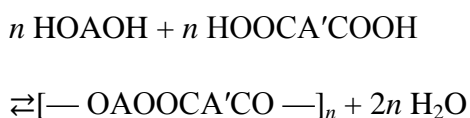


## Lecture #9: Polycondensation reactions

### Polycondensation

a process for the production of polymers from bifunctional and polyfunctional compounds (monomers), accompanied by the elimination of low-molecular weight by-products (for example, water, alcohols, and hydrogen halides). A typical example of polycondensation is the synthesis of a complex polyester:



where A and A' are glycol and dicarboxylic acid groups, respectively.

The process is called

homopolycondensation if the minimum possible number of monomer types for a given case participates. This number is usually two, as in the reaction shown above, although it may be unity, for example:



If at least one monomer more than the number required for the given reaction participates in polycondensation, the process is called copolycondensation. Polycondensation in which only bifunctional compounds participate leads to the formation of linear macromolecules and is called linear polycondensation. If molecules with three or more functional groups participate in polycondensation, three-dimensional structures are formed and the process is called three-dimensional polycondensation. In cases where the degree of completion of polycondensation and the mean length of the macromolecules are limited by the equilibrium concentration of the reagents and reaction products, the process is called equilibrium (reversible) polycondensation. If the limiting factors are kinetic rather than thermodynamic, the process is called nonequilibrium (irreversible) polycondensation.

Polycondensation is often complicated by side reactions, in which both the original monomers and the polycondensation products (oligomers and polymers) may participate. Such reactions include the reaction of monomer or oligomer with a monofunctional compound (which may be present as an impurity), intramolecular cyclization (ring closure), and degradation of the macromolecules of the resultant polymer. The rate competition of polycondensation and the side reactions determines the molecular weight, yield, and molecular weight distribution of the polycondensation polymer.

Polycondensation is characterized by disappearance of the monomer in the early stages of the process and a sharp increase in molecular weight, in spite of a slight change in the extent of conversion in the region of greater than 95-percent conversion.

A necessary condition for the formation of macromolecular polymers in linear polycondensation is the equivalence of the initial functional groups that react with one another.

Polycondensation is accomplished by one of three methods: (1) in a melt, when a mixture of the initial compounds is heated for a long period to 10°–20°C above the melting (softening) point of the resultant polymer; (2) in solution, when the monomers are present in the same phase in the solution state; (3) on the phase boundary between two immiscible liquids, in which one of the initial compounds is found in each of the liquid phases (interphase polycondensation).

Polycondensation processes play an important role in nature and technology. Polycondensation or similar reactions are the basis for the biosynthesis of the most important biopolymers—proteins, nucleic acids, and cellulose. Polycondensation is widely used in industry for the production of polyesters (polyethylene terephthalate, polycarbonates, and alkyd resins), polyamides, phenol-formaldehyde resins, urea-formaldehyde resins, and certain silicones. In the period 1965–70, polycondensation acquired great importance in connection with the development of industrial production of a series of new polymers, including heat-resistant polymers (polyarylates, aromatic polyimides, polyphenylene oxides, and polysulfones).

**Condensation polymers** are any kind of polymers formed through a condensation reaction—where molecules join together—losing small molecules as by-products such as water or methanol, as opposed to addition polymers which involve the reaction of unsaturated monomers. Types of condensation polymers include polyamides, polyacetals and polyesters.

Condensation polymerization, a form of step-growth polymerization, is a process by which two molecules join together, resulting in loss of small molecules which are often water. The type of

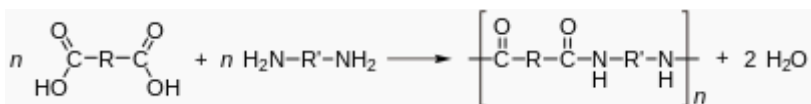
end product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.

Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower molecular weight. Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three-dimensional polymers which are crosslinked.

Dehydration synthesis often involves joining monomers with an -OH (hydroxyl) group and a freely ionized -H on either end (such as a hydrogen from the -NH<sub>2</sub> in nylon or proteins). Normally, two or more different monomers are used in the reaction. The bonds between the hydroxyl group, the hydrogen atom and their respective atoms break forming water from the hydroxyl and hydrogen, and the polymer.

Polyester is created through ester linkages between monomers, which involve the functional groups carboxyl and hydroxyl (an organic acid and an alcohol monomer).

Nylon is another common condensation polymer. It can be manufactured by reacting diamines with carboxyl derivatives. In this example the derivative is a di-carboxylic acid, but di-acyl chlorides are also used. Another approach used is the reaction of di-functional monomers, with one amine and one carboxylic acid group on the same molecule:



General chemical structure of one type of condensation polymer

The carboxylic acids and amines link to form peptide bonds, also known as amide groups. Proteins are condensation polymers made from amino acid monomers. Carbohydrates are also condensation polymers made from sugar monomers such as glucose (ie. cellulose<sup>[1]</sup> or glycogen) and galactose.

Condensation polymerization is occasionally used to form simple hydrocarbons. This method, however, is expensive and inefficient, so the addition polymer of ethene (polyethylene) is generally used.

Condensation polymers, unlike addition polymers, may be biodegradable. The peptide or ester bonds between monomers can be hydrolysed by acid catalysts or bacterial enzymes breaking the polymer chain into smaller pieces.

The most commonly known condensation polymers are proteins, fabrics such as nylon, silk, or polyester.

**References:**

**<http://encyclopedia2.thefreedictionary.com/Polycondensation>**

**[https://en.wikipedia.org/wiki/Condensation\\_polymer](https://en.wikipedia.org/wiki/Condensation_polymer)**