from Part C, and one from Part D).

Question #5

The creep deformation of a polymer under constant stress (σ) can be represented by a model consisting of a Kelvin-Voight element (spring with E_1, dashpot with η_1) in series with a single spring (E_2).

a) What is the expression for the total strain ε?

b) Immediately after applying the stress, the strain is 0.002. After 1000 seconds, the strain is 0.004. After a very long time, the strain approaches 0.006 asymptotically. What is the retardation time $\tau_1 = \eta_1/E_1$?

c) If the applied stress is removed after 1000 seconds, sketch the creep and recovery curves. (Note that it needn't be a perfect plot. Just give a general idea, making use of some of the landmarks given in the problem statement.)

Question #6

Two different polymers (A and B) were tested in an extension test at a constant rate. Polymer A showed a stress-strain curve similar to a Kelvin-Voight element with an elastic modulus of 1.0 x 10^8 dynes/cm^2 and a relaxation time of 1.0 x 10^5 seconds. Polymer B showed a stress-strain curve corresponding to a Maxwell element with an elastic modulus of 1.0 x 10^{10} dynes/cm^2 and a relaxation time of 2.0 seconds.

For each polymer, calculate the following:

a) the maximum extension before rupture
b) the tensile strength

PART D: ANSWER QUESTIONS 7 (20 marks)

Note: Four questions constitute a complete paper

(with one from Part A, one from Part B, one from Part C, and one from Part D).

Question #7

a) A polymer has the following characteristics: $\overline{M_n} = 50{,}000$ and $\overline{M_w} = 25{,}000$

Is this polymer more likely to be synthesized via the step-growth mechanism or the chain-growth mechanism? Explain.

b) From the following data, determine the crystallinity of Sample C:

Sample	Crystallinity	Density [g/cm^3]
A	80%	0.960
B	70%	0.930
C	?	0.950

c) What would be the effect of pressure on (i) the glass transition temperature of a polymer and (ii) the viscosity of a polymer in the melt state? Justify your answer.

d) Propose three methods for increasing the stiffness of polyethylene which is to be used at room temperature.