Step-Growth Polymerization: Multifunctional Monomers

Multifunctional monomers may be used in polymerizations to form branched or crosslinked chains. One of the most common examples of this is polyurethanes. Linear polyurethanes are formed by the reaction of difunctional alcohols with difunctional isocyanates:

$$\text{HO-A-OH} + \text{OCN-B-NCO} \longrightarrow \text{-[O-A-O-OC-NH-B-NH-CO]}_n\text{-}$$

Typically, a small amount of multifunctional (3 or more) alcohol or isocyanate is added in order to provide for branching or crosslinking.

We will simulate this polymerization simulation using three sets of paper clips, silver clips representing the diol monomer (HO-A-OH), gold clips representing the diisocyanate monomer (OCN-B-NCO), and large silver clips representing four functional alcohol monomers (tetraols). For simplicity, assume that each monomer unit has mass 1.

Initial Configuration

Place 30 diol, 50 diisocyanate, and 10 tetraol monomer molecules on a piece of paper to represent the monomer units and label each *position* with one number, 1 through 100. Each tetraol must be labelled with *two* numbers: the tetraols have twice the number of functional units and thus twice the probability of reacting compared to the diols and diisocyanates.

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-isocyanate connection (silver-gold or gold-silver connection). If you are unable to make an alcohol-isocyanate connection, continue generating random numbers until you can. Form polymer chains and branched units where each diol and diisocyanate mer unit is connected with at most two other mer units; however, each tetraol is connected with at most four other mer units! Be sure to maintain an alternating structure ...alcohol-isocyanate-alcohol-isocyanate -... As your molecules grow, ensure that numbers associated with each molecule are equal to half the molecular functionality (one number for difunctional, two numbers for tetrafunctional, three numbers for six-functional, etc.).

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. Did you obtain a branched chain structure? a crosslinked structure? What key parameters control the extent of branching or crosslinking?
3. 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. Consider carefully two parameters, the concentration of the tetraol and the stoichiometric balance between alcohol and isocyanate. (The concentrations given above resulted in perfect stoichiometric balance, why?) How do $\bar{M}_n$ and $\bar{M}_w$ change with the variations you have tried? How does the molecular structure vary?

Different functionalities (3, 4, 5, ...) of the alcohol or isocyanate are available for commercial polymerizations. What are the effects of using these types of functionalities?