Problem Set #2
Chemical Engineering 160/260
Due Friday, February 9, 2001

3-5 The benzoyl peroxide initiated polymerization of a monomer follows the simplest kinetic scheme, that is, $R_p = k_p[M](f k_d[I]/k_t)^{1/2}$ with all rate constants and *f* being independent of conversion. For a polymerization system with $[M]_O = 2$ M and $[I]_O = 10^{-2}$ molar, the limiting conversion p_∞ is 10%. To increase p_∞ to 20%:

a. Would you increase or decrease $[M]_O$ and by what factor?
b. Would you increase or decrease $[I]_O$ and by what factor? How would the rate and degree of polymerization be affected by the proposed changes in $[I]_O$**?**
c. Would you increase or decrease the reaction temperature for the case of thermal initiated polymerization? For the case of photopolymerization (assuming that an increase in temperature does not cause thermal decomposition of initiator)?

E_d, E_p, and E_t are 64, 32, and 8 kJ/mole, respectively.

3-6 For a radical polymerization with bimolecular termination, the polymer produced contains 1.30 initiator fragments per polymer molecule. Calculate the relative extents of termination by disproportionation and coupling, assuming that no chain transfer reactions occur.

3-7 A solution 0.20 molar in monomer and 4.0×10^{-3} M in a peroxide initiator is heated at 60°C. How long will it take to achieve conversion? $k_P = 145$ liters/ mole-sec, $k_t = 7.0 \times 10^7$ liters/ mole-sec, $f = 1$, and the initiator half-life is 44 hr.

3-17 A radical chain polymerization following $R_p = k_p[M](f k_d[I]/k_t)^{1/2}$ shows the indicated conversions for specified initial monomers and initiator concentrations and reaction times:

Experiment	Temperature (°C)	[M] (moles/liter)	$[I] \times 10^3$ (moles/liter)	Reaction Time (min)	Conversion (%)
1	60	1.00	2.5	500	50
2	80	0.50	1.0	700	75
3	60	0.80	1.0	600	40
4	60	0.25	10.0	?	50

Calculate the reaction time for 50% conversion in Experiment 4. Calculate the overall activation energy for the rate of polymerization.

6-3 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?

6-7 Consider the radical copolymerization of a benzene solution that is 1.5 M in styrene and 3.0 M in methyl acrylate.

a. What is the initial copolymer composition if the polymerization is carried out at 60°C using benzoyl peroxide at a concentration of 5.0×10^{-4} M? How is the copolymer composition affected if 3.0×10^{-4} M benzoyl peroxide is used?

6-8 List the following monomers in order of their increasing tendency toward alternation with 1,3-butadiene in radical copolymerization:

a. *n*-Butyl vinyl ether
b. Methyl methacrylate
c. Methyl acrylate
d. Styrene
e. Maleic anhydride
f. Vinyl acetate
g. Acrylonitrile

Explain the relative alternating tendencies in these copolymerizations.