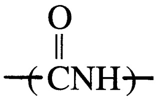
Lecture 1

Polymerization

INTRODUCTION

Polymerization is a reaction in which chain-like macromolecules are formed by combining small molecules (monomers).

Monomers are the building blocks of these large molecules called polymers. One natural polymer is cellulose (the most abundant organic compound on earth), a molecule made of many simple glucose units (monomers) joined together through a glycoside linkage.[1] Proteins, the material of life, are polypeptides made of α-amino acids attached by an amide



$-\!\left(\overset{\overset{\displaystyle O}{\|}}{C}NH\right)\!-$ linkage.

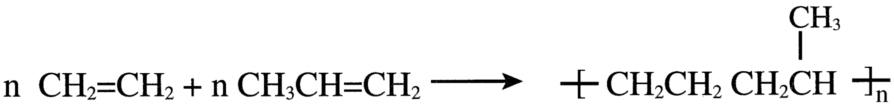
The polymer industry dates back to the 19th century, when natural polymers, such as cotton, were modified by chemical treatment to produce artificial silk (rayon). Work on synthetic polymers did not start until the beginning of the 20th century. In 1909, L. H. Baekeland prepared the first synthetic polymeric material using a condensation reaction between formaldehyde and phenol. Currently, these polymers serve as important thermosetting plastics (phenol formaldehyde resins). Since Baekeland's discovery, many polymers have been synthesized and marketed. Many modern commercial products (plastics, fibers, rubber) derive from polymers. The huge polymer market directly results from extensive work in synthetic organic compounds and catalysts. Ziegler's discovery of a coordination catalyst in the titanium family paved the road for synthesizing many stereoregular polymers with improved properties. This chapter reviews the chemistry involved in the synthesis of polymers.

MONOMERS, POLYMERS, AND COPOLYMERS

A *monomer* is a reactive molecule that has at least one functional group (e.g. -OH, -COOH, $-NH_2$, -C=C-). Monomers may add to themselves as in the case of ethylene or may react with other monomers having different functionalities. A monomer initiated or catalyzed with a specific catalyst polymerizes and forms a macromolecule—a polymer. For example, ethylene polymerized in presence of a coordination catalyst produces a linear homopolymer (linear polyethylene):

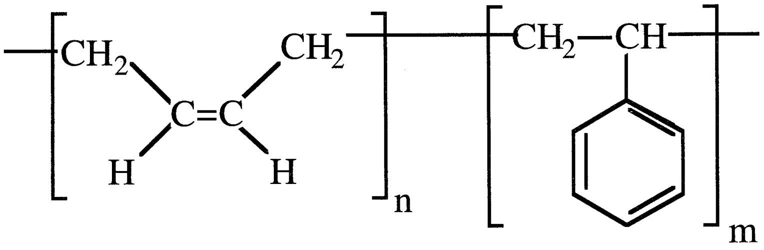
$$n\,CH_2{=}CH_2 \rightarrow \left[CH_2{-}CH_2 \right]_n \text{ (Linear polyethylene)}$$

A *copolymer,* on the other hand, results from two different monomers by addition polymerization. For example, a thermoplastic polymer with better properties than an ethylene homopolymer comes from copolymerizing ethylene and propylene:



$$n\;CH_2{=}CH_2 + n\,CH_3CH{=}CH_2 \longrightarrow \left[CH_2CH_2\,CH_2\overset{\overset{CH_3}{|}}{C}H \right]_n$$

Block copolymers are formed by reacting two different *prepolymers,* which are obtained by polymerizing the molecules of each monomer separately. A block copolymer made of styrene and butadiene is an important synthetic rubber:

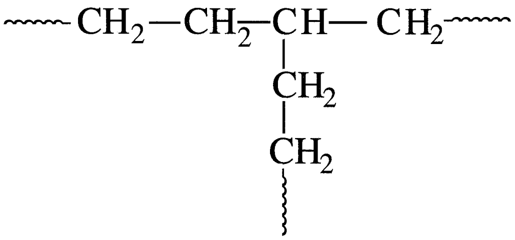


Alternating copolymers have the monomers of one type alternating in a regular manner with the monomers of the other, regardless of the composition of the reactants. For example, an alternate copolymer of vinyl acetate and vinyl chloride could be represented as:

$$—CH_2\overset{\overset{OAC}{|}}{C}HCH_2\overset{\overset{Cl}{|}}{C}HCH_2\overset{\overset{OAC}{|}}{C}HCH_2\overset{\overset{Cl}{|}}{C}H—$$

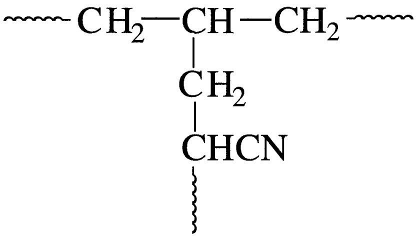
Random copolymers have the different monomer molecules distributed randomly along the polymer chain.

A polymer molecule may have just a linear chain or one or more branches protruding from the polymer backbone. Branching results mainly from chain transfer reactions (see "Chain Transfer Reactions" later in this chapter) and affects the polymer's physical and mechanical properties. Branched polyethylene usually has a few long branches and many more short branches



$$\sim CH_2-CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_2\\ \wr}}{CH}-CH_2\sim$$

Intentional branching may improve the properties of the product polymer through grafting. A *graft copolymer* can be obtained by creating active sites on the polymer backbone. The addition of a different monomer then reacts at the active site and forms a branch. For example, polyethylene irradiated with gamma rays and then exposed to a reactive monomer, such as acrylonitrile, produces a polyethylene-polymer with acrylonitrile branches:[2,3]



$$\sim CH_2-\underset{\substack{|\\ CH_2\\ |\\ CHCN\\ \wr}}{CH}-CH_2\sim$$

Crosslinked polymers have two or more polymer chains linked together at one or more points other than their ends. The network formed improves the mechanical and physical properties of the polymer.

Crosslinking may occur during the polymerization reaction when multifunctional groups are present (as in phenol-formaldehyde resins) or through outside linking agents (as in the vulcanization of rubber with sulfur).

POLYMERIZATION REACTIONS

Two general reactions form synthetic polymers: chain addition and condensation.

Addition polymerization requires a chain reaction in which one monomer molecule adds to a second, then a third and so on to form a macromolecule. Addition polymerization monomers are mainly low molecular-weight olefinic compounds (e.g., ethylene or styrene) or conjugated diolefins (e.g., butadiene or isoprene).

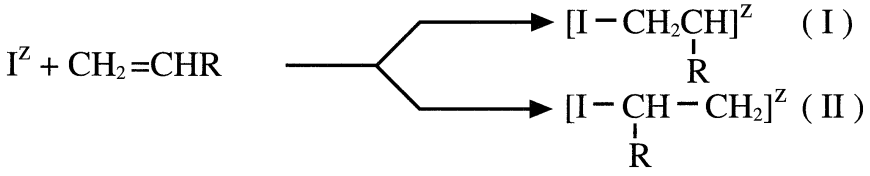
Condensation polymerization can occur by reacting either two similar or two different monomers to form a long polymer. This reaction usually releases a small molecule like water, as in the case of the esterification of a diol and a diacid. In condensation polymerization where ring opening occurs, no small molecule is released (see "Condensation Polymerization" later in this chapter).

ADDITION POLYMERIZATION

Addition polymerization is employed primarily with substituted or unsubstituted olefins and conjugated diolefins. Addition polymerization initiators are free radicals, anions, cations, and coordination compounds. In addition polymerization, a chain grows simply by adding monomer molecules to a propagating chain. The first step is to add a free radical, a cationic or an anionic initiator (I^Z) to the monomer. For example, in ethylene polymerization (with a special catalyst), the chain grows by attaching the ethylene units one after another until the polymer terminates. This type of addition produces a linear polymer:

$$I^Z + CH_2{=}CH_2 \rightarrow I\left[CH_2{-}CH_2\right]^z$$

Branching occurs especially when free radical initiators are used due to chain transfer reactions (see following section, "Free Radical Polymerizations"). For a substituted olefin (such as vinyl chloride), the addition primarily produces the most stable intermediate (I). Intermediate (II) does not form to any appreciable extent:

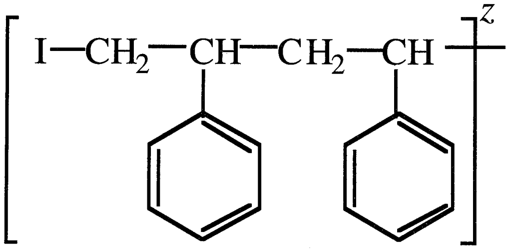


$$I^Z + CH_2{=}CHR \longrightarrow \begin{cases} [I-CH_2\underset{R}{CH}]^Z & (I) \\ [I-\underset{R}{CH}-CH_2]^Z & (II) \end{cases}$$

I^z = a free radical $I^\bullet$, cation I^+, or an anion I^-
R = alkyl, phenyl, Cl, etc.

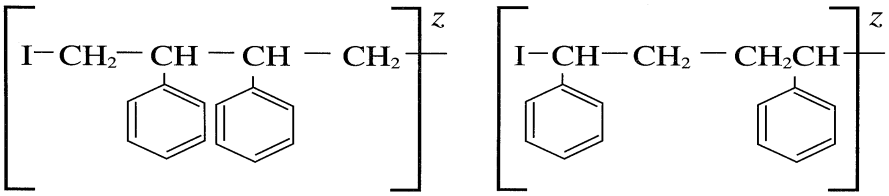
Propagation then occurs by successive monomer molecules additions to the intermediates. Three addition modes are possible: (a) Head to tail; (b) Head to head, and (c) tail to tail.

The head-to-tail addition mode produces the most stable intermediate. For example, styrene polymerization mainly produces the head-to-tail intermediate:



Head to-tail mode

Head-to-head or tail-to-tail modes of addition are less likely because the intermediates are generally unstable:

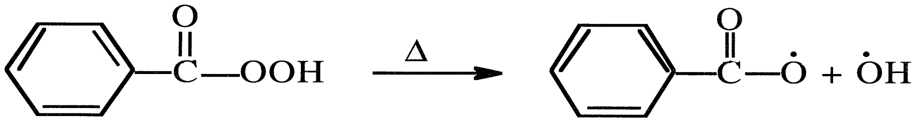


Head-to-head mode   Tail-to-tail mode

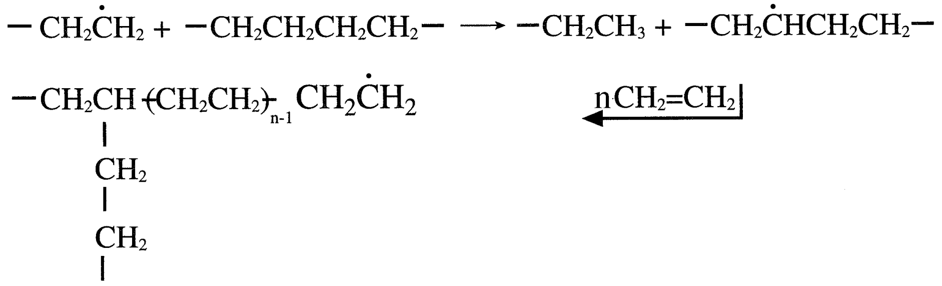
Chain growth continues until the propagating polymer chain terminates.

Free Radical Polymerization

Free radical initiators can polymerize olefinic compounds. These chemical compounds have a weak covalent bond that breaks easily into two free radicals when subjected to heat. Peroxides, hydroperoxides and azo compounds are commonly used. For example, heating peroxybenzoic acid forms two free radicals, which can initiate the polymerization reaction:

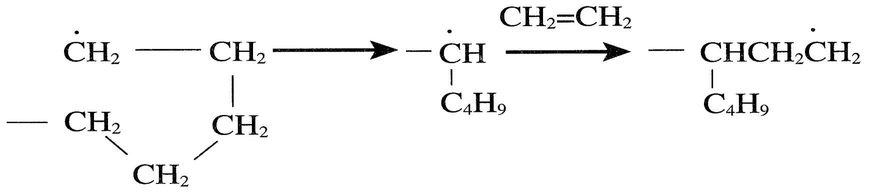


Free radicals are highly reactive, short lived, and therefore not selective. Chain transfer reactions often occur and result in a highly branched product polymer. For example, the polymerization of ethylene using an organic peroxide initiator produces highly branched polyethylene. The branches result from the abstraction of a hydrogen atom by a propagating polymer intermediate, which creates a new active center. The new center can add more ethylene molecules, forming a long branch:



$$-CH_2\dot{C}H_2 + -CH_2CH_2CH_2CH_2- \longrightarrow -CH_2CH_3 + -CH_2\dot{C}HCH_2CH_2-$$

Intermolecular chain transfer reactions may occur between two propagating polymer chains and result in the termination of one of the chains. Alternatively, these reactions take place by an intramolecular reaction by the coiling of a long chain. Intramolecular chain transfer normally results in short branches:[4]



Free radical polymers may terminate when two propagating chains combine. In this case, the tail-to-tail addition mode is most likely.

Polymer propagation stops with the addition of a chain transfer agent. For example, carbon tetrachloride can serve as a chain transfer agent:

$$—CH_2—\dot{C}H_2 + CCl_4 \rightarrow —CH_2—CH_2Cl + \dot{C}Cl_3$$

The $\dot{C}Cl_3$ free radical formed can initiate a new polymerization reaction.

Lecture 2

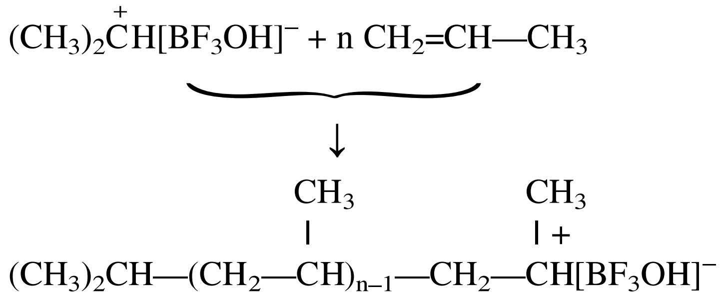
Cationic Polymerization

Strong protonic acids can affect the polymerization of olefins (Chapter 3). Lewis acids, such as $AlCl_3$ or BF_3, can also initiate polymerization. In this case, a trace amount of a proton donor (cocatalyst), such as water or methanol, is normally required. For example, water combined with BF_3 forms a complex that provides the protons for the polymerization reaction.

An important difference between free radical and ionic polymerization is that a counter ion only appears in the latter case. For example, the intermediate formed from the initiation of propene with BF_3-H_2O could be represented as

$$H^{+}[BF_3OH]^{-} + CH_2{=}CH{-}CH_3 \longrightarrow (CH_3)_2\overset{+}{C}H[BF_3OH]^{-}$$

The next step is the insertion of the monomer molecules between the ion pair.

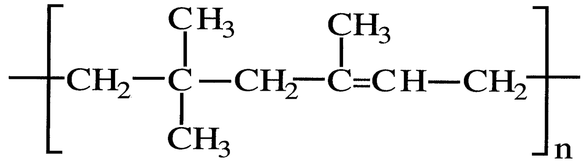


$$\underbrace{(CH_3)_2\overset{+}{C}H[BF_3OH]^- + n\,CH_2{=}CH{-}CH_3}_{\displaystyle\downarrow}$$

$$(CH_3)_2CH{-}(CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}H})_{n-1}{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|\,+}{C}H}[BF_3OH]^-$$

In ionic polymerizations, reaction rates are faster in solvents with high dielectric constants, which promote the separation of the ion pair.

Cationic polymerizations work better when the monomers possess an electron-donating group that stabilizes the intermediate carbocation. For example, isobutylene produces a stable carbocation, and usually copolymerizes with a small amount of isoprene using cationic initiators. The product polymer is a synthetic rubber widely used for tire inner tubes:

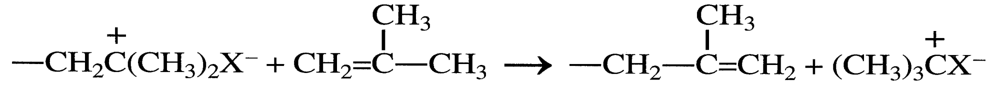


$$\left[CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH-CH_2 \right]_n$$

Cationic initiators can also polymerize aldehydes. For example, BF_3 helps produce commercial polymers of formaldehyde. The resulting polymer, a polyacetal, is an important thermoplastic (Chapter 12):

$$-\!\!\left[CH_2-O \right]\!\!-$$

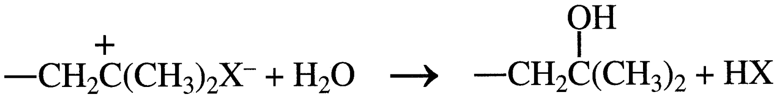
In general, the activation energies for both cationic and anionic polymerization are small. For this reason, low-temperature conditions are normally used to reduce side reactions.[5] Low temperatures also minimize chain transfer reactions. These reactions produce low-molecular weight polymers by disproportionation of the propagating polymer:



$$-CH_2\overset{+}{C}(CH_3)_2X^- + CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 \longrightarrow -CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + (CH_3)_3\overset{+}{C}X^-$$

X^- represents the counter ion.

Cationic polymerization can terminate by adding a hydroxy compound such as water:

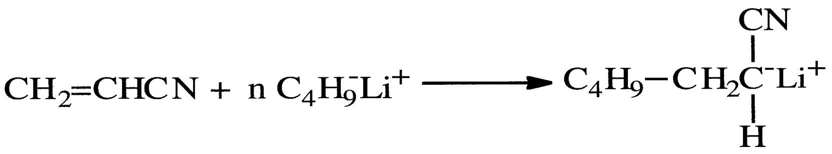


$$\text{—}CH_2\overset{+}{C}(CH_3)_2X^- + H_2O \longrightarrow \text{—}CH_2\overset{\displaystyle OH}{\overset{|}{C}}(CH_3)_2 + HX$$

Anionic Polymerization

Anionic polymerization is better for vinyl monomers with electron withdrawing groups that stabilize the intermediates. Typical monomers best polymerized by anionic initiators include acrylonitrile, styrene, and butadiene. As with cationic polymerization, a counter ion is present with the propagating chain. The propagation and the termination steps are similar to cationic polymerization.

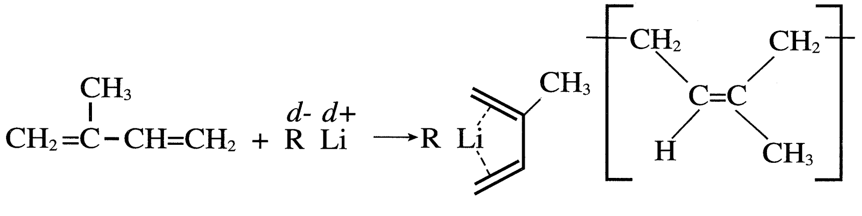
Many initiators, such as alkyl and aryllithium and sodium and lithium suspensions in liquid ammonia, effect the polymerization. For example, acrylonitrile combined with n-butyllithium forms a carbanion intermediate:



$$CH_2{=}CHCN + n\ C_4H_9^-Li^+ \longrightarrow C_4H_9{-}CH_2\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CN}{\overset{|}{C}}}}{}^-Li^+$$

Chain growth occurs through a nucleophilic attack of the carbanion on the monomer. As in cationic polymerizations, lower temperatures favor anionic polymerizations by minimizing branching due to chain transfer reactions.

Solvent polarity is also important in directing the reaction bath and the composition and orientation of the products. For example, the polymerization of butadiene with lithium in tetrahydrofuran (a polar solvent) gives a high 1,2 addition polymer.[6] Polymerization of either butadiene or isoprene using lithium compounds in nonpolar solvent such as n-pentane produces a high cis-1,4 addition product. However, a higher cis-1,4-polyisoprene isomer was obtained than when butadiene was used. This occurs because butadiene exists mainly in a transoid conformation at room temperature[7] (a higher cisoid conformation is anticipated for isoprene):



A complex of isoprene with RLi (cisoid)

cis- 1,4-Polyisoprene

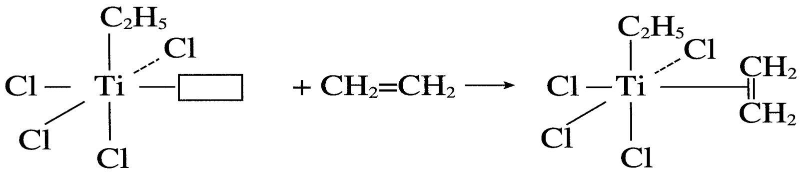
Coordination Polymerization

Polymerizations catalyzed with coordination compounds are becoming more important for obtaining polymers with special properties (linear and stereospecific). The first linear polyethylene polymer was prepared from a mixture of triethylaluminum and titanium tetrachloride (Ziegler catalyst) in the early 1950s. Later, Natta synthesized a stereoregular polypropylene with a Ziegler-type catalyst. These catalyst combinations are now called Zieglar-Natta catalysts.

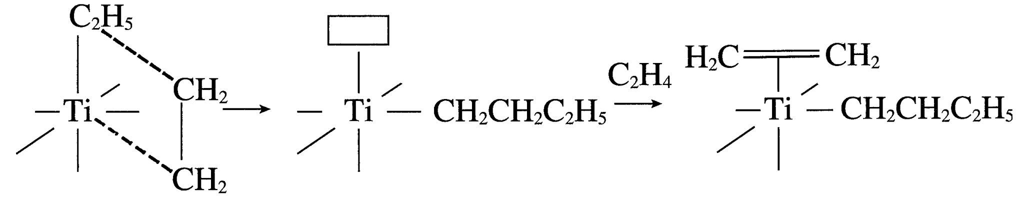
In coordination polymerization, the bonds are appreciably covalent but with a certain percentage of ionic character. Bonding occurs between a transition metal central ion and the ligand (perhaps an olefin, a diolefin or carbon monoxide) to form a coordination complex. The complex reacts further with the ligand to be polymerized by an insertion mechanism. Different theories about the formation of coordination complexes have been reviewed by Huheey.[8] In recent years, much interest has been centered on using late transition metals such as iron and cobalt for polymerization. Due to their lower electrophilicity, they have greater tolerence for polar functionality. It was found that the catalyst activity and the polymer branches could be modified by altering the bulk of the ligand that surrounds the central metal. Such a protection reduces chain-transfer reactions and results in a high molecular-weight polymer. An example of these catalysts are pyridine bis-imine ligands complexed with iron and cobalt salts.[9]

Ziegler-Natta catalysts currently produce linear polyethylene (nonbranched), stereoregular polypropylene, cis-polybutadiene, and other stereoregular polymers.

In polymerizing these compounds, a reaction between α-$TiCl_3$ and triethylaluminum produces a five coordinate titanium (III) complex arranged octahedrally. The catalyst surface has four Cl anions, an ethyl group, and a vacant catalytic site (□) with the Ti(III) ion in the center of the octahedron. A polymerized ligand, such as ethylene, occupies the vacant site:



The next step is the cis insertion of the ethyl group, leaving a vacant site. In another step, ethylene occupies the vacant site. This process continues until the propagating chain terminates:



When propylene is polymerized with free radicals or some ionic initiators, a mixture of three stereo-forms results (Figure 11-1).[10] These forms are

Atactic—the methyl groups are randomly distributed.

Isotactic—all methyl groups appear on one side of the polymer chain.

Syndiotactic—the methyl groups alternate regularly from one side to the other.

The isotactic form of propylene has better physical and mechanical properties than the three tactic form mixture (obtained from free radical polymerization). Isotactic polypropylene, in which all of the stereo cen-

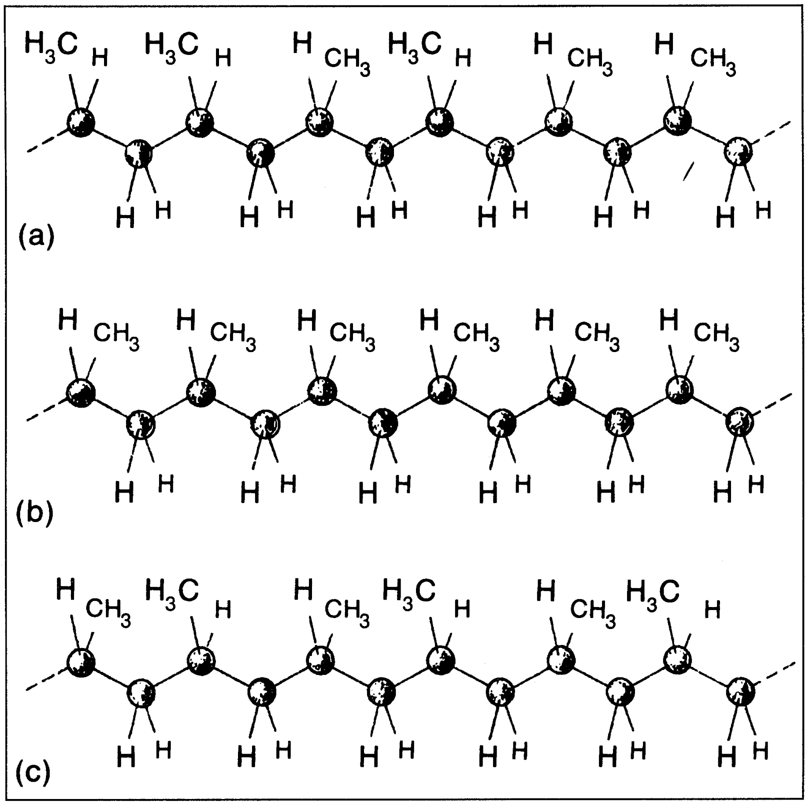
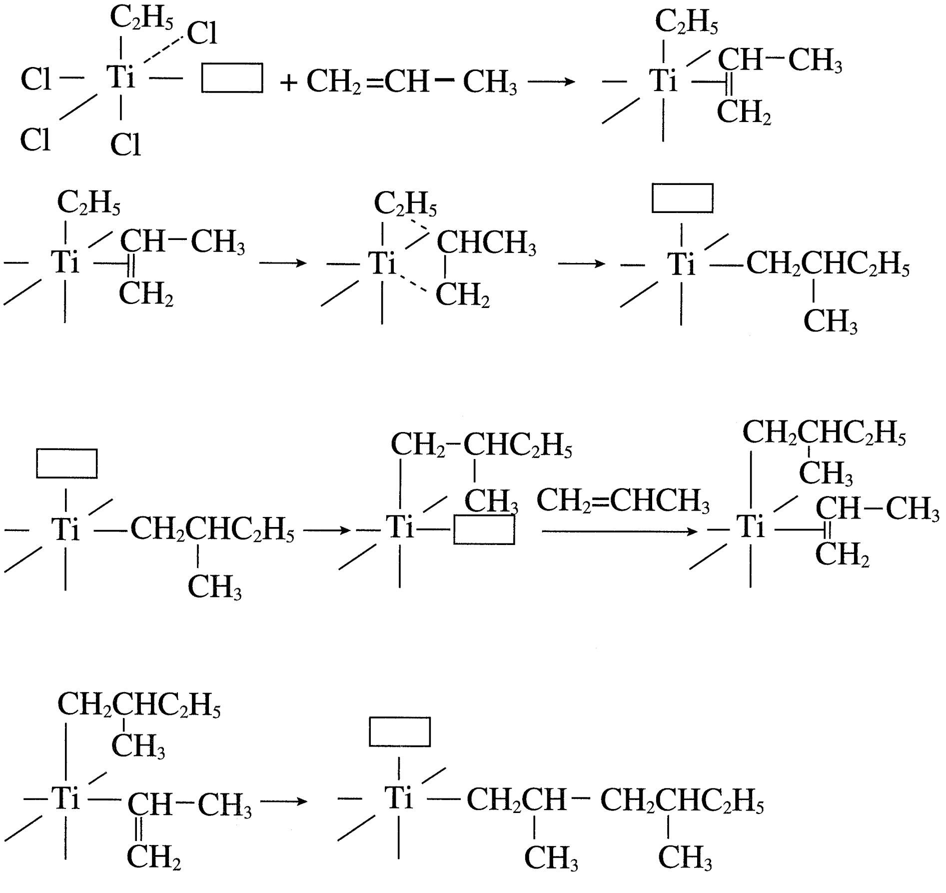


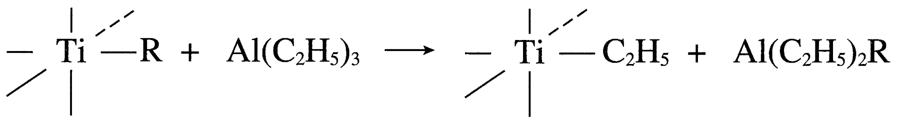
Figure 11-1. Propylene can undergo polymerization in three different ways to form atactic (a), isotactic (b), or syndiotactic polypropylene (c).[10]

ters of the polymer are the same, is a crystalline thermoplastic. By contrast, atactic polypropylene, in which the stereo centers are arranged randomly, is an amorphous gum elastomer. Polypropylene consisting of blocks of atactic and isotactic stereo sequences is rubbery.[11] Polymerizing propylene with Ziegler-Natta catalyst produces mainly isotactic polypropylene. The Cosse-Arlman model explains the formation of the stereoregular type by describing the crystalline structure of $\alpha TiCl_3$ as a hexagonal close packing with anion vacancies.[12] This structure allows for cis insertion. However, due to the difference in the steric requirements, one of the vacant sites available for the ligand to link with the titanium catalyst which has a greater affinity for the propagating polymer than the other site. Accordingly, the growing polymer returns rapidly back to that site as shown here:



The propagating polymer then terminates, producing an isotactic polypropylene. Linear polyethylene occurs whether the reaction takes place by insertion through this sequence or, as explained earlier, by ligand occupation of any available vacant site. This course, however, results in a syndiotactic polypropylene when propylene is the ligand.

Adding hydrogen terminates the propagating polymer. The reaction between the polymer complex and the excess triethylaluminum also terminates the polymer. Treatment with alcohol or water releases the polymer:

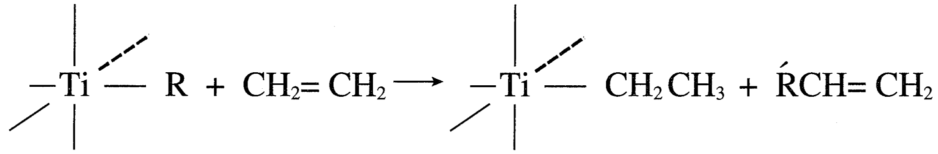


$$-Ti-R + Al(C_2H_5)_3 \longrightarrow -Ti-C_2H_5 + Al(C_2H_5)_2R$$

$$Al(C_2H_5)_2R + H_2O \longrightarrow RH + Al(C_2H_5)_2OH$$

R= growing polymer

A chain transfer reaction between the monomer and the growing polymer produces an unsaturated polymer. This occurs when the concentration of the monomer is high compared to the catalyst. Using ethylene as the monomer, the termination reaction has this representation:



$$-Ti-R + CH_2=CH_2 \longrightarrow -Ti-CH_2CH_3 + RCH=CH_2$$

A new generation coordination catalysts are metallocenes. The chiral form of metallocene produces isotactic polypropylene, whereas the achiral form produces atactic polypropylene. As the ligands rotate, the catalyst produces alternating blocks of isotactic and atactic polymer much like a miniature sewing machine which switches back and forth between two different kinds of stitches.[11]

Lecture 3

CONDENSATION POLYMERIZATION
(Step-Reaction Polymerization)

Though less prevalent than addition polymerization, condensation polymerization produces important polymers such as polyesters, polyamides (nylons), polycarbonates, polyurethanes, and phenol-formaldehyde resins (Chapter 12).

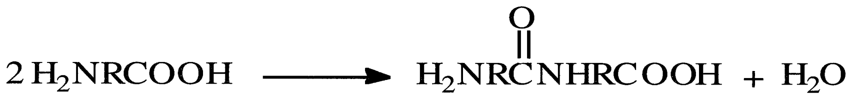
In general, condensation polymerization refers to

1. A reaction between two different monomers. Each monomer possesses at least two similar functional groups that can react with the functional groups of the other monomer. For example, a reaction of a diacid and a dialcohol (diol) can produce polyesters:

$$\mathrm{HO\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OH + HOR'OH \longrightarrow HO\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OR'OH + H_2O}$$

A similar reaction between a diamine and a diacid can also produce polyamides.

2. Reactions between one monomer species with two different functional groups. One functional group of one molecule reacts with the other functional group of the second molecule. For example, polymerization of an amino acid starts with condensation of two monomer molecules:

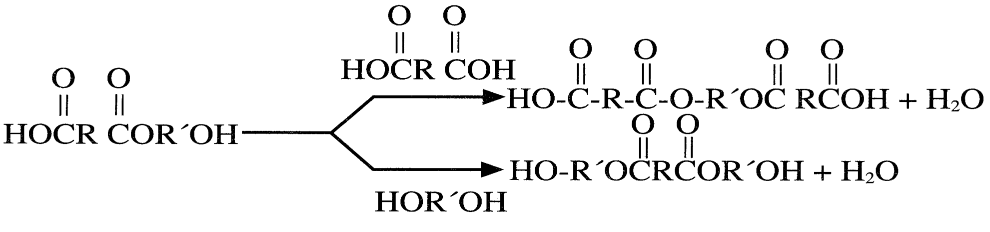


$$2\,\mathrm{H_2NRCOOH \longrightarrow H_2NR\overset{\overset{O}{\|}}{C}NHRCOOH + H_2O}$$

In these two examples, a small molecule (water) results from the condensation reaction.

Ring opening polymerization of lactams can also be considered a condensation reaction, although a small molecule is not eliminated. This type is noted later in this chapter under “Ring Opening Polymerization.”

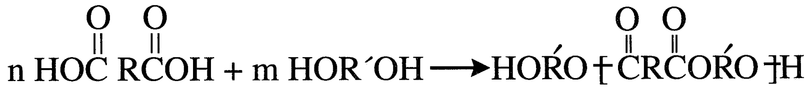
Condensation polymerization is also known as step-reaction polymerization because the reactions occur in steps. First, a dimer forms, then a trimer, next a tetramer, and so on until the polymer terminates. Although step polymerizations are generally slower than addition polymerizations, with long reaction times required for high conversions, the monomers disappear fast. The reaction medium contains only dimers, trimers, tetramers, and so on. For example, the dimer formed from the condensation of a diacid and a diol (reaction previously shown) has hydroxyl and carboxyl endings that can react with either a diacid or a diol to form a trimer:



$$\mathrm{HO\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OR'OH \xrightarrow{HO\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OH} HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R'O\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OH + H_2O}$$

$$\mathrm{HO\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OR'OH \xrightarrow[HOR'OH]{} HO\text{-}R'O\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OR'OH + H_2O}$$

The compounds formed continue condensation as long as the species present have different endings. The polymer terminates by having one of the monomers in excess. This produces a polymer with similar endings. For example, a polyester formed with excess diol could be represented:



$$n\,HO\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OH + m\,HOR'OH \longrightarrow HOR'O\left[\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OR'O\right]H$$

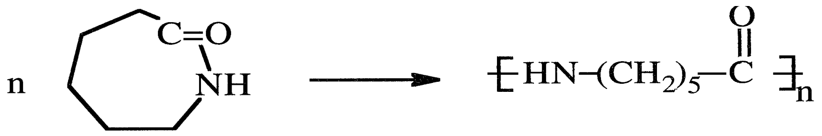
where m > n and $\left[\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}OR'O\right]$ is the repeating unit.

In these reactions, the monomers have two functional groups (whether one or two monomers are used), and a linear polymer results. With more than two functional groups present, crosslinking occurs and a thermosetting polymer results. Example of this type are polyurethanes and urea formaldehyde resins (Chapter 12).

Acid catalysts, such as metal oxides and sulfonic acids, generally catalyze condensation polymerizations. However, some condensation polymers form under alkaline conditions. For example, the reaction of formaldehyde with phenol under alkaline conditions produces methylolphenols, which further condense to a thermosetting polymer.

RING OPENING POLYMERIZATION

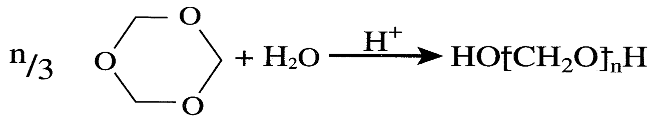
Ring opening polymerization produces a small number of synthetic commercial polymers. Probably the most important ring opening reaction is that of caprolactam for the production of nylon 6:



$$n\,(\text{caprolactam}) \longrightarrow \left[HN-(CH_2)_5-\overset{\overset{O}{\|}}{C}\right]_n$$

Although no small molecule gets eliminated, the reaction can be considered a condensation polymerization. Monomers suitable for polymerization by ring opening condensation normally possess two different functional groups within the ring. Examples of suitable monomers are lactams (such as caprolactam), which produce polyamides, and lactons, which produce polyesters.

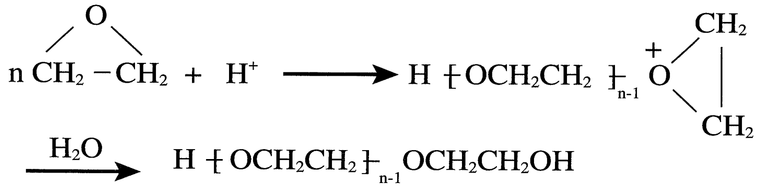
Ring opening polymerization may also occur by an addition chain reaction. For example, a ring opening reaction polymerizes trioxane to a polyacetal in the presence of an acid catalyst. Formaldehyde also produces the same polymer:



$$^{n}/_{3}\ \text{Trioxane} + H_2O \xrightarrow{H^+} HO[CH_2O]_nH$$

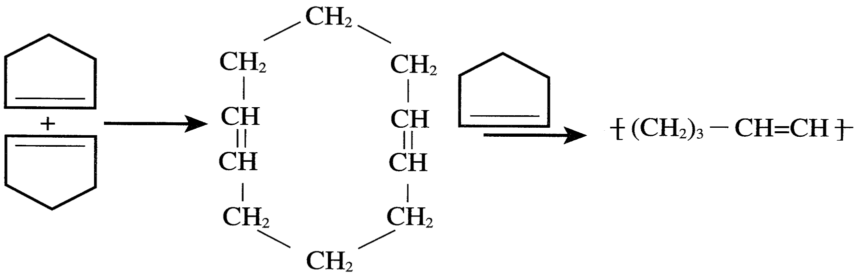
Trioxane

Monomers used for ring opening polymerization (by addition) are cyclic compounds that open easily with the action of a catalyst during the reaction. Small strained rings are suitable for this type of reaction. For example, the action of a strong acid or a strong base could polymerize ethylene oxide to a high molecular-weight polymer.



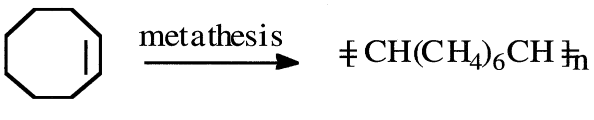
These water soluble polymers are commercially known as carbowax.

The ring opening of cycloolefins is also possible with certain coordination catalysts. This simplified example shows cyclopentene undergoing a first-step formation of the dimer cyclodecadiene, and then incorporating additional cyclopentene monomer units to produce the solid, rubbery polypentamer:[13]



Cyclodecadiene Polypentamer

Another example is the metathesis of cyclooctene, which produces polyoctenylene, an elastomor known as trans-polyoctenamer:[14]



Chemische Werke Huls produces the polymer for use in blends with some conventional rubbers.[15] This metathetic reaction has become an important synthetic tool in the polymer field.[13,16] Catalyzed polymerization of cycloolefins has been reviewed by Tsonis.[17]

POLYMERIZATION TECHNIQUES

Polymerization reactions can occur in bulk (without solvent), in solution, in emulsion, in suspension, or in a gas-phase process. Interfacial polymerization is also used with reactive monomers, such as acid chlorides.

Polymers obtained by the *bulk technique* are usually pure due to the absence of a solvent. The purity of the final polymer depends on the purity of the monomers. Heat and viscosity are not easily controlled, as in other polymerization techniques, due to absence of a solvent, suspension, or emulsion medium. This can be overcome by carrying the reaction to low conversions and strong agitation. Outside cooling can also control the exothermic heat.

In *solution polymerization,* an organic solvent dissolves the monomer. Solvents should have low chain transfer activity to minimize chain transfer reactions that produce low-molecular-weight polymers. The presence of a solvent makes heat and viscosity control easier than in bulk polymerization. Removal of the solvent may not be necessary in certain applications such as coatings and adhesives.

Emulsion polymerization is widely used to produce polymers in the form of emulsions, such as paints and floor polishes. It also used to polymerize many water insoluble vinyl monomers, such as styrene and vinyl chloride. In emulsion polymerization, an agent emulsifies the monomers. Emulsifying agents should have a finite solubility. They are either ionic, as in the case of alkylbenzene sulfonates, or nonionic, like polyvinyl alcohol.

Water is extensively used to produce emulsion polymers with a sodium stearate emulsifier. The emulsion concentration should allow micelles of large surface areas to form. The micelles absorb the monomer molecules activated by an initiator (such as a sulfate ion radical $SO\bullet_4^-$). X-ray and light scattering techniques show that the micelles start to increase in size by absorbing the macromolecules. For example, in the free radical polymerization of styrene, the micelles increased to 250 times their original size.

In *suspension polymerization,* the monomer gets dispersed in a liquid, such as water. Mechanical agitation keeps the monomer dispersed. Initiators should be soluble in the monomer. Stabilizers, such as talc or polyvinyl alcohol, prevent polymer chains from adhering to each other and keep the monomer dispersed in the liquid medium. The final polymer appears in a granular form.

Suspension polymerization produces polymers more pure than those from solution polymerization due to the absence of chain transfer reactions. As in a solution polymerization, the dispersing liquid helps control the reaction's heat.

Interfacial polymerization is mainly used in polycondensation reactions with very reactive monomers. One of the reactants, usually an acid chloride, dissolves in an organic solvent (such as benzene or toluene), and the second reactant, a diamine or a diacid, dissolves in water. This technique produces polycarbonates, polyesters, and polyamides. The reaction occurs at the interface between the two immiscible liquids, and the polymer is continuously removed from the interface.

PHYSICAL PROPERTIES OF POLYMERS

The properties of polymers determine whether they can be used as a plastic, a fiber, an elastomer, an adhesive, or a paint.

Important physical properties include the density, melt flow index, crystallinity, and average molecular weight. Mechanical properties of a polymer, such as modulus (the ratio of stress to strain), elasticity, and breaking strength, essentially follow from the physical properties.

The following sections describe some important properties of polymers.

CRYSTALLINITY

A polymer's tendency to have order and form crystallites derives from the regularity of the chains, presence (or absence) and arrangement of bulky groups, and the presence of secondary forces, such as hydrogen bonding. For example, isotactic polystyrene with phenyl groups arranged on one side of the polymer backbone is highly crystalline, while the atactic form (with a random arrangement of phenyl groups) is highly amorphous. Polyamides are also highly crystalline due to strong hydrogen bonding. High-density polyethylene exhibits no hydrogen bonding, but its linear structure makes it highly crystalline. Low-density polyethylene, on the other hand, has branches and a lower crystallinity. It does not pack as easily as the high-density polymer.

The mechanical and thermal behaviors depend partly on the degree of crystallinity. For example, highly disordered (dominantly amorphous) polymers make good elastomeric materials, while highly crystalline polymers, such as polyamides, have the rigidity needed for fibers. Crystallinity of polymers correlates with their melting points.

MELTING POINT

The freezing point of a pure liquid is the temperature at which the liquid's molecules lose transitional freedom and the solid's molecules become more ordered within a definite crystalline structure. Polymers, however, are non-homogeneous and do not have a definite crystallization temperature.

When a melted polymer cools, some polymer molecules line up and form crystalline regions within the melt. The rest of the polymer remains amorphous. The temperature at which these crystallites disappear when the crystalline polymer is gradually heated is called the crystalline melting temperature, T_m. Further cooling of the polymer below T_m changes the amorphous regions into a glass-like material. The temperature at which this change occurs is termed the glass transition temperature, T_g. Elastomeric materials usually have a low T_g (low crystallinity), while highly crystalline polymers, such as polyamides, have a relatively high T_g.

VISCOSITY

The viscosity of a substance measures its resistance to flow. The melt viscosity of a polymer increases as the molecular weight of the polymer rises. Polymers with high melt viscosities require higher temperatures for processing.

The melt flow index describes the viscosity of a solid plastic. It is the weight in grams of a polymer extruded through a defined orifice at a specified time. The melt viscosity and the melt flow index can measure the extent of polymerization. A polymer with a high melt flow index has a low melt viscosity, a lower molecular weight, and usually a lower impact tensile strength.

MOLECULAR WEIGHT

Polymerization usually produces macromolecules with varying chain lengths. As a result, polymers are described as polydisperse systems. Commercial polymers have molecular weights greater than 5,000 and contain macromolecules with variable molecular weights. The methods for determining the average molecular weights of polymers include measuring some colligative property, such as viscosity or sedimentation. Different methods do not correlate well, and determining the average molecular weight requires more than one method. Two methods normally determine the *number average* and the *weight average* molecular weights of the polymer.

Number Average Molecular Weight

The number average molecular weight (M_n) is related to the number of particles present in a sample. It is calculated by dividing the sum of the weights of all the species present (monomers, dimers, trimers, and so on) by the number of species present:

$$M_n = \frac{W}{\sum N_i} = \frac{\sum N_i M_i}{\sum N_i}$$

i = degree of polymerization (dimer, trimers, etc.)
N_i = number of each polymeric species
M_i = molecular weight of each polymer species
W = total weight of all polymer species.

M_n depends not on the molecular sizes of the particles but on the number of particles. Measuring colligative properties such as boiling point elevation, freezing point depression, and vapor pressure lowering can determine the number of particles in a sample.

Weight Average Molecular Weight

The weight average molecular weight (M_w) is the sum of the products of the weight of each species present and its molecular weight, divided by the sum of all the species' weights:

$$M_w = \frac{\sum W_i M_i}{W} = \frac{\sum W_i M_i}{\sum N_i M_i}$$

W_i = weight of each polymeric species
M_i = molecular weight of each polymeric species

Substituting $N_i M_i = W_i$, the weight average molecular weight can be defined as

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Larger, heavier molecules contribute more to M_w than to M_n. Light scattering techniques and ultracentrifugation can determine M_w.

The following simple example illustrates the difference between M_n and M_w: Suppose a sample has six macro-molecules. Three of them have a molecular weight = 1.0×10^4, two have a molecular weight = 2.0×10^4, and one has a molecular weight = 3.0×10^4:

$$M_n = \frac{(3.0+4.0+3.0)10^4}{6} = 1.7 \times 10^4$$

$$M_w = \frac{3(1.0\times10^4)^2 + 2(2.0\times10^4)^2 + 1(3.0\times10^4)^2}{3(1.0\times10^4) + 2(2.0\times10^4) + 1(3.0\times10^4)} = 2.0\times10^4$$

In monodispersed systems $M_n = M_w$.

The difference in the value between M_n and M_w. indicates the polydispersity of the polymer system. The closer M_n is to M_w, the narrower the molecular weight spread. Molecular weight distribution curves for polydispersed systems can be obtained by plotting the degree of polymerization i versus either the number fraction, N_i, or the weight fraction, W_i.

CLASSIFICATION OF POLYMERS

Synthetic polymers may be classified into addition or condensation polymers according to the type of reaction. A second classification depends on the monomer type and the linkage present in the repeating unit into polyolefins, polyesters, polyamides, etc. Other classifications depend on the polymerization technique (bulk, emulsion, suspension, etc.) or on the polymer's end use. The latter classifies polymers into three broad categories: plastics, elastomers, and synthetic fibers.

Plastics

Plastics are relatively tough substances with high molecular weight that can be molded with (or without) the application of heat. In general, plastics are subclassified into *thermoplastics,* polymers that can be resoftened by heat, and *thermosets,* which cannot be resoftened by heat.

Thermoplastics have moderate crystallinity. They can undergo large elongation, but this elongation is not as reversible as it is for elastomers. Examples of thermoplastics are polyethylene and polypropylene.

Thermosetting plastics are usually rigid due to high crosslinking between the polymer chains. Examples of this type are phenol-fomaldehyde and polyurethanes. Crosslinking may also be promoted by using chemical agents such as sulfur or by heat treatment or irradiation with gamma rays, ultraviolet light, or energetic electrons. Recently, high energy ion beams were found to increase the hardness of the treated polymer drastically.[18]

Synthetic Rubber

Synthetic rubber (elastomers) are high molecular weight polymers with long flexible chains and weak intermolecular forces. They have low crystallinity (highly amorphous) in the unstressed state, segmental mobility, and high reversible elasticity. Elastomers are usually crosslinked to impart strength.

Synthetic Fibers

Synthetic fibers are long-chain polymers characterized by highly crystalline regions resulting mainly from secondary forces (e.g., hydrogen bonding). They have a much lower elasticity than plastics and elastomers. They also have high tensile strength, a light weight, and low moisture absorption.

Lecture 4

THERMOPLASTICS AND ENGINEERING RESINS

Thermoplastics are important polymeric materials that have replaced or substituted many naturally-derived products such as paper, wood, and steel. Plastics possess certain favorable properties such as light weight, corrosion resistance, toughness, and ease of handling. They are also less expensive. The major use of the plastics is in the packaging field. Many other uses include construction, electrical and mechanical goods, and insulation. One growing market that evolved fairly recently is engineering thermoplastics. This field includes polymers with special properties such as high thermal stability, toughness, and chemical and weather resistance. Nylons, polycarbonates, polyether sulfones, and polyacetals are examples of this group.

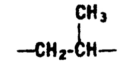
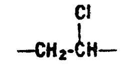
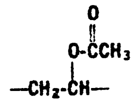
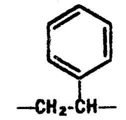
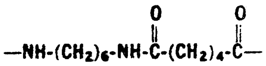
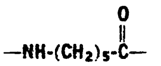
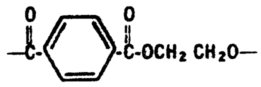
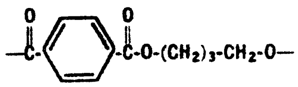
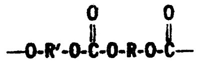
Another important and growing market for plastics is the automotive field. Many automobile parts are now made of plastics. Among the most used polymers are polystyrene polymers and copolymers, polypropylene, polycarbonates, and polyvinyl chloride. These materials reduce the cost and the weight of the cars. As a result, gasoline consumption is also reduced.

Most big-volume thermoplastics are produced by addition polymerization. Other thermoplastics are synthesized by condensation. Table 12-1 shows the major thermoplastics.[3]

POLYETHYLENE

Polyethylene is the most extensively used thermoplastic. The ever-increasing demand for polyethylene is partly due to the availability of the monomer from abundant raw materials (associated gas, LPG, naphtha). Other factors are its relatively low cost, ease of processing the polymer, resistance to chemicals, and its flexibility. World production of all polyethylene grades, approximately 100 billion pounds in 1997, is predicted

Table 12-1
Major thermoplastic polymers

Name	Family	Formula	Melting temp.	Density
Low-density polyethylene	Polyolefin	$-CH_2-$	110 (T_m)	0.910
High-density polyethylene	Polyolefin	$-CH_2-$	120 (T_m)	0.950
Polypropylene	Polyolefin	 $-CH_2-\overset{CH_3}{\overset{\vert}{C}}H-$	175 (T_m)	0.902
Polyvinyl chloride	Vinyl	 $-CH_2-\overset{Cl}{\overset{\vert}{C}}H-$	100 (T_g)	1.35
Polyvinyl acetate	Vinyl	 $-CH_2-\overset{O-\overset{O}{\overset{\Vert}{C}}CH_3}{\overset{\vert}{C}}H-$	—	—
Polystyrene	Styrenic		100 (T_g)	1.05
Acrylonitrilebutadiene styrene	Styrenic	—	—	—
Acrylonitrile styrene	Styrenic	—	—	—
Polymethylmethacrylate	Acrylic	—	—	—
Polyhexamethylene-adipate	Polyamide	 $-NH-(CH_2)_6-NH-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-$	265 (T_m)	1.14
Polycaprolactam	Polyamide	 $-NH-(CH_2)_5-\overset{O}{\overset{\Vert}{C}}-$	225 (T_m)	1.14
Polyethylene-terephthalate	Polyester		270 (T_m)	—
Polybutylene-terephthalate	Polyester		250 (T_m)	1.3
Polycarbonates	Polyester	 $-O-R'-O-\overset{O}{\overset{\Vert}{C}}-O-R-O-\overset{O}{\overset{\Vert}{C}}-$	190 (T_g)	1.2
Polyacetals	Polyethers	$-O-CH_2-O-R-$	181 (T_m)	—

to reach 300 billion pounds in 2015, the largest increase for linear low density polyethylene.[4]

High-pressure polymerization of ethylene was introduced in the 1930s. The discovery of a new titanium catalyst by Karl Ziegler in 1953 revolutionized the production of linear unbranched polyethylene at lower pressures. The two most widely used grades of polyethylene are low-density polyethylene (LDPE) and high-density polyethylene (HDPE). Currently, a new LDPE grade has been introduced. It is a linear, low-density grade (LLDPE) produced like the high-density polymer at low pressures.

Polymerizing ethylene is a highly exothermic reaction. For each gram of ethylene consumed, approximately 3.5 KJ (850 cal) are released:[5]

$$nCH_2{=}CH_2 \rightarrow \left[CH2{-}CH_2 \right]_n \qquad \Delta H = -92 KJ/mol$$

When ethylene is polymerized, the reactor temperature should be well controlled to avoid the endothermic decomposition of ethylene to carbon, methane, and hydrogen:

$$CH_2{=}CH_2 \rightarrow 2C + 2H_2$$

$$CH_2{=}CH_2 \rightarrow C + CH_4$$

Low-Density Polyethylene

Low-density polyethylene (LDPE) is produced under high pressure in the presence of a free radical initiator. As with many free radical chain addition polymerizations, the polymer is highly branched. It has a lower crystallinity compared to HDPE due to its lower capability of packing.

Polymerizing ethylene can occur either in a tubular or in a stirred autoclave reactor. In the stirred autoclave, the heat of the reaction is absorbed by the cold ethylene feed. Stirring keeps a uniform temperature throughout the reaction vessel and prevents agglomeration of the polymer.

In the tubular reactor, a large amount of reaction heat is removed through the tube walls.

Reaction conditions for the free radical polymerization of ethylene are 100–200°C and 100–135 atmospheres. Ethylene conversion is kept to a low level (10–25%) to control the heat and the viscosity. However, overall conversion with recycle is over 95%.

The polymerization rate can be accelerated by increasing the temperature, the initiator concentration, and the pressure. Degree of branching and molecular weight distribution depend on temperature and pressure. A higher density polymer with a narrower molecular weight distribution could be obtained by increasing the pressure and lowering the temperature.

The crystallinity of the polymer could be varied to some extent by changing the reaction conditions and by adding comonomers such as vinyl acetate or ethyl acrylate. The copolymers have lower crystallinity but better flexibility, and the resulting polymer has higher impact strength.[6]

High-Density Polyethylene

High-density polyethylene (HDPE) is produced by a low-pressure process in a fluid-bed reactor. Catalysts used for HDPE are either of the Zieglar-type (a complex of $Al(C_2H_5)_3$ and α-$TiCl_4$) or silica-alumina impregnated with a metal oxide such as chromium oxide or molybdenum oxide.

Reaction conditions are generally mild, but they differ from one process to another. In the newer Unipol process (Figure 12-1) used to produce both HDPE and LLDPE, the reaction occurs in the gas phase.[7] Ethylene and the comonomers (propene, 1-butene, etc.) are fed to the reactor containing a fluidized bed of growing polymer particles. Operation temperature and pressure are approximately 100°C and 20 atmospheres. A single-stage centrifugal compressor circulates unreacted ethylene. The circulated gas fluidizes the bed and removes some of the exothermic reaction heat. The product from the reactor is mixed with additives and then pelletized. New modifications for gas-phase processes have been reviewed by Sinclair.[8]

The polymerization of ethylene can also occur in a liquid-phase system where a hydrocarbon diluent is added. This requires a hydrocarbon recovery system.

High-density polyethylene is characterized by a higher crystallinity and higher melting temperature than LDPE due to the absence of branching.

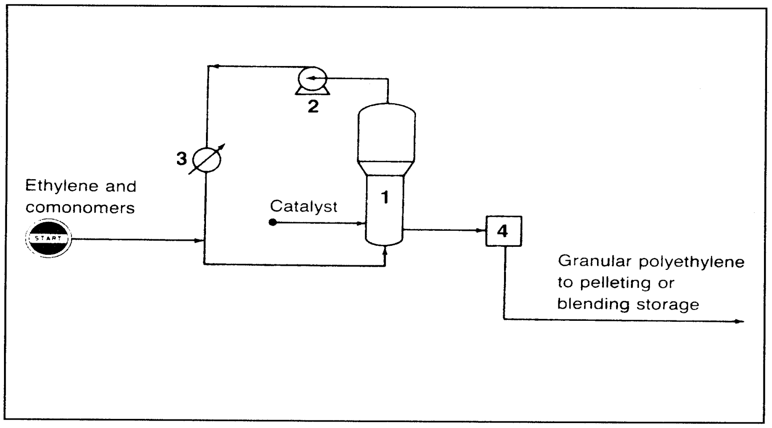


Figure 12-1. The Union Carbide Unipol process for producing HDPE[7]: (1) reactor, (2) single-stage centrifugal compressor, (3) heat exchanger, (4) discharge tank.

Some branching could be incorporated in the backbone of the polymer by adding variable amounts of comonomers such as hexene. These comonomers modify the properties of HDPE for specific applications.

Linear Low-Density Polyethylene

Linear low-density polyethylene (LLDPE) is produced in the gas phase under low pressure. Catalysts used are either Ziegler type or new generation metallocenes. The Union Carbide process used to produce HDPE could be used to produce the two polymer grades. Terminal olefins (C_4–C_6) are the usual comonomers to effect branching.

Developments in the gas-fluidized-bed polymerization reduced investments for high pressure processes used for LDPE. The new technology lowers capital and operating costs and reduces reactor purge/waste streams. Specific designed nozzles are located within the fluidized bed to disperse the hydrocarbons within the bed. The liquid injected through the nozzles quickly evaporates, hence removing the heat of polymerization. These processes can produce a wide range of polymers with different melt flow indices (MFI of <0.01 to >100) and densities of 890–970 Kg/m^3. Types of reactors and catalysts used for HDPE and LLDPE have been reviewed by Chinh and Power.[9]

LLDPE has properties between HDPE and LDPE. It has fewer branches, higher density, and higher crystallinity than LDPE.

Properties and Uses of Polyethylenes

Polyethylene is an inexpensive thermoplastic that can be molded into almost any shape, extruded into fiber or filament, and blown or precipitated into film or foil. Polyethylene products include packaging (largest market), bottles, irrigation pipes, film, sheets, and insulation materials.

Currently, high density polyethylene is the largest-volume thermoplastic. The 1997 U.S. production of HDPE was 12.5 billion pounds. LDPE was 7.7 billion pounds and LLDPE was 6.9 billion pounds.[10]

Because LDPE is flexible and transparent, it is mainly used to produce film and sheets. Films are usually produced by extrusion. Calendering is mainly used for sheeting and to a lesser extent for film production.

HDPE is important for producing bottles and hollow objects by blow molding. Approximately 64% of all plastic bottles are made from HDPE.[11] Injection molding is used to produce solid objects. Another important market for HDPE is irrigation pipes. Pipes made from HDPE

Lecture 5

POLYPROPYLENE

Polypropylene (PP) is a major thermoplastic polymer. Although polypropylene did not take its position among the large volume polymers until fairly recently, it is currently the third largest thermoplastic after PVC. The delay in polypropylene development may be attributed to technical reasons related to its polymerization. Polypropylene produced by free radical initiation is mainly the atactic form. Due to its low crystallinity, it is not suitable for thermoplastic or fiber use. The turning point in polypropylene production was the development of a Ziegler-type catalyst by Natta to produce the stereoregular form (isotactic).

Catalysts developed in the titanium-aluminum alkyl family are highly reactive and stereoselective. Very small amounts of the catalyst are needed to achieve polymerization (one gram catalyst/300,000 grams polymer). Consequently, the catalyst entrained in the polymer is very small, and the catalyst removal step is eliminated in many new processes.[12] Amoco has introduced a new gas-phase process called "absolute gas-phase" in which polymerization of olefins (ethylene, propylene) occurs in the total absence of inert solvents such as liquefied propylene in the reactor. Titanium residues resulting from the catalyst are less than 1 ppm, and aluminum residues are less than those from previous catalysts used in this application.[13]

Table 12-2
Important properties of polyethylenes

Polymer	Melting point range °C	Density g/cm^3	Degree of crystal-linity %	Stiffness modules psi × 10^3
Branched, Low density	107–121	0.92	60–65	25–30
Medium density	—	0.935	75	60–65
Linear, High density				
Ziegler type	125–132	0.95	85	90–110
Phillips type	—	0.96	91	130–150

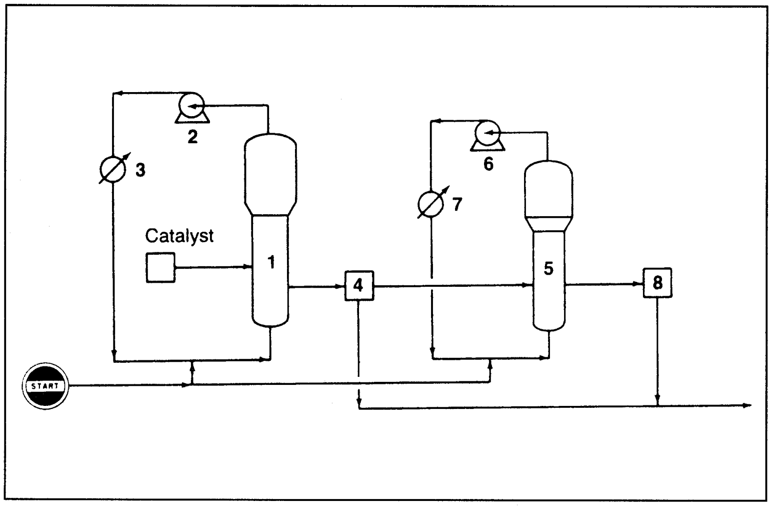


Figure 12-2. The Union Carbide gas-phase process for producing polypropylene[14]: (1) reactor, (2) centrifugal compressor, (3) heat exchanger, (4) product discharge tank (unreacted gas separated from product), (5) impact reactor, (6) compressor, (7) heat exchanger, (8) discharge tank (copolymer separated from reacted gas).

Polypropylene could be produced in a liquid or in a gas-phase process. Until 1980, the vertically stirred bed process of BASF was the only large-scale commercial gas phase process.[8] In the Union Carbide/Shell gas phase process (Figure 12-2), a wide range of polypropylenes are made in a fluidized bed gas phase reactor.[14] Melt index, atactic level, and molecular weight distribution are controlled by selecting the proper catalyst, adjusting operating conditions, and adding molecular weight control agents. This process is a modification of the polyethylene process (discussed before), but a second reactor is added. Homopolymers and random copolymers are produced in the first reactor, which operates at approximately 70°C and 35 atmospheres. Impact copolymers are produced in the second reactor (impact reactor) after transferring the polypropylene resin from the first reactor. Gaseous propylene and ethylene are fed to the impact reactor to produce the polymers' rubber phase. Operation of the impact reactor is similar to the initial one, but the second operates at lower pressure (approximately 17 atmospheres). The granular product is finally pelletized.

Random copolymers made by copolymerizing equal amounts of ethylene and propylene are highly amorphous, and they have rubbery properties.

An example of the liquid-phase polymerization is the Spheripol process (Figure 12-3), which uses a tubular reactor.[7] Copolymerization

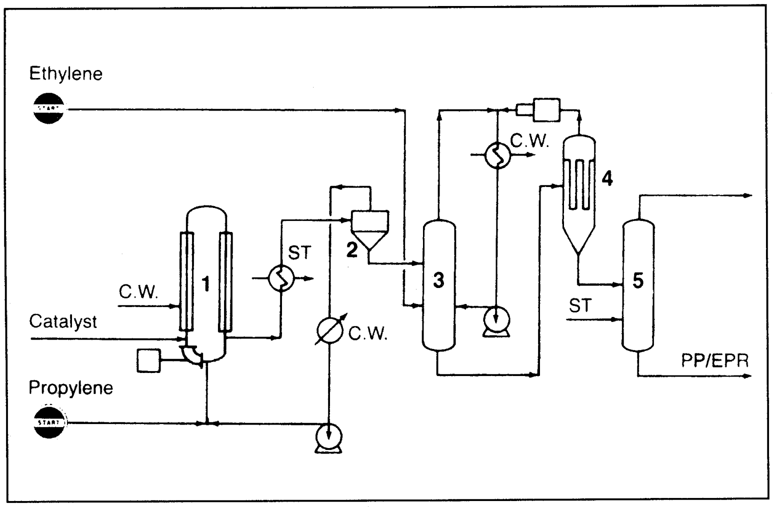


Figure 12-3. The Himont Inc. Spheripol process for producing polypropylene in a liquid-phase[7]: (1) tubular reactor, (2,4) two-stage flash pressure system (to separate unreacted monomer for recycle), (3) heterophasic copolymerization gas-phase reactor, (5) stripper.

occurs in a second gas phase reactor. Unreacted monomer is flashed in a two-stage pressure system and is recycled back to the reactor. Polymer yields of 30,000 or more Kg/Kg of supported catalyst are attainable, and catalyst residue removal from the polymer is not required. The product polymer has an isotactic index of 90–99%.

New generation metallocene catalysts can polymerize propylene in two different ways. Rigid chiral metallocene produce isotactic polypropylene whereas the achiral forms of the catalysts produce atactic polypropylene. The polymer microstructure is a function of the reaction conditions and the catalyst design.[15] Recent work has shown that the rate of ligand rotation in some unbridged metallocenes can be controlled so that the metallocene oscillates between two stereochemical states. One isomer produces isotactic polypropylene and the other produces the atactic polymer. As a result, alternating blocks of rigid isotactic and flexible atactic polypropylene grow within the same polymer chain.[16]

Properties and Uses of Polypropylene

The properties of commercial polypropylene vary widely according to the percentage of crystalline isotactic polymer and the degree of polymerization. Polypropylenes with a 99% isotactic index are currently produced.

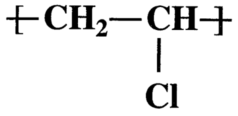
Articles made from polypropylene have good electrical and chemical resistance and low water absorption. Its other useful characteristics are its light weight (lowest thermoplastic polymer density), high abrasion resistance, dimensional stability, high impact strength, and no toxicity. Table 12-3 shows the properties of polypropylene.

Polypropylene can be extruded into sheets and thermoformed by solid-phase pressure forming into thin-walled containers. Due to its light weight and toughness, polypropylene and its copolymers are extensively used in automobile parts.

Improvements in melt spinning techniques and film filament processes have made polypropylene accessible for fiber production. Low-cost fibers made from polypropylene are replacing those made from sisal and jute.

World demand for polypropylene is expected to be 30 billion pounds by 2002. This is the strongest growth forecast for any of the major thermoplastics (5.9%). Many of the resins new applications particularly in packaging come at the expense of PS and PVC, the two resins that have been the subject of regulatory restrictions related to solid waste issues and potential toxicity.[17]

Polyvinyl Chloride



$$-\!\!\left[CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}} \right]\!\!-$$

Polyvinyl chloride (PVC) is one of the most widely used thermoplastics. It can be extruded into sheets and film and blow molded into bottles. It is used in many common items such as garden hoses, shower curtains, irrigation pipes, and paint formulations.

PVC can be prepolymerized in bulk to approximately 7–8% conversion. It is then transferred to an autoclave where the particles are polymerized to a solid powder. Most vinyl chloride, however, is polymerized

Table 12-3
Properties of Polypropylene

Density, g/cm^3	0.90–0.91
Fill temperature, max. °C	130
Tensile strength, psi	3,200–5,000
Water absorption, 24 hr., %	0.01
Elongation, %	3–700
Melting point, T_m °C	176
Thermal expansion, 10^{-5} in./in. °C	5.8–10
Specific volume, cm^3/lb	30.4–30.8

in suspension reactors made of stainless steel or glass-lined. The peroxide used to initiate the reaction is dispersed in about twice its weight of water containing 0.01–1% of a stabilizer such as polyvinyl alcohol.[18]

In the European Vinyls Corp. process (Figure 12-4), vinyl chloride monomer (VCM) is dispersed in water and then charged with the additives to the reactor.[19] It is a stirred jacketed type ranging in size between 20–105m^3. The temperature is maintained between 53–70°C to obtain a polymer of a particular molecular weight. The heat of the reaction is controlled by cooling water in the jacket and by additional reflux condensers for large reactors. Conversion could be controlled between 85–95% as required by the polymer grade. At the end of the reaction, the PVC and water slurry are channelled to a blowdown vessel, from which part of unreacted monomer is recovered. The rest of the VCM is stripped, and the slurry is centrifuged to separate the polymer from both water and the initiator.

Polyvinyl chloride can also be produced in emulsion. Water is used as the emulsion medium. The particle size of the polymer is controlled using the proper conditions and emulsifier. Polymers produced by free radical initiators are highly branched with low crystallinity.

Vinyl chloride can be copolymerized with many other monomers to improve its properties. Examples of monomers used commercially are vinyl acetate, propylene, ethylene, and vinylidine chloride. The copolymer with ethylene or propylene (T_g = 80°C), which is rigid, is used for

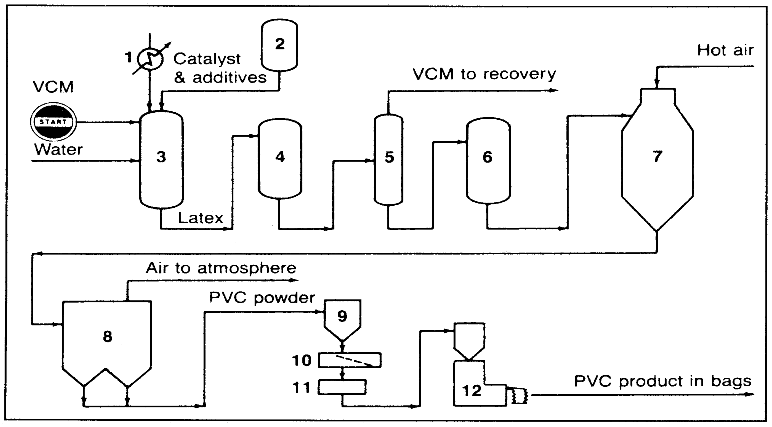


Figure 12-4. The European Vinyls Corp. process for producing polyvinyl chloride using suspension polymerization[19]: (1) reactor, (2) blow-down vessels (to separate unreacted monomer), (3) stripping column, (4) reacted monomer recovery, (5) slurry centrifuge, (6) slurry drier.

blow molding objects. Copolymers with 6–20% vinyl acetate (T_g = 50–80°C) are used for coatings.

Properties and Uses of Polyvinyl Chloride

Two types of the homopolymer are available, the flexible and the rigid. Both types have excellent chemical and abrasion resistance. The flexible types are produced with high porosity to permit plasticizer absorption. Articles made from the rigid type are hard and cannot be stretched more than 40% of their original length. An important property of PVC is that it is self-extinguishing due to presence of the chlorine atom.

Flexible PVC grades account for approximately 50% of PVC production. They go into such items as tablecloths, shower curtains, furniture, automobile upholstery, and wire and cable insulation.

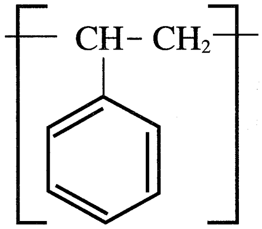
Many additives are used with PVC polymers such as plasticizers, antioxidants, and impact modifiers. Heat stabilizers, which are particularly important with PVC resins, extend the useful life of the finished product. Plastic additives have been reviewed by Ainsworth.[20]

Rigid PVC is used in many items such as pipes, fittings roofing, automobile parts, siding, and bottles.

The 1997 U.S. production of PVC and its copolymers was approximately 14 billion pounds.

Lecture 6

POLYSTYRENE



Polystyrene (PS) is the fourth big-volume thermoplastic. Styrene can be polymerized alone or copolymerized with other monomers. It can be polymerized by free radical initiators or using coordination catalysts. Recent work using group 4 metallocene combined with methylaluminoxane produce stereoregular polymer. When homogeneous titanium catalyst is used, the polymer was predominantly syndiotactic. The heterogeneous titanium catalyst gave predominantly the isotactic.[21] Copolymers with butadiene in a ratio of approximately 1:3 produces SBR, the most important synthetic rubber.

Copolymers of styrene-acrylonitrile (SAN) have higher tensile strength than styrene homopolymers. A copolymer of acrylonitrile, butadiene, and styrene (ABS) is an engineering plastic due to its better mechanical properties (discussed later in this chapter). Polystyrene is produced either by free radical initiators or by use of coordination catalysts. Bulk, suspension, and emulsion techniques are used with free radical initiators, and the polymer is atactic.

In a typical batch suspension process (Figure 12-5), styrene is suspended in water by agitation and use of a stabilizer.[14] The polymer forms beads. The bead/water slurry is separated by centrifugation, dried, and blended with additives.

Properties and Uses of Styrene Polymers

Polystyrene homopolymer produced by free radical initiators is highly amorphous (T_g = 100°C). The general purpose rubber (SBR), a block copolymer with 75% butadiene, is produced by anionic polymerization.

The most important use of polystyrene is in packaging. Molded polystyrene is used in items such as automobile interior parts, furniture, and home appliances. Packaging uses plus specialized food uses such as containers for carryout food are growth areas. Expanded polystyrene foams, which are produced by polymerizing styrene with a volatile solvent such as pentane, have low densities. They are used extensively in insulation and flotation (life jackets).

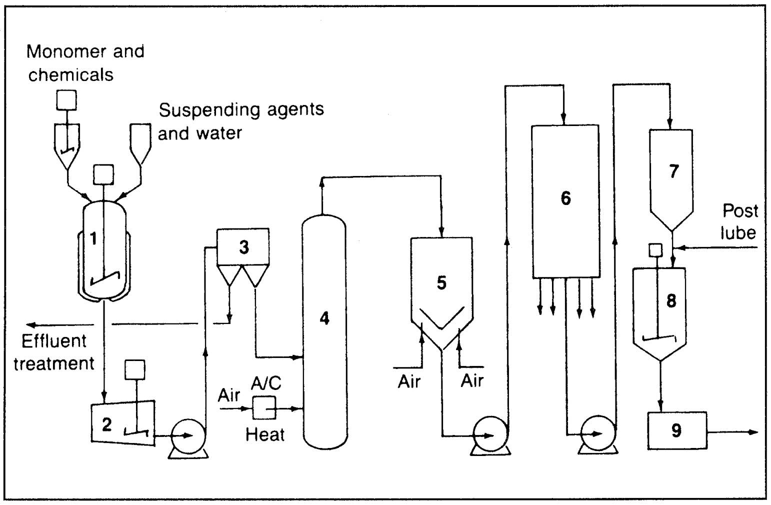


Figure 12-5. The Lummus Crest Inc. process for producing polystyrene[14]: (1) reactor, (2) holding tank (Polystyrene beads and water), (3) centrifuge, (4) pneumatic drier, (5) conditioning tank, (6) screening of beads, (7,8) lubrication and blending, (9) shipping product.

SAN (T_g = 105°C) is stiffer and has better chemical and heat resistance than the homopolymer. However, it is not as clear as polystyrene, and it is used in articles that do not require optical clarity, such as appliances and houseware materials.

ABS has a specific gravity of 1.03 to 1.06 and a tensile strength in the range of 6 to 7.5×10^3 psi. These polymers are tough plastics with outstanding mechanical properties. A wide variety of ABS modifications are available with heat resistance comparable to or better than polysulfones and polycarbonates (noted later in this section). Another outstanding property of ABS is its ability to be alloyed with other thermoplastics for improved properties. For example, ABS is alloyed with rigid PVC for a product with better flame resistance.

Among the major applications of ABS are extruded pipes and pipe fittings, appliances such as refrigerator door liners, and in molded automobile bodies.

World polystyrene production in 1997 was approximately 10 million tons. The demand is forecasted to reach 13 million tons by 2002.[22] The 1997 U.S. production of polystyrene polymers and copolymers was approximately 6.6 billion pounds. ABS, SAN, and other styrene copolymers were approximately 3 billion pounds for the same year.

NYLON RESINS

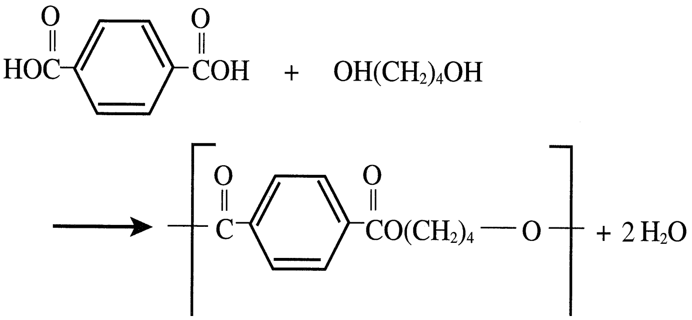
Nylon resins are important engineering thermoplastics. Nylons are produced by a condensation reaction of amino acids, a diacid and a diammine, or by ring opening lactams such as caprolactam. The polymers, however, are more important for producing synthetic fibers (discussed later in this chapter).

Important properties of nylons are toughness, abrasion and wear resistance, chemical resistance, and ease of processing. Reinforced nylons have higher tensile and impact strengths and lower expansion coefficients than metals. They are replacing metals in many of their applications. Objects made from nylons vary from extruded films used for pharmaceutical packaging to bearings and bushings, to cable and wire insulation.

THERMOPLASTIC POLYESTERS

Thermoplastic polyesters are among the large-volume engineering thermoplastics produced by condensation polymerization of terephthalic acid with ethylene glycol or 1,4-butanediol. These materials are used to produce film for magnetic tapes due to their abrasion and chemical resistance, low water absorption, and low gas permeability. Polyethylene terephthalate (PET) is also used to make plastic bottles (approximately 25% of plastic bottles are made from PET). Similar to nylons, the most important use of PET is for producing synthetic fibers (discussed later).

Polybutylene terephthalate (PBT) is another thermoplastic polyester produced by the condensation reaction of terephthalic acid and 1,4-butanediol:

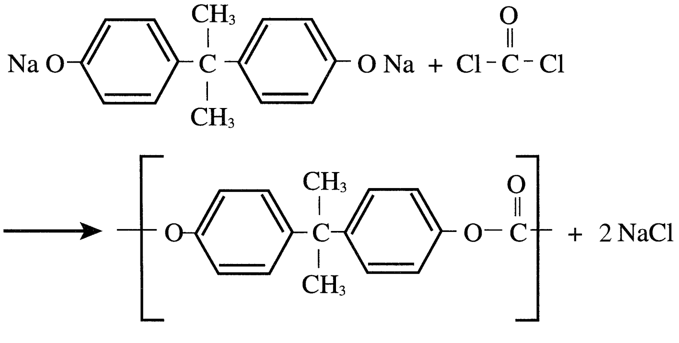


The polymer is either produced in a bulk or a solution process. It is among the fastest growing engineering thermoplastics, and leads the market of reinforced plastics with an annual growth rate of 7.3%.[23]

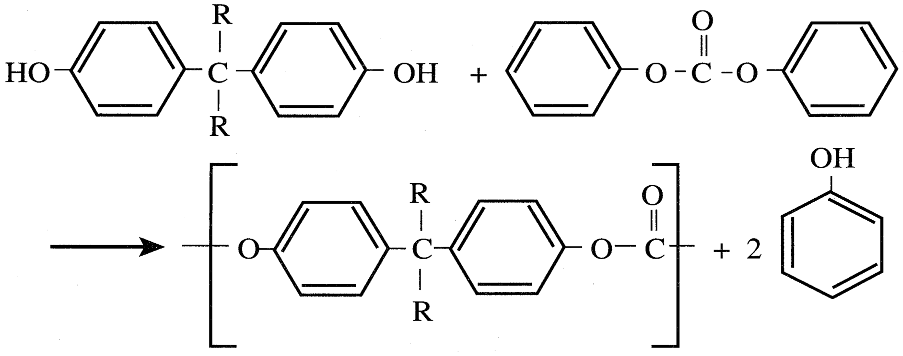
The 1997 U.S. production of thermoplastic polyesters was approximately 4.3 billion pounds.

POLYCARBONATES

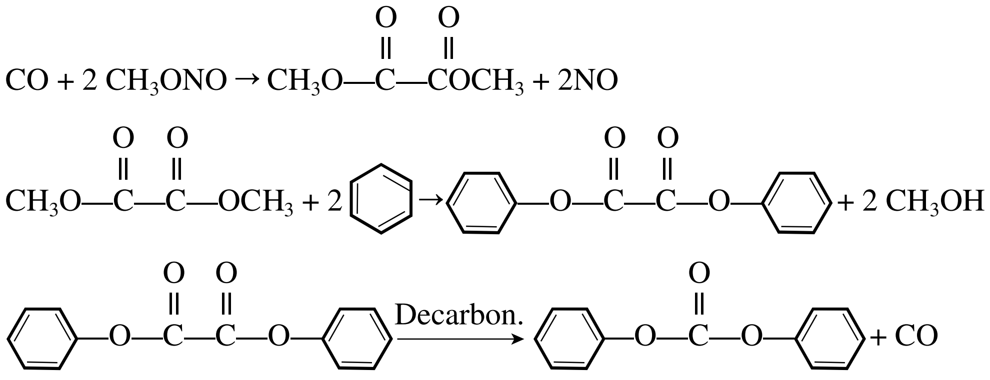
Polycarbonates (PC) are another group of condensation thermoplastics used mainly for special engineering purposes. These polymers are considered polyesters of carbonic acid. They are produced by the condensation of the sodium salt of bisphenol A with phosgene in the presence of an organic solvent. Sodium chloride is precipitated, and the solvent is removed by distillation:



Another method for producing polycarbonates is by an exchange reaction between bisphenol A or a similar bisphenol with diphenyl carbonate:



Diphenol carbonate is produced by the reaction of phosgene and phenol. A new approach to diphenol carbonate and non-phosgene route is by the reaction of CO and methyl nitrite using Pd/alumina. Dimethyl carbonate is formed which is further reacted with phenol in presence of tetraphenox titanium catalyst. Decarbonylation in the liquid phase yields diphenyl carbonate.


$$CO + 2\,CH_3ONO \rightarrow CH_3O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 + 2NO$$

However, the reaction is equilibrium constained and requires a complicated processing scheme.[24]

Properties and Uses of Polycarbonates

Polycarbonates, known for their toughness in molded parts, typify the class of polymers known as engineering thermoplastics. These materials, designed to replace metals and glass in applications demanding strength and temperature resistance, offer advantages of light weight, low cost, and ease of fabrication.[25]

Materials made from polycarbonates are transparent, strong, and heat- and break-resistant. However, these materials are subject to stress cracking and can be attacked by weak alkalies and acids. Table 12-4 compares the properties of polycarbonates with other thermoplastic resins.[25]

Polycarbonates are used in a variety of articles such as laboratory safety shields, street light globes, and safety helmets. The maximum usage temperature for polycarbonate objects is 125°C.

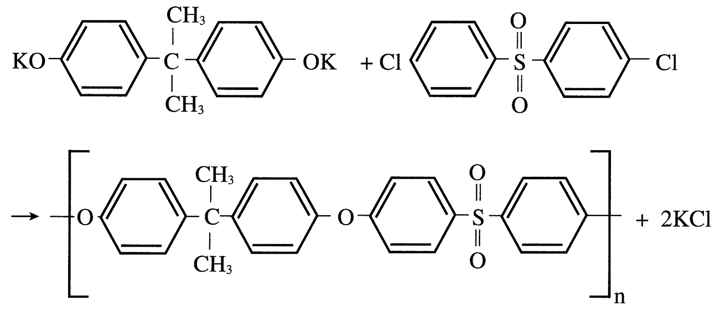
POLYETHER SULFONES

Polyether sulfones (PES) are another class of engineering thermoplastics generally used for objects that require continuous use of temperatures around 200°C. They can also be used at low temperatures with no change in their physical properties.

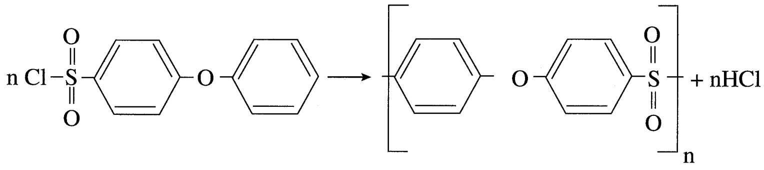
Table 12-4
Properties of polycarbonates compared with some thermoplastics[25]

Resin	Melting or glass transition temperature (°C)	tensile strength (MPa)	compressive strength (MPa)	flexural strength (MPa)	Izod impact, 1/8 in. (J/m)
PPO, impact modified	100–110	117–127	124–162	179–200	43–53
PC	149	65	86	93	850
PC, 30% glass	149	131	124	158	106
PC-ABS	149	48–50	76	89–94	560
Nylon 6/6, impact modified	240–260	48–55			160–210
Nylon 6/6, 33% glass	265	151–193	202	282	117–138
PBT	232–267	56	59–100	82–115	43–53
PBT, 30% glass	232–267	117–131	124–162	179–200	69–85
Acetal, homopolymer	181		124	96	69–122
ABS, impact modified	100–110	33–43	31–55	55–76	347–400
PPO, impact modified	135	48–55	69	56–76	320–370
PPO, 30% reinforced	100–110	117–127	123	138–158	90–112

Polyether sulfones can be prepared by the reaction of the sodium or potassium salt of bisphenol A and 4,4′-dichlorodiphenyl sulfone. Bisphenol A acts as a nucleophile in the presence of the deactivated aromatic ring of the dichlorophenylsulfone. The reaction may also be catalyzed with Friedel-Crafts catalysts; the dichlorophenyl sulfone acts as an electrophile:



Polyether sulfones could also be prepared using one monomer:



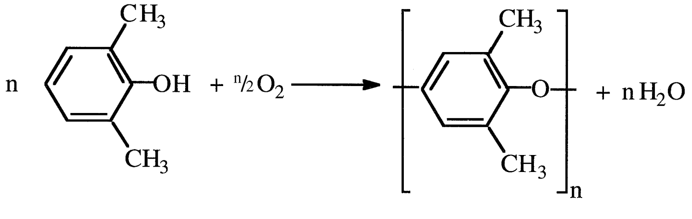
Properties and Uses of Aromatic Polyether Sulfones

In general, properties of polyether sulfones are similar to those of polycarbonates, but they can be used at higher temperatures. Figure 12-6 shows the maximum use temperature for several thermoplastics.[26]

Aromatic polyether sulfones can be extruded into thin films and foil and injection molded into various objects that need high-temperature stability.

POLY(PHENYLENE) OXIDE

Polyphenylene oxide (PPO) is produced by the condensation of 2,6-dimethylphenol. The reaction occurs by passing oxygen in the phenol solution in presence of Cu_2Cl_2 and pyridine:



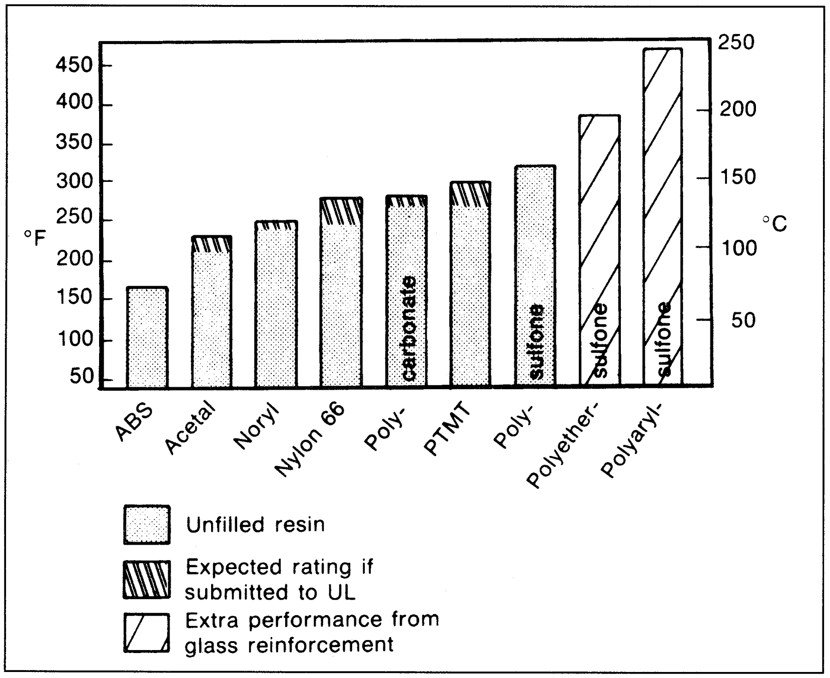
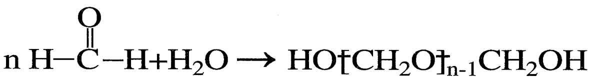


Figure 12-6. Maximum continuous use temperature of some engineering thermoplastics.[26]

PPO is an engineering thermoplastic with excellent properties. To improve its mechanical properties and dimensional stability, PPO can be blended with polystyrene and glass fiber. Articles made from PPO could be used up to 330°C: it is mainly used in items that require higher temperatures such as laboratory equipment, valves, and fittings.

POLYACETALS

Polyacetals are among the aliphatic polyether family and are produced by the polymerization of formaldehyde. They are termed polyacetals to distinguish them from polyethers produced by polymerizing ethylene oxide, which has two -CH_2- groups between the ether group. The polymerization reaction occurs in the presence of a Lewis acid and a small amount of water at room temperature. It could also be catalyzed with amines:



$$n\,H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + H_2O \longrightarrow HO{+}CH_2O{+}_{n-1}CH_2OH$$

Polyacetals are highly crystalline polymers. The number of repeating units ranges from 500 to 3,000. They are characterized by high impact resistance, strength, and a low friction coefficient.