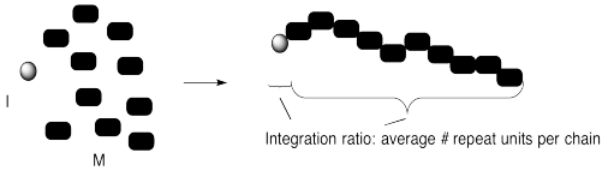
12.6: Polymer Synthesis

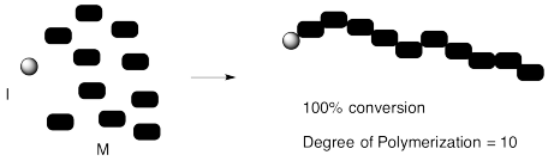
Macromolecules are very large molecules. Their molecular weights can range from the thousands to the millions. Typically they are constructed from small, repeating units linked together in some way.

How many repeating units are there in a chain? Because of the way synthetic polymers are made, we may be able to predict how long the chain is by the conditions we choose when we make it. Polymers are frequently made through the action of an initiator, which gets the monomer units to start attaching to each other. Without the initiator, the monomers just sit there. (There are exceptions; nylon 6-6 and other condensation polymers are sometimes made just by mixing two different kinds of monomers together, without an initiator.)

If each initiator in the process starts its own chain growing, then the ratio of monomers to intiators that we start with may tell us the chain length we will end up with.

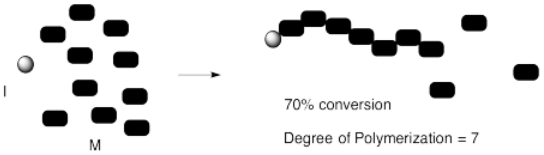


We can confirm that outcome experimentally by measuring the ratio of monomer to initiator in the polymer that is produced. That evidence is sometimes obtained by integration of a ^{1}H NMR spectrum. The "degree of polymerization" is the measured number of repeating units in the chain. In the case below, we started with 10 monomers per initiator and ended up with DP = 10.

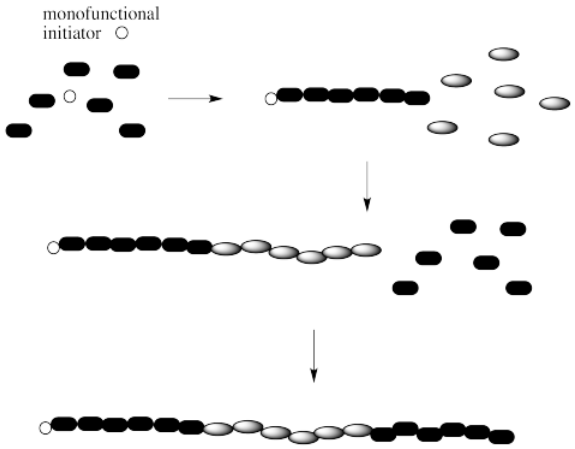


Things don't always work out that way. Maybe for some reason the chain stops growing unexpectedly (an event that is often called "chain death"). Maybe we stopped the reaction a little too early, before all the monomers had time to react. Maybe there is a reverse reaction, in which a polymer can break down into monomers again, and we end up at some balance between polymer formation and polymer breakdown (an "equilibrium").

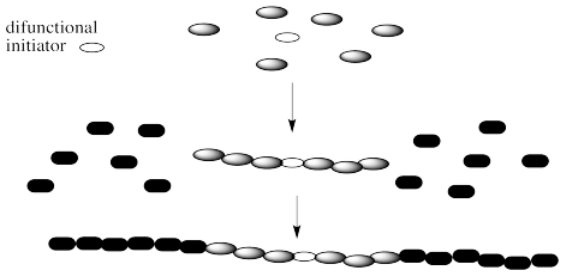
In that case, the degree of polymerization might not reflect the original monomer to initiator ratio. It might also depend upon the percent conversion -- that is, how much of the original monomers were converted into polymer. If we start with 10 monomers per initiator, but only 70% of the monomers are enchained in the reaction, then the degree of polymerization will be 7, not 10.



If we are dealing with a block copolymer, we may be interested in more than just the total number of monomers in the chain. We may instead be interested in the ratio of one monomer to the other (for example, A:B:A = 6:6:6 in the example below).



Note that there are a couple of different ways of making block copolymers. We can simply start growing the chain from one end, as shown above. Alternatively, we might start with a difunctional initiator. That's an initiator that starts gorwing the chain in two directions at once. The result is called a "telechelic polymer". This method of growth can be more efficient in some cases.



Exercise 12.6.1

Explain why a telechelic polymer might grow more quickly than a regular one.

Answer

The telechelic polymer has two growing ends per chain, so it grows twice as fast as a normal chain.

Exercise 12.6.2

If a polymerization is performed using a 500:1 ratio of initiators to monomers and the reaction reaches 85% conversion, what is the degree of polymerization?

Answer

If this chain reached 100% conversion, then the degree of polymerization would be 500. At 85% conversion, DP = 425.