Chem 654, Spring 2003
Handout

PS#2 revised, 02/06/03

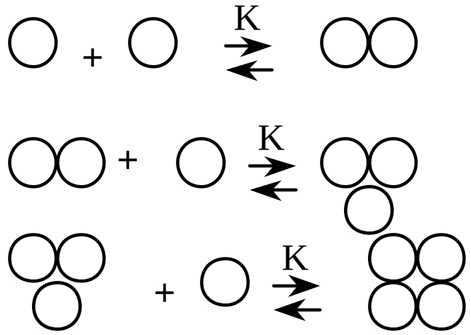
Problem Set 2. due 02/17/03

A. (1) Consider the self-association phenomenon of a monodisperse polymer where the equilibrium constant is the same for each step such that the multiple equilibria

$$M + M \overset{K}{\rightleftarrows} M_2\ ;$$

$$M_2 + M \overset{K}{\rightleftarrows} M_3\ ;$$

$$M_3 + M \overset{K}{\rightleftarrows} M_4\ ;$$



$$\vdots$$

$$M_x + M \overset{K}{\rightleftarrows} M_{x+1}\ ;$$

hold, assuming the solution to be ideal, i.e., the activity coefficient is unity for each species. Find the distribution function expression for x-mer, X_x, in terms of K and the equilibrium unimer concentration, $[M]_e$. Assuming the density of the unimer density does not change upon association, calculate the number average and weight average molar masses of the equilibrium mixture if the unimer molar mass is 10 kg/mol, the unimer concentration at the start, $[M]_o=0.04$ M and $K=9.5\cdot10^3(\text{mol/L})^{-1}$.

(2) Derive the expression for the mole fraction of x-mer if the equilibrium constant for the first step, K', is very different from that of the rest, such that K >> K', which represents the case of cooperative association.

B. A free radical polymerization of styrene in toluene as the solvent is carried out at 85°C with benzoyl peroxide as the initiator. It has been shown that the termination is exclusively via recombination. Assume that there is no chain transfer reaction, and the steady state approximation can be made. With the following data provided,

(1) calculate the time required to have 1% of the monomer polymerized;
(2) find the residual monomer concentration at the end of polymerization, i.e., $t\rightarrow\infty$;
(3) calculate the instantaneous number average degrees of polymerization when 1% and 5% of monomer polymerized, respectively; and
(4) plot $\ln([M]/[M]_o)$ vs. t and $[M]/[M]_o$ vs. $[I]/[I]_o$

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Data:

a. The initiation is via the first order decomposition of benzoyl peroxide with 100% efficiency, and $k_d = 1.2\cdot 10^{-4}\ s^{-1}$ at 85°C.

b. $k_2/k_3^{1/2} = 2.3\cdot 10^{-2}\ L^{1/2}/mol^{1/2}\ \cdot s^{1/2}$, where $k_2 = k_p$ and $k_3 = k_t$.

c. $[M]_o = 0.1$ M, the initial monomer concentration

d. $[I]_o = 0.1$ mM, the initial concentration of initiator

C. For a free radical polymerization with the initiation rate νI and the termination taking place exclusively by the recombination of free radical species,

(a) show that the chain length distribution of the resulting polymer is given by

$$X_x = (x-1)\alpha^{x-2}(1-\alpha)^2 \qquad (2 \le x \le \infty) \tag{1}$$

under the assumptions that

1) the global steady-state approximation,

$$\frac{d}{dt}[\sum_{x=1}^{\infty}(RM_x\bullet)] = 0 \qquad (2),$$

such that $\nu_i = k_t(M\bullet)^2$, where $(M\bullet) \equiv \sum_{x=1}^{\infty}(RM_x\bullet)$ (3)

2) the local steady-state approximation,

$$\frac{d}{dt}(RM_x\bullet) = 0, \qquad (x=1, 2, 3, \cdots) \qquad (4),$$

3) a long kinetic chain legth,

$$\nu \equiv \frac{\nu_p}{\nu_i} = \frac{k_p(M)(M\bullet)}{k_t(M\bullet)^2} = \frac{k_p(M)}{k_t(M\bullet)} = \frac{k_p(M)}{(\nu_i k_t)^{1/2}} >> 1 \tag{5}$$

hold, so that

$$\alpha \equiv \frac{k_p(M)}{k_p(M) + (\nu_i k_p)^{1/2}} \le 1 \tag{6}$$

(b) show that weight fraction of x-mer is given by

$$W_x = \frac{1}{2}x(x-1)\alpha^{x-2}(1-\alpha)^3 \tag{7}$$

(c) Plot W_x vs. x with x_n=1000 and compare it to that of MPD at the same x_n=1000.