

## Imbalanced Step Growth Reaction

We have discussed that a limitation to producing high- $M$  products via step-growth (condensation) reactions is stoichiometry mismatch and the related problem of impurities. As you might have noticed during lecture, the theory has been worked out for mismatched reactions. Consider a reaction between AA (diol) and BB (diacid) to produce a polyester. An imbalance ratio,  $r$ , is defined as:

$$r = n_A/n_B$$

where  $n_A$  and  $n_B$  are the number of functional groups of type A and B, respectively, at the start of the reaction. The maximum value of  $r$  is unity (i.e., if A groups really exceed B groups, then the definition of  $r$  inverts). The number average degree of polymerization in such a case is:

$$\sigma_n = \frac{1+r}{1+r-2pr}$$

where  $p$  is the usual extent of reaction ( $0 < p < 1$ ).

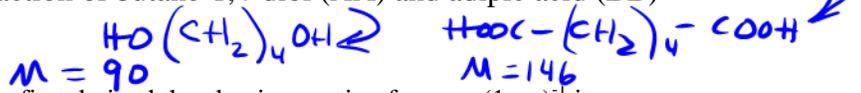
- a. Write an equation for  $\sigma_n$  when  $p = 1$ .

$$\sigma_n \xrightarrow{p=1} \frac{1+r}{1+r-2r} = \frac{1+r}{1-r}$$

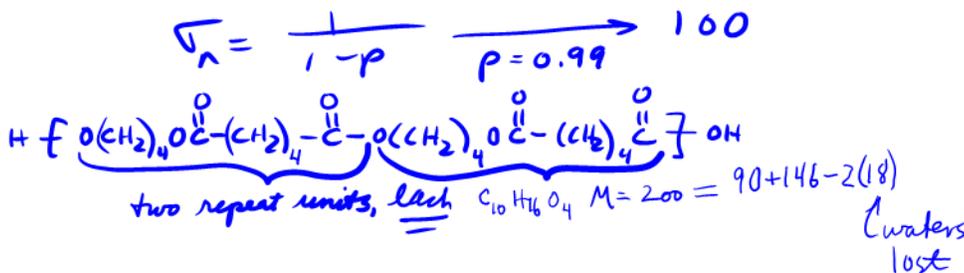
- b. Write an equation for  $\sigma_n$  when  $r = 1$  (should look familiar).

$$\sigma_n \xrightarrow{r=1} \frac{2}{2-2p} = \frac{1}{1-p}$$

- c. Compute  $\sigma_n$  and  $M_n$  for the reaction of butane-1,4-diol (AA) and adipic acid (BB) if  $p = 0.99$  and  $r = 1.00$ .

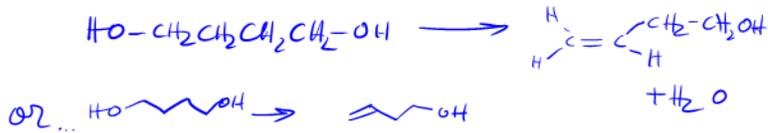


Hint: Be careful, because when we first derived the classic equation for  $\sigma_n = (1-p)^{-1}$  it was for AB polymerization. That gave us the (number average of) number of AB units in the polymer. Now we get the (number average of the) sum of AA plus BB units in the polymer...which is twice the number of the AABB repeat units (neglecting end effects). It may be easier to think of  $\sigma_n$  as the number of "average monomers" and compute an "average monomer" mass  $M_0 = (M_{0,AA} + M_{0,BB})/2$ . It also may be time to dig out that textbook...or some other textbook that contains this very problem!



To see how the equation behaves, let us suppose  $p = 0.5$ , 50% of -COOH groups are reacted.  $\sigma_n = 2$  and it clearly means AABB is the main component. So  $M_n = 2 \times M_0$ , adjusted =  $2 \times 100$

- d. Write a dehydration reaction for the 1,4-diol to give an olefin impurity that does not participate in this condensation reaction.



- e. A scale-up chemist is trying to make a polyester of butane-1,4-diol and adipic acid with  $M_n = 6000$ . She assumes that the reaction is perfectly balanced, but unknown to her 0.5% of the 1,4-diol has decomposed to unreactive olefin. What will be the value of  $p$  when she stops the reaction and what actual  $M_n$  will be obtained?

$$r = 0.995$$

$$\bar{v}_n, \text{ desired} = \frac{6000}{100} = 60 = \frac{1}{1-p}$$

$$\Rightarrow p_{\text{desired}} = 1 - \frac{1}{60} = 0.98\bar{3}$$

$$\bar{v}_n = \frac{1+r}{1+r-2pr} \quad \frac{1+0.995}{1.995-2(0.98\bar{3})(0.995)} = 51.4$$

$$M_n \approx 5140$$

- f. After MALDI confirms that the mass is lower than expected, the chemist decides to assay the butane-1,4-diol for impurity and finds the 0.5% unreactive component. To what value of  $p$  should the reaction be run to compensate and reach the desired  $M_n$  of 6000?

$$\bar{M}_n = \frac{1+r}{1+r-2pr} \quad \rightarrow \quad p = \frac{-1}{2r} \left( \frac{1+r}{\bar{M}_n} - 1+r \right) = \frac{1+r}{2r} \left( 1 - \frac{1}{\bar{M}_n} \right)$$

$$p \Rightarrow \frac{1+0.995}{2(0.995)} \left( 1 - \frac{1}{60} \right) = 0.986$$

- g. How could the chemist assay the butane-1,4-diol for that impurity? Be as specific as possible, taking advantage of your team's capabilities.

HPLC?

FTIR looking for C=C stretches

- h. How would you run the reaction, monitor its progress, and stop it when you reached a particular value of  $p$ ? (Give conditions, specify instruments involved, etc.).

My Guess: Target that carbonyl in FTIR-equipped reactor.