All the monomers from which addition polymers are made are alkenes or functionally substituted alkenes. The most common and thermodynamically favored chemical transformations of alkenes are addition reactions. Many of these addition reactions are known to proceed in a stepwise fashion by way of reactive intermediates, and this is the mechanism followed by most polymerizations. A general diagram illustrating this assembly of linear macromolecules, which supports the name chain growth polymers, is presented here. Since a pi-bond in the monomer is converted to a sigma-bond in the polymer, the polymerization reaction is usually exothermic by 8 to 20 kcal/mol. Indeed, cases of explosively uncontrolled polymerizations have been reported.

It is useful to distinguish four polymerization procedures fitting this general description.

- Radical Polymerization The initiator is a radical, and the propagating site of reactivity (*) is a carbon radical.
- Cationic Polymerization The initiator is an acid, and the propagating site of reactivity (*) is a carbocation.
- Anionic Polymerization The initiator is a nucleophile, and the propagating site of reactivity (*) is a carbanion.
- Coordination Catalytic Polymerization The initiator is a transition metal complex, and the propagating site of reactivity (*) is a terminal catalytic complex.

Radical Chain-Growth Polymerization

Virtually all of the monomers described above are subject to radical polymerization. Since this can be initiated by traces of oxygen or other minor impurities, pure samples of these compounds are often "stabilized" by small amounts of radical inhibitors to avoid unwanted reaction. When radical polymerization is desired, it must be started by using a radical initiator, such as a peroxide or certain azo compounds. The formulas of some common initiators, and equations showing the formation of radical species from these initiators are presented below.

By using small amounts of initiators, a wide variety of monomers can be polymerized. One example of this radical polymerization is the conversion of styrene to polystyrene, shown in the following diagram. The first two equations...
illustrate the initiation process, and the last two equations are examples of chain propagation. Each monomer unit adds to
the growing chain in a manner that generates the most stable radical. Since carbon radicals are stabilized by substituents
of many kinds, the preference for head-to-tail regioselectivity in most addition polymerizations is understandable. Because
radicals are tolerant of many functional groups and solvents (including water), radical polymerizations are widely used in
the chemical industry.

In principle, once started a radical polymerization might be expected to continue unchecked, producing a few extremely
long chain polymers. In practice, larger numbers of moderately sized chains are formed, indicating that chain-terminating
reactions must be taking place. The most common termination processes are Radical Combination and
Disproportionation. These reactions are illustrated by the following equations. The growing polymer chains are colored
blue and red, and the hydrogen atom transferred in disproportionation is colored green. Note that in both types
of termination two reactive radical sites are removed by simultaneous conversion to stable product(s). Since the
concentration of radical species in a polymerization reaction is small relative to other reactants (e.g. monomers, solvents
and terminated chains), the rate at which these radical-radical termination reactions occurs is very small, and most
growing chains achieve moderate length before termination.

The relative importance of these terminations varies with the nature of the monomer undergoing polymerization. For
acrylonitrile and styrene combination is the major process. However, methyl methacrylate and vinyl acetate are terminated
chiefly by disproportionation.

Another reaction that diverts radical chain-growth polymerizations from producing linear macromolecules is called chain
transfer. As the name implies, this reaction moves a carbon radical from one location to another by an intermolecular or
intramolecular hydrogen atom transfer (colored green). These possibilities are demonstrated by the following equations
Chain transfer reactions are especially prevalent in the high pressure radical polymerization of ethylene, which is the method used to make LDPE (low density polyethylene). The 1º-radical at the end of a growing chain is converted to a more stable 2º-radical by hydrogen atom transfer. Further polymerization at the new radical site generates a side chain radical, and this may in turn lead to creation of other side chains by chain transfer reactions. As a result, the morphology of LDPE is an amorphous network of highly branched macromolecules.

**Cationic Chain-Growth Polymerization**

Polymerization of isobutylene (2-methylpropene) by traces of strong acids is an example of cationic polymerization. The polyisobutylene product is a soft rubbery solid, \( T_g \approx -70^\circ C \), which is used for inner tubes. This process is similar to radical polymerization, as demonstrated by the following equations. Chain growth ceases when the terminal carbocation combines with a nucleophile or loses a proton, giving a terminal alkene (as shown here).

Monomers bearing cation stabilizing groups, such as alkyl, phenyl or vinyl can be polymerized by cationic processes. These are normally initiated at low temperature in methylene chloride solution. Strong acids, such as HClO4, or Lewis acids containing traces of water (as shown above) serve as initiating reagents. At low temperatures, chain transfer reactions are rare in such polymerizations, so the resulting polymers are cleanly linear (unbranched).

**Anionic Chain-Growth Polymerization**

Treatment of a cold THF solution of styrene with 0.001 equivalents of n-butyllithium causes an immediate polymerization. This is an example of anionic polymerization, the course of which is described by the following equations. Chain growth may be terminated by water or carbon dioxide, and chain transfer seldom occurs. Only monomers having anion stabilizing substituents, such as phenyl, cyano or carbonyl are good substrates for this polymerization technique. Many of the resulting polymers are largely isotactic in configuration, and have high degrees of crystallinity.

Species that have been used to initiate anionic polymerization include alkali metals, alkali amides, alkyl lithiiums
and various electron sources. A practical application of anionic polymerization occurs in the use of superglue. This material is methyl 2-cyanoacrylate, CH2=C(CN)CO2CH3. When exposed to water, amines or other nucleophiles, a rapid polymerization of this monomer takes place.

### Ziegler-Natta Catalytic Polymerization

An efficient and stereospecific catalytic polymerization procedure was developed by Karl Ziegler (Germany) and Giulio Natta (Italy) in the 1950's. Their findings permitted, for the first time, the synthesis of unbranched, high molecular weight polyethylene (HDPE), laboratory synthesis of natural rubber from isoprene, and configurational control of polymers from terminal alkenes like propene (e.g. pure isotactic and syndiotactic polymers). In the case of ethylene, rapid polymerization occurred at atmospheric pressure and moderate to low temperature, giving a stronger (more crystalline) product (HDPE) than that from radical polymerization (LDPE). For this important discovery these chemists received the 1963 Nobel Prize in chemistry.

Ziegler-Natta catalysts are prepared by reacting certain transition metal halides with organometallic reagents such as alkyl aluminum, lithium and zinc reagents. The catalyst formed by reaction of triethylaluminum with titanium tetrachloride has been widely studied, but other metals (e.g. V & Zr) have also proven effective. The following diagram presents one mechanism for this useful reaction. Others have been suggested, with changes to accommodate the heterogeneity or homogeneity of the catalyst. Polymerization of propylene through action of the titanium catalyst gives an isotactic product; whereas, a vanadium based catalyst gives a syndiotactic product.

#### Contributors