Problem 1 (20%)

Describe and explain the differences in structure of polyethylene (PE) and polypropylene (PP) derived from (a) free radical polymerization, and (b) Ziegler-Natta catalyst. Show the chain conformation of PE and PP in the crystalline form.

Problem 2 (20%)

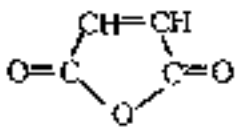
a) Consider the following monomer reactivity ratios for the copolymerization of various pairs of monomers:

10%

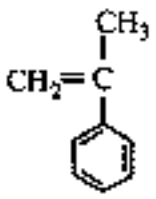
M_1	r_1	M_2	r_2	T(°C)
Maleic anhydride	0.015	styrene	0.040	50
α-methyl styrene	0.38	styrene	2.3	-
allyl acetate	0	styrene	90±10	60
ethyl vinyl ether	0	styrene	90±20	60

Describe the reasons why the following monomers can hardly homopolymerize (i.e. monomer reactivity ratio r_1 is nearly close to zero).

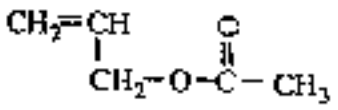
1). maleic anhydride



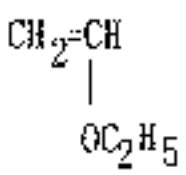
2). α-methyl styrene



3). allyl acetate



4). ethyl vinyl ether



b) The sodium naphthalene (initiator) polymerization of styrene is carried out in

10% tetrahydrofuran solution. A living polymer with two reactive ends is formed as a result. Please give the chemical structure of this living polymer (polystyrene), and the final polymers resulted from the following reactions:

1). Add large amount of epoxide, and then water.

2.) Add excessive amount of carbon dioxide (dry ice), and then water.

3.) Add appropriate amount of 1,3-butadiene, and then water.

Problem 3 (20%)

For condensation polymerization:

5% (a) Derive the equations for the number-average and weight-average degrees of polymerization in terms of the extent of reaction. What is the ratio of these terms as the reaction goes to 100% conversion?

5% (b) Sketch the curves of the mole fraction N_x and the weight fraction W_x of x-mers as a function of x for three different values of the extent of reaction p for a difunctional monomer.

5% (c) How does the number-average and weight-average molecular weights depend upon the extent of polymerization?

5% (d) In order to obtain high molecular weight (M_n =50,000) condensation polymers the extent of reaction must be essentially 100%. Discuss several precautions that must be taken in order to achieve this kind of efficiency?

Problem 4 (20%)

5% (a) Please explain why polymer solubility in a given liquid is lower than the

solubility of its monomer in the same liquid? Does molecular weight of the polymer also play a role in the solubility? Why?

5% (b) Please describe the conformation change and chain motion of a polymer as it experiences a glass transition and melting transition.

10% (c) Please describe the time-temperature superposition principle and its practical applications for amorphous polymers.

Problem 5 (20%)

12% (a) Experiments were carried out to measure X_{max}, the maximum crystallinity, in a serious of random copolymers of ethylene and propylene. Linear PE gave X_{max}=95%. Introduction 4 CH_3- groups per 100 main-chain carbon atoms reduced X_{max} to 50%, and at 20 CH_3- groups per 100 main-chain carbons X_{max} = 0%. Calculate the weight fraction of polypropylene in the copolymer in order to obtain 50% and 0% crystallinity.

8% (b) The glass transition T_g(K) of a random copolymer is given to a good approximation by

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where W_1 and W_2 are weight fractions of the comonomers, and T_{g1} and T_{g2} are glass transition temperatures of the corresponding homopolymers. Calculate T_g of the non-crystalline ethylene-propylene copolymers, taking T_g= -120°C for polyethylene and T_g= -19°C for polypropylene.