Problem Set 3

1. ATRP of 5.0 M styrene is carried out at 110ºC using 1-phenylethyl bromide (0.050 M) and CuBr (0.050 M) in the presence of 4,4'-di(5-nonyl)-2,2'-bipyridine (0.10 M). The number-average molecular weight at 72% conversion is 7150. Compare the observed molecular weight to the theoretical value expected for this polymerization.

2. Describe how NMP (Nitroxide-mediated polymerization) is used to synthesize a block copolymer of styrene and 4-vinylpyridine.

3. Describe the components of an emulsion polymerization system on a macroscopic level. Compare the pros and cons of emulsion polymerization as a process condition in comparison to bulk and solution polymerization.

4. Quantitatively compare the rate and degree of polymerization of styrene polymerized in bulk at 60ºC with an emulsion polymerization (case 2 behavior: n=0:5) containing 1:0 $\times 10^{15}$ polymer particles per milliliter. Assume that [M]= 5:0 molar, Ri = 5.0×10^{12} radicals per milliliter per second, and all rate constants are the same for both systems. Kt = 6×10^{7} L mol^{-1} s^{-1}. For each polymerization system, indicate the various ways (if any) by which the polymerization rate can be affected without affecting the degree of polymerization.

5. Consider the following monomers and initiating systems:

Initiating Systems	Monomers
$(\phi CO_2)_2$	$\phi CH{=}CH_2$
$(CH_3)_3CCOOH + Fe^{2+}$	$CH_2{=}CHCN$
Na + naphthalene	$CH_2{=}C(CH_3)_2$
H_2SO_4	$CH_2{=}CH{-}O{-}n\text{-}C_4H_9$
$BF_3 + H_2O$	$CH_2{=}CH{-}Cl$
$n\text{-}C_4H_9Li$	$CH_2{=}C(CH_3){-}CO_2CH_3$
	$CH_2{=}O$
	$CF_2{=}S$

What is the actual initiating species that initiates polymerization for each of the initiating systems? Show equations. Which initiating system(s) can be used to polymerize each of the various monomers? Explain. What general reaction conditions (e.g., temperature, solvent) are required for each polymerization?

6. A monomer Z is polymerized in the presence of an initiating system Y. The following experimental observations are made:
a. The degree of polymerization decreases as the reaction temperature increases.
b. The degree of polymerization is affected by the solvent used.
c. The degree of polymerization is first-order in monomer concentration.
d. The rate of polymerization increases as the reaction temperature increases.

Is this polymerization proceeding by a step, radical chain, cationic chain, or anionic chain mechanism? Discuss clearly how each experimental observation is consistent with your answer.

7. Consider the following monomer reactivity ratios for the copolymerization of various pairs of monomers:

Case	r_1	r_2
1	0.1	0.2
2	0.1	10
3	0.1	3
4	0	0.3
5	0	0
6	0.8	2
7	1	15

What is the composition of the copolymer that would be formed at low conversion from equimolar mixtures of the two monomers in each case?

8. Explain the following observations:
a. A small amount of epichlorohydrin greatly increases the rate of the polymerization of tetrahydrofuran by BF3 even though epichlorohydrin is much less basic than tetrahydrofuran.
b. The addition of small amounts of water to the polymerization of oxetane by BF3 increases the polymerization rate but decreases the degree of polymerization.