# Chain Growth Polymerization with Chain Transfer to Monomer

Chain growth polymerization is used to produce many common polymers such as polystyrene, poly(methyl methacrylate), and poly(vinyl chloride). These polymerizations begin with the reaction of an initiator fragment with a monomer unit to form an active chain:

$$I^* + M \longrightarrow IM^*$$

where * indicates the active site (a radical, anion, cation). Monomer units add sequentially to this active site to form a polymer chain:

$$IM^* + M \longrightarrow IMM^*$$
$$IMM^* + M \longrightarrow IMMM^*$$
$$\cdots$$

At the beginning of this polymerization, the initiator rapidly generates active sites onto which monomer units add sequentially. During some polymerizations, growth of a chain may be terminated by chain transfer to monomer, which "kills" the active chain and begins a new one:

$$IMMM^* + M \longrightarrow IMMM + M^*$$

We will conduct this polymerization using red paper clips to represent the initiator fragments, silver paper clips to represent monomer units which simply add to the chain, and blue paper clips to represent monomer units where chain transfer to monomer happens to occur. Each monomer unit has a mass 1 and the mass of the initiator fragment is neglected.

## Initial Configuration

Place ten red initiator fragments on a piece of paper and label them with the numbers 1 to 10. Count out 90 silver and 10 blue paper clips to represent monomers which are available to react. Mix the monomers in a cup or box.

## Polymerization

Use a random number generator (die, tables, calculator, computer) to generate a random number between 1 and 10, inclusive. Draw at random a monomer unit from the mixture of monomers. If a silver monomer is drawn, simply add that monomer to the chain indicated by the random number. If a blue monomer is drawn, chain transfer to monomer occurs: a) the chain indicated by the random number is "killed" and removed from the set of active growing chains. b) The blue monomer becomes active and occupies the position vacated by the dead chain. Form linear polymer chains. You should always have exactly ten active chains; however, keep the dead ones as they contribute to the molecular weight distribution.

## 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 chains (unreacted monomers are not included in this average, but dead chains are)

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 $w(i)$.
2. How does $\bar{M}_n$ vary with the extent of reaction? Chain transfer to monomer is frequently regarded as detrimental, but in some special cases can actually be desirable. Can you describe such a situation?

## Variations

Try different probabilities for chain transfer to monomer (initial concentrations of the blue monomer). How do $\bar{M}_n$ and $\bar{M}_w$ change with the new parameters you have tried? How can the probability of chain transfer be used to control the molecular weight of the final polymer?

Another type of transfer is chain transfer to polymer. In this case the active site at the end of a growing chain attacks the backbone of another chain (either growing or dead). The active site is thus transferred to the backbone of another chain. Can you devise a set of rules which will provide for accurate replication of chain transfer to polymer? What key change in the chain structure occurs under these circumstances?

Termination of active sites may occur during polymerization reactions. For example, termination by coupling happens when two active sites at two chain ends come together, joining the chains and terminating both active sites. Can you devise a set of rules which will provide for accurate replication of termination by coupling?