

### Problem 24.

If catalyzed:

$$R_p = -\frac{dc}{dt} = kc^2$$

$$\frac{dc}{c^2} = -kdt$$

$$\frac{1}{c} - \frac{1}{c_0} = kt$$

$$\frac{1}{c} = kt + \frac{1}{c_0}$$

If uncatalyzed:

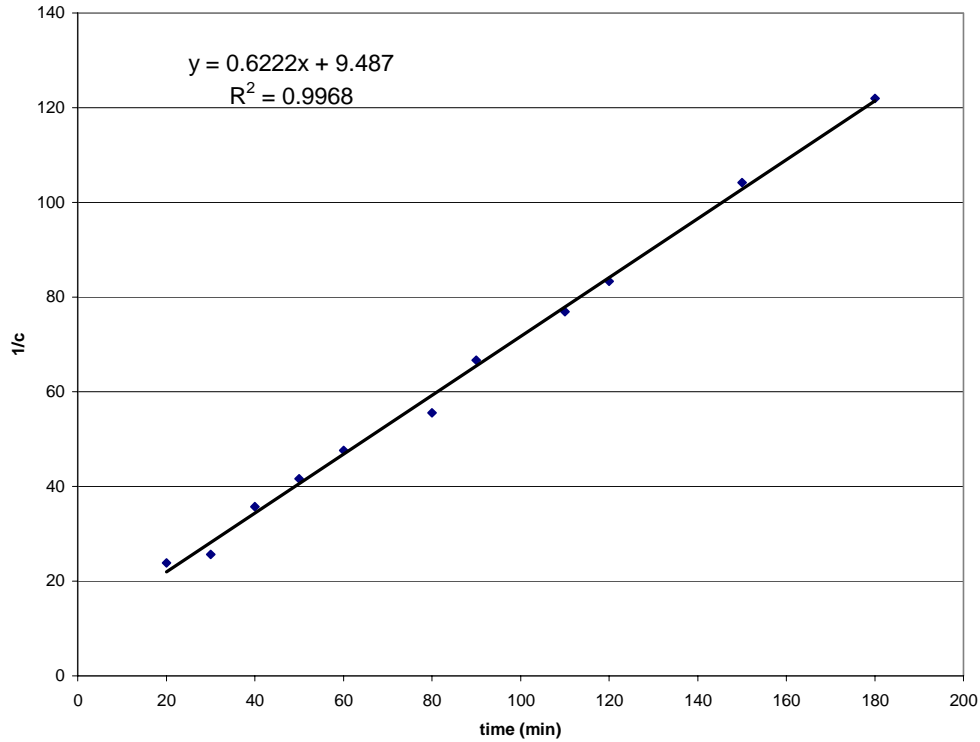
$$R_p = -\frac{dc}{dt} = kc^3$$

$$\frac{dc}{c^3} = -kdt$$

$$\frac{1}{c^2} - \frac{1}{c_0^2} = 2kt$$

$$\frac{1}{c^2} = 2kt + \frac{1}{c_0^2}$$

Plot both  $1/c$  and  $1/c^2$  vs.  $t$  and test for linearity.

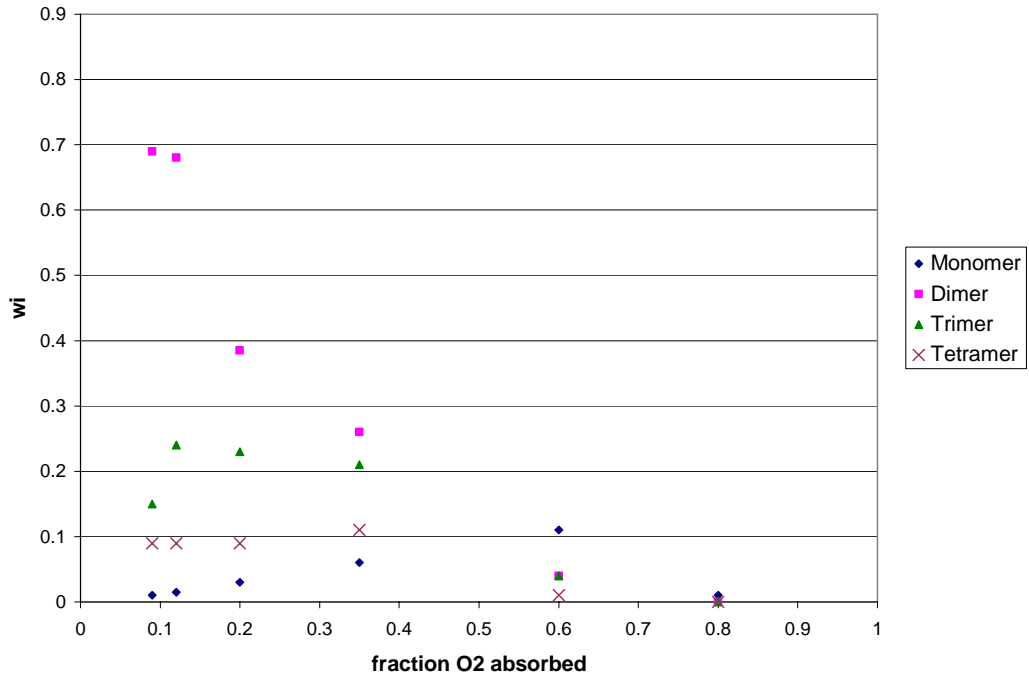


So the data indicate catalyzed conditions. From the fit,  $k = 0.62 \text{ min}^{-1}$

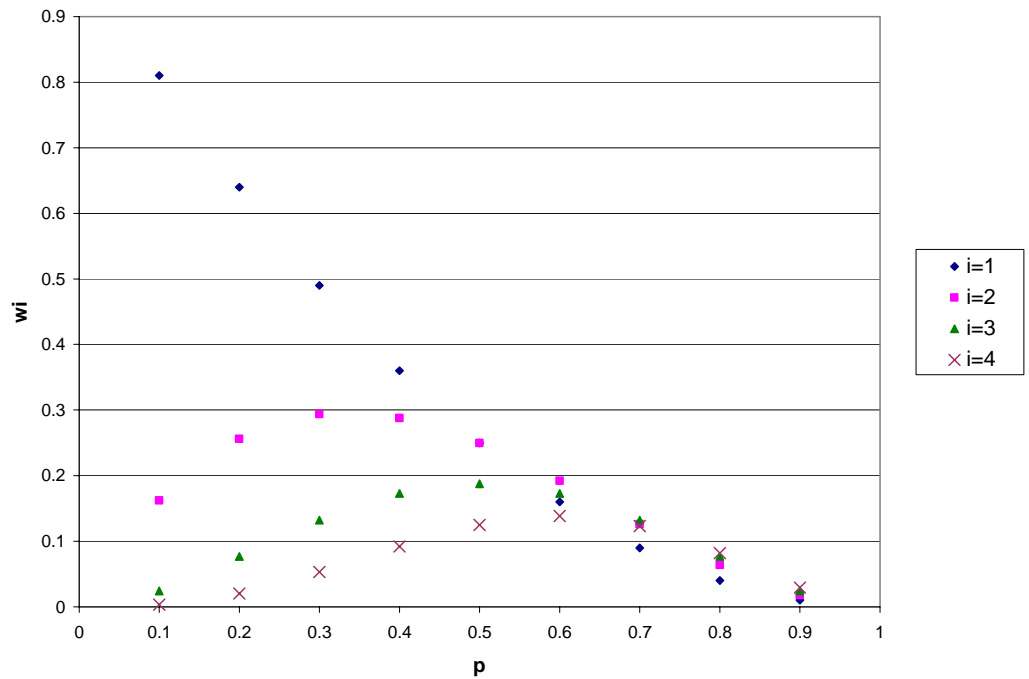
A possible name for the polymer synthesized is poly(4-propylenepiperidine-2,6-dione)

### Problem 25.

From the data:



From theory:

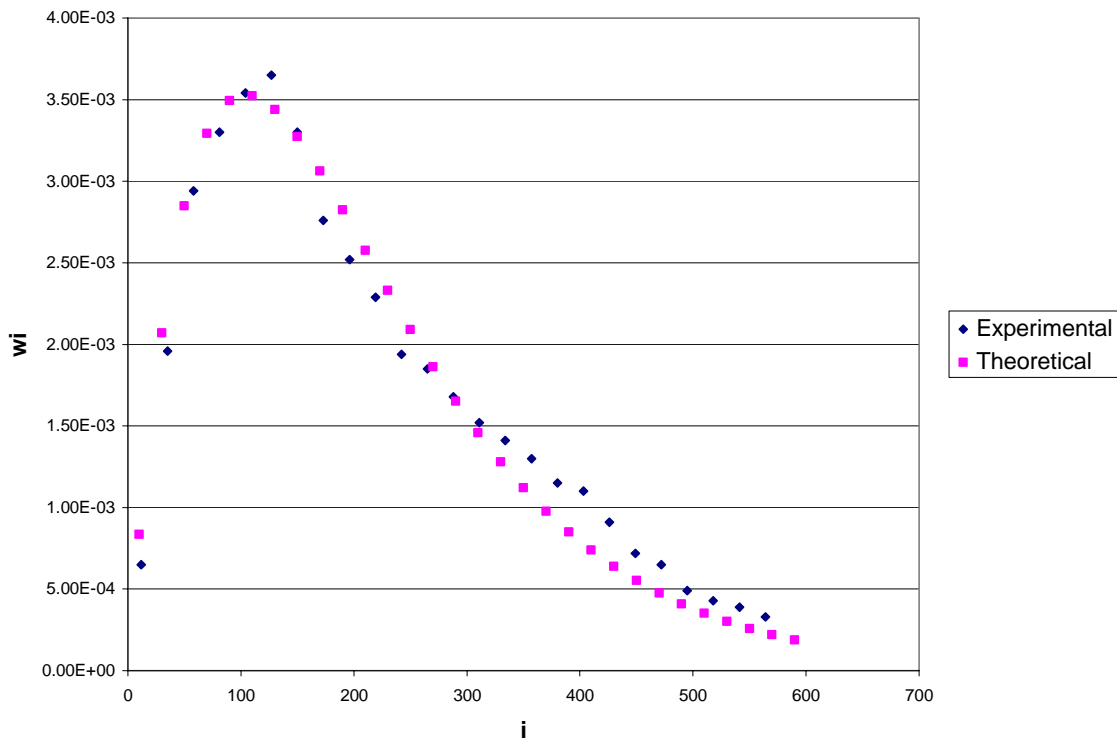


The discrepancies in the plot (dimer curve shaped as  $i=1$  theory curve, etc.) can be explained by the fact that the dimer was the starting point for the experiment. Otherwise, there is very good agreement between the two curves.

**Problem 26.**

$$N_w = \frac{\sum_i i w_i}{\sum_i w_i}; \text{ To find } p: N_w = \frac{1+p}{1-p}$$

$$N_w = 208.6; p = .9904$$



A smaller value of  $p$  would increase the maximum  $w_i$  but also result in a narrower distribution, which would reduce the accuracy of the prediction even further at large  $i$ .

**Problem 27.**

$$K = \frac{[OCO][H_2O]}{[COOH][OH]}$$

Under conditions of stoichiometric balance:

$$K = \frac{[OCO][H_2O]}{[COOH]^2} = \frac{(p[COOH]_0)[H_2O]}{\{(1-p)[COOH]_0\}^2}$$

Simplify and solve for  $[H_2O]$ :

$$[H_2O] = K \frac{(1-p)^2 [COOH]_0}{p} = K [COOH]_0 \left( \frac{1-p}{1} \right) \left( \frac{1-p}{p} \right)$$

Since  $DP_n = \frac{1}{1-p}$  and  $\frac{p}{1-p} = DP_n - 1$ :

$$[H_2O] = K \frac{[COOH]_0}{DP_n (DP_n - 1)}$$

**Problem 28.**

$$R_p = -\frac{d[COOH]}{dt} = k_f[RC(OH)_2^+][R'OH] - k_d[RC(OH)_2OR'H^+]$$

Find the rate of appearance/disappearance of the intermediate:

$$\frac{d[RC(OH)_2OR'H^+]}{dt} = -k_r[RC(OH)_2OR'H^+] - k_d[RC(OH)_2OR'H^+] + k_f[RC(OH)_2^+][R'OH]$$

Via PSSA, set the rate equal to zero and solve for the concentration of the intermediate:

$$0 = -(k_r + k_d)[RC(OH)_2OR'H^+] + k_f[RC(OH)_2^+][R'OH]$$

$$(k_r + k_d)[RC(OH)_2OR'H^+] = k_f[RC(OH)_2^+][R'OH]$$

$$[RC(OH)_2OR'H^+] = \frac{k_f[RC(OH)_2^+][R'OH]}{(k_r + k_d)}$$

Insert into initial rate equation and simplify:

$$R_p = k_f[RC(OH)_2^+][R'OH] - k_d \frac{k_f[RC(OH)_2^+][R'OH]}{(k_r + k_d)}$$

$$R_p = k_f[RC(OH)_2^+][R'OH] \left( 1 - \frac{k_d}{(k_r + k_d)} \right)$$

Using the following equation for the equilibrium constant:

$$K_{eq} = \frac{[RC(OH)_2^+]}{[RCOOH][HA]}$$

and rearranging, the final answer is obtained:

$$R_p = k_f K_{eq} [HA][RCOOH][R'OH] \left( \frac{k_r}{k_r + k_d} \right)$$

The rate equation reduces to the expression obtained in class when  $k_r \gg k_d$  which was the assumption made during the in class derivation.

**Problem 29.**

$$x_i(p) = p^{(i-1)}(1-p)$$

$$p = \frac{k[A]_0 t}{1 + k[A]_0 t}$$

To find the maximum in time as a function of p, take the derivative with respect to time and set equal to zero.

$$\frac{\partial x_i}{\partial t} = \frac{\partial x_i}{\partial p} \frac{\partial p}{\partial t} = \left( (1-p)(i-1)p^{i-2} - p^{i-1} \right) \frac{\partial p}{\partial t} = 0$$

Since  $\frac{\partial p}{\partial t}$  is independent of p, we can divide through leaving:

$$\left( (1-p)(i-1)p^{i-2} - p^{i-1} \right) = 0$$

Divide by  $p^{i-2}$ :

$$\left( (1-p)(i-1) - p \right) = 0$$

$$p = \frac{i-1}{i}$$

Rearranging:

$$i = \frac{1}{1-p} = N_n$$

So the maximum mole fraction in time of a specific i-mer is related to the number average degree of polymerization

For absolute amount:

$$n_i = m_0 p^{i-1} (1-p)^2$$

Similarly:

$$\frac{\partial n_i}{\partial t} = \frac{\partial n_i}{\partial p} \frac{\partial p}{\partial t} = m_0 \left( (1-p)^2 (i-1) p^{i-2} - 2(1-p) p^{i-1} \right) \frac{\partial p}{\partial t} = 0$$

$$(1-p)^2 (i-1) p^{i-2} - 2(1-p) p^{i-1} = 0$$

$$(1-p)(i-1) - 2p = 0$$

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

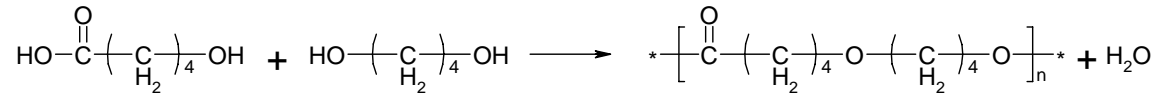
Rearranging:

$$i = \frac{1+p}{1-p} = N_w$$

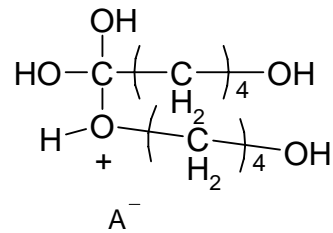
So the maximum amount in time of a specific i-mer is related to the weight average degree of polymerization.

**Problem 30.**

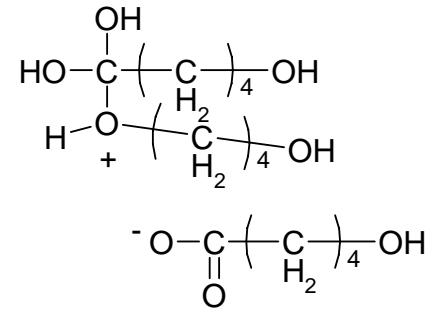
(a)



Acid-catalyzed intermediate:



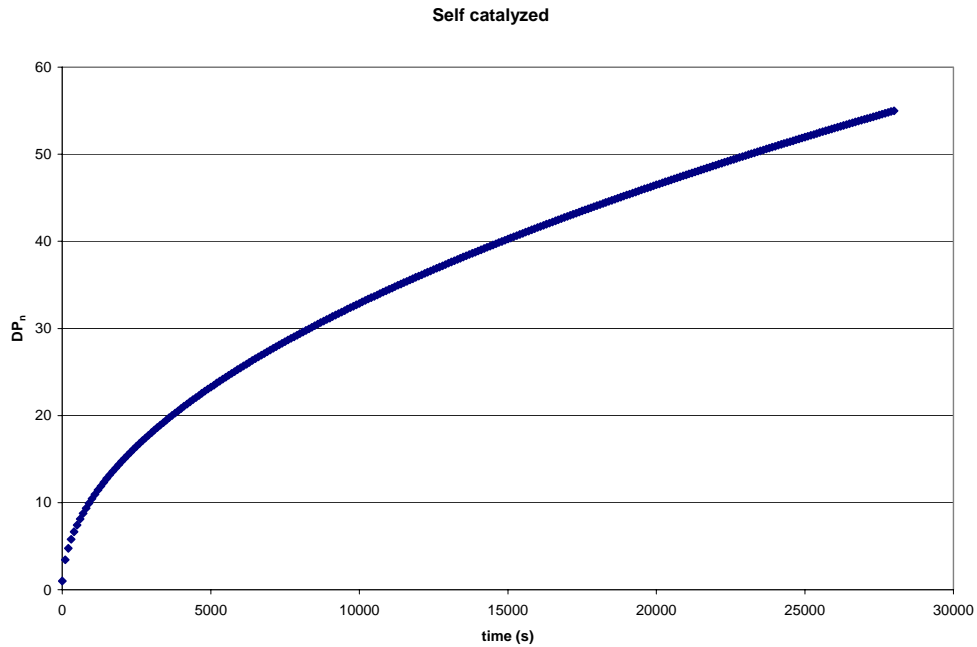
Self-catalyzed intermediate:



(b)

For self-catalyzed:

$$DP_n^2 = 1 + 2[A]_0^2 kt$$



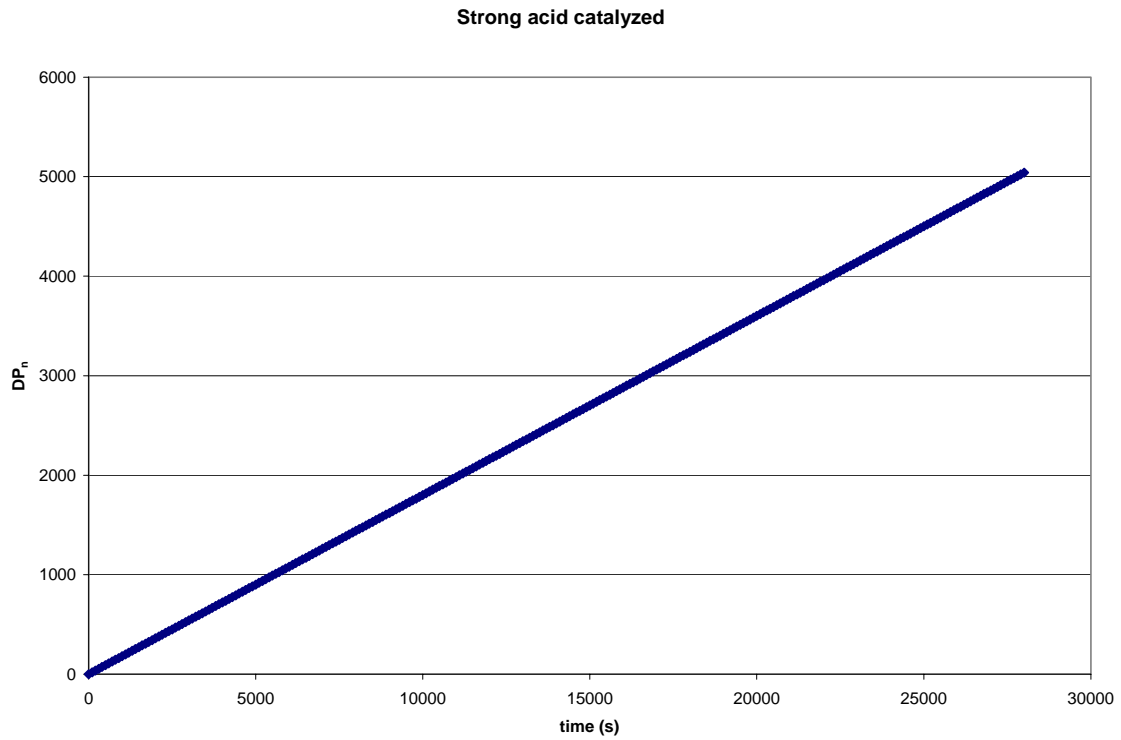
It would take 231.5 hours to obtain a number average degree of polymerization of 300



(c)

For acid catalyzed:

$$N = 1 + [A]_0 kt$$



It would only take 0.5 hours to reach a number average degree of polymerization of 300.

(d)

In the self catalyzed reaction, catalyst is lost as monomer is consumed, resulting in a leveling off of the reaction. This effect is not observed for the strong acid catalyzed reaction.