

## II. CHEMISTRY OF POLYMERIZATION REACTIONS

### Functionality

Large molecular complexes can be built up in two possible ways: either by an association of small molecules by means of secondary bonds (van der Waals forces, etc.) or by continuous chemical reactions between small molecules, thus establishing strong chemical bonds between them. In the first case, those molecular associations which exist, for instance, in water, alco-

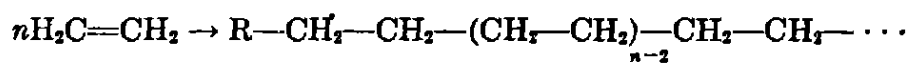
hols, and organic acids are extremely sensitive to disturbances of physical or chemical nature, since the forces binding the molecules are relatively weak (3,000–6,000 cal per mole); the dissociation energy of primary chemical bonds, however, has an entirely different order of magnitude (50,000–100,000 cal per mole). Natural and synthetic high polymers consist of large molecules built up by chemical bonds of the latter type.

The conception of low-molecular-weight organic molecules linking up to give a polymer molecule poses the question of the nature of the reactions that produce such polymers and the types of molecules that are capable of undergoing these reactions. The number of polymeric substances found in nature and produced artificially, and especially the variety of properties exhibited by them, seemed at first to indicate an almost unlimited number of possibilities in both respects. In later investigations, however, and primarily through the brilliant contributions of Carothers,<sup>1</sup> it was shown that two basic principles determine whether polymerization will occur at all. The first of these establishes the concept of *polyfunctionality* of a molecule as a requirement for the formation of polymer; the second divides all polymerization reactions into two distinct types: "addition" and "condensation" polymerizations. Later on though, some polymerization reactions were discovered which show characteristics of both types simultaneously. With the aid of these two principles, it becomes possible to choose from the set of presently available molecules those which possess the structure necessary for the formation of macromolecules by either one of the two typical reactions.

A molecule is called bi- or polyfunctional if two or more reactive or functional groups either are present at the beginning of the reaction or appear in the course of it. A monofunctional material can react at one point, a bifunctional material at two points, and a polyfunctional material at many points. Simple examples of bi- or polyfunctional molecules are hydroxy or amino acids, di- or polyalcohols, -amines, or -acids. These molecules interact with each other through their chemically active groups; but since two or more of them are located on each molecule, the reaction continues in two or three directions and linear or tridimensional molecules are formed. Figure 15-1 illustrates schematically the reaction between two monofunctional molecules, which does not produce macromolecules (*a*), whereas bifunctional monomers lead to linear-chain molecules (*b*), and the reaction of trifunctional molecules produces complicated networklike structures (*c*).

Another type of bifunctionality is exhibited by a large group of molecules containing double or triple bonds. Under the influence of heat or light energy, or if subjected to other forms of radiation, the two second-

order (or  $\pi$ ) electrons of the double bond may go into an excited state and may thus become available for a bifunctional reaction of the molecule. The over-all reaction may be expressed as



Another way to induce bifunctionality in a double-bond molecule is to create high polarity in its originally neutral or only slightly polar structure.

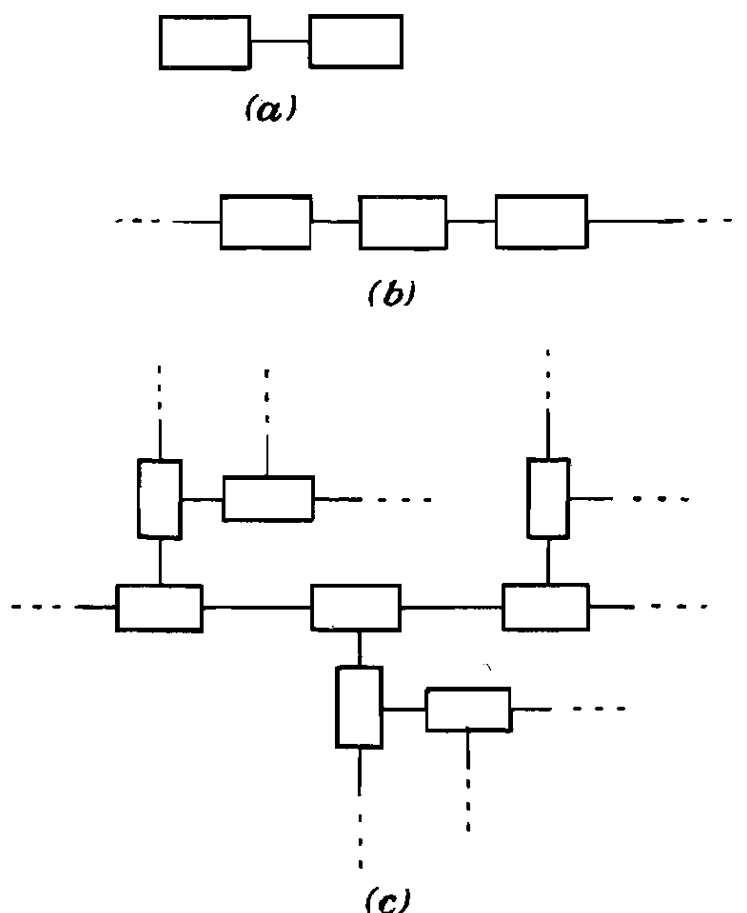


FIG. 15-1. Reactions of (a) monofunctional, (b) bifunctional, and (c) polyfunctional molecules.

This can be achieved by introducing a highly polar molecule such as, for instance, boron trifluoride,  $\text{BF}_3$ , into the reaction mixture under appropriate reaction conditions. It has been found that ionic polymerizations of this type require the presence of a small amount of a cocatalyst such as, for instance, water, which forms a highly polar molecular compound with the main catalyst. If such a highly polar compound approaches a monomer molecule containing a double bond, a charge separation may take place in the latter by a displacement of the two  $\pi$  electrons. These electrons will now be located at one specific site of the molecule, causing it to be negatively charged there and resulting in the formation of a positive charge at an opposite site. Figure 15-2a illustrates the charge separation in a schematic

form and shows also how the new "bifunctional" molecule can be the beginning of a polymer chain.

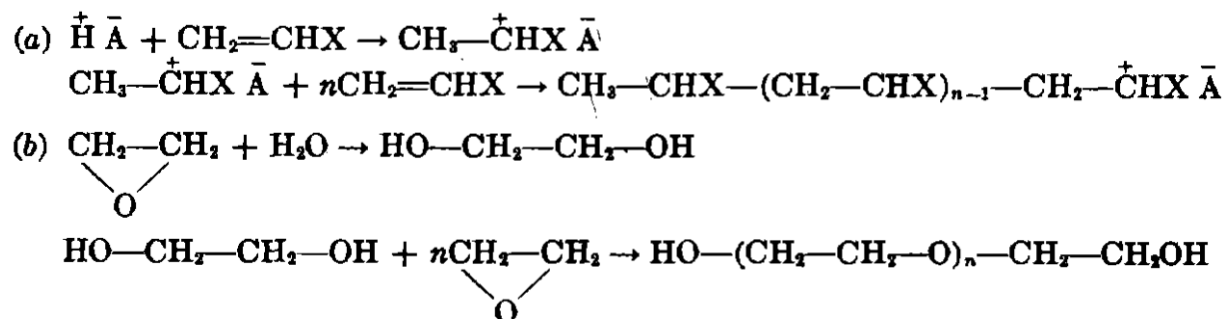
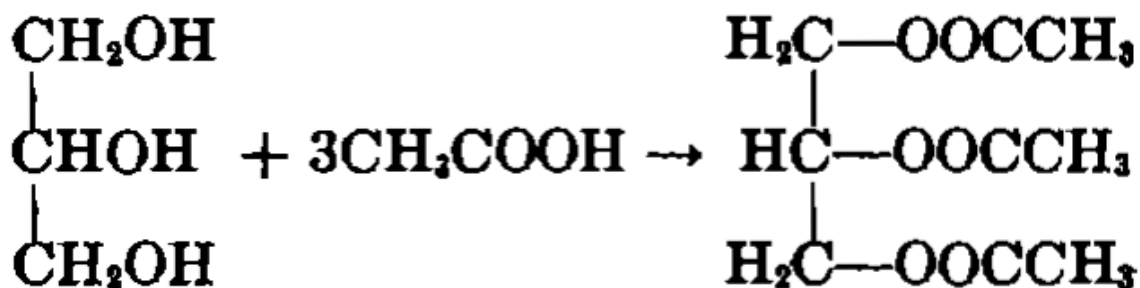


FIG. 15-2. Examples of polymer chain initiation by bifunctional molecules.

Bifunctional molecules may result from the opening of three—or more—membered rings, as for instance in the case of the formation of polymer molecules from ethylene oxide or tetrahydrofuran. An illustration of the over-all reaction scheme is given in Fig. 15-2b.

It must be emphasized again that polymer formation can be achieved only in a reaction where *all* participating molecules are bi- or polyfunctional. Monofunctional groups reacting with bi- or polyfunctional groups do not lead to polymer formation as can be seen from the reaction of glycerine with acetic acid:



The influence of the functionality concept in determining polymer structure is decisive. In any reaction where the average functionality of the product is less than the average functionality of the reactants, polymerization does not take place. If it is equal in the product to that of the reactants, a polymer is formed; it is linear in structure and grows to a finite size. If, however, the average functionality of the product is greater than that of the reactants, then the reaction, if carried far enough, produces a tridimensional network polymer. The tridimensional and the linear polymers differ sharply in many of their physical and chemical characteristics, particularly in their solution properties and their fusibility. In general, linear polymers are thermoplastic; they are fusible and soluble in appropriate solvents. Tridimensional network polymers are thermosetting; they may imbibe solvents and swell, forming a gel-like material, but they will not dissolve. They do not melt but, upon continuous heating, decompose and break down chemically.