**Chem 654, Spring 2003**
**Handout**



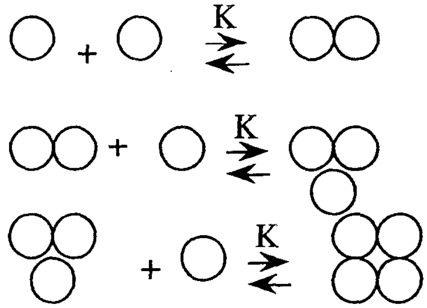
Solutions to
**Problem Set 2. due 02/17/03**

**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

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

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

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



$$\vdots$$

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

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 equili brium 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 $K=9.5\cdot 10^3(\mathrm{mol/L})^{-1}$.

(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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## Handout

PS#1-2

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,

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

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

2) the local steady-state approximation,

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

3) a long kinetic chain legth,

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

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.

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Solutions to
Problem Set #2

A.(i) Molar concentration of each species at the equilibrium is expressed by $[M]_e \equiv [M]$, the monomer concentration, and the equilibrium constant $K$.

$[M_2] = K[M]^2$, $[M_3] = K[M][M_2] = K^2[M]^3$, $[M_4] = K[M][M_3] = K^3[M]^4$ $\cdots$ $[M_x] = K^{x-1}[M]^x$.

The total concentration of all species, $\sum_{x=1}^{\infty}[M_x] = \sum_{x=1}^{\infty} K^{x-1}[M]^x = [M]\sum_{x=1}^{\infty} p^{x-1}$

(where $p \equiv K[M]$ assumed to be less than unity that needs confirmation for consistency)

$$= \frac{[M]}{(1 - K[M])}$$

The mole fraction of $x$-mer,

$$X_x = \frac{[M_x]}{\sum_{x=1}^{\infty}[M_x]} = \frac{K^{x-1}[M]^x}{\frac{[M]}{(1-K[M])}} = (K[M])^{x-1}(1-K[M])$$

$$= p^{x-1}(1-p),$$ it is another MPD.

$[M]$ is evaluated by mass conservation,

$$[M]_0 = 4\cdot 10^{-2}\,M = \sum_{x=1}^{\infty} x[M_x] = [M]\sum x(K[M])^{x-1}$$

$$= \frac{[M]}{(1-K[M])^2}, \quad \because \sum_{x=1}^{\infty} x p^{x-1} = \frac{1}{(1-p)^2}$$

$$[M]_0(1-K[M])^2 = [M], \quad K^2[M]_0[M]^2 - (2K[M]_0+1)[M] + [M]_0 = 0$$

$$K^2[M]_0 = 3.61\cdot 10^6, \quad 2K[M]_0 + 1 = 7.61\cdot 10^2$$

$$\therefore [M] = \frac{7.61\cdot 10^2 \pm 0.39\cdot 10^2}{7.22\cdot 10^6} = \begin{cases} 10^{-4}, & K[M] = 0.95 < 1 \\ 1.11\cdot 10^{-4}, & K[M] = 1.05 > 1 \end{cases}$$

Thus, $\underline{[M] = 10^{-4}\,M}$ to be consistent with the assumption.

$$x_n = \frac{1}{1-K[M]} = \frac{1}{1-0.95} = 20, \quad M_n = 2\cdot 10^5 = 200\ \text{kg/mol}$$

$$x_w = \frac{1+K[M]}{1-K[M]} = \frac{1.95}{0.05} = 39, \quad M_w = 390\ \text{kg/mol}$$

A.(2) $[M_2]=K'[M]^2,\ [M_3]=K[M][M_2]=K'K[M]^3,\ [M_4]=K'K^2[M]^4,$

$\ldots\ [M_x]=K'K^{x-2}[M]^x, \quad 2\le x\le\infty$

$$\sum_{x=1}^{\infty}[M_x]=[M]+\sum_{x=2}^{\infty}K'K^{x-2}[M]^x + [M]+[M]\cdot K'[M]$$

$$=[M]+K'[M]^2\sum_{x=2}^{\infty}(K[M])^{x-2}=[M]\left\{1+\frac{K'[M]}{1-K[M]}\right\}$$

The mole fraction of x-mer: $$X_x=\frac{[M_x]}{\sum_{x=1}^{\infty}M_x}=\frac{K'K^{x-2}[M]^x}{[M]\left\{1+\frac{K'[M]}{1-K[M]}\right\}}$$

assuming $K(M)<1$

$$=\frac{p'p^{x-2}}{\frac{1-p+p'}{1-p}} \quad \text{where } p\equiv K[M]<1,\quad p'\equiv K'[M]<<1$$

$$\approx p'p^{x-2} \quad \text{for } 2\le x\le\infty \text{ since } p'<<p$$

$$X_1=\frac{[M]}{[M]\left\{1+\frac{p'}{1-p}\right\}}=\frac{1-p}{1-p+p'}\lesssim 1$$

B $\nu_p=-\dfrac{d[M]}{dt}=\dfrac{k_p}{k_t^{1/2}}\nu_i^{1/2}[M],\quad \nu_i=2fk_d[I]=2k_d[I]$

$-\dfrac{d[I]}{dt}=k_d[I],\quad [I]=[I]_0e^{-k_dt}$

$\therefore \nu_i=2k_d[I]_0e^{-k_dt},\quad \nu_i^{1/2}=(2k_d[I]_0)^{1/2}e^{-k_dt/2}$

$\therefore \nu_p=\left(\dfrac{k_p}{k_t^{1/2}}\right)(2k_d[I]_0)^{1/2}e^{-k_dt/2}\cdot[M]$

$$-\int_{[M]_0}^{[M]}\frac{d[M]}{[M]}=-\ln\frac{[M]}{[M]_0}=\left\{\left(\frac{k_p}{k_t}\right)^{1/2}(2k_d[I]_0)^{1/2}\right\}\int_0^t e^{-k_dt/2}dt$$

$$=\{\quad\}\left(-\frac{2}{k_d}\right)(e^{-k_dt/2}-1)$$

$$\ln\frac{[M]}{[M]_0}=\frac{2^{3/2}}{k_d^{1/2}}\left(\frac{k_p}{k_t^{1/2}}\right)[I]_0^{1/2}\cdot(e^{-k_dt/2}-1)=5.92\cdot10^{-2}(e^{-k_dt/2}-1)$$

(1) $t$ when $[M]/[M]_0=0.99$, time required to polymerize 1% of $[M]_0$

$$\ln(0.99)=5.92\cdot10^{-2}(e^{-k_dt/2}-1)=5.92\cdot10^{-2}(e^{-6\cdot10^{-5}t}-1)$$

$t=3084\,s\approx 51\,min$

(2) $[M]_\infty$ ? , $\ln\frac{[M]_\infty}{[M]_0} = 5.92\cdot10^{-2}(-1)$, $[M]_\infty = [M]_0 e^{-0.0592}$

$= 10^{-1}\cdot 0.943$

$= 0.0943\,M$

(3) $X_n$ when $[M] = 0.99[M]_0 = 9.9\cdot10^{-2}$, 1% polymerized

$$X_n = \frac{2k_p[M]}{k_t^{1/2}\,\nu_i^{1/2}} = \frac{2\cdot 2.3\cdot10^{-2}\cdot 9.9\cdot10^{-2}}{1.29\cdot10^{-4}} = \underline{\underline{35}}$$

$\nu_i^{1/2} = [2\cdot1.2\cdot10^{-4}\cdot10^{-4}]^{1/2}\cdot e^{-1.2\cdot10^{-4}\cdot3.08\cdot10^{3}/2}$

$X_n$ when $[M] = 0.95[M]_0 = 9.5\cdot10^{-2}$, 5% polymerized

$\ln(0.95) = 5.92\cdot10^{-2}(e^{-1.2\cdot10^{-4}t/2} - 1)$, $e^{-6\cdot10^{-5}t} = 0.134$, $t = 33{,}500\,s$
$\approx 9.3\,h$

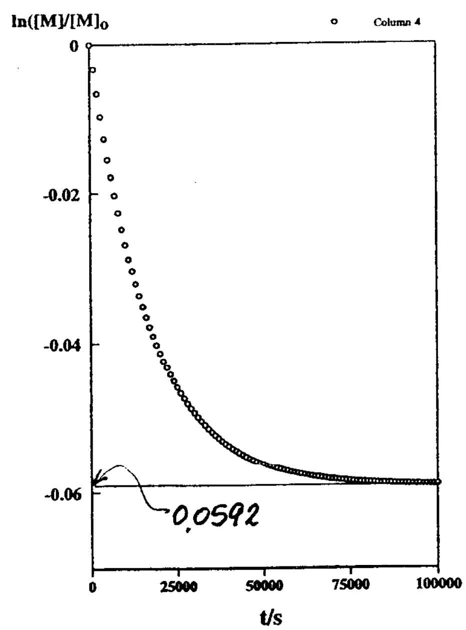
$\nu_i^{1/2}(t = 9.3\,h) = 2.08\cdot10^{-5}$

$1.55\cdot10^{-4}\cdot0.134$

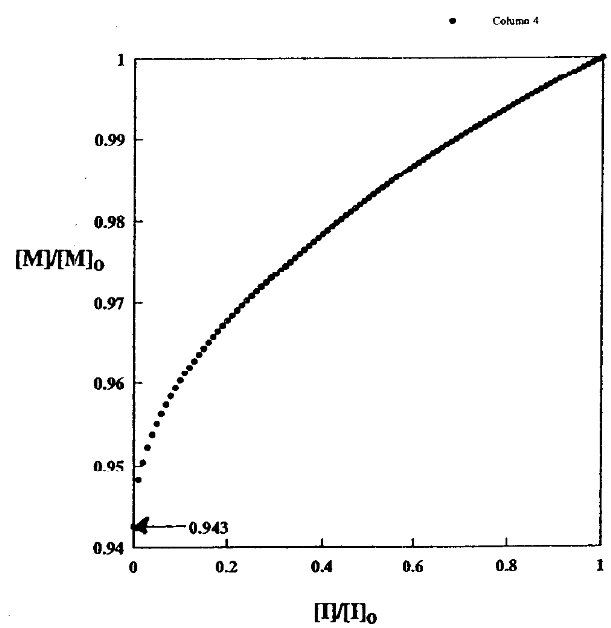
$$X_n = \frac{2k_p[M]}{k_t^{1/2}\,\nu_i^{1/2}} = \frac{2\cdot2.3\cdot10^{-2}\cdot0.095}{2.08\cdot10^{-5}} = \underline{\underline{210}}$$

(4)

**ln([M]/[M]$_0$) vs. t for a free radical polymerization with benzoyl peroxide as the initiator**




**Monomer ratio vs. Initiator ratio for dead-end free radical polymerization**



C. (a) From the global s.s. approximation, (2),

$$\frac{d}{dt}\left[\sum_{x=1}^{\infty}(RM_x^{\bullet})\right]=0, \quad \nu_i - k_t\left[\sum_{x=1}^{\infty}(RM_x^{\bullet})\right]^2=0$$

$$(M\bullet)\equiv\sum_{x=1}^{\infty}(RM_x^{\bullet})=(\nu_i/k_t)^{1/2}$$

From the local s.s. approx, (3)

$$\frac{d}{dt}(RM_x\bullet)=0=k_p(RM_{x-1}\bullet)(M)-k_p(RM_x^{\bullet})(M)-k_t(RM_x^{\bullet})(M\bullet)$$

$$(RM_x^{\bullet})[k_p(M)+k_t(M\bullet)]=k_p(RM_{x-1}^{\bullet})(M)$$

$$(RM_x^{\bullet})=\left(\frac{k_p(M)}{k_p(M)+k_t(M\bullet)}\right)(RM_{x-1}\bullet)=\alpha(RM_{x-1}^{\bullet})$$

where $\alpha \lesssim 1$

Thus, $(RM_x\bullet) \quad \alpha(RM_{x-1}^{\bullet})=\alpha^2(RM_{x-2}\bullet)=\cdots=\alpha^{x-1}(RM\bullet)$

By the reco ation only, the smallest species is RPR from (RM•)+(RM•)

The rate of polymer formation is

$$\frac{d(RP_xR)}{dt}=\frac{1}{2}k_t\sum_{j=1}^{x-1}(RM_j\bullet)(RM_{x-j}\bullet)=\frac{1}{2}k_t\sum_{j=1}^{x-1}[\alpha^{j-1}(RM\bullet)][\alpha^{x-j-1}(RM\bullet)]$$

$$=\frac{1}{2}k_t(RM\bullet)^2\sum_{j=1}^{x-1}\alpha^{j-1}\cdot\alpha^{x-j-1}=\frac{1}{2}k_t(RM\bullet)^2(\underbrace{\alpha^{x-2}+\alpha^{x-2}+\cdots+\alpha^{x-2}}_{(x-1)\text{ terms}})$$

$$=\frac{1}{2}k_t(RM\bullet)^2(x-1)\alpha^{x-2}$$

$X_x \propto \frac{d(RP_xR)}{dt}$, $X_x=B(x-1)\alpha^{x-2}$ where $B$ is the normalization const

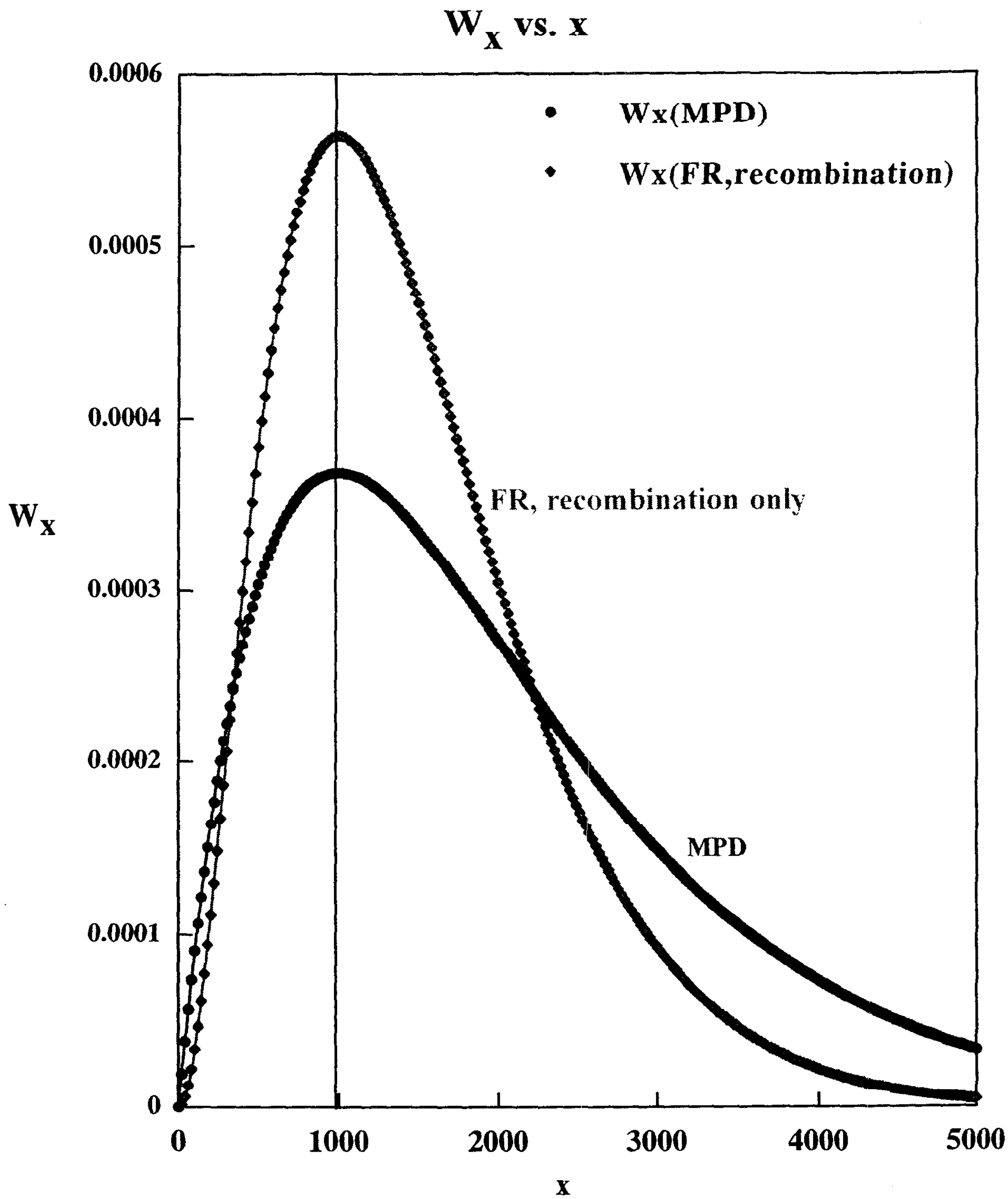
$$1=\sum_{x=2}^{\infty}B(x-1)\alpha^{x-2}=B[1\cdot\alpha^0+2\cdot\alpha+3\alpha^2+\cdots]=\frac{B}{(1-\alpha)^2}, \quad B=(1-\alpha)^2$$

$$\therefore X_x=(1-\alpha)^2(x-1)\alpha^{x-2} \quad (2\le x\le\infty) \quad Q.E.D.$$

(b) $$W_x=\frac{xX_x}{\sum xX_x}=\frac{x(x-1)\alpha^{x-2}(1-\alpha)^2}{(1-\alpha)^2\sum x(x-1)\alpha^{x-2}}=\frac{x(x-1)\alpha^{x-2}(1-\alpha)^2}{(1-\alpha)^2\frac{2}{(1-\alpha)^3}}=\frac{1}{2}x(x-1)\alpha^{x-2}(1-\alpha)^3$$

$$\sum x(x-1)\alpha^{x-2}=\frac{2}{(1-\alpha)^3}$$

(c)



$W_x$ vs. x
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
Wx(MPD)
Wx(FR,recombination)
FR, recombination only
MPD
$W_x$
0
1000
2000
3000
4000
5000
x