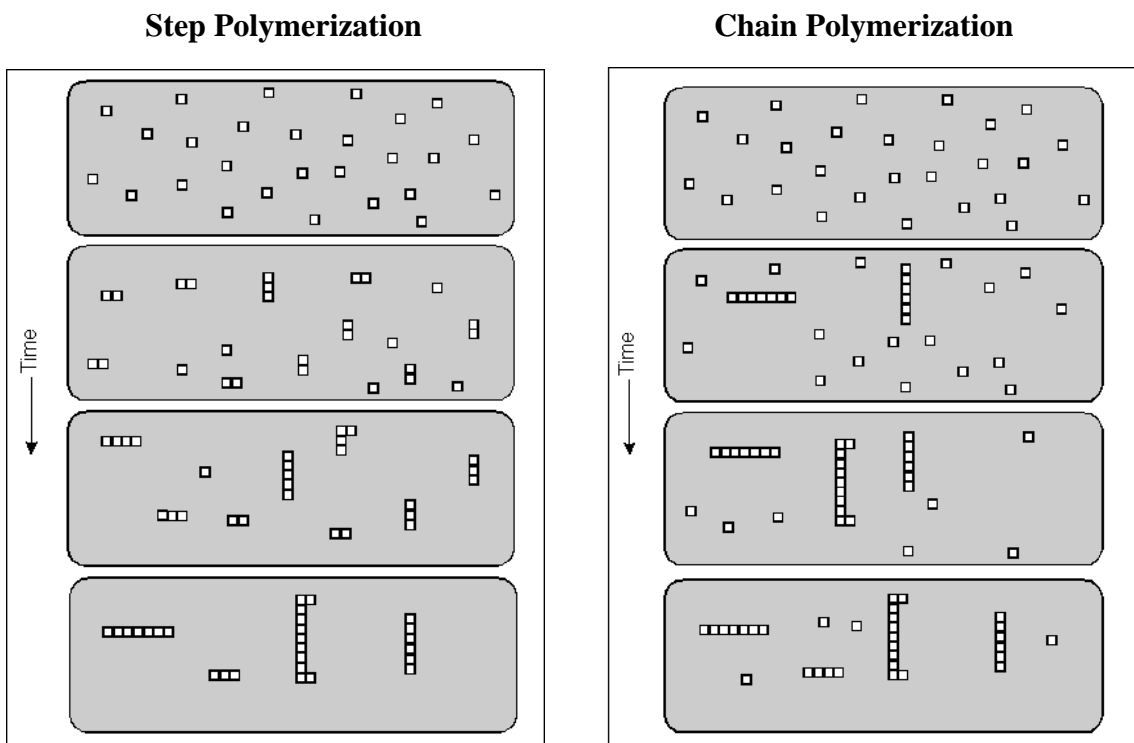


Step and Chain Polymerization



- Any two molecular species can react.
 - Monomer disappears early.
 - Polymer MW rises throughout.
 - Growth of chains is usually slow (minutes to days).
 - Long reaction times increase MW, but yield of polymer hardly changes.
 - All molecular species are present throughout.
 - Usually (but not always) polymer repeat unit has fewer atoms than had the monomer.
- Growth occurs *only* by addition of monomer to active chain end.
 - Monomer is present throughout, but its concentration decreases.
 - Polymer begins to form immediately.
 - Chain growth is usually very rapid (second to microseconds).
 - MW and yield depend on mechanism details.
 - Only monomer and polymer are present during reaction.
 - Usually (but not always) polymer repeat unit has the same atoms as had the monomer
-

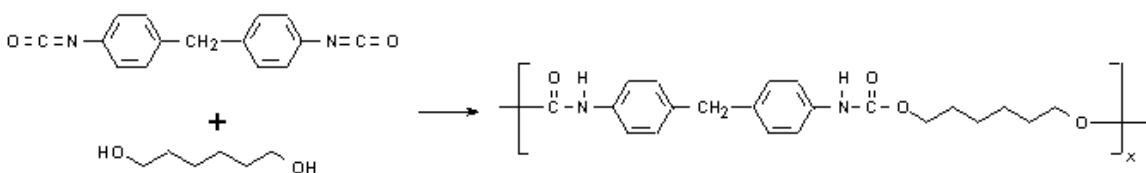
Condensation vs. Addition

[Carothers](#) originally classified polymers based on a comparison of the atoms in the monomer to the atoms in the polymer repeat unit.

- Condensation polymers had fewer atoms in the repeat unit (i.e., some small molecule was emitted during polymerization).
- Addition polymers had the same atoms as their monomers.

There are many exceptions for this to be useful.

- Step polymerization by addition of alcohols to diisocyanates to form polyurethanes:



- Chain polymerization (ring opening of heterocycle) with loss of CO_2 to form polypeptide.

