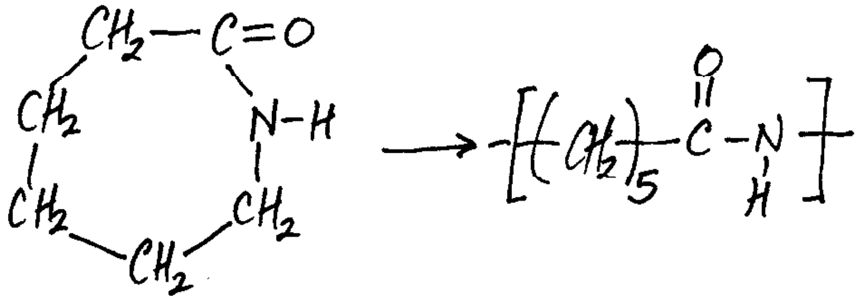
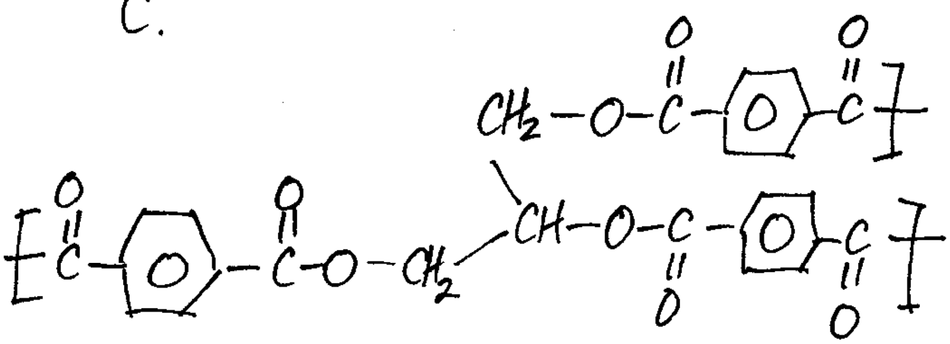
Chem 654 / Exam #1
Key

(1) A. $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\bullet$

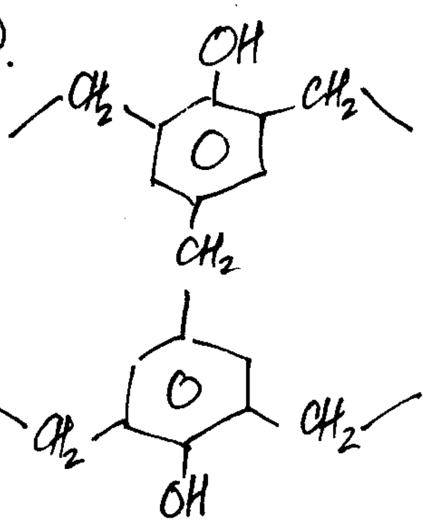
B.



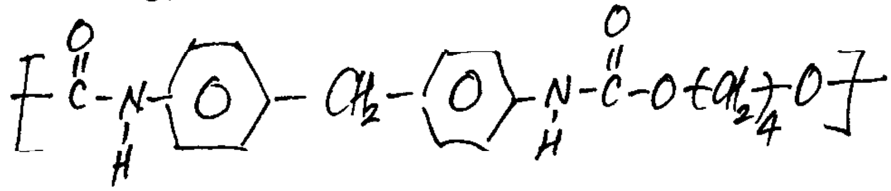
C.



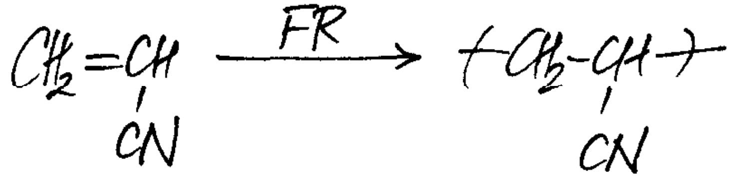
D.



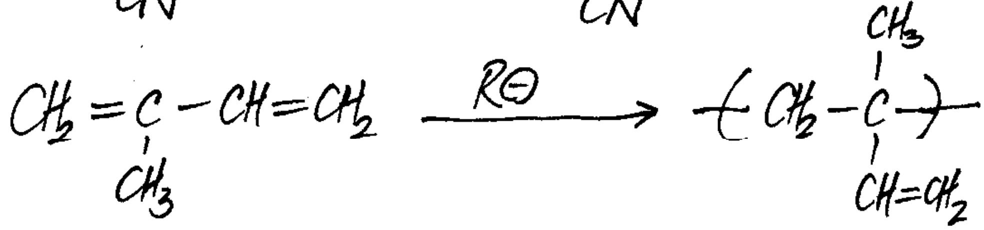
E.



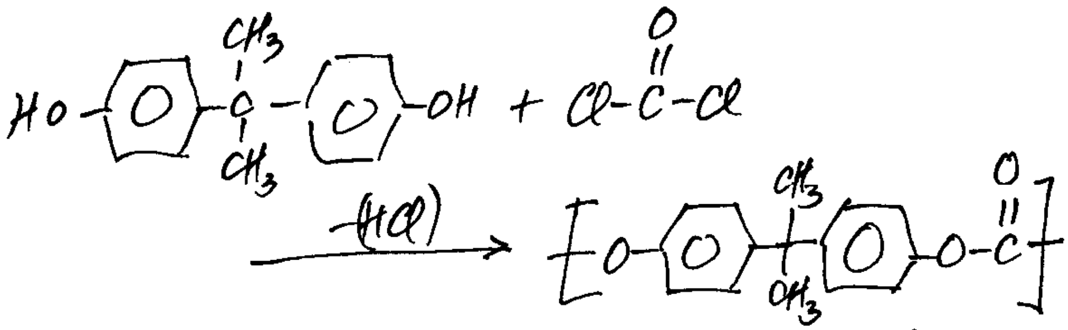
(2) A.



B.

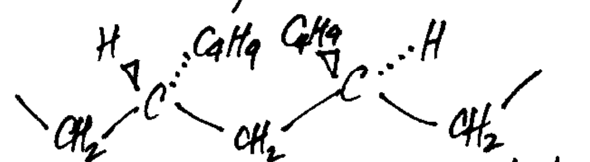


C.



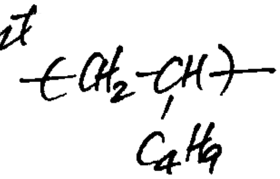
polycarbonate

D.

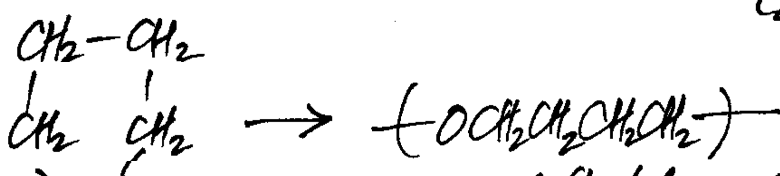


most likely syndiotactic

or just

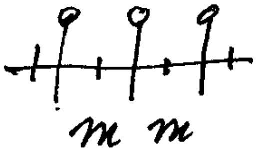


E.

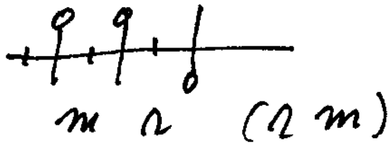


poly(butylene oxide)

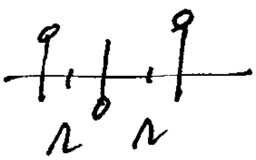
(3)

A. 

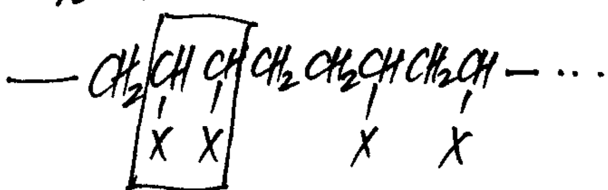
$$P(mm) = \frac{2!}{2!0!} p_m^2 = p_m^2$$



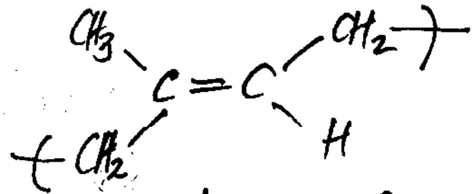
$$P(mr) = \frac{2!}{1!1!} p_m(1-p_m) = 2p_m(1-p_m)$$



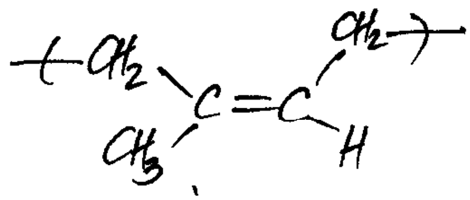
$$P(rr) = \frac{2!}{0!2!} p_m^0 (1-p_m)^2 = (1-p_m)^2$$

B. 

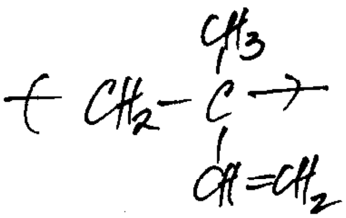
HH defect

C. 

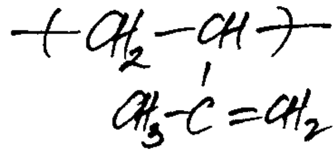
trans-1,4



cis-1,4



1,2 addition



3,4-addition

D. In free radical polymerization,

$$\frac{d(R_x^{\cdot})}{dt} = 0 \quad \text{for } 1 \le x \le \infty$$

E. Polycondensation $X_x = p^{x-1}(1-p)$ where p as the extent of reaction is indept of chain length, i.e., the same p for $1 \le x \le \infty$

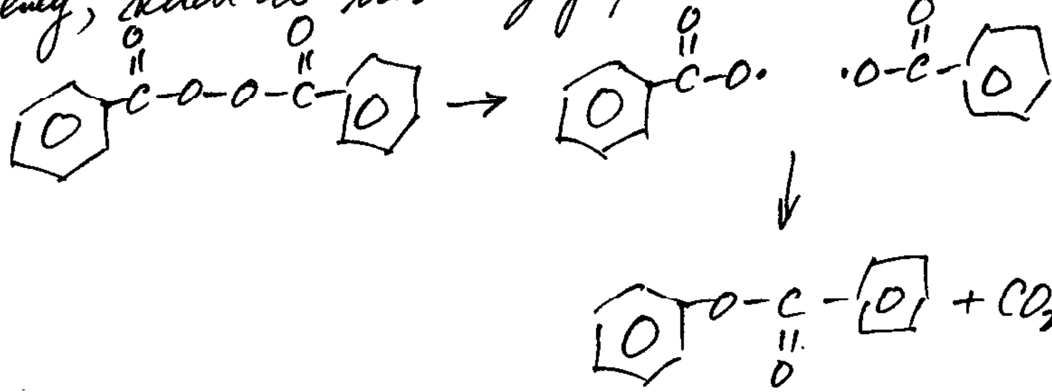
F. $x_w/x_n = M_w/M_n \equiv PDI$

G. Free radical mechanism for termination, one chain gets reduced while its collision partner gets oxidized,

$$\sim\sim CH_2CHX\cdot \;+\; \cdot XCH{-}CH_2\sim\sim \;\longrightarrow\; \sim CH_2CH_2X \;+\; \underset{\displaystyle X}{\overset{}{CH}}{=}CH\sim\sim$$

reduced oxidized

H. Free radical initiator fragments recombine within such a cage, resulting in a reduced initiator efficiency, such as in benzoyl peroxide



within a solvent cage

I. Some monomers can self initiate to start polymerization

$$\underset{\displaystyle X}{CH_2{=}CH} + \underset{\displaystyle X}{CH_2{=}CH} \xrightarrow{\Delta} \underset{\displaystyle X}{CH_3{-}CH\cdot} + CH{\equiv}C{-}X$$

free radical or other stable species

J. mercaptan or chlorohydrocarbon can act as the chain transfer agents

$$\sim\sim\cdot + RSH \longrightarrow \sim\sim H + RS\cdot$$

$$\sim\sim\cdot + CCl_3H \longrightarrow \sim\sim H + CCl_3\cdot$$

(4)

A. a) i) no loop forming side reaction

ii) principle of equal reactivity such that

$$\frac{C_0 - C_t}{C_0} = p \text{ which is indep't of } x\text{, chain length}$$

iii) When $p \lesssim 1$, $q \equiv 1-p \gtrsim 0$, such that $1-p \approx e^{-q}$

b) i) Steady-state approximation for

$$\frac{d}{dt}\sum_{x=1}^{\infty}(RM_x^{\bullet}) = 0 \quad \text{and} \quad \frac{d(RM_x^{\bullet})}{dt} = 0$$

such that $(RM_x^{\bullet}) = (R^{\bullet})\alpha^{x-1}$

$$\alpha = \frac{k_p(M)}{k_p(M) + (\nu_i k_t)^{1/2}} \lesssim 1$$

ii) $RM_x^{\bullet} + RM_y^{\bullet} \longrightarrow RP_{x+y}R$, recombination only

iii) $1-\alpha \equiv q \gtrsim 0$, such that $1-\alpha \approx e^{-q}$

c) i) no initiation or termination such that all reactions have the same rate constant k

ii) $x \approx \nu$ where all $X(x)$ is populated such that

$$X_x = \frac{e^{-\nu}\nu^{x-1}}{(x-1)!} \approx \frac{e^{-(x-\nu)^2/2\nu}}{\sqrt{2\pi\nu}}$$

B. $$W(x) = \frac{x X(x)}{\int_0^{\infty} x X(x)\,dx} = \frac{x X(x)}{Q_1}, \quad Q_1/Q_0 = x_n,\ Q_0 = 1$$

$\therefore x_n = Q_1$

a) $$W(x) = \frac{x q e^{-qx}}{(1/q)} = x q^2 e^{-qx}$$

b) $$W(x) = \frac{x^2 q^3 e^{-qx}}{(2/q)} = \frac{1}{2} x^2 q^3 e^{-qx}$$

c) $$W(x) = x e^{-(x-\nu)^2/2\nu}/\sqrt{2\pi\nu} \cdot \nu = \frac{x e^{-(x-\nu)^2/2\nu}}{\sqrt{2\pi\nu^3}}$$

a) $x_w = \int_0^\infty x\, W(x)\, dx = q^2 \int_0^\infty x^2 e^{-qx} dx = q^2 \frac{2!}{q^3} = \frac{2}{q}$

$x_w / x_n = {}^{2}/_{q} \big/ {}^{1}/_{q} = 2$

b) $x_w = \frac{1}{2} q^3 \int_0^\infty x^3 e^{-qx} dx = \frac{1}{2} q^3 \cdot \frac{3!}{q^4} = \frac{3}{q}$

$x_w / x_n = {}^{3}/_{q} \big/ {}^{2}/_{q} = 3/2 = 1.5$

c) $x_w = \frac{1}{\sqrt{2\pi\nu^3}} \int_0^\infty x^2 e^{-(x-\nu)^2/2\nu} dx = \frac{1}{\sqrt{2\pi\nu^3}} \int_{-\infty}^\infty (u+\nu)^2 e^{-u^2/2\nu} du$

$x - \nu = u$

$dx = d\nu$

$x = 0,\ u = -\nu \to -\infty$

$x = \infty,\ u = \infty$

$$= \frac{2}{\sqrt{2\pi\nu^3}} \left\{ \frac{1}{2^2 \left(\frac{1}{2\nu}\right)} \sqrt{\frac{\pi}{\frac{1}{2\nu}}} + \nu^2 \frac{1}{2} \sqrt{\frac{\pi}{\frac{1}{2\nu}}} \right\}$$

$$= \frac{1}{\cancel{\sqrt{2\pi\nu}}\,\nu} \left\{ \nu \cancel{\sqrt{2\pi\nu}} + \nu^2 \cancel{\sqrt{2\pi\nu}} \right\} = 1 + \nu$$

$x_w / x_n = \frac{\nu + 1}{\nu} = 1 + \frac{1}{\nu} \approx 1$

C. $W(x)$ maximizes when $x = x_n$

a) $\frac{dW(x)}{dx} = q^2 \left(e^{-qx} + x(-q) e^{-qx} \right) = 0$

$1 = q x_{max}, \quad x_{max} = \frac{1}{q} = x_n$

b) $\frac{dW(x)}{dx} = \frac{1}{2} q^3 \left(2x e^{-qx} + x^2(-q) e^{-qx} \right) = 0$

$2 = q x_{max}, \quad x_{max} = \frac{2}{q} = x_n$

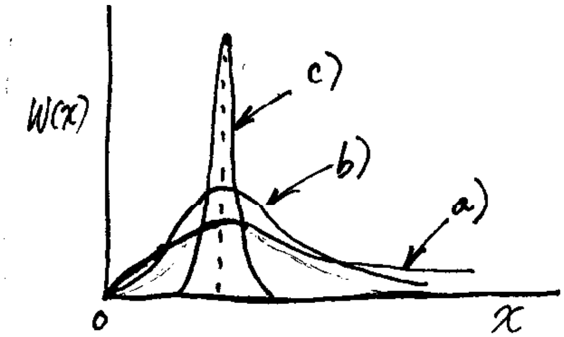
c) $e^{-(x-\nu)^2/2\nu} \to e^0$ when $x = \nu = x_n$

(4) D. a) $W(\frac{1}{q}) = \frac{1}{q}\cdot q^2 \cdot e^{-q\frac{1}{q}} = qe^{-1} = q/e$

b) $W(\frac{2}{q}) = \frac{1}{2}\left(\frac{2}{q}\right)^2 q^3 e^{-q\frac{2}{q}} = \frac{1}{2}\frac{4}{q^2}\, q^3 \cdot e^{-2} = 2q/e^2$

c) $W(\nu) = \frac{\nu}{\sqrt{2\pi\nu}\cdot\nu}\, e^0 = \frac{1}{\sqrt{2\pi\nu}}$

E.



a) $W(\frac{1}{q}) = \frac{1}{10^3\cdot e} = 3.7\cdot 10^{-4}$

b) $W(\frac{2}{q}) = \frac{4}{10^3\cdot e} = 1.5\cdot 10^{-3}$

c) $W(\nu) = \frac{1}{\sqrt{2\pi\cdot 10^3}} = 1.3\cdot 10^{-2}$

not necessary

(5) A. $F_1 = \frac{-d(M_1)/dt}{-\frac{d(M_1)}{dt} - \frac{d(M_2)}{dt}} = \frac{d(M_1)}{d(M_1)+d(M_2)}$

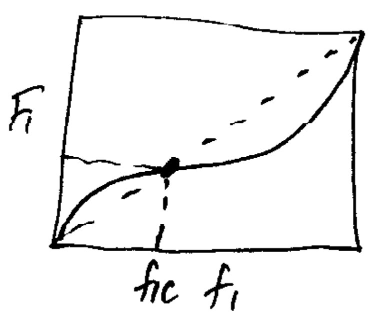
B. Steady state approximation for (R_1) and (R_2)

$$-\frac{d(R_1)}{dt} = k_{12}(R_1)(M_2) - k_{21}(R_2)(M_1) = 0$$

$$-\frac{d(R_2)}{dt} = -k_{12}(R_1)(M_2) + k_{21}(R_2)(M_1) = 0$$

$$\therefore\ k_{12}(R_1)(M_2) = k_{21}(R_2)(M_1)$$

C



f_{1c} : azeotropic composition

$$f_{1c} = \frac{r_1 f_{1c}^2 + f_{1c}(1-f_{1c})}{r_1 f_{1c}^2 + 2f_{1c}(1-f_{1c}) + r_2(1-f_{1c})^2}, \qquad f_{1c} = \frac{1-r_2}{2-(r_1+r_2)}$$

This should suffice

D. $f_{1c} = \frac{1}{3}$

$$\frac{1}{3} = \frac{r_1\left(\frac{1}{3}\right)^2 + \left(\frac{1}{3}\right)\left(\frac{2}{3}\right)}{r_1\left(\frac{1}{3}\right)^2 + 2\left(\frac{1}{3}\right)\left(\frac{2}{3}\right) + r_2\left(\frac{2}{3}\right)^2} = \frac{r_1\frac{1}{9} + \frac{2}{9}}{r_1\frac{1}{9} + \frac{4}{9} + r_2\frac{4}{9}} = \frac{r_1 + 2}{r_1 + 4 + 4r_2}$$

$3r_1 + 6 = r_1 + 4 + 4r_2$, $2r_1 + 2 = 4r_2$, $\underline{\underline{r_1 + 1 = 2r_2}}$

E.