Problem Set 1

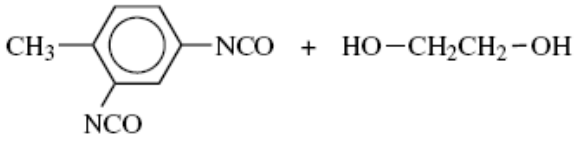
1. Show by equations the overall chemical reactions involved in the synthesis of polymers from

a. $CH_2=CH-CO_2H$

b. 

c. $H_2N-(CH_2)_5-NH_2 \; + \; ClCO-(CH_2)_6-COCl$

d. $HO-(CH_2)_5-CO_2H$

e. 

f. $CH_2=CH-F$

2. Can any other monomer(s) be used to obtain the same polymer structure for any of these polymers?

3. How would you experimentally determine whether the polymerization of an unknown monomer X was proceeding by a step or a chain mechanism?

4. A sample of polystyrene is composed of a series of fraction of different-sized molecules:

Fraction	Weight Fraction	Molecular Weight
A	0.10	12,000
B	0.19	21,000
C	0.24	35,000
D	0.18	49,000
E	0.11	73,000
F	0.08	102,000
G	0.06	122,000
H	0.04	146,000

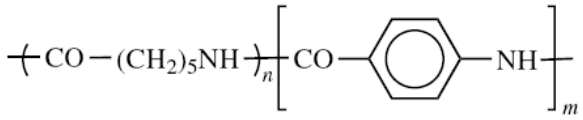
Calculate the number-average and weight-average molecular weights of this polymer sample. Draw a molecular weight distribution curve.

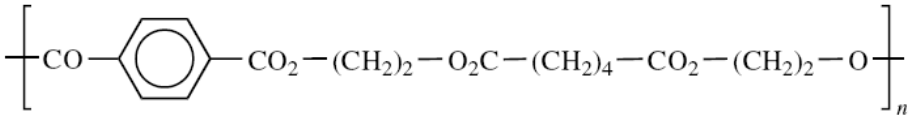
5. Derive an expression for the rate of polymerization of stoichiometric amounts of adipic acid and hexamethylene diamine. Indicate the assumptions inherent in the derivation. Derive an expression for the rate of polymerization of nonstoichiometric amounts of the two reactants.

6. A 21.3-g sample of poly(hexamethylene adipamide) is found to contain $2{:}50\times10^{-3}$ mol of carboxyl groups by both titration with base and infrared spectroscopy. From these data the polymer is calculated to have a number-average molecular weight of 8520. What assumption is made in the calculation? How can one experimentally obtain the correct value of Mn?

7. The polymerization between equimolar amounts of a diol and diacid proceeds with an equilibrium constant of 200. What will be the expected degree of polymerization and extent of reaction if the reaction is carried out in a closed system without removal of the by-product water? To what level must [H2O] be lowered in order to obtain a degree of polymerization of 200 if the initial concentration of carboxyl groups is 2 M?

8. Describe by means of equations how random and block copolymers having the following compositions could be synthesized:

a. 

b. 

9. More practice on calculation.

TABLE 1. Polystyrene Molecular Weight Information

Fraction	Molecular Weight (M_x g/mol)	Mass (g)
1	20,000	0.30
2	40,000	0.90
3	60,000	2.20
4	80,000	6.00
5	100,000	7.00
6	120,000	4.00
7	140,000	1.80
8	160,000	0.90

(I). As a quality control engineer for a leading producer of polystyrene, your job is to ensure that each batch has a similar molecular weight distribution. A sample of a batch of polystyrene yields the molecular weight information as shown above. For this sample, calculate the:
(a) M_n (b) M_w (c) PDI

(II). Suppose instead that the polystyrene sample contained an equal number of molecules of reach molecular weight fraction listed in Table 1. Calculate the:
(a) M_n (b) M_w (c) PDI