

1

INTRODUCTION

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules which combine with each other to form polymer molecules are termed *monomers* and the reactions by which they combine are termed *polymerizations*. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule. When one speaks of polymers, one is concerned with materials whose molecular weights may reach into the millions. Most of the polymers, however, that one usually encounters either in the laboratory or in practical applications will usually fall into the 5,000–200,000 molecular weight range.

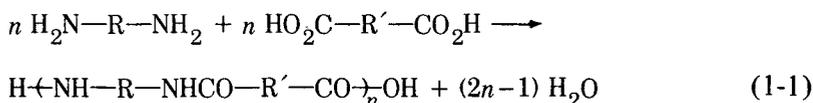
1-1 TYPES OF POLYMERS AND POLYMERIZATIONS

There has been and still is considerable confusion concerning the classification of polymers. This is especially the case for the beginning student. During the development of polymer science, two classifications of polymers have come into use. One classification divides

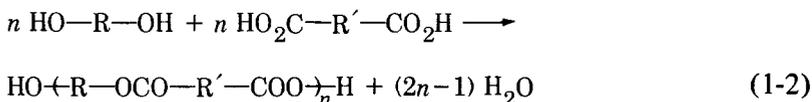
polymers into *condensation* and *addition* polymers and the other divides them into *step* and *chain* polymers. Confusion and error arise because the two classifications are usually used interchangeably without careful thought. The terms condensation and step are usually used synonymously as are the terms addition and chain. Although these terms can often be used synonymously as noted, this is not always the case because the two classifications arise from two different bases of classification. The condensation-addition classification is primarily applicable to the composition or structure of polymers. The step-chain classification is based on the mechanism of the polymerization reactions.

1-1a Polymer Composition and Structure

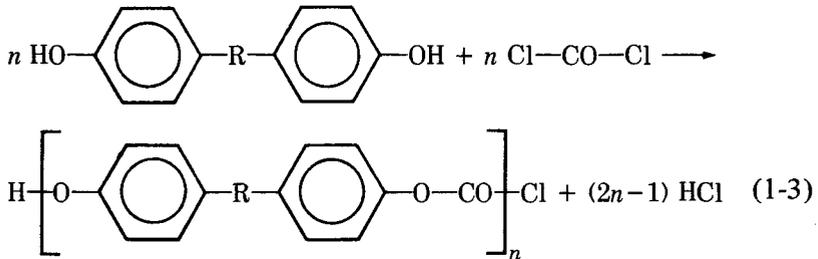
Polymers were originally classified by Carothers [1] in 1929 into condensation and addition polymers on the basis of the compositional difference between the polymer and the monomer(s) from which it was synthesized. Condensation polymers were those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water. An example of such a condensation polymer is the polyamides formed from diamines and diacids with the elimination of water according to



where R and R' are aliphatic or aromatic groupings. The unit in parentheses in the polyamide formula repeats itself many times in the polymer chain and is termed the *repeating unit* or *base unit* [2]. The composition of the repeating unit differs from that of the two monomers by the elements of water. The polyamide synthesized from hexamethylene diamine, $\text{R} = (\text{CH}_2)_6$, and adipic acid, $\text{R}' = (\text{CH}_2)_4$, is the extensively used fiber and plastic known commonly as nylon-6,6 or poly(hexamethylene adipamide). Other examples of condensation polymers are the polyesters formed from diacids and diols with the elimination of water



and the polycarbonates from the reaction of an aromatic dihydroxy reactant and phosgene with the elimination of hydrogen chloride



The common condensation polymers and the reactions by which they are formed are shown in Table 1-1. It should be noted from Table 1-1 that for many of the condensation polymers, there are different combinations of reactants which can be employed for their synthesis. Thus, polyamides can be synthesized by the reactions of diamines with diacids or diacyl chlorides and by the self-condensation of amino acids. Similarly, polyesters can be synthesized from diols by esterification with diacids or ester interchange with diesters.

Some naturally occurring polymers such as cellulose, starch, wool, and silk are classified as condensation polymers since one can postulate their synthesis from certain hypothetical reactants by the elimination of water. Thus, cellulose can be thought of as the polyether formed by the dehydration of glucose. Carothers included such polymers by defining condensation polymers as those in which the formula of the repeating unit lacks certain atoms which are present in the monomer(s) from which it is formed or to which it may be degraded. In this sense, cellulose is considered a condensation polymer since its hydrolysis yields glucose which contains the repeating unit of cellulose plus the elements of water

