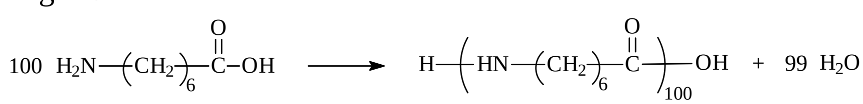
Problems 1-11, Chapter 11, Allcock and Lampe
ANSWER KEY

1. (a) $\overline{M}_n = 57{,}143$ g/mol
   (b) $\overline{M}_w = 83{,}333$ g/mol

2. (a) $\overline{M}_n = 108{,}538$ g/mol
   (b) $\overline{M}_w = 137{,}358$ g/mol
   (Each fraction was assigned the mid-point molecular weight.)

3. $M_o = 100$ g/mol
   (a) $$p = \frac{\overline{M}_w / M_o - 1}{\overline{M}_w / M_o + 1} = 0.989$$
   (b) $\overline{M}_n = \overline{M}_w / (1 + p) = 9{,}250 \text{ g/mol}$ 9,250 g/mol
   (c) Average number of structural units in the polymer molecules =
   $\overline{X}_n = \overline{M}_n / M_o = 92.5$
   (d) $\text{Prob}\,(185) = p^{x-1}(1-p) = 1.463 \times 10^{-3}$

4. (k at 187°C should be taken as 2.74 x10^{-2} kg/mol-min)
   $M_o = 127$ g/mol
   (a) 

   (b) E_p = 34.6 kcal/mol; A_p = 7.49 x10^{14} kg/mol-min
   (c) $\overline{X}_n = \overline{M}_n / M_o = 33.4$
   $$p = \frac{\overline{X}_n - 1}{\overline{X}_n + 1} = 0.942$$
   (d) $$p = \frac{\overline{M}_w / M_o - 1}{\overline{M}_w / M_o + 1} = 0.989$$

5. (a) From Problem 4, the reaction is second order. Therefore,
   $$-\frac{d[\text{COOH}]}{dt} = k_2[\text{COOH}]^2$$
   Integration yields:
   $$\frac{1}{[\text{COOH}]} - \frac{1}{[\text{COOH}]_o} = k_2 \text{t}$$
   But,
   $$\overline{X}_n = \frac{1}{1-p} = \frac{[\text{COOH}]_o}{[\text{COOH}]}$$, and combination yields:
   $$\overline{X}_n = k_2[\text{COOH}]_o t + 1$$

Now, we will modify the expression to account for the presence of 0.65 mol% of caproic acid.
Let $r = [NH_2]_o/[COOH]_o = 1/1.0065 = 0.9822$. Amine and carboxylic acid groups are consumed in equimolar amounts; thus,

$$[\mathrm{COOH}]_o - [\mathrm{COOH}] = [\mathrm{NH}_2]_o - [\mathrm{NH}_2]$$

and we have,

$$[\mathrm{NH}_2] = (\mathrm{r}-1)[\mathrm{COOH}]_o + [\mathrm{COOH}]$$

Therefore,

$$-\frac{d[\mathrm{COOH}]}{dt} = k_2[\mathrm{COOH}]\{(\mathrm{r}-1)[\mathrm{COOH}]_o + [COOH]\}$$

Separating variables, integrating, and rearranging yields:

$$\int_{[\mathrm{COOH}]_o}^{[\mathrm{COOH}]} \frac{\mathrm{d}[\mathrm{COOH}]}{[\mathrm{COOH}]\{(\mathrm{r}-1)[\mathrm{COOH}]_o + [\mathrm{COOH}]\}} = -k_2\int_0^t dt$$

$$\ln\frac{(\mathrm{r}-1)[\mathrm{COOH}]_o + [\mathrm{COOH}]}{\mathrm{r}[\mathrm{COOH}]} = (\mathrm{r}-1)[\mathrm{COOH}]_o k_2 t, \quad r < 1$$

Or, in terms of the conversion, p, of the minority groups (NH_2):

$$\ln\frac{1-p}{1-rp} = (r-1)[COOH]_o k_2 t, \quad r < 1$$

(In this particular case, $r = 0.9822$)

(b) (Assume that this question refers to the case for which caproic acid is absent.) From Problem 4, the value of the second-order rate constant, k_2, is 2.74 x10^{-2} kg/mol-min.

$$t = \frac{\dfrac{\overline{\mathrm{M}}_n - 18}{\mathrm{M}_o} - 1}{[\mathrm{COOH}]_o k_2} = 539 \text{ min}$$

(c) The average degree of polymerization in (b) above is 49.78, and hence, the conversion is 0.9799.
12,718 g/mol represents a degree of polymerization of 100.

$$W_x = x(1-p)^2 p^{x-1} = 5.41 \times 10^{-3}$$

Neglecting the weight of water contained in the terminal groups, the total mass of polymer molecules is 419.1 g (3.3 mol of aminocaproic acid repeat units at 127 g/mol each). Thus, 5.41 x10^{-3} × 419.1 g = 2.27 g of polyamide has a molecular weight of 12, 718 g/mol.

6. (a) Let $A = 2[COOH]_o^2 k_3$. The integrated rate expression for an uncatalyzed polyesterification is given as follows:

$$\frac{1}{(1-p)^2} = 1 + At$$

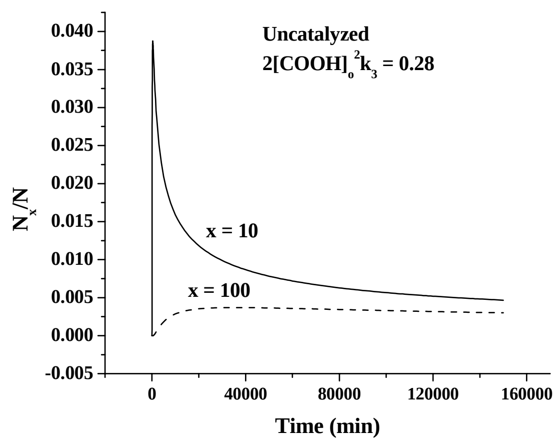
Solve for p:

$$p = 1 - \frac{1}{\sqrt{1+At}} = \frac{\sqrt{1+At}-1}{\sqrt{1+At}}$$

Combine with equation for Prob (x):

$$\text{Prob}(x) = \frac{N_x}{N} = \frac{\left(\sqrt{1+At}-1\right)^{x-1}}{\left(\sqrt{1+At}\right)^x}$$

The following is a plot of the mole fraction of polymer with x = 10 and x = 100 as a function of reaction time, with A = 0.28 (this value of A was chosen by setting $[COOH]_o$ = 8 eq/kg and k_3 = 0.0022 kg^2/eq^2-min):



(b) Let $B = [COOH]_o k_2$. The integrated rate expression for an acid-catalyzed polyesterification is given as follows:

$$\frac{1}{(1-p)} = 1 + Bt$$

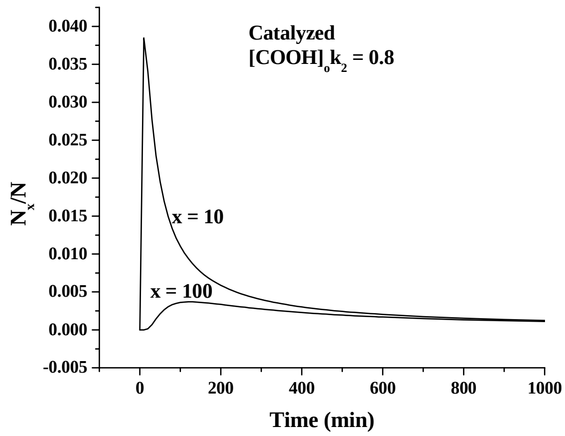
Solve for p:

$$p = 1 - \frac{1}{1+Bt} = \frac{Bt}{1+Bt}$$

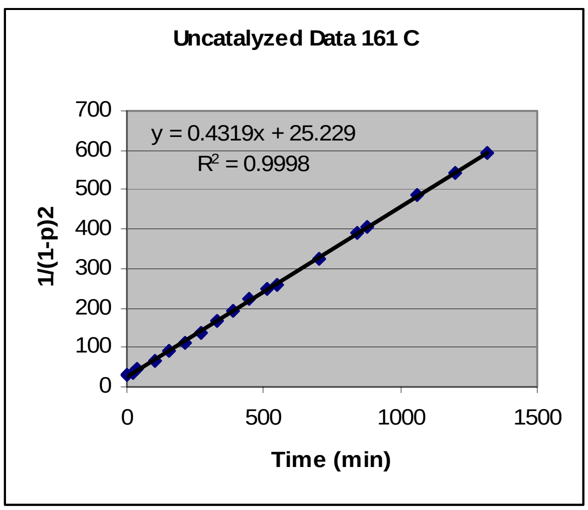
Combine with equation for Prob (x):

$$\text{Prob}(x) = \frac{N_x}{N} = \frac{(Bt)^{x-1}}{(1+Bt)^x}$$

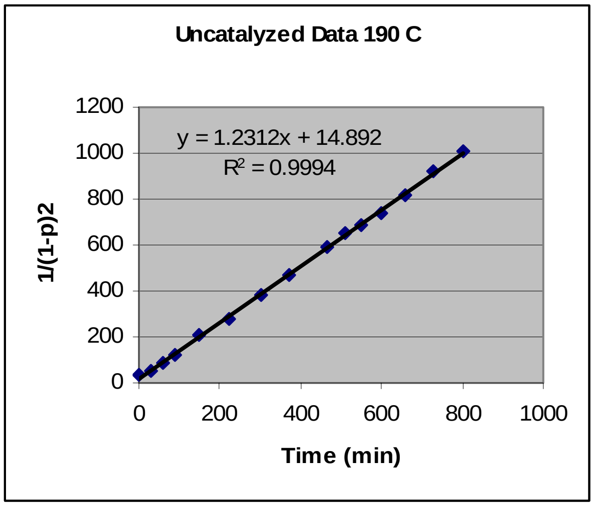
The following is a plot of the mole fraction of polymer with x = 10 and x = 100 as a function of reaction time, with *B* = 0.8 (this value of *B* was chosen by setting $[COOH]_o$ = 8 eq/kg and k_2 = 0.1 kg/eq-min):



7. (a) The following is a plot of the uncatalyzed data at 161°C. The slope obtained by linear regression is 0.4391 min^{-1}. The slope = $2[COOH]_o^2 k_3$; therefore, if $[COOH]_o$ = 6.24 eq/kg, then $k_3 = 5.55 \times 10^{-3}$ kg^2/eq^2-min.



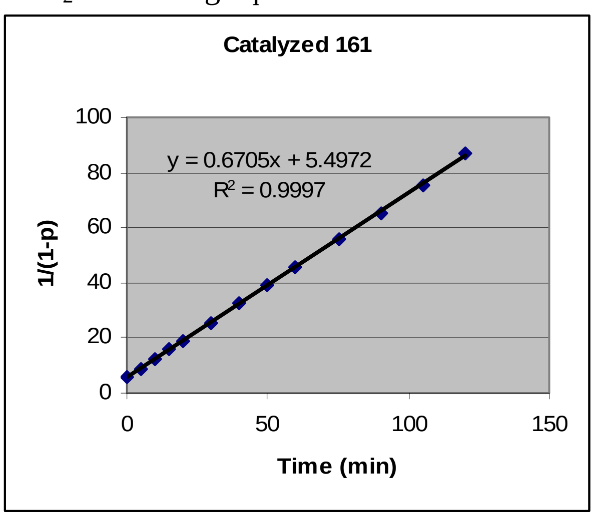
Below is a plot of the uncatalyzed data at 190°C. The slope obtained by linear regression is 1.2312 min^{-1}. The slope = $2[COOH]_o^2 k_3$; therefore, if $[COOH]_o$ = 6.24 eq/kg, then $k_3 = 1.58 \times 10^{-2}$ kg^2/eq^2-min.



190°C = 463K; 161°C = 434K

$$E_{act} = -R\ln\frac{k_{3,190}}{k_{3,161}}\left(\frac{1}{463}-\frac{1}{434}\right)^{-1} = 14.4\ \frac{\text{kcal}}{\text{mol}}$$

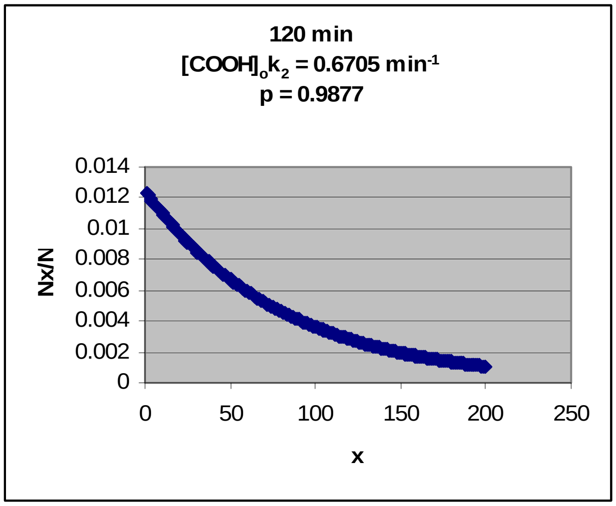
(b) Below is a plot of the catalyzed data at 161°C. The slope obtained by linear regression is 0.6705 min^{-1}. The slope = $[COOH]_o k_2$; therefore, if $[COOH]_o$ = 6.24 eq/kg, then k_2 = 0.107 kg/eq-min.

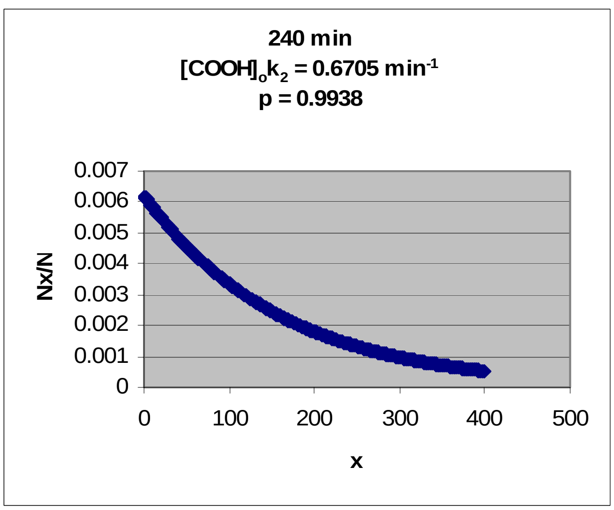


8. For the catalyzed polyesterification, $[COOH]_o k_2$ = 0.6705 min^{-1}. Recall from Problem 6 that for $B = [COOH]_o k_2$, the following distribution function holds:

$$\text{Prob}(x) = \frac{N_x}{N} = \frac{(Bt)^{x-1}}{(1+Bt)^x}$$

The following are plots of this function at 120 min (p=0.9877) and 240 min (p=0.9938):





Let $B = [\text{COOH}]_o k_2$. Recall, the integrated rate expression for an acid-catalyzed polyesterification is given as follows:

$$\frac{1}{(1-p)} = 1 + Bt$$

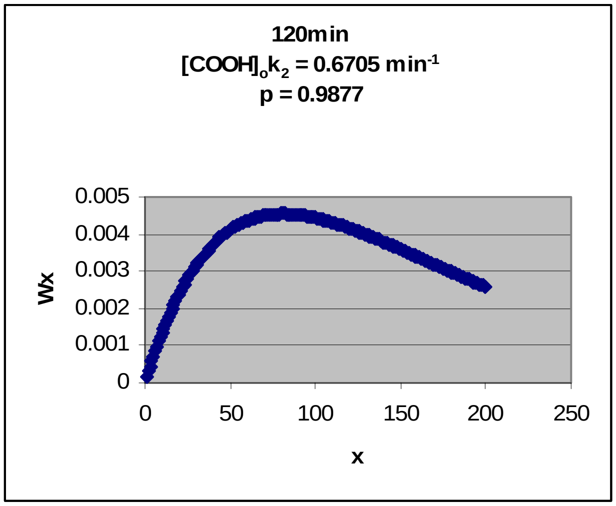
Solve for p:

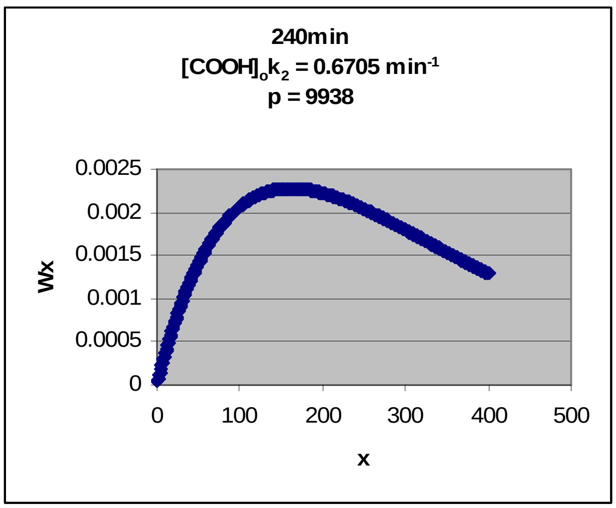
$$p = 1 - \frac{1}{1+Bt} = \frac{Bt}{1+Bt}$$

Combine with $W_x = x(1-p)^2 p^{x-1}$:

$$W_x = x(1+Bt)^{-2}\left(\frac{Bt}{1+Bt}\right)^{x-1}$$

The following are plots of this function at 120 min (p=0.9877) and 240 min (p=0.9938):





9. $$r = \frac{N_A}{N_B} = \frac{[\text{Acid}]_o}{[\text{Diol}]_o} = \frac{1-0.0085}{1} = 0.9915$$

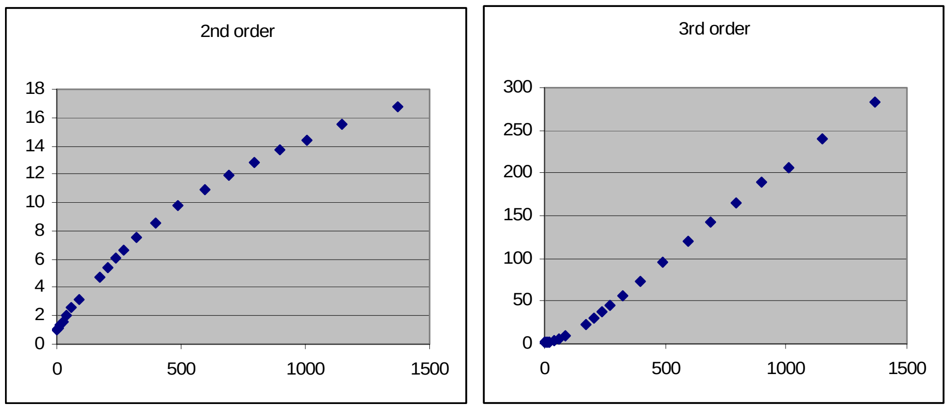
$$\left(\overline{X}_n\right)_{max} = \frac{1+r}{1-r} = \frac{1.9915}{0.0085} = 234.3$$

For this particular A-A, B-B system, M_o = 142.2 g/mol. At full conversion, all molecules will have an odd number of structural units with decanediol units on both ends; hence, $\overline{X}_n = 2n+1$, and $n = \dfrac{r}{1-r}$.

$\overline{M}_n = (\overline{X}_n - 1)M_o + M_{eg}$, where M_{eg} is the molecular weight of the end groups. In this particular case, this represents one decanediol structural unit plus one water = 174.3 g/mol. Therefore, $\overline{M}_n$ = 33,348 g/mol. $\overline{M}_w \cong 2\overline{M}_n$ =66,696 g/mol.

Alternatively, for high degrees of polymerization, $\overline{M}_n$ is very accurately approximated by:
$\overline{M}_n = \overline{X}_n \cdot M_o = 33{,}317$ g/mol. And, $\overline{M}_w \cong 2\overline{M}_n$ =66,635 g/mol.

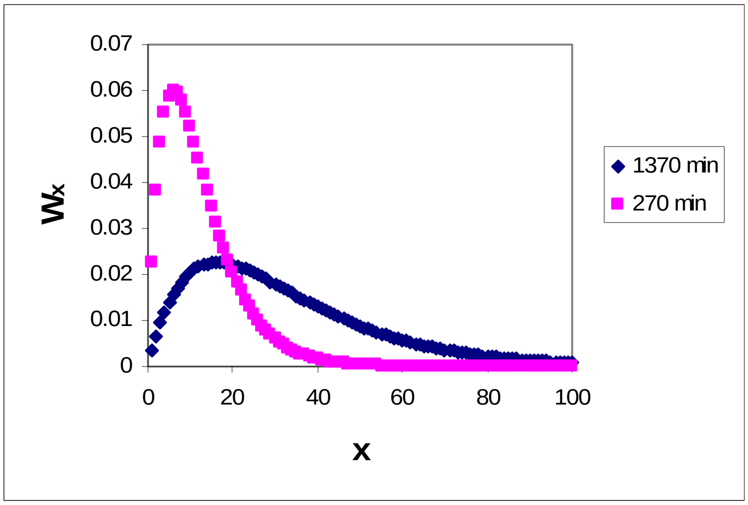
10. (a) The reaction is 3rd order.



(b)
$$[COOH]_o = \frac{2\,(\text{eq/mol})}{(\text{FW}_{\text{DEG}} + \text{FW}_{\text{AA}})(\text{g/mol})} 1000\left(\frac{\text{g}}{\text{kg}}\right) = 7.93\,\frac{eq}{kg}$$

The slope of the 3rd order plot (from the linear portion above p = 0.8) is, by linear regression, equal to 0.22 min^{-1}. Therefore, $k_3 = 1.75 \times 10^{-3}$ kg^2/eq^2-min.

(c) Below are plots of the function $W_x = x(1-p)^2 p^{x-1}$, at 270 min (p=0.85) and 1370 min (p=0.9405).



11. Allcock offers no solution for this system. Regarding the Carother's approach, he does not instruct the reader of how to calculate f_{avg} for non-stoichiometrically balanced systems. However, a solution is given in the notes (material taken from Odian).

$$f_{\text{avg}} = \frac{2\sum \text{N}_\text{i}(\text{A})\text{f}_\text{i}(\text{A})}{\sum \text{N}_\text{i}} = \frac{2[(5\cdot 2)]}{5+4+1} = \frac{20}{10}$$

$$p_c = \frac{2}{f_{avg}} = 1.0$$

Regarding the statistical approach, Allcock likewise offers no solution. His analysis apparently applies only to systems in which the branching monomer contains the type of group (i.e., A or B) that is in the minority. Again, however, a solution can be found in Odian (p. 110, 4th Ed.).

$$p_c = \frac{1}{\left[r\left(f_{w,A}-1\right)\left(f_{w,B}-1\right)\right]^{1/2}} \frac{1}{\left[\frac{10}{11}(2-1)\left(\frac{25}{11}-1\right)\right]^{1/2}} = 0.93$$

Here, $f_{w,A}$ and $f_{w,B}$ are the weight-average functionalities of the A and B containing molecules, given by:

$$f_{w,A} = \frac{\sum f_{A_i}^2 N_{A_i}}{\sum f_{A_i} N_{A_i}} \qquad f_{w,B} = \frac{\sum f_{B_i}^2 N_{B_i}}{\sum f_{B_i} N_{B_i}}$$

This approach provides (coincidentally perhaps) the answer given by Allcock.