

## Polymerization Reactions

Polymerization reactions are either *condensation* reactions or *addition* reactions. The polymer formation in condensation polymerization proceeds

### Condensation Polymerization:

stepwise, the various intermediates, dimer, trimer, etc., existing as stable molecules until the next reaction step. Small molecules, usually water, are split off at each step of the reaction.

### Addition Polymerization:

Addition polymerization is characterized by the fact that the reaction from monomer to polymer occurs without elimination of by-products. During the addition reaction, no stable compounds are formed because the intermediates are comparatively short-lived radicals or ions. The formation of the polymer chain is usually accomplished in a fraction of a second and in one single sweep. Polymerization at the double bond is a typical addition reaction of this type. Certain addition reactions, which proceed by first opening the ring of a cyclic compound, follow a stepwise procedure. Thus they occupy a position in between the two reaction types, showing certain similarities to each.

### Copolymerization:

- Random
- Alternating

A form of addition polymerization is that of copolymerization in which two or more different monomers are linked together, either at random or alternating, to form one single copolymer chain or network:

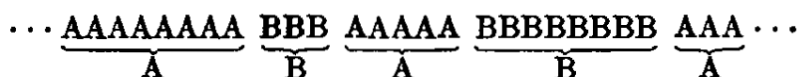
... AABABBBBABABBAAABBBAB ... random  
... ABABABABABABABAB ... alternating

### Special Types of Copolymerization

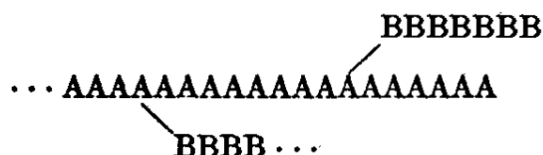
Recently two special types of copolymerization have been investigated intensely and have shown promise for use in large-scale industrial production. They are called block polymerization and graft polymerization,

## Block Polymerization:

In block polymerization, sequences of one type of monomer are prepolymerized and then joined to the prepolymerized sequences of another monomer:



A typical example of graft polymerization is one in which sequences of monomer B are grafted onto the main chain consisting of A units:



Finally a type of addition polymerization calling for the employment of stereospecific catalysts has recently aroused much interest in the laboratory as well as in industry. With the aid of such catalysts, an addition polymerization yields certain polymers in which the main chain as well as the chemical substituents are situated in a highly ordered spatial pattern. Polymers of physical and chemical characteristics are thus obtained which contrast markedly from those formed in normal polymerizations.