

### CHAPTER III



#### CONDENSATION (STEPWISE) POLYMERIZATION AND PHENOLIC RESINS

Condensation polymerization is the process by which the polymer is built up by successive reactions between monomer molecules and the growing polymer with liberation of small molecules such as water, hydrogen chloride, sodium chloride or ammonia.

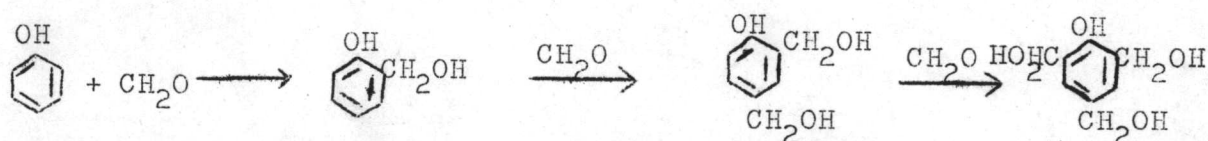
Carothers and Kienle were the American workers who first gave the important fundamental concept of functionality of monomers. The atoms or groups of atoms in a molecule which can react with another molecule and thereby give rise to a primary valency link are designated functional groups. The number of such groups in a simple molecule is known as the functionality of the molecule.

Reactant pairs where each partner has a functionality of unity can only react to form small, non-polymeric molecules. Reactant pairs where each is bifunctional can form only chain polymers, which will remain soluble and thermoplastic. Reactant pairs where one is at least bifunctional and the other at least trifunctional will give rise to highly branched polymers, which will finally form three-dimensional networks which are insoluble and do not melt. Such polymers are called thermosetting plastics (thermosetting resins)

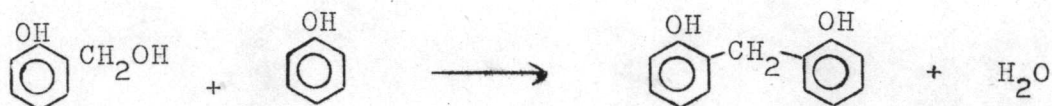
It is clear that complete reaction would mean that the whole system had been converted to a single giant molecule. Experimentally, when bifunctional reactants and system of higher functionality were reacted, even if stoichiometrically equivalent amounts of functional groups were present, it was not possible to drive the reaction to completion. In the system of bifunctionality, however, a single chain molecule would have already been formed while one of each kind of functional group remained at opposite ends of the chain.

Phenol-furfural reaction is an example of the condensation polymerization. Since phenol is trifunctional monomer, then products of this reaction are thermosetting resins. The most important thermosetting resins, both from an historical stand-point and in current commercial application, are formaldehyde condensation products with phenol (phenolic resins). Mechanisms of such reaction are suggested as following: (16)

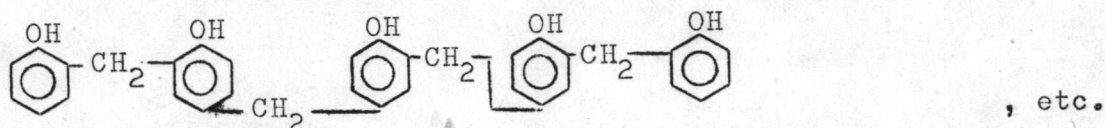
The first step in the reaction is the formation of addition compounds known as methylol derivatives, the reaction taking place at the ortho or para position:



This step is called methylolation. In the presence of acid catalysts, and with the mole ratio of formaldehyde to phenol less than 1, the methylol derivatives condense with phenol to form, first, dihydroxy-diphenyl methane:



and, on further condensation and methylene bridge formation, fusible and soluble linear low polymers called novolac are formed. The structure is as follows :

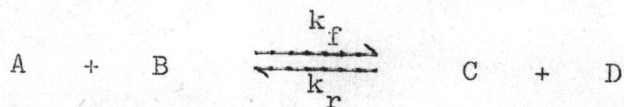


where ortho and para links occur at random. Molecular weights may range as high as 1,000 corresponding to about ten phenyl residues. These materials do not themselves react further to give crosslinked resins, but must be reacted with more formaldehyde to raise its mole ratio to phenol above unity.

Furfural, which in itself is a thermosetting resin by virtue of its aldehyde group and reactive furan ring, may replace part of the formaldehyde in phenolic resins. Although such thermosetting resins are commonly used in place of, or blended with, phenol-formaldehyde resins, there are several important differences in the preparative techniques<sup>(17)</sup>. For example, the commonly used phenol-formaldehyde novolacs are formed by reacting formaldehyde with a slight molar excess of phenol in the presence of an acid catalyst. Similar conditions employed to polymerize furfural and phenol give gels, unless a large excess of phenol is present to inhibit acid degradation of the furfurals.

The nature of products from the reaction with hydrochloric acid as a catalyst depends upon the proportion of the acid employed, mole ratio of furfural to phenol, temperature and other conditions. For example, the resin obtained with an excess of phenol was soluble in acetone and alcohol, and remained jelly-like when cooled, even after it had been heated for a number of days.

In the kinetic study of stepwise polymerization, it typically involves equilibrium reactions of the type



where the rate of the forward and reverse reactions are  $k_f[A][B]$  and  $k_r[C][D]$ , respectively. At equilibrium these rates are equal, whence

$$K = \frac{k_r}{k_f} = \frac{[A][B]}{[C][D]}$$

If the system is far from equilibrium, as in the initial stages of polymerization, the reverse reaction is very slow, and changes in the concentrations of the reactions may be considered to result from the forward reaction alone.