Step-Growth Polymerization: Two Difunctional Monomers with Different Functionalities

Difunctional monomers with different functionalities polymerize to form many of the most common polymers, including nylons, polyesters, and polyurethanes. For example, poly(ethylene terephthalate) may be formed by the reaction of ethylene glycol with terephthalic acid:

$$\text{HO-CH}_2\text{CH}_2\text{-OH} + \text{HOOC-}\phi\text{-COOH} \longrightarrow$$
$$\text{H-[O-CH}_2\text{CH}_2\text{-OOC-}\phi\text{-CO]}_n\text{-OH} + \text{water}$$

During this polymerization, every monomer and growing chain has exactly two functionalities, which may be two -OH units, two -COOH units, or one of each.

We will simulate this polymerization using two sets of paper clips, silver paper clips representing the diol monomer (ethylene glycol) and gold paper clips representing the diacid monomer (terephthalic acid). For simplicity, assume that each monomer unit has mass 1 and neglect the mass of water.

Initial Configuration

Place 50 diol and 50 diacid paper clips on a piece of paper to represent the monomer units and label each *position* with one number, 1 through 100.

Polymerization

Use a random number generator (die, tables, calculator, computer) to generate a random number between 1 and the maximum number of molecules in your sample (or between 1 and 100, discarding the results with no associated molecule). Generate a second random number; join the two molecules only if you are able to make an alcohol-acid connection (silver-gold or gold-silver connection). If you are unable to make an alcohol-acid connection, continue generating random numbers until you can. Form linear polymer chains where the structure alternates: ...alcohol-acid-alcohol-acid...

Quantification of the Molecular Weight

At the start, and at regular intervals after approximately five reactions, calculate the following for your mixture:

- the extent of reaction
- the number average molecular weight of the growing chains (unreacted monomers are included in this average)

Think carefully about the most simple and efficient way to do each calculation.

Questions

1. What are the final $\bar{M}_n$ and $\bar{M}_w$ for this polymerization? What is the polydispersity? Sketch the molecular weight distribution $w(i)$. What would be different in a real polymerization with 10^{23} monomer units?
2. How does $\bar{M}_n$ vary with the extent of reaction? Can you derive an equation that gives $\bar{M}_n$ as a function of X? How does this compare with your results?

Variations

Try different initial concentrations of each of the monomers, for example 60 diol and 40 diacid monomer molecules. What are the final $\bar{M}_n$ and $\bar{M}_w$ for these polymerizations? What structural differences are there between these results and a perfect stoichiometric balance of 50/50? What are the advantages of maintaining perfect stoichiometric balance: Why might you want to deliberately use an imbalance?

These types of reactions usually have an equilibrium constant, rather than being irreversible. What precautions to you need to take to ensure that the reaction proceeds to completion?