Chem 654, Spring 2003
Handout

PS#3, 02/20/03

Problem Set 2. due 03/03/03

A. (1) Consider the kinetic scheme for anionic polymerization with the initiation step already seeded such that all rate constants k are the same, and (I) = (A_1)

$$I + M \xrightarrow{k} A_2 \tag{1}$$

$$A_2 + M \xrightarrow{k} A_3$$

$$A_3 + M \xrightarrow{k} A_4$$

$$\vdots$$

$$A_{x-1} + M \xrightarrow{k} A_x$$

Initial conditions: t = 0, (M)=$(M)_o$, and (I) = $(I)_o$, (A_2)=(A_2) = · · · = 0.

Also, $\sum_{x=1}^{\infty} A_x = (I)_o$ throughout the polymerization since no termination takes place.

Hence, $$(M) = (M)_o e^{-k(I)_o t} \tag{2}$$

$$x_n = 1 + \frac{(M)_o - (M)}{(I)_o} = 1 + \frac{(M)_o}{(I)_o}[1 - e^{-k(I)_o t}], \tag{3}$$

$$\nu \equiv x_n - 1, \text{ such that } d\nu = k(M)dt, \text{ where } \nu \text{ is called eigenzeit.} \tag{4}$$

a) Show that the mole fraction of x-mer in discrete form is given by the Poisson distribution:

$$X_x = \frac{e^{-\nu}\nu^{x-1}}{(x-1)!}, \qquad (1 \le x \le \infty) \tag{5}$$

b) Prove that the continuous form of mole fraction of x-mer for the Poisson distribution in the limit of $\nu >> 1$, is

$$X(x) = \frac{e^{-(x-\nu)^2/2\nu}}{(2\pi\nu)^{1/2}}, \qquad (0 \le x \le \infty) \tag{6}$$

with the aid of Stirling's approximation,

$$x! \approx \sqrt{2\pi} \cdot x^{x+1/2} \cdot e^{-x} \tag{7}$$

c) Show that the continuous form of weight fraction of x-mer for the Poisson distribution is given by

$$W(x) = \frac{x \cdot e^{-(x-\nu)^2/2\nu}}{(2\pi\nu^3)^{1/2}} \tag{8}$$

and evaluate x_n , x_w and x_z with the continuous forms of the distribution.

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B. The kinetic scheme for a copolymerization by the free radical mechanism is given by the following.

$$\begin{aligned}
&\sim\sim\sim\sim\sim M_1\bullet \;+\; M_1 \xrightarrow{k_{11}} \sim\sim\sim\sim\sim M_1\bullet \\
&\sim\sim\sim\sim\sim M_1\bullet \;+\; M_2 \xrightarrow{k_{12}} \sim\sim\sim\sim\sim M_2\bullet \\
&\sim\sim\sim\sim\sim M_2\bullet \;+\; M_1 \xrightarrow{k_{21}} \sim\sim\sim\sim\sim M_1\bullet \\
&\sim\sim\sim\sim\sim M_2\bullet \;+\; M_2 \xrightarrow{k_{22}} \sim\sim\sim\sim\sim M_2\bullet
\end{aligned} \qquad (9)$$

a) Show that the instantaneous composition of comonomer 1 in the copolymer, F_1, is

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (10)$$

provided that $k_{21}(M_1)(M_2\bullet) = k_{12}(M_2)(M_1\bullet)$ and where f_1 is the composition of 1 in the monomer feed, and r_1 and r_2 are defined as

$$r_1 \equiv \frac{k_{11}}{k_{12}} \quad \text{and } r_2 \equiv \frac{k_{22}}{k_{21}} \qquad (11)$$

b) Plot f_1 vs. F_1 for three cases,

1) $r_1 = 0.8$ and $r_2 = 0.2$,
2) $r_1 = 10$ and $r_2 = 0.1$
3) $r_1 = 0.1$ and $r_2 = 10$

c) Prove that

$$\frac{f(1-F)}{F} = r_2 - r_1 (f^2 / F) \qquad (12)$$

where $F \equiv F_1/F_2$ and $f \equiv f_1/f_2$.

d) Plot f_1 vs. F_1 for $r_1 r_2 = 1$, and $r_1 = 10, 5, 2, 1, 0.5, 0.2, 0.1$

e) Compute r_1 and r_2 for styrene and vinyl acetate copolymerization by Q-e scheme and compare them with the experimental values.

C. Another commonly encountered distribution function in polymer science is the binomial distribution, where the elemental probability for a particular outcome at a given trial is p and that of not having the outcome is q=1-p. An example is rolling of a die where p=1/6 for getting 6 and q=5/6 for not getting 6. Ideal coin tossing is another example where p=q=1/2 for head or tail. The probability for getting x times out of n trials for the particular outcome is given by

$$\mathbf{P}(x, n) = \frac{n!}{x!(n-x)!} p^x q^{n-x} \tag{13}$$

a) Show that $\mathbf{P}(x, n)$ is normalized for $0 \le x \le n$.
b) When applied to coin tossing problem, p=q=1/2, evaluate $\mathbf{P}(4, 4)$, $\mathbf{P}(3, 4)$, $\mathbf{P}(2, 4)$, $\mathbf{P}(1, 4)$, and $\mathbf{P}(0, 4)$.
c) Plot $\mathbf{P}(4, 4)$, $\mathbf{P}(3, 4)$ and $\mathbf{P}(2, 4)$ as functions of p for $0 \le p \le 1$.
d) Consider pentad sequence analysis of binomial stereoplacement of a vinyl polymer. Plot the probabilities of four distinct sequences, rrrr, rrrm, mrrm, rmrm as functions of elemental meso placement probability, p_m for $0 \le p_m \le 1$.
e) Show that the binomial distribution for p=q=1/2 as n approaches infinity, is given by

$$\mathbf{P}(m, n) = \sqrt{\frac{2}{\pi n}} \cdot \exp[-m^2/2n] \tag{14}$$

where $m \equiv n-2x$. Hint: Use Stirling's approximation given above, (7).

f) Plot $\mathbf{P}(m, 1000)$ vs. m.