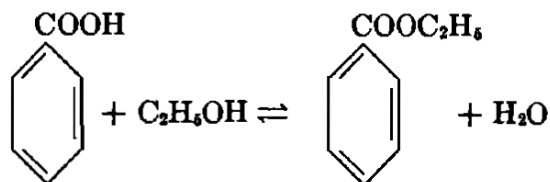


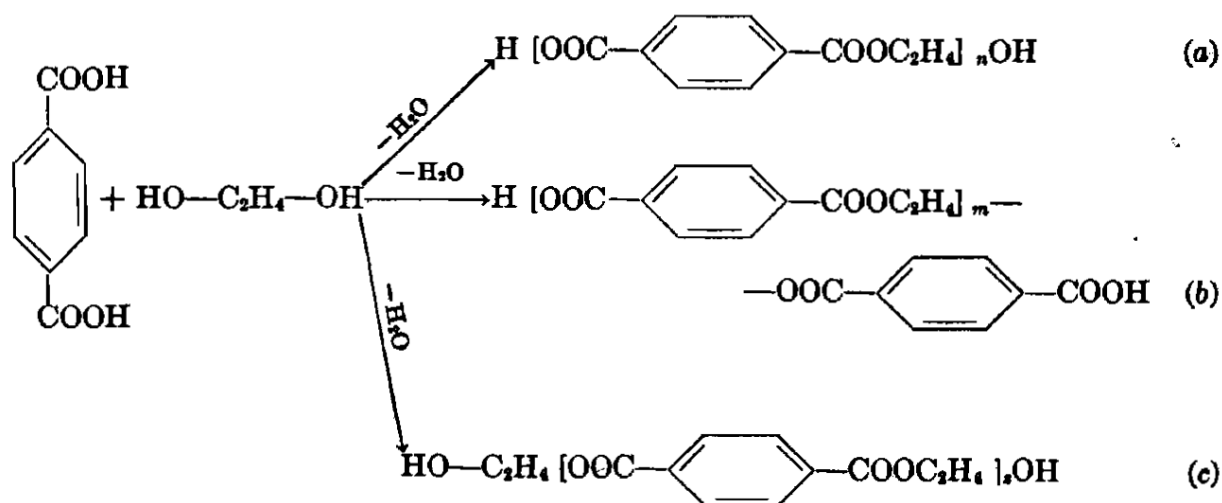
POLYCONDENSATION

Polycondensation proceeds fundamentally in the same manner as condensations between low-molecular-weight substances. For instance, the

energy of activation for polyesterifications and for polyamide formations lies between 15,000 and 30,000 cal per mole. These data come fairly close to the energy of activation for esterification and amidation of monofunctional molecules. The same acidic or basic catalysts are effective in the formation of a condensation-polymer molecule and of a low-molecular-weight condensation product. The mechanism of the polyreaction presents all characteristics of a step reaction; i.e., the chains grow proportionally to the reaction time, and each of the chain molecules is stable at any stage of the propagation process. Condensations between low-molecular-weight compounds are equilibrium reactions. In polycondensations the same principles hold true, though certain complications do arise. Consider, for instance, the esterification of benzoic acid with ethyl alcohol:



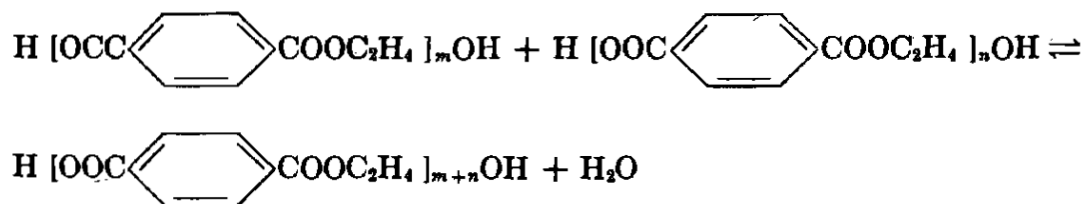
Under given conditions of temperature, pressure, and initial reactant concentration, the reaction will proceed at a certain measurable rate and reach an equilibrium. In a polycondensation, employing bifunctional reactants of a similar character, i.e., terephthalic acid and ethylene glycol, three types



of polymer molecules are formed. Type *a* is a polymer with one terminal carboxyl and one terminal hydroxyl, *b* is a polymer with two terminal carboxyls, and *c* is a polymer with two terminal hydroxyls. The prevalence of each type is critically dependent on the initial concentrations of the reactants. Molecules of type *a* appear in appreciable amounts only when the molar ratio of reactants is unity. An excess of acid causes all the polymer to be of type *b*, and an excess of glycol leads to molecules of type *c*. The quantity *n* or *m* or *z* in the above formulas is called the degree of polymerization \overline{DP} and depends in part on reactant concentration. If all the acid molecules are used up, the polymerization does not proceed further. If

there is a molar excess of glycol, this may occur at a time when the \overline{DP} is not very large.

The conditions of esterification are such that there is a certain tendency of the polymerized molecule to hydrolyze and thus to depolymerize. In the reaction



the possibility of hydrolysis is very great. There are only two places where the ester bond may form, but there are $m + n$ sites at which the ester bond may be hydrolyzed. As a result, even though the tendency toward esterification as opposed to hydrolysis may be very high, let us say 200:1, the reaction proceeds no further after a certain \overline{DP} is attained, because the number of places at which hydrolysis may take place is so large.

This leads to serious problems in the industrial production of polyesters and polyamides where it is essential to remove the last traces of water during polymerization in order to attain a molecular weight high enough for the polymer to form a useful material. Figure 15-3 illustrates the relationship between the amount of water present at a certain stage of a polyester

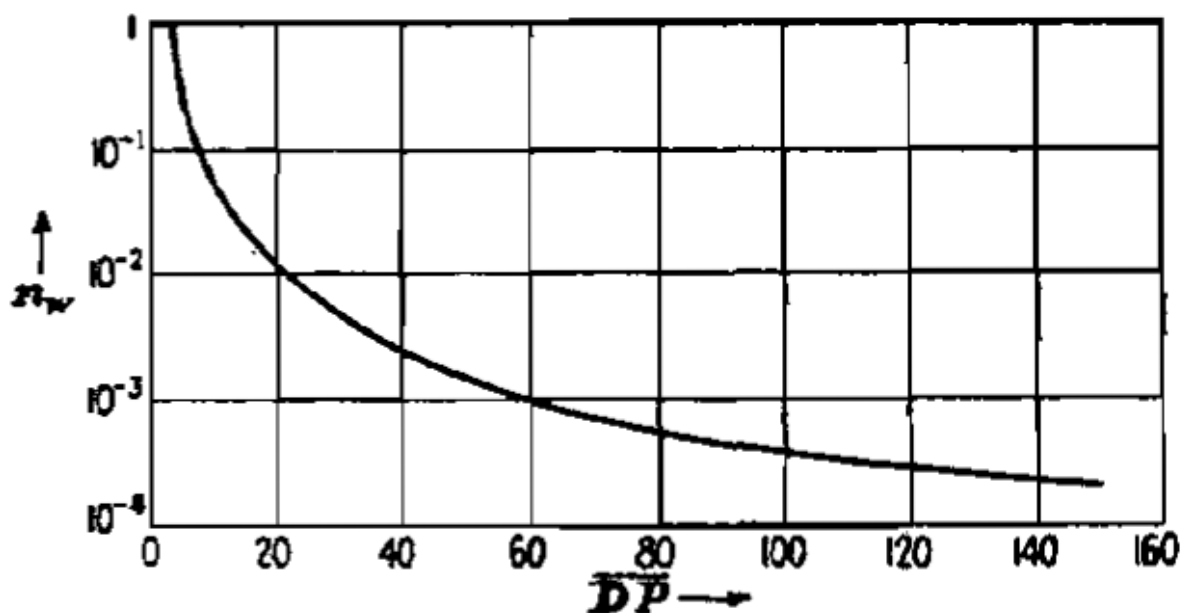


FIG. 15-3. Relationship between water content (mole fractions) and average polymerization degree in polyesters.

reaction and the average degree of polymerization of the polymer at that stage.

While systems of sufficiently high functionality usually lead to gelation and consequently to the formation of infusible and insoluble materials, this gelation may be prevented by including an adequate excess of one of the reacting components. For example, a stoichiometric reaction between glycerine and phthalic acid yields a large tridimensional network polymer, while in a reaction involving a molar excess of glycerine only a limited and considerably less extensive network is formed in which all the remaining end groups are hydroxyl. The excess glycerine serves to esterify

all the acid groups before the critical infinite network forms. Such a molecule is pictured below.

