

3.5 a

$$R_p = k_p [M] (f k_d [I] / k_t)^{\frac{1}{2}}$$

The integrated form of this equation is

$$-\ln \frac{[M]}{[M]_0} = \frac{2k_d}{k_t^{1/2}} \left( \frac{f[I]_0}{k_d} \right)^{\frac{1}{2}} \left( 1 - \exp^{-\frac{k_d t}{2}} \right) = -\ln(1 - P)$$

$$\text{At } t \rightarrow \infty, [M] \rightarrow [M]_{\infty}, P \rightarrow P_{\infty}$$

$$-\ln(1 - P_{\infty}) = \frac{2k_d}{k_t^{1/2}} \left( \frac{f[I]_0}{k_d} \right)^{\frac{1}{2}}$$

The question asked how a change in  $[M]_0$  could be used to increase  $P_{\infty}$ : regarding the equation above then the question is how  $[M]_0$  affects the rate constants  $k_d$ ,  $k_t$ ,  $k_p$ , since  $f$  and  $[I]_0$  are independent of the initial monomer concentration.  $k_d$  depends on the initiator chemistry, temperature and/or light only and is first order not on monomer concentration (this could be different if for example the monomer and initiator both absorbed at the wavelength used to initiate).  $k_t$  depends on the ability of two radical chains to come into proximity and then to react. This should not be affected by the amount of monomer present provided viscosity does not change appreciably (one could argue that with increasing monomer concentration a radical chain is less likely to react with another chain and more likely to react with a monomer, just statistically speaking, but this effect is included in  $R_p$  already by  $[M]$  term.)  $k_p$  does not depend on  $[M]$  as  $R_p$  is first order in  $[M]$ , so  $k_p$  cannot have any  $[M]$  dependence.

So we are led to conclude that we cannot modify  $P_{\infty}$  by changing  $[M]_0$ .

Note that  $P_{\infty} = 1 - \frac{[M]_{\infty}}{[M]_0}$ . Since  $[M]_{\infty}$  does not change  $P_{\infty}$  we must conclude that  $[M]_{\infty}$  scales with  $[M]_0$ .

3.5 b). We can use the dead-end technique to answer this portion of the question. In the problem it is clear that steady state applies since we are only 10-20% converted. So

$$R_i = R_t \text{ and } \frac{d[M_0]}{dt} = 0$$

From the rate equation for propagation,

$$-\frac{d[M]}{dt} = R_p = \frac{k_p[M] \left( f \frac{k_d[I]}{k_t} \right)^{1/2}}{k_t} *$$

Assume initiation is first order in  $[I]$ , so  $-\frac{d[I]}{dt} = k_d[I]$  and

$[I] = [I]_0 e^{-k_d t}$ . Substituting into \* and integrating with the initial condition  $[M] = [M_0]$  at  $t = 0$ ,

$$-\ln \frac{[M]}{[M_0]} = \frac{2k_p}{k_t^{1/2}} \left( \frac{f[I]_0}{k_d} \right)^{1/2} \left( 1 - \exp \frac{-k_d t}{2} \right)$$

We consider for this problem  $t \rightarrow \infty$ , so the exponential term disappears:

$$** \quad -\ln \frac{[M]_\infty}{[M_0]} = \frac{2k_p}{k_t^{1/2}} \left( \frac{f[I]_0}{k_d} \right)^{1/2} = 2k_p \left( \frac{f}{k_d k_t} \right)^{1/2} [I_0]^{1/2}$$

Case 1:  $p_\infty = 0.1$

By definition,  $p_\infty = \frac{[M_0] - [M_\infty]}{[M_0]}$ , so  $\frac{[M_\infty]}{[M_0]} = 1 - p_\infty$

$$-\frac{\ln(0.9)}{[I]_0^{1/2}} = 2k_p \left( \frac{f}{k_d k_t} \right)^{1/2}$$

Case 2:  $p_\infty = 0.2$

$$-\frac{\ln(0.8)}{[I]_2^{1/2}} = 2k_p \left( \frac{f}{k_d k_t} \right)^{1/2}$$

$$\therefore \frac{\ln(0.9)}{[I_0]_1^{1/2}} / \frac{\ln(0.8)}{[I_0]_2^{1/2}} = 1 \Rightarrow \text{over}$$

Rate constants and  $f$  do not depend on concentration of initiator to first approximation, so these two quantities are equal.

$$\therefore \frac{[I_0]_2}{[I_0]_1} = \left[ \frac{\ln(0.8)}{\ln(0.9)} \right]^2 = 4.4856$$

So we need to increase the initiator concentration by  $\sim 4\frac{1}{2}$  times to increase conversion. This result is consistent with intuition which says we need more initiator to polymerise more monomer if the kinetic chain length is fixed.

Effects on  $R_p$ ,  $DP$ ?

$$R_p \Rightarrow \text{Increases } R_p \text{ by a factor of } \sqrt{\frac{[I_0]_2}{[I_0]_1}} = 2.12$$

$$DP \Rightarrow \overline{DP}_n = \frac{k_p^2 [M]^2}{R_p} (k_t) \propto \frac{1}{R_p} \text{ (Audit, eqn 6.64)}$$

So the degree of polymerization decreases by a factor of 2.12

c) Thermally initiated:

Temperature affects  $k_d$  exponentially if the initiator is thermally homolysed. But it also affects all the rates, so we need to consider  $k_t$  and  $k_p$  as well.

Returning to \*\*, we can take the ratio for the 10% and 20% conversion rates:

$$A \equiv \frac{\ln[0.9]}{\ln[0.8]} = \frac{\left( \frac{k_p}{(k_d k_t)^{1/2}} \right)_{10\%}}{\left( \frac{k_p}{(k_d k_t)^{1/2}} \right)_{20\%}}$$

Taking the log of both sides and noting that all the  $k_p$  behave Arrheniusly  $k = A \exp^{-E/RT}$

$$\ln A = \ln \left[ \frac{k_p}{(k_d k_t)^{1/2}} \right]_{10\%} - \left( \frac{E_{RP}}{RT} \right)_{10\%} - \ln \left[ \frac{k_p}{(k_d k_t)^{1/2}} \right]_{20\%} + \left( \frac{E_{RP}}{RT} \right)_{20\%}$$

The  $A_p/A_d/A_t$  values should be independent of temperature.

Also  $E_{RP}$  = total activation energy for polymerization rate is

independent of temperature. So

$$\ln A = \frac{E_{RP}}{R} \left[ \frac{1}{T_{20\%}} - \frac{1}{T_{10\%}} \right]$$

Let  $T_{20\%} = f T_{10\%}$ . We wish to see whether  $f > 1$  or  $< 1$ .

$$\ln A = \frac{E_{RP}}{R} \left[ \frac{T_{10\%} - T_{20\%}}{T_{10\%} T_{20\%}} \right] = \frac{E_{RP}}{R} \left[ \frac{1-f}{f T_{10\%}} \right]$$

Solving for  $f$ :

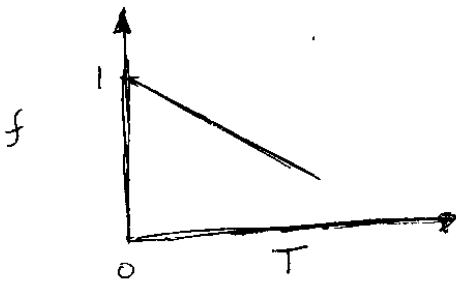
$$\frac{R \ln A}{E_{RP}} f T_{10\%} + f = 1$$

$$f = \frac{1}{\left( \frac{R \ln A}{E_{RP}} T_{10\%} + 1 \right)}$$

Plugging in values,

$$f \approx \frac{1}{1.56E^3 T + 1}$$

Note that we cannot determine  $f$  exactly without knowing the reference temperature.



$f$  is  $> 1$  for all values of  $T$ . Therefore  $T_{20\%} > T_{10\%}$  and we need to decrease the temperature.

Photochemically Initiated:

Temperature has no effect on  $K_d$  in the ideal case.

We proceed in the same manner, but  $k_{d10\%} = k_{d20\%}$

$$\text{So } \ln A = \frac{E_p - \frac{E_t}{2}}{R} \left[ \frac{1-f}{f T_{10\%}} \right], \text{ where now } E_p - \frac{E_t}{2} = 28 \text{ kJ/mol.}$$

So basically since  $E_p - \frac{E_t}{2} > 0$  an increase in temperature will have the desired effect to increase conversion. However  $f$  may need to be large in this case because there is no effect on the initiator.

3.6

$$f = 1.3 = \frac{\# \text{ fragment initiators}}{\# \text{ polymer molecules}} \leftarrow \text{propagating (prior to coupling/disproportionation)}$$

$a$  = fraction of propagating chains undergoing coupling

$1-a$  = fraction of propagating chains undergoing disproportionation

Then for a system w/  $n$  propagating polymer molecules,

$$f = \frac{\frac{an}{2} + (1-a)n}{\frac{an}{2} + (1-a)n} = \frac{2}{2-a}$$

disproportionation yields  $(1-a)n$  fragments per  $(1-a)n$  molecules

coupling yields  $an$  fragments per  $\frac{an}{2}$  molecules

$$\therefore a = \frac{2f-2}{f}$$

$$= \frac{2(1.3)-2}{1.3}$$

$$= 0.462$$

$\therefore$  46.2% coupling  
53.8% disproportionation

Problem 3-7

Given  $[M]_0 = 0.2 M$

$[I]_0 = 4 \times 10^{-3} M$

$T = 60^\circ C$

$k_p = 145 \frac{L}{mol \cdot s}$

$k_t = 7 \times 10^7 \frac{L}{mol \cdot s}$

$f = 1$

$t_{1/2} = 44 \text{ hr.} \longrightarrow k_d = \frac{\ln 2}{t_{1/2}} = 0.0158 \text{ hr}^{-1} \cdot \frac{\text{hr}}{60^2 \text{ s}} = 4.376 \times 10^{-6} \text{ s}^{-1}$

Determine time to 50% conversion.

$$-\ln \frac{[M]}{[M]_0} = \frac{2 k_p}{(k_t)^{1/2}} \left( \frac{f [I]_0}{k_d} \right)^{1/2} (1 - e^{-k_d t/2})$$
 Rudin eqn 6-35

$-\ln(1-p) =$

$-\ln(0.5) = \frac{2 (145) \frac{L}{mol \cdot s}}{\sqrt{7 \times 10^7 \frac{L}{mol \cdot s}}}$

$\left( \frac{1.4 \times 10^{-3} \frac{mol}{L}}{4.376 \times 10^{-6} \text{ s}^{-1}} \right)^{1/2} (1 - e^{-k_d t/2})$

Solve w/ Maple (eg).

$t = 137.5 \text{ hr}$

```

> eqn1 := -ln(1-p) = 2*kp/sqrt(kt) * (f*I0/kd)^(1/2) * (1-exp(-kd*t/2));
                                kp * sqrt(f*I0/kd) * (1 - e^(-1/2*kd*t))
                                -----
                                sqrt(kt)
eqn1 := -ln(1-p) = 2 *
> kp:=145;                                kp := 145
> kd:=4.376*10^(-6);                        kd := .4376000000 10^-5
> kt:=7*10^7;                               kt := 70000000
> I0:=4*10^(-3);                            I0 := 1/250
> f:=1;                                     f := 1
> p:=0.5;                                   p := .5
> eqn1;
                                .6931471806 = .0001252539114 * sqrt(70000000) * (1 - e^(-2.188000000 10^-5*t))
> solve(eqn1, t)/60^2;
                                137.4961989
>

```

Problem 3.17

a) Determine time for Case 4...

The integrated form of the polymerization rate equation can be written as

$$-\ln \frac{[M]}{[M_0]} = 2 k_p \left( \frac{f [I_0]}{k_t k_d} \right)^{1/2} (1 - \exp^{-k_d t/2})$$

Let  $V \equiv \frac{k_p f^{1/2}}{(k_t)^{1/2}}$ , and  $\frac{[M]}{[M_0]} = 1 - p$  % conversion

$$-\ln(1-p) = \frac{2V[I_0]^{1/2}}{k_d^{1/2}} (1 - \exp^{-k_d t/2})$$

Consider cases #1 and #3. These are both at 60°C, and we can use the given values for  $p$ ,  $[I_0]$  and  $t$  to solve for  $V$  and  $k_d$ . This is done on the attached maple spreadsheet.

The formulas are reproduced below:

$$\textcircled{1} -\ln(0.5) = \frac{2V}{k_d^{1/2}} (2.5 \times 10^{-3})^{1/2} (1 - \exp^{-\frac{k_d}{2}(500 \cdot 60)})$$

↑ in seconds

$$\textcircled{2} -\ln(0.6) = \frac{2V}{k_d^{1/2}} (1 \times 10^{-3})^{1/2} (1 - \exp^{-k_d/2(600 \cdot 60)})$$

Solving for  $V$  and  $k_d$  yields

$$k_d = 2.0778 \times 10^{-5} \text{ Hz}$$

$$V = 0.118 \left( \frac{\text{L}}{\text{mol} \cdot \text{s}} \right)^{1/2}$$

Now consider case 4. These values should be the same for this case since temperature is the same. Thus for 4 we have

$$-\ln(0.5) = \frac{2(0.118) \left( \frac{\text{L}}{\text{mol} \cdot \text{s}} \right)^{1/2} \cdot (10^{-2} \frac{\text{mol}}{\text{L}})^{1/2}}{(2.0778 \times 10^{-5})^{1/2} \text{ s}^{1/2}} \left( 1 - \exp^{-\frac{2.0778 \times 10^{-5} \text{ s}^{-1}}{2} t} \right)$$

Part a)

3-17

```
> eqnA:=-ln(1-p1)=2*V/kd^(1/2)*I1^(1/2)*(1-exp(-kd*t1/2));  
eqnA:=-ln(1-p1)=2 *  $\frac{V\sqrt{I1}(1-e^{(-1/2 kd t1)})}{\sqrt{kd}}$   
> eqnB:=-ln(1-p2)=2*V/kd^(1/2)*I2^(1/2)*(1-exp(-kd*t2/2));  
eqnB:=-ln(1-p2)=2 *  $\frac{V\sqrt{I2}(1-e^{(-1/2 kd t2)})}{\sqrt{kd}}$   
> p1:=.5;  
p1 := .5  
> p2:=.4;  
p2 := .4  
> t1:=500*60;  
t1 := 30000  
> t2:=600*60;  
t2 := 36000  
> I1:=2.5*10^(-3);  
I1 := .002500000000  
> I2:=1*10^(-3);  
I2 :=  $\frac{1}{1000}$   
> eqnA;  
.6931471806 = .1000000000 *  $\frac{V(1-e^{(-15000 kd)})}{\sqrt{kd}}$   
> eqnB;  
.5108256238 =  $\frac{1}{500} \frac{V\sqrt{1000}(1-e^{(-18000 kd)})}{\sqrt{kd}}$   
> solve({eqnA, eqnB}, {kd, V});  
{V=.1439549775+.09056236635 I, kd=.0001334345371+.0004566694167 I},  
{V=.1179915251, kd=.00002077846770}  
> V:=.1179915251;  
V := .1179915251  
> kd:=.2077846770e-4;  
kd := .00002077846770  
> eqnC:=-ln(1-p3)=2*V/kd^(1/2)*I3^(1/2)*(1-exp(-kd*t3/2));  
eqnC:=-ln(1-p3)=51.76950964 *  $\sqrt{I3}(1-e^{(-.00001038923385 t3)})$   
> p3:=.5;  
p3 := .5  
> I3:=10*10^(-3);
```



```

t3 := 1/100
> eqnC;
.6931471806 = .5176950964 * sqrt(100) * (1 - e^(-.00001038923385 * t3))
> solve(eqnC, t3)/60;
230.5985265
>

```

3.17b Find the activation energy for the rate of polymerization.

$$R_p = k_p [M] \left( \frac{f k_d [I]}{k_t} \right)^{\frac{1}{2}}. \text{ Since } k_* = A_* \exp^{-E_*/RT}, \text{ (Arrhenius) then}$$

$$\ln R_p = \ln \left\{ A_p \left( \frac{A_d}{A_t} \right)^{\frac{1}{2}} \right\} + \ln (f [I]^{\frac{1}{2}} [M]) - \frac{E_A}{RT}, \text{ with } E_A = \text{the desired activation energy.}$$

It should be clear from this equation that we need to use the data given at two different temperatures. Subtracting  $\ln R_p$  at 80°C from that at 60°C gives

$$(\ln R_p)_{60^\circ\text{C}} - (\ln R_p)_{80^\circ\text{C}} = \ln \left( \frac{f [I]^{\frac{1}{2}} [M]_{60^\circ\text{C}}}{f [I]^{\frac{1}{2}} [M]_{80^\circ\text{C}}} \right) - \frac{E_A}{R} \left[ \frac{1}{333} - \frac{1}{353} \right]$$

$$\ln \frac{(R_p)_{60}}{(R_p)_{80}} = \ln \left[ \frac{(2.5 \times 10^{-3})^{\frac{1}{2}} (1)}{(10^{-3})^{\frac{1}{2}} (0.5)} \right] - E_A (2.0464 \times 10^{-5})$$

↑ in  $\frac{\text{J}}{\text{mol}}$

$$\ln \frac{(R_p)_{60}}{(R_p)_{80}} = 1.15129 - E_A (2.0464 \times 10^{-5})$$

Now to be fully rigorous we'd need to know  $(R_p)_{60^\circ\text{C}}$  and  $(R_p)_{80^\circ\text{C}}$ . To former we can already calculate from the information obtained in solving part a).

$$(R_p)_{60^\circ\text{C}} = [M] V [I]^{\frac{1}{2}} k_d^{\frac{1}{2}} = \left( 1 \frac{\text{mol}}{\text{L}} \right) \left( 2.5 \times 10^{-3} \frac{\text{mol}}{\text{L}} \right)^{\frac{1}{2}} (0.118) \left( \frac{\text{L}}{\text{mol s}} \right)^{\frac{1}{2}} (2.0778 \times 10^4)$$

$$(R_p)_{60^\circ\text{C}} = 2.6894 \times 10^{-5} \frac{\text{mol}}{\text{L s}} \quad *$$

3.17b cont.

However to obtain the latter we'd need to determine  $V$  and  $k_d$  as in part a) at  $80^\circ\text{C}$ . This would require another row in the table with time  $[M]$  and  $[I]$  all at  $80^\circ\text{C}$ .

Plugging these values back into  $(R_p)_{80^\circ\text{C}}$  and substituting into \* above would allow us to rigorously obtain  $E_R$ .

A less exact/rigorous treatment is to estimate  $R_p$  values using the definition  $R_p = -\frac{d[M]}{dt}$ . Assuming  $R_p$  is constant

over the interval specified then  $R_p = -\frac{\Delta M}{\Delta t}$ ,

$$(R_p)_t = -\frac{[M] - [M_0]}{t}, \quad [M] = [M_0](1 - p)$$

$$= -\frac{[M_0]}{t} (1 - p - 1) = \frac{p[M_0]}{t}$$

$$R_p(60^\circ\text{C}) = \frac{(0.5)(1 \frac{\text{M}}{\text{L}})}{500 \text{ min}} = 0.001 \frac{\text{M}}{\text{Lmin}} = 1.67 \times 10^{-5} \frac{\text{M}}{\text{Ls}}$$

$$R_p(80^\circ\text{C}) = \frac{(0.75)(0.5 \frac{\text{M}}{\text{L}})}{700 \text{ min}} = 5.357 \times 10^{-4} \frac{\text{M}}{\text{Lmin}}$$

Solving for  $E_R$  from \* gives  $E_R \sim 25.76 \text{ kJ/mol}$

6-3. Use the simple copolymer equation  
(eg Rudin 7-14)

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}, \quad F_2 = 1 - F_1$$

Here  $f_1 = f_2 = 0.5$ .

The compositions in each case are shown in the table below:

Case	r1	r2	F1	F2
1	0.1	0.2	0.478	0.522
2	0.1	10	0.091	0.909
3	0.1	3	0.216	0.784
4	0	0.3	0.435	0.565
5	0	0	0.500	0.500
6	0.8	2	0.375	0.625
7	1	15	0.111	0.889

$$f_1 = 0.5$$

$$f_2 = 0.5$$

Problem #6-7

$$\left. \begin{array}{l} \text{Styrene} = 1, \quad = [1.5M] \\ \text{Methyl Acrylate} = 2, \quad = [3.0M] \end{array} \right\} \begin{array}{l} f_1 = \frac{1.5}{3+1.5} = \frac{1}{3} \\ f_2 = \frac{3}{4.5} = \frac{2}{3} \end{array}$$

From odian, Table 6-2  $r_1 = 0.19$   
 $r_2 = 0.80$

$$\therefore F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$\boxed{\begin{array}{l} F_1 = 29.6\% \text{ Styrene} \\ F_2 = 70.4\% \text{ Methyl acrylate} \end{array}}$$

The composition will be independent of initiator concentration.

Problem #6-8.

Determine the tendency toward alternation of the given monomers w/ 1,3 butadiene.

We need to calculate  $r_1$  and  $r_2$  values, where

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

Note that this is an empirical, approximate method, but it should show the trends we need to answer the question.

$$r_1 r_2 = \exp[-(e_1 - e_2)^2]$$

There is an excellent table in Odian, pg 491 (1991 version) which has all the info needed. So let  $r_1 =$  butadiene and  $r_2 =$  2nd monomer.

Monomer 1	Q	e			
1,3 butadiene	1.7	-0.5			
Monomer 2	Q	e	r1	r2	r1*r2
n-butyl vinyl ether	0.038	-1.5	73.759	0.005	0.368
methyl methacrylate	0.78	0.4	1.390	0.320	0.445
methyl acrylate	0.45	0.64	2.136	0.128	0.273
styrene	1	-0.8	1.975	0.463	0.914
maleic anhydride	0.86	3.69	0.243	0.000	0.000
vinyl acetate	0.026	-0.88	79.066	0.011	0.866
acrylonitrile	0.48	1.23	1.491	0.034	0.050

When, for example  $r_1 > 1$ , this means a radical ending in a butadiene monomer will prefer to add another butadiene molecule, rather than monomer 2. Thus w/ n-butyl vinyl ether and vinyl acetate we'd expect to get mostly blocks of butadiene. The case will be worse w/ n-butyl vinyl ether as its  $r_2$  value is lower.

The best alternator will be maleic anhydride, for which  $r_1, r_2 < 0$  and  $r_1 r_2 \sim 0$ . We would expect a very high

degree of alternation in this case. The other five are more complicated. We cannot simply rank them according to  $r_1, r_2$  products being closer to zero because this only works when both  $r_1$  and  $r_2$  are less than zero. Otherwise there is a tendency for block formation, as in this case butadiene is favored to add to radical ends terminating in either butadiene or monomer two. We would expect then those pairs being closest to ideal ( $r_1 \sim r_2 \sim 1, r_1 r_2 = 1$ ) to be better alternating as they obey bernoullian statistics and will tend less towards higher butadiene incorporation.

