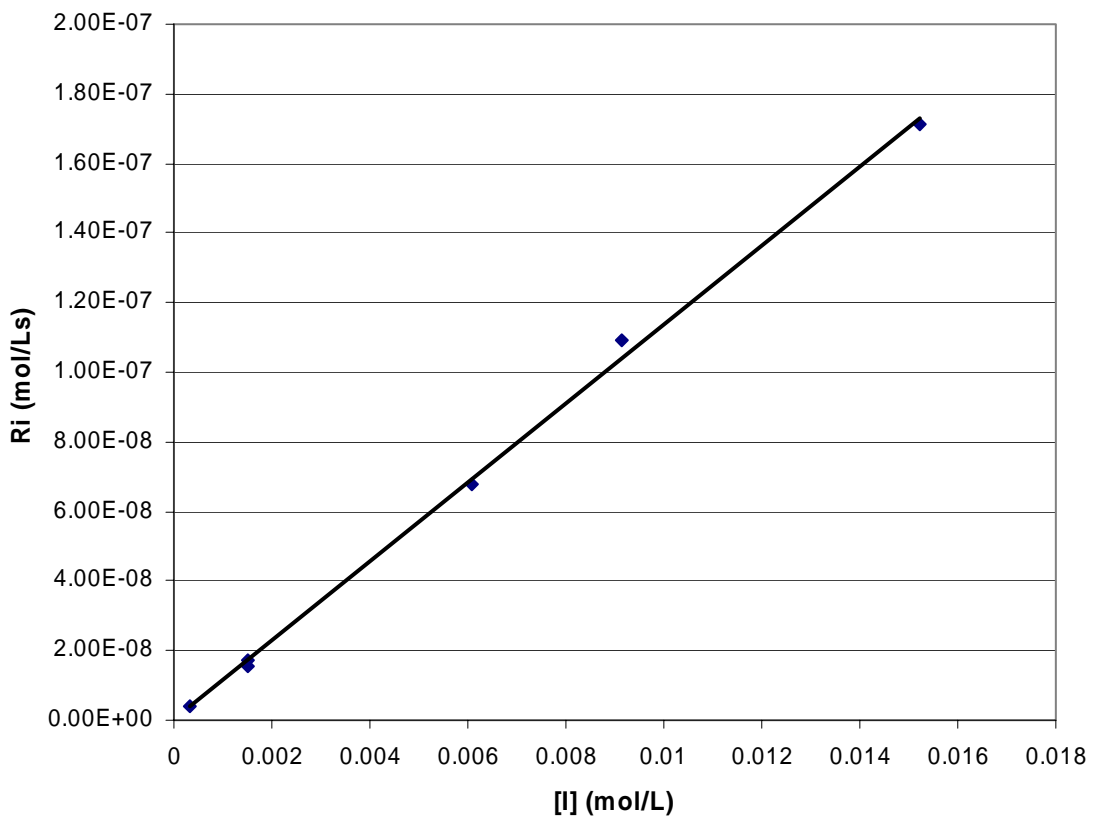


**Problem 39.**

$$R_i = \frac{R_p}{\bar{V}} = 2fk_d[I]$$

$$M_{0, \text{AIBN}} = 164 \text{ g/mol}$$

$$k_d = 0.0388 \text{ hr}^{-1} \left( \frac{1 \text{ hr}}{3600 \text{ s}} \right) = 1.078 \times 10^{-5} \text{ s}^{-1}$$



$$\text{Slope of line} = 1.14 \times 10^{-5} = 2fk_d$$

$$\text{Thus } f = 0.53$$

**Problem 40.**

$$\bar{\tau} = \frac{1}{2(fk_t k_d [I])^{1/2}} \Rightarrow (fk_d [I])^{1/2} = \frac{1}{2\bar{\tau} k_t^{1/2}}$$

$$R_p = k_p [M] \frac{1}{k_t^{1/2}} (fk_d [I])^{1/2} \Rightarrow [M] = \frac{2R_p \bar{\tau} k_t}{k_p}$$

Run	[M] (mol/L)
5	16.1
6	13.5
8	13.5
12	17.8
13	14.3

Double check with  $R_i$  values provided:

$$R_p = k_p [M] \left( \frac{R_i}{2k_t} \right)^{1/2} \Rightarrow [M] = \frac{R_p}{k_p} \left( \frac{2k_t}{R_i} \right)^{1/2}$$

Run	[M] (mol/L)
5	16.3
6	13.1
8	13.4
12	18.0
13	14.4

These values agree quite well with those calculated above.

**Problem 41.**

At higher conversions, the polymer radicals are larger (on average) than at low conversions. This leads to a slight increase in the viscosity, and given that the termination of active radical chains is diffusion limited, the rate constant of termination ( $k_t$ ) drops accordingly. This decrease in termination rate accounts for the increased lifetime observed for radicals at higher conversions. This is a rather mild example of the auto-acceleration, known as the Trommsdorff effect, discussed in section 3.4B of the text.

**Problem 42.**

$$N_n = \frac{2 - \alpha}{1 - p}$$

$$\frac{N_w}{N_n} = \frac{4 - 3\alpha - \alpha p + 2p}{(2 - \alpha)^2}$$

The results are presented in the table below:

$N_n$	$N_w/N_n$	$p$	$\alpha$
1129	1.60	0.998	0.191
924	1.67	0.998	0.316
674	1.73	0.998	0.419
609	1.74	0.997	0.436

**Problem 43.**

For disproportionation:

$$x_i = (1-p)p^{i-1} \quad (\text{equation 3.7.16})$$

For combination:

$$x_i = (i-1)(1-p)^2 p^{i-2} \quad (\text{equation 3.7.26})$$

Derivation of number average degree of polymerization expression:

$$N_n = \sum_{i=1}^{\infty} ix_i = \alpha \sum_{i=1}^{\infty} i(1-p)p^{i-1} + (1-\alpha) \sum_{i=1}^{\infty} i(i-1)(1-p)^2 p^{i-2}$$

$$N_n = \alpha(1-p) \sum_{i=1}^{\infty} ip^{i-1} + (1-\alpha)(1-p)^2 \sum_{i=1}^{\infty} i(i-1)p^{i-2} = \alpha(1-p) \frac{1}{(1-p)^2} + (1-\alpha)(1-p)^2 \frac{2}{(1-p)^3}$$

$$N_n = \frac{\alpha}{1-p} + \frac{2(1-\alpha)}{1-p} = \frac{2-\alpha}{1-p}$$

Note that:

$$\sum_{i=1}^{\infty} i(i-1)p^{i-2} = \frac{d}{dp} \left( \sum_{i=1}^{\infty} ip^{i-1} \right) = \frac{d}{dp} \left( \frac{1}{(1-p)^2} \right) = \frac{2}{(1-p)^3}$$

Now derive the equation for the PDI:

$$\text{Given: } w_i = \frac{ix_i}{N_n}$$

Therefore:

$$\frac{N_w}{N_n} = \frac{1}{N_n} \frac{\sum_{i=1}^{\infty} iw_i}{\sum_{i=1}^{\infty} w_i} = \frac{1}{N_n} \frac{\sum_{i=1}^{\infty} \frac{i^2 x_i}{N_n}}{\sum_{i=1}^{\infty} \frac{ix_i}{N_n}} = \frac{1}{N_n} \frac{\sum_{i=1}^{\infty} i^2 x_i}{\sum_{i=1}^{\infty} ix_i}$$

Substituting:

$$\frac{N_w}{N_n} = \frac{1-p}{2-\alpha} \left[ \frac{\alpha \sum_{i=1}^{\infty} i^2 (1-p) p^{i-1} + (1-\alpha) \sum_{i=1}^{\infty} i^2 (i-1) (1-p)^2 p^{i-2}}{\alpha \sum_{i=1}^{\infty} i (1-p) p^{i-1} + (1-\alpha) \sum_{i=1}^{\infty} i (i-1) (1-p)^2 p^{i-2}} \right]$$

$$\frac{N_w}{N_n} = \frac{1-p}{2-\alpha} \left[ \frac{\alpha (1-p) \sum_{i=1}^{\infty} i^2 p^{i-1} + (1-\alpha) (1-p)^2 \sum_{i=1}^{\infty} i^2 (i-1) p^{i-2}}{\alpha (1-p) \sum_{i=1}^{\infty} i p^{i-1} + (1-\alpha) (1-p)^2 \sum_{i=1}^{\infty} i (i-1) p^{i-2}} \right]$$

$$\frac{N_w}{N_n} = \frac{1-p}{2-\alpha} \left[ \frac{\alpha (1-p) \frac{1+p}{(1-p)^3} + (1-\alpha) (1-p)^2 \left( \frac{1}{(1-p)^3} + \frac{3(1+p)}{(1-p)^4} \right)}{\alpha (1-p) \frac{1}{(1-p)^2} + (1-\alpha) (1-p)^2 \frac{2}{(1-p)^3}} \right]$$

Note that:

$$\sum_{i=1}^{\infty} i^2 (i-1) p^{i-2} = \frac{d}{dp} \left( \sum_{i=1}^{\infty} i^2 p^{i-1} \right) = \frac{d}{dp} \left( \frac{1+p}{(1-p)^3} \right) = \frac{1}{(1-p)^3} + \frac{3(1+p)}{(1-p)^4}$$

Now simplify terms and obtain the final expression:

$$\frac{N_w}{N_n} = \frac{1-p}{2-\alpha} \left[ \frac{\alpha \frac{1+p}{(1-p)^2} + (1-\alpha) \left( \frac{1-p}{(1-p)^2} + \frac{3(1+p)}{(1-p)^2} \right)}{\alpha \frac{1}{1-p} + (1-\alpha) \frac{2}{1-p}} \right]$$

$$\frac{N_w}{N_n} = \frac{1-p}{2-\alpha} \left[ \frac{\alpha \frac{1+p}{1-p} + (1-\alpha) \frac{4+2p}{1-p}}{\alpha + 2(1-\alpha)} \right] = \frac{\alpha(1+p) + (1-\alpha)(4+2p)}{(2-\alpha)(2-\alpha)}$$

$$\frac{N_w}{N_n} = \frac{4-3\alpha - \alpha p + 2p}{(2-\alpha)^2}$$

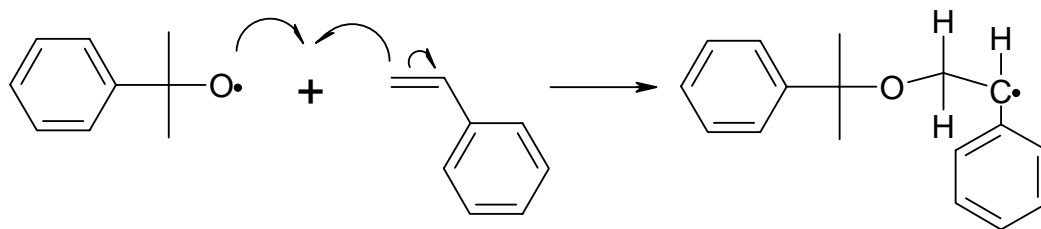
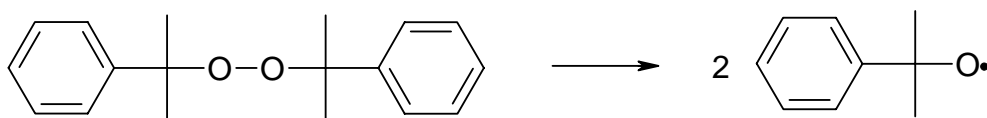
**Problem 44.**

solvent	$\bar{v}$	$\bar{v}_{tr}$	[SX]/[M]	$C_{sx}$
t-butyl alcohol	6580	3709	2.56	0.000046
methyl isobutyl ketone	6670	510	0.492	0.003681
diethyl ketone	6670	147	0.583	0.01144
chloroform	920	93	0.772	0.01252

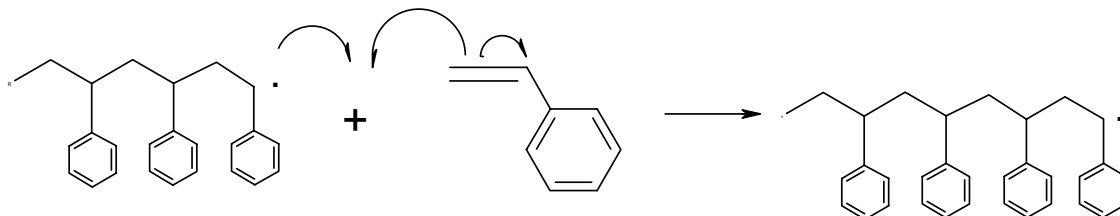
From the values of the kinetic chain length without chain transfer, it is clear that the reaction does not proceed the same in chloroform relative to the other solvents.

**Problem 45.**

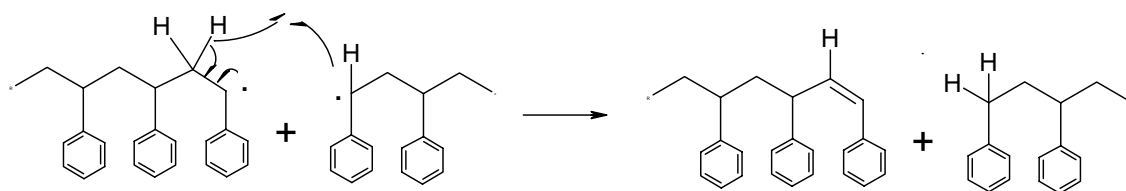
(a)



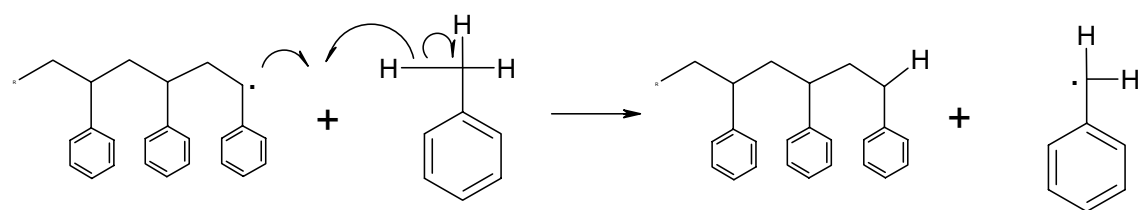
(b)



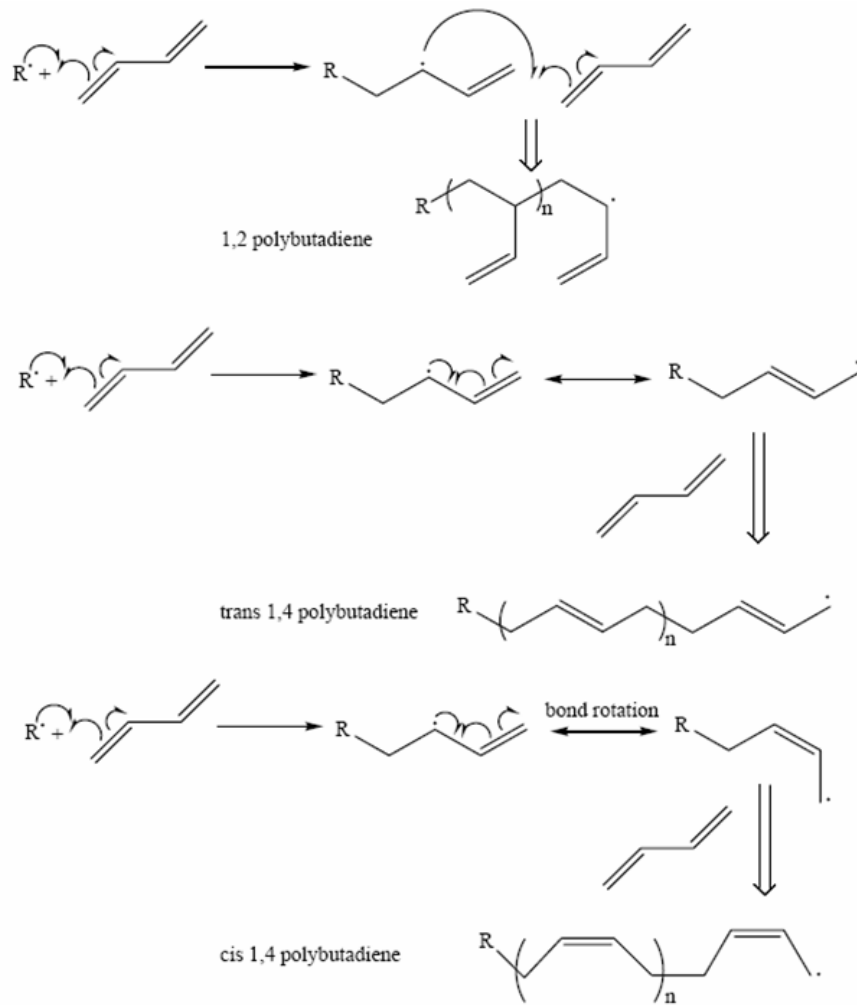
(c)



(d)



**Problem 46.**





**Problem 47.**

$$[I] = 0.04 \text{ M}$$

$$[M]_0 = 2.0 \text{ M}$$

$$M_0 \text{ of styrene} = 104 \text{ g/mol}$$

$$R_i = 1.6 \times 10^{-10} \text{ Ms}^{-1}$$

$$R_p = 6.4 \times 10^{-7} \text{ Ms}^{-1}$$

**Note: polymerization is run at 60°C, which is not explicit in the problem statement**

(a)

$$fk_d = \frac{R_i}{2[I]} = \frac{1.6 \times 10^{-10} \text{ Ms}^{-1}}{2(0.04 \text{ M})} = 2.0 \times 10^{-9} \text{ s}^{-1}$$

$$R_p = k_p [M] \left( \frac{fk_d [I]}{k_t} \right)^{1/2}$$

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M](fk_d [I])^{1/2}} = \frac{R_p}{[M] \left( \frac{R_i}{2} \right)^{1/2}} = \frac{6.4 \times 10^{-7} \text{ Ms}^{-1}}{2.0 \text{ M} \left( \frac{1.6 \times 10^{-10} \text{ Ms}^{-1}}{2} \right)^{1/2}} = 0.036 \text{ (Ms)}^{-1/2}$$

(b)

$$\bar{v} = \frac{R_p}{R_i} = \frac{6.4 \times 10^{-7} \text{ Ms}^{-1}}{1.6 \times 10^{-10} \text{ Ms}^{-1}} = 4000$$

(c)

$$\frac{1}{\bar{v}_r} = \frac{1}{\bar{v}} + C_M = \frac{1}{4000} + 0.85 \times 10^{-4} = 3.35 \times 10^{-4}$$

$$\bar{v} = N_n = 2.99 \times 10^3$$

$$M_n = N_n M_0 = 2.99 \times 10^3 (104 \text{ g/mol}) = 3.10 \times 10^5 \text{ g/mol}$$

(d)

$$\frac{1}{\bar{v}_r} = \frac{1}{\bar{v}} + C_T \frac{[T]}{[M]}$$

$$[T] = \left( \frac{1}{\bar{v}_r} - \frac{1}{\bar{v}} \right) \frac{[M]}{C_T} = \left( \frac{1}{\frac{40000 \text{ g/mol}}{104 \text{ g/mol}}} - \frac{1}{4000} \right) \frac{2.0 \text{ M}}{9.0 \times 10^{-3}} = 0.521 \text{ M} \cong 77 \text{ g/L CCl}_4$$

(e)

$$E_{app}^* = E_p^* + \frac{E_d^*}{2} - \frac{E_t^*}{2}$$

Values presented in Chapter 3 of the text:

$$E_p^* = 26,000 \text{ J/mol (at } 60^\circ\text{C)}$$

$$E_t^* = 8,000 \text{ J/mol (at } 60^\circ\text{C)}$$

$$E_d^* = 146,900 \text{ J/mol (at } 100^\circ\text{C)}$$

Assume the activation energies at  $100^\circ\text{C}$  are equivalent to those presented in the text.

Thus,  $E_{app}^* = 95,500 \text{ J/mol}$

Also presented in chapter 3 of the text:

$$k_p = 1.65 \times 10^2 \text{ (Ms)}^{-1} \text{ (} 60^\circ\text{C)}$$

$$k_t = 6.0 \times 10^7 \text{ (Ms)}^{-1} \text{ (} 60^\circ\text{C)}$$

$$k_d = 8.8 \times 10^{-7} \text{ s}^{-1} \text{ (} 100^\circ\text{C)}$$

Use these values to solve for the prefactors  $A_p$ ,  $A_t$ , and  $A_d$

$$k_p = 1.65 \times 10^2 \text{ (Ms)}^{-1} = A_p e^{\frac{-26000}{8.314(333)}}$$

$$A_p = 1.98 \times 10^6 \text{ (Ms)}^{-1}$$

$$k_t = 6.0 \times 10^7 \text{ (Ms)}^{-1} = A_t e^{\frac{-8000}{8.314(333)}}$$

$$A_t = 1.08 \times 10^9 \text{ (Ms)}^{-1}$$

$$k_d = 8.80 \times 10^{-7} \text{ s}^{-1} = A_d e^{\frac{-146900}{8.314(373)}}$$

$$A_d = 3.29 \times 10^{14} \text{ s}^{-1}$$

Find  $k_d$  at  $60^\circ\text{C}$  to determine  $f$ :

$$k_d = 3.29 \times 10^{14} \text{ s}^{-1} e^{\frac{-146900}{8.314(333)}} = 2.98 \times 10^{-9} \text{ s}^{-1}$$

$$f = \frac{fk_d}{k_d} = \frac{2.0 \times 10^{-9} \text{ s}^{-1}}{2.98 \times 10^{-9} \text{ s}^{-1}} = 0.671$$

Calculate  $R_p$  at 100 °C:

$$\ln R_p = \ln A_p \left( \frac{A_d}{A_t} \right)^{1/2} - \frac{E_{app}^*}{RT} + \ln(f[I]^{1/2}[M])$$

$$\ln R_p = \ln[1.98 \times 10^6 \left( \frac{3.29 \times 10^{14}}{1.08 \times 10^9} \right)^{1/2}] - \frac{95500}{8.314(373)} + \ln[(0.671)(0.04)^{1/2}(2)]$$

$$R_p = 2.5 \times 10^{-6} \text{ Ms}^{-1}$$

(f)

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} \left( \frac{R_i}{2} \right)^{1/2} [M]$$

$$-\frac{d[M]}{[M]} = \frac{k_p}{k_t^{1/2}} \left( \frac{R_i}{2} \right)^{1/2} dt$$

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

$$\ln \frac{[M]}{[M]_0} = \frac{k_p}{k_t^{1/2}} \left( \frac{R_i}{2} \right)^{1/2} t$$

$$k_t = 1.08 \times 10^9 (\text{Ms})^{-1} e^{\frac{-8000}{8.314(373)}} = 8.19 \times 10^7 (\text{Ms})^{-1}$$

$$k_p = 1.98 \times 10^6 (\text{Ms})^{-1} e^{\frac{-26000}{8.314(373)}} = 4.52 \times 10^2 (\text{Ms})^{-1}$$

$$t = 18000 \text{ s}$$

Calculate  $R_i$  @ 100 °C:

$$R_i = 2fk_d[I] = 2(8.80 \times 10^{-7} \text{ s}^{-1})(0.671)(0.04 \text{ M}) = 4.72 \times 10^{-8} \text{ Ms}^{-1}$$

$$\ln \frac{[M]_0}{[M]} = \frac{4.52 \times 10^2 (\text{Ms})^{-1}}{(8.19 \times 10^7 (\text{Ms})^{-1})^{1/2}} \frac{(4.72 \times 10^{-8} \text{ Ms}^{-1})^{1/2}}{\sqrt{2}} (18000 \text{ s})$$

$$\frac{[M]_0}{[M]} = 1.15 \Rightarrow [M] = \frac{2.0 \text{ M}}{1.15} = 1.74 \text{ M}$$

$$p = \frac{[M]_0 - [M]}{[M]_0} = \frac{2.0 - 1.74}{2.0} = 0.13$$

**Problem 48.**

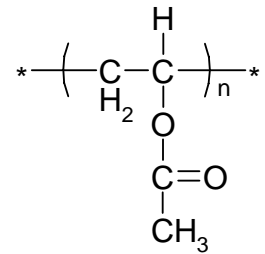
Calculate moles of polystyrene:

$$\frac{3.22g}{(1.52 \times 10^4)(104g/mol)} = 2.04 \times 10^{-6} mol$$

Convert polystyrene activity to a per mole basis:

$$\frac{203 counts min^{-1}}{2.04 \times 10^{-6} mol} = 9.95 \times 10^7 counts min^{-1} mol^{-1}$$

Since AIBN has two radical fragments per molecule and the polystyrene has roughly the same activity on a per mole basis as the AIBN, one can conclude that each polystyrene chain contains two AIBN radical fragments. This evidence suggests that combination is the primary mode of termination.

**Problem 49.**

$$N_n = 100000$$

Oxidation of the 1,2-diol linkages yields poly(vinyl alcohol) with  $N_n = 200$

$$\frac{100000}{200} \approx 500 \text{ chains formed after oxidation of each PVA chain}$$

Therefore, initial PVA chains were cleaved 499 times on average.

$$\frac{499}{100000} (100) = 0.5\% \text{ head-to-head linkages in the original polymer}$$

99.5% of the linkages are head-to-tail

**Problem 50.**

$a$  = fraction of chains terminated by combination

$(1-a)$  = fraction of chains terminated by disproportionation

$b$  = average # of initiator fragments per polymer molecule

$$a = \frac{2b - 2}{b} = \frac{2(1.4) - 2}{2} = 0.40 \text{ (combination)}$$

$$1 - a = 0.60 \text{ (disproportionation)}$$