

ME 495 MANUFACTURING METHODS OF PLASTICS

Chapter 1
INTRODUCTION
TO POLYMERS

1. INTRODUCTION

There is perhaps no class of materials more characteristic of the impact of the modern engineering technology on everyday life than polymers. Of the three basic types of materials (metals, ceramics and polymers), polymers are the newest and at the same time the oldest known to humans. The word *polymer* is derived from the words *poly* (meaning *many*) and *meres* (meaning *parts*). **A polymer can be defined as a compound consisting of long-chain molecule that is composed of a large number of repeating units of identical structure.** There may be thousands of units in a single polymer molecule. Most polymers are based on carbon and are therefore considered organic materials. However, the group also includes a number of inorganic polymers.

Polymers form the living organisms and vital processes of all life on earth. To ancient humans, biological polymers were source of food, shelter, and many of their implements. Certain polymers, such as proteins, cellulose, and silk, are found in nature, while many others, including polystyrene, polyethylene and nylon, are produced only by synthetic routes. The synthetic fibres, principally nylon and polyester, are good substitutes for the naturally occurring fibres such as cotton, wool, and silk. In some cases, naturally occurring polymers can also be produced synthetically (e.g., natural rubber: *Hevea* which is known as *polyisoprene* in its synthetic form). Nearly all of the polymeric materials used in engineering are synthetic; they are made by chemical processing. Many polymers, including polyethylene, are simply compounds of hydrogen and carbon. Others contain oxygen (e.g., acrylics), nitrogen (e.g., nylons), fluorine (fluoroplastics), and silicon (silicones).



Although polymers can be separated into plastics and rubbers, the word *plastics* is used as a common synonym for polymers. The name is derived from the extensive formability of most polymeric products during fabrication. In reality, plastics are the commercial materials derived from synthetic polymers other than rubbers (elastomers) and fibres. A typical commercial plastic resin may contain two or more polymers in addition to various additives and fillers.

For our purposes in covering polymers as a technical subject, it is appropriate to divide them into the following three categories:

(1) *Thermoplastic polymers*, or *thermoplastics* (TP), as they are often called, are solid materials at room temperature, but they become viscous liquids when heated to temperatures of only a few hundred degrees. This characteristic allows them to be easily and economically shaped into products. They can be subjected to this heating and cooling cycle repeatedly without significant degradation of the polymer.

(2) *Thermosetting polymers*, or *thermosets* (TS), cannot tolerate repeated heating cycles as thermoplastics can. When initially heated, they soften and flow for molding; but the elevated temperatures also produce a chemical reaction that hardens the material into an infusible solid. If reheated, thermosetting polymers degrade and char rather than soften.

(3) Elastomers. These are the rubbers. Elastomers (E) are polymers that exhibit extreme elastic extensibility when subjected to relatively low mechanical stress. Some elastomers can be stretched by a factor of 10 and yet completely recover to their original shape. Although their properties are very different from thermosets, they share a similar molecular structure, which is different from the thermoplastics.

Thermoplastics are commercially the most important of the three types, constituting around 70% of the tonnage of all synthetic polymers produced. Thermosets and elastomers share the remaining 30% about evenly, with a slight edge for the former. Common TP polymers include polyethylene, polyvinyl chloride, polypropylene, polystyrene, and nylon. Examples of TS polymers are phenolics, epoxies, and certain polyesters. The most common example given for elastomers is natural (vulcanized) rubber; however, synthetic rubbers exceed the tonnage of natural rubber.



Although the classification of polymers into TP, TS, and E categories will suit our purposes adequately for organizing the topic in this chapter, we should note that the three types sometimes overlap: certain polymers that are normally thermoplastic can be made into thermosets; and some polymers can be either thermosets or elastomers (we indicated that their molecular structures are similar); and some elastomers are thermoplastic. However, these are exceptions to the general classification scheme.

The growth in applications of synthetic polymers is truly impressive. On a volumetric basis, current annual usage of polymers exceeds that of metals. The reasons for the commercial and technological importance of polymers include the following:

*Plastics can be formed by molding into intricate part geometries, usually with no further processing required. They are very compatible with *net shape* processing.

*Plastics possess an attractive list of properties for many engineering applications where strength is not a factor:

- (1) low density relative to metals and ceramics;
- (2) good strength-to-weight ratios for certain (but not all) polymers;
- (3) high corrosion resistance; and
- (4) low electrical and thermal conductivity.

*On a volumetric basis, polymers are cost competitive with metals.

*On a volumetric basis, polymers generally require less energy to produce than metals. This is generally true because the temperatures for working these materials are much lower than for metals.

*Certain plastics are translucent and/or transparent, which makes them competitive with glass in some applications.

*Polymers are widely used in composite materials.

On the negative side, polymers in general have the following limitations:

1. low strength, relative to metals and ceramics;
2. low modulus of elasticity or stiffness (in the case of elastomers, of course, this may be a desirable characteristic);
3. service temperatures are limited to only a few hundred degrees because of the softening of thermoplastic polymers or degradation of thermosetting polymers;
4. some polymers degrade when subjected to sunlight and other forms of radiation; and
5. plastics exhibit viscoelastic properties, which can be a distinct limitation in load-bearing applications.

2. FUNDAMENTALS OF POLYMER SCIENCE AND TECHNOLOGY

The backbone of every organic material is the chain of carbon atoms. There are four electrons in the outer shell of a carbon atom as shown in Fig 1.1. Each atom can form a covalent bond with another carbon atom or with a foreign atom. The elements encountered most frequently, and their valencies are: **valence 1:** H, F, Cl, Br, I; **valence 2:** O, S; **valence 3:** N; **valence 4:** C, Si.

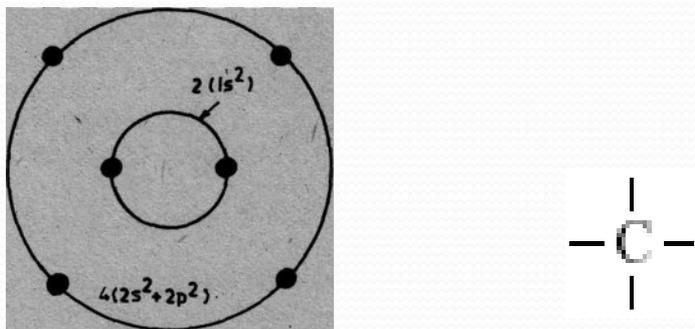
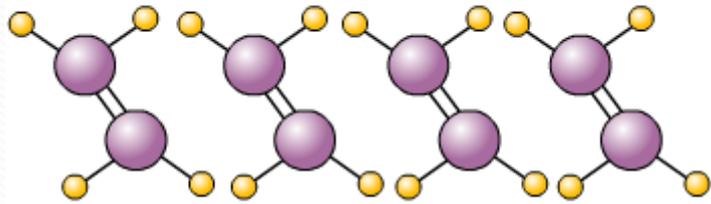


Fig 1.1 Carbon atom(a) electron structure (b) bonds

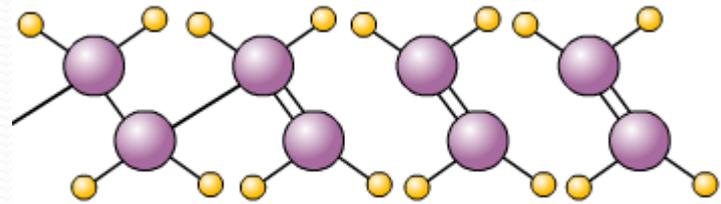


A vital point in making the long carbon chains is that two molecules of a material such as ethylene can be taken, which has two carbon to carbon bonds, one bond in each molecule is opened up, and the molecules are joined to create a chain.

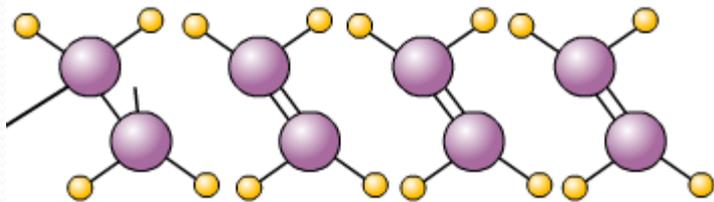
After the two **mers** (a unit consisting of relatively few atoms, joined to other units to form a **polymer**) are joined, there are still two free bonds available for joining the other mers. The process goes on, linking mers together until it is stopped by the addition of another chemical called **terminator**.



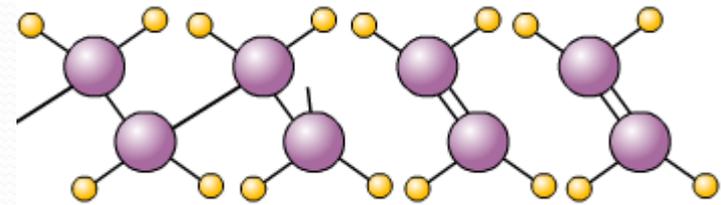
1. Ethylene mers



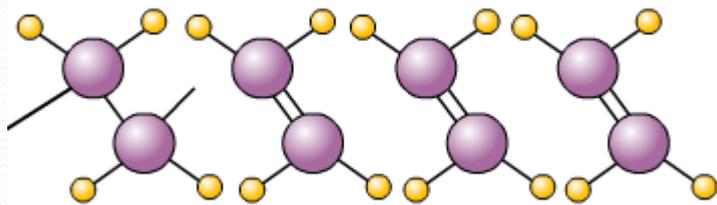
4. Combined mers (polymer)



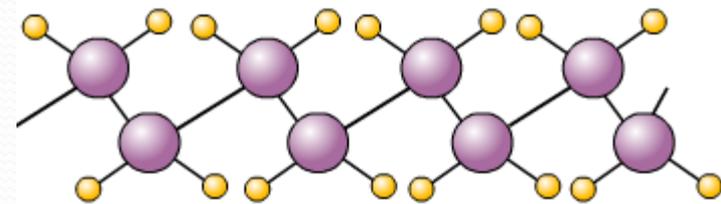
2. Bond opening



5. Opening another bond



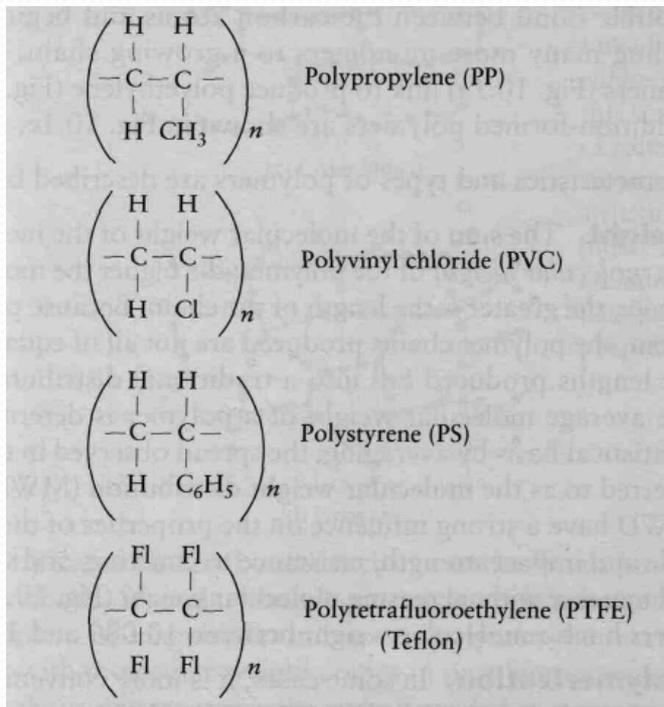
3. Linking to the other mer



6. Completed polymer (polyethylene)

Figure 2

The mer must have sufficient number of bonds which can be opened up for attachment to other mers of the same or different formula, this number is called as **functionability**. For example, C_2H_4 is bifunctional (functionability = 2). For polymerization the mers must be at least bifunctional.



Mer	Polymer
Ethylene	Polyethylene
Propylene	Polypropylene
Vinylchloride	Polyvinylchloride, PVC
Styrene	Polystyrene
Tetrafluoroethylene	Polytetrafluoroethylene
Methylacrylatemethylacrylate	Polymethylacrylate

Figure 5 Some Examples of Common Monomers:

The degree of polymerization (DP) is the molecular weight of the polymer divided by the molecular weight of the mer. It gives the number of mers in the molecule or its average length. Larger molecules results higher bond strengths and, therefore higher melting or softening temperatures.

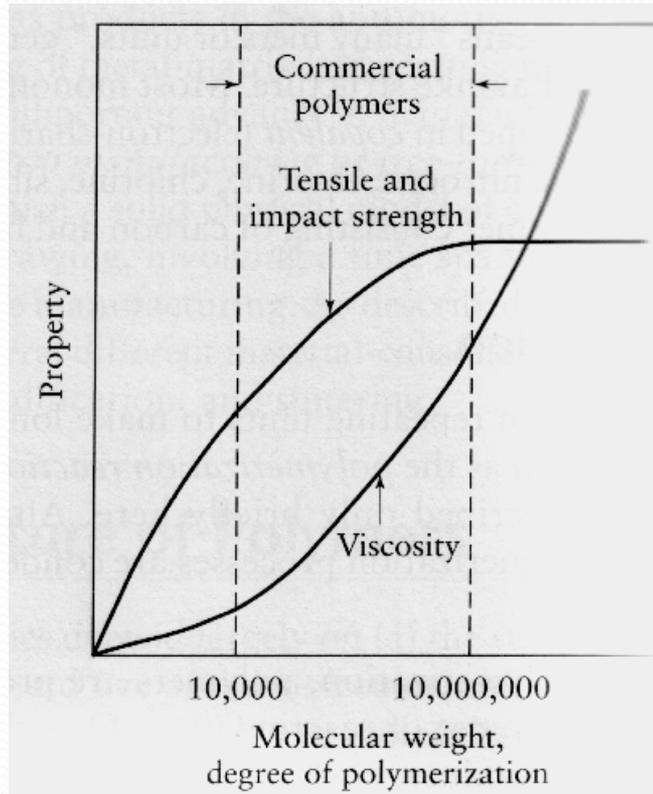


TABLE Typical Values of Degree of Polymerization (DP) and Molecular Weight (MW) for Selected Thermoplastic Polymers.

Polymer	DP(<i>n</i>)	MW
Polyethylene	10,000	300,000
Polystyrene (PS)	3,000	300,000
Polyvinyl chloride (PVC)	1,500	100,000
Nylon	120	15,000
Polycarbonate	200	40,000

Figure 6



A mass of polymer material consists of many macromolecules; the analogy of a bowl of just-cooked spaghetti (without sauce) is sometimes used to visualize the relationship of the individual molecules to the bulk material. Entanglement among the long strands helps to hold the mass together, but atomic bonding is more significant. The bonding between macromolecules in the mass is due to Van der Waals and other secondary bonding types. Thus, the aggregate polymer material is held together by forces that are substantially weaker than the primary bonds holding the molecules together. This explains why plastics in general are not nearly as stiff and strong as metals or ceramics.

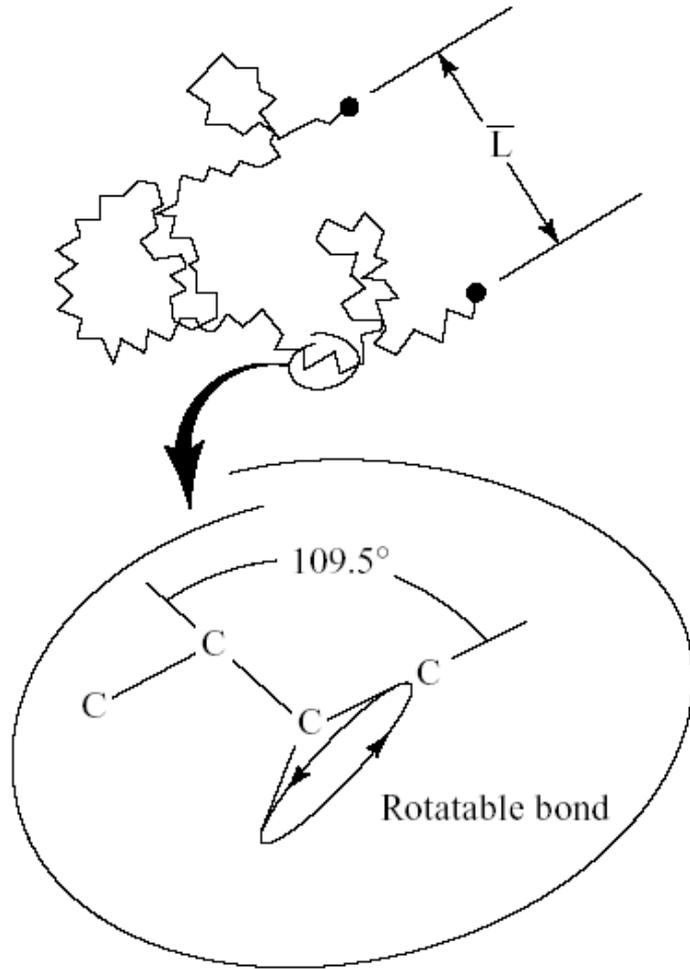


Figure 7

A straight line is used to represent the structure in two dimensions, but this is not the actual situation; each bond is at 109° to the next. When stress is applied, these interwinded molecules stretch to provide elongation that can be thousands of times greater than it would be in a typical crystal of a metal or ceramic.

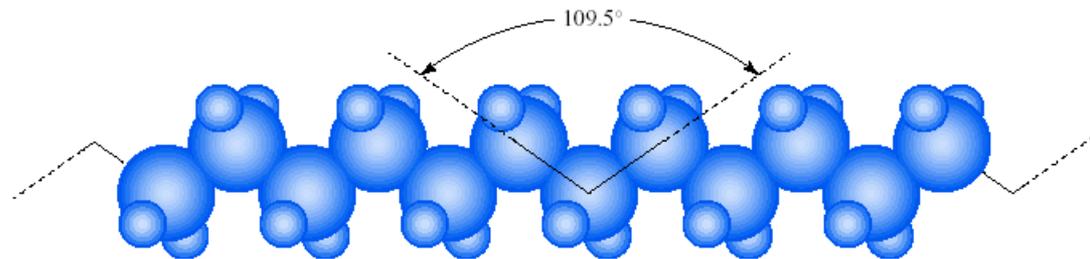


Figure 8

When a thermoplastic polymer is heated, it softens. The heat energy causes the macromolecules to become thermally agitated, exciting them to move relative to each other within the polymer mass (here, the bowl of spaghetti analogy loses its appeal). The material begins to behave like a viscous liquid, viscosity decreasing (fluidity increasing) with rising temperature.





THE END OF FIRST LECTURE

POLYMERIZATION MECHANISMS

1. Addition Polymerization: An initiator is added to the polymer which attracts one of the electrons of carbon double bond. The other electron of the bond then becomes unsatisfied and it attracts an electron from another mer and so the molecule grows. Finally, the chain is stopped when two growing segments meet or when one growing segment meets the terminator.

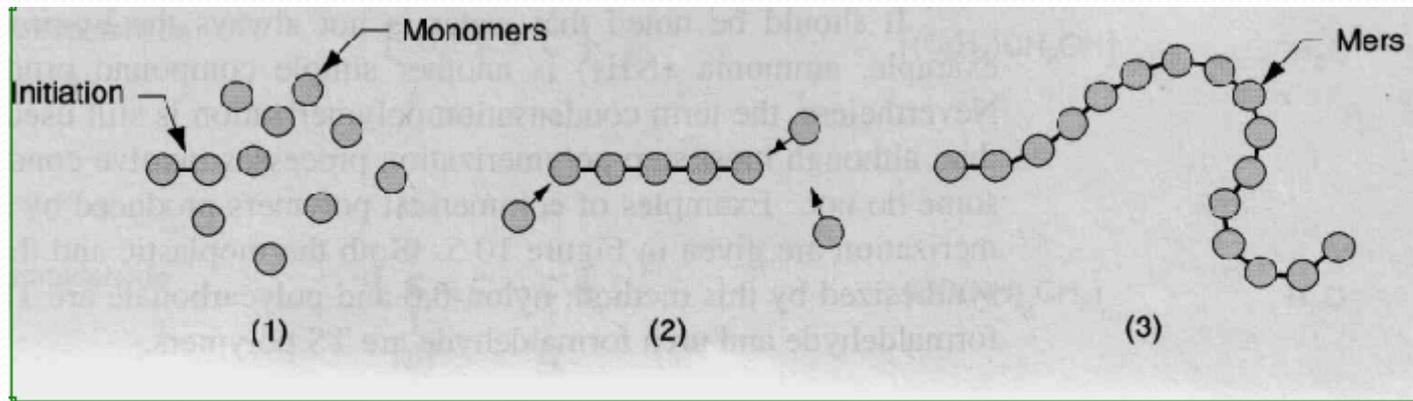


Figure 9 Model of addition (chain) polymerization



The rate of addition polymerization can be very rapid (e.g., polymerization of isobutylene using hydrogen peroxide can take place in a few seconds, yielding polymers comprising thousands of mers). For this reason, the process is also named Chain Reaction Polymerization.

A variety of chemicals, including organic substances, can be used as initiators and **retarders** to modify the reaction rate.

Polymer	Monomer	Repeating mer	Chemical formula
Polypropylene	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} $	$ \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---} \text{C} - \text{C} \text{---} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \right]_n $	$(\text{C}_3\text{H}_6)_n$
Polyvinyl chloride	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{Cl} \end{array} $	$ \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---} \text{C} - \text{C} \text{---} \\ \quad \\ \text{H} \quad \text{Cl} \end{array} \right]_n $	$(\text{C}_2\text{H}_3\text{Cl})_n$
Polystyrene	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} $	$ \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---} \text{C} - \text{C} \text{---} \\ \quad \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array} \right]_n $	$(\text{C}_8\text{H}_8)_n$
Polytetrafluoroethylene (Teflon)	$ \begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C} = \text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array} $	$ \left[\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{---} \text{C} - \text{C} \text{---} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right]_n $	$(\text{C}_2\text{F}_4)_n$
Polyisoprene (natural rubber)	$ \begin{array}{c} \text{H} \quad \text{H} \quad \quad \text{H} \\ \quad \quad \quad \\ \text{C} - \text{C} = \text{C} - \text{C} \\ \quad \quad \quad \\ \text{H} \quad \quad \text{CH}_3 \quad \text{H} \end{array} $	$ \left[\begin{array}{c} \text{H} \quad \text{H} \quad \quad \text{H} \\ \quad \quad \quad \\ \text{---} \text{C} - \text{C} = \text{C} - \text{C} \text{---} \\ \quad \quad \quad \\ \text{H} \quad \quad \text{CH}_3 \quad \text{H} \end{array} \right]_n $	$(\text{C}_5\text{H}_8)_n$

Figure 10 Some typical polymers formed by addition (chain) polymerization

2. Condensation Polymerization(Step-Reaction Polymerization): Two or more different molecules have to get together in each step if the molecule is to grow. This process is much slower than addition polymerization. This reaction can produce either a chain like molecule or a network structure.

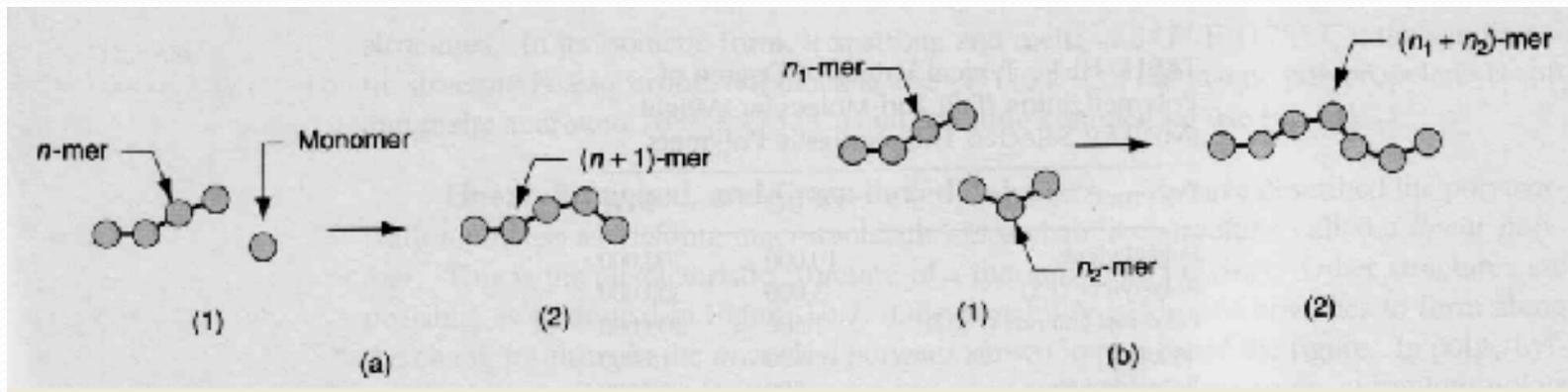


Figure 11. Model of step polymerization

Polymer	Repeating unit	Chemical formula	Condensate
Nylon-6, 6	$\left[\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{H} \end{array} \right]_6 - \text{N} - \begin{array}{c} \text{H} \\ \\ \text{O} \\ \\ \text{C} \end{array} - \left[\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{H} \end{array} \right]_4 - \begin{array}{c} \text{O} \\ \\ \text{C} \end{array} - \text{N} - \begin{array}{c} \text{H} \\ \\ \text{O} \\ \\ \text{C} \end{array} - \text{N} \right]_n$	$[(\text{CH}_2)_6(\text{CONH})_2(\text{CH}_2)_4]_n$	H_2O
Polycarbonate	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{C}_6\text{H}_4) - \text{C} - (\text{C}_6\text{H}_4) - \text{O} - \text{C} - \text{O} \\ \qquad \qquad \qquad \\ \text{CH}_3 \qquad \qquad \qquad \text{O} \end{array} \right]_n$	$(\text{C}_3\text{H}_6(\text{C}_6\text{H}_4)_2\text{CO}_3)_n$	HCl
Phenol formaldehyde	$\left[\begin{array}{c} \text{H} \\ \\ \text{C}_6\text{H}_4 - \text{C} \\ \qquad \qquad \\ \text{OH} \qquad \qquad \text{H} \end{array} \right]_n$	$[(\text{C}_6\text{H}_4)\text{CH}_2\text{OH}]_n$	H_2O
Urea formaldehyde	$\left[\begin{array}{c} \text{NH} \qquad \text{H} \\ \qquad \qquad \\ \text{C} = \text{O} - \text{C} \\ \qquad \qquad \\ \text{NH} \qquad \qquad \text{H} \end{array} \right]_n$	$(\text{CO}(\text{NH})_2\text{CH}_2)_n$	H_2O

Figure 12 Some typical polymers formed by step (condensation) polymerization

POLYMER STRUCTURES AND COPOLYMERS

There are structural differences among polymer molecules, even molecules of the same polymer. In this section we examine three aspects of molecular structure: (1) Stereoregularity, (2) branching and cross-linking, and (3) copolymers.

1. Stereoregularity *Stereoregularity* is concerned with the spatial arrangement of the atoms and groups of atoms in the repeating units of the polymer molecule. An important aspect of stereoregularity is the way the atom groups are located along the chain for a polymer that has one of the H atoms in its mers replaced by some other atom or atom group. Polypropylene is an example; it is similar to polyethylene except that CH_3 is substituted for one of the four H atoms in the mer.

Three tactic arrangements are possible, as illustrated in Figure 13:

- (a) *isotactic*, in which the odd atom groups are all on the same side;
- (b) *syndiotactic*, in which the atom groups alternate on opposite sides;
- and
- (c) *atactic*, in which the groups are randomly along either side.

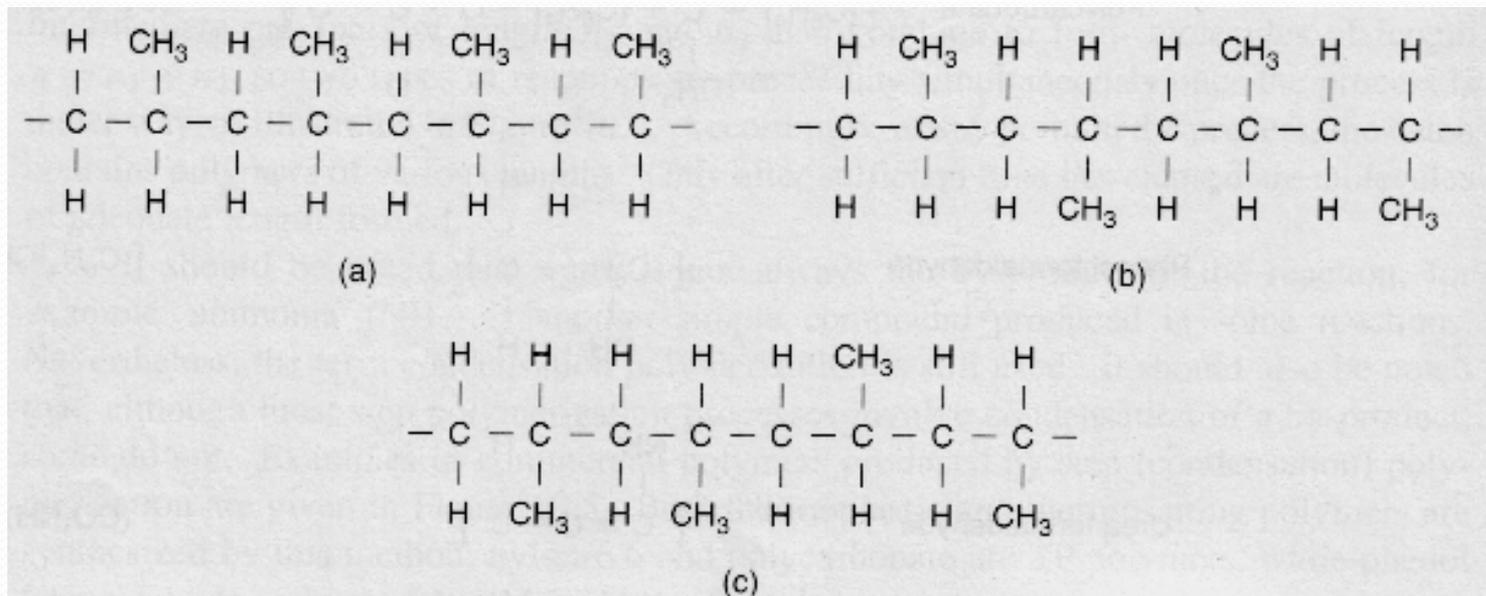
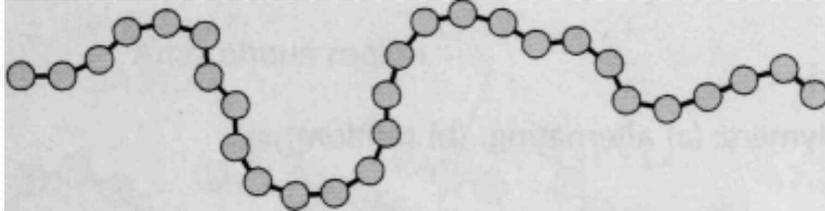


Figure 13 Possible arrangement of atom groups in polypropylene
 (a) isotactic (b) syndiotactic (c) atactic

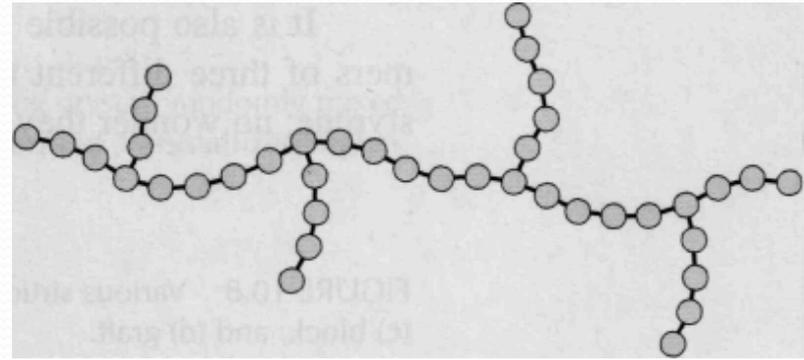


The tactic structure is important in determining the properties of the polymer. It also influences the tendency of a polymer to crystallize. Continuing with our polypropylene example, this polymer can be synthesized in any of the three tactic structures. In its isotactic form it is strong and melts at 175°C; the syndiotactic structure is also strong, but melts at 131°C; but atactic polypropylene is soft and melts at around 75°C and has little commercial use.

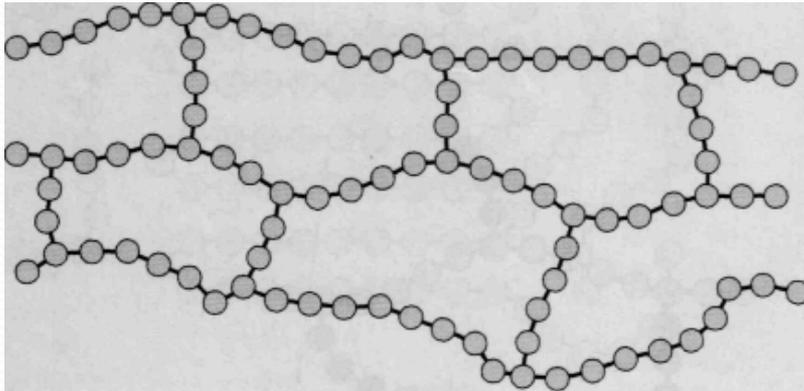
2. Linear, Branched, and Cross-linked Polymers We have described the polymerization process as yielding macromolecules of a chainlike structure, called a *linear polymer*. This is the characteristic structure of a thermoplastic polymer. Other structures are possible, as portrayed in Figure 14. One possibility is for side branches to form along the chain, resulting in the *branched polymer* shown in part (b) of the figure. In polyethylene, this occurs because hydrogen atoms are replaced by carbon atoms at random points along the chain, initiating the growth of a branch chain at each location. For certain polymers, primary bonding occurs between branches and other molecules at certain connection points to form *cross-linked polymers*, as pictured in Figure 14(c) and (d). Cross-linking occurs because a certain proportion of the monomers used to form the polymer are capable of bonding to adjacent monomers on more than two sides, thus allowing branches from other molecules to attach. Lightly cross-linked structures are characteristic of elastomers.



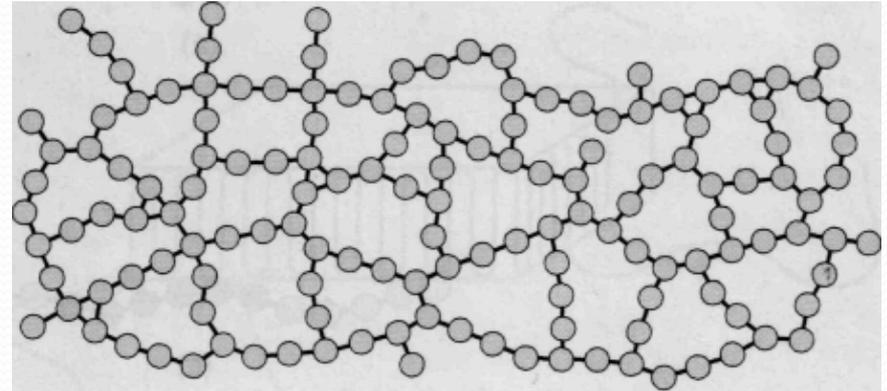
(a)



(b)



(c)



(d)

Figure 14 Various structures of polymer molecules: (a) linear, characteristic of thermoplastics; (b) branched, (c) loosely cross-linked as in an elastomer, and (d) tightly cross-linked or networked structure as in a thermoset.



When the polymer is highly cross-linked we refer to it as having a *network structure*, as in part (d) of the figure: in effect, the entire mass is one gigantic macromolecule. Thermosetting plastics take this structure after curing.

The presence of branching and cross-linking in polymers has a significant effect on properties. It is the basis of the difference between the three categories of polymers: TP, TS, and E. Thermoplastic polymers always possess linear or branched structures or a mixture of the two. Branches increase entanglement among the molecules, usually making the polymer stronger in the solid state and more viscous at a given temperature in the plastic or liquidy state. Thermosetting plastics and elastomers are cross-linked polymers.



Cross-linking causes the polymer to become chemically set; the reaction cannot be reversed. The effect is to permanently change the structure of the polymer; upon heating, it degrades or burns rather than melts. Thermosets possess a high degree of cross-linking, while elastomers possess a low degree of cross-linking. Thermosets are hard and brittle while elastomers are elastic and resilient.

3. **Copolymers** Polyethylene is a *homopolymer*, so is polypropylene, polystyrene, and many other common plastics; their molecules consist of repeating mers that are all the same type. *Copolymers* are polymers whose molecules are made of repeating units of two different types. An example is the copolymer synthesized from ethylene and propylene to produce a copolymer with elastomeric properties. The ethylene-propylene copolymer can be represented as follows:



where n and m range between 10 and 20 and the proportions of the two constituents are around 50% each. :The combination of polyethylene and polypropylene with small amounts of diene is an important synthetic rubber.



Copolymers can possess different arrangements of their constituent mers. The possibilities are shown in Figure 15:

(a) *alternating copolymer*, in which the mers repeat every other place;

(b) *random*, in which the mers are in random order, the frequency depending on the relative proportions of the starting monomers;

(c) *block*, in which mers of the same type tend to group themselves into long segments along the chain; and

(d) *graft*, in which mers of one type are attached as branches to a main backbone of mers of the other type. The ethylene-propylene diene rubber, mentioned previously, is a block type.

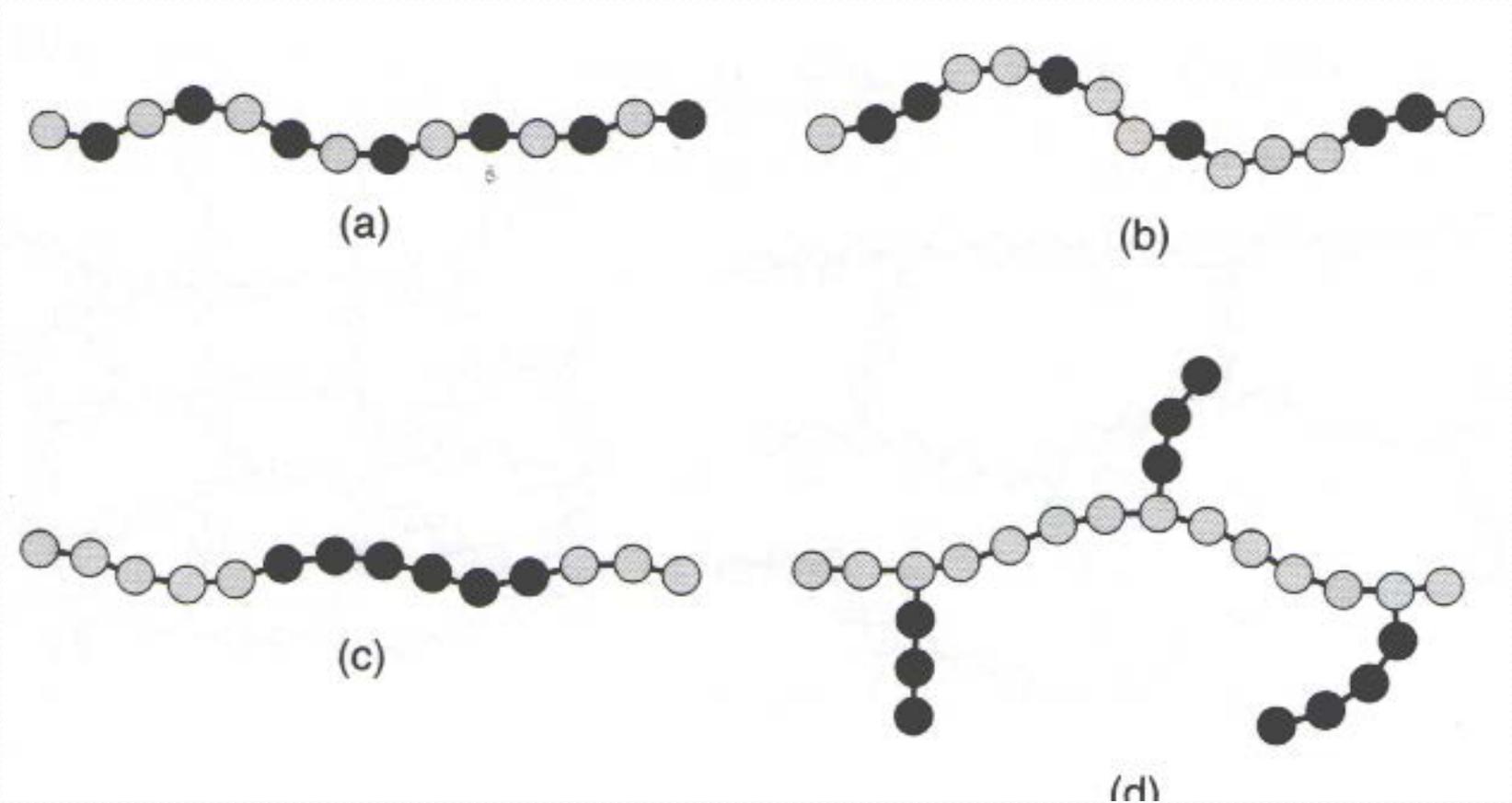


Figure 15 Various structures of copolymers:
a) alternating, (b) random, (c) block, and (d) graft.



Synthesis of copolymers is analogous to alloying of metals to form solid solutions. As with metallic alloys, differences in the ingredients and structure of copolymers can have a substantial effect on properties. An example is the polyethylene-polypropylene mixture we have been discussing. Each of these polymers alone is fairly stiff; yet a 50-50 mixture of the two forms a copolymer of random structure that is very rubbery.

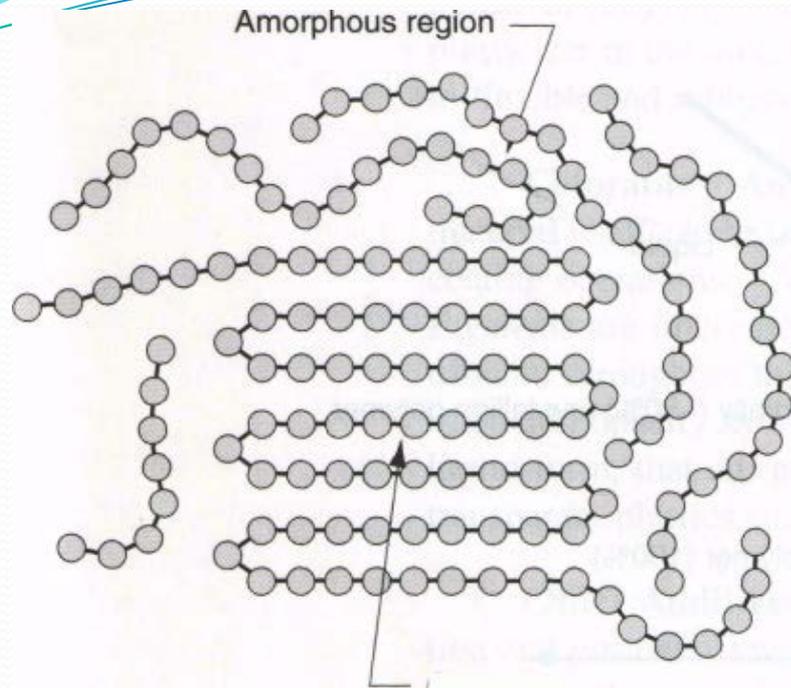
It is also possible to synthesize *ternary polymers*, or *terpolymers*, which consist of mers of three different types. An example is the plastic ABS (acrylonitrile-butadiene-styrene; no wonder they call it ABS).

Crystallinity Both amorphous and crystalline structures are possible with polymers, although the tendency to crystallize is much less than for metals or nonglass ceramics. Not all polymers can form crystals. For those that can, the *degree of crystallinity* (the proportion of crystallized material in the mass) is always less than 100%. As crystallinity increases in a polymer, so do (1) density, (2) stiffness, strength, and toughness, and (3) heat resistance. In addition, (4) if the polymer is transparent in the amorphous state, it becomes opaque when partially crystallized. A number of polymers are transparent, but they must be in the amorphous (glassy) state in order to possess this property. Some of these effects can be illustrated by the differences between low- and high-density polyethylene, presented in Table 2. The underlying reason for the property differences between these materials is the degree of crystallinity.

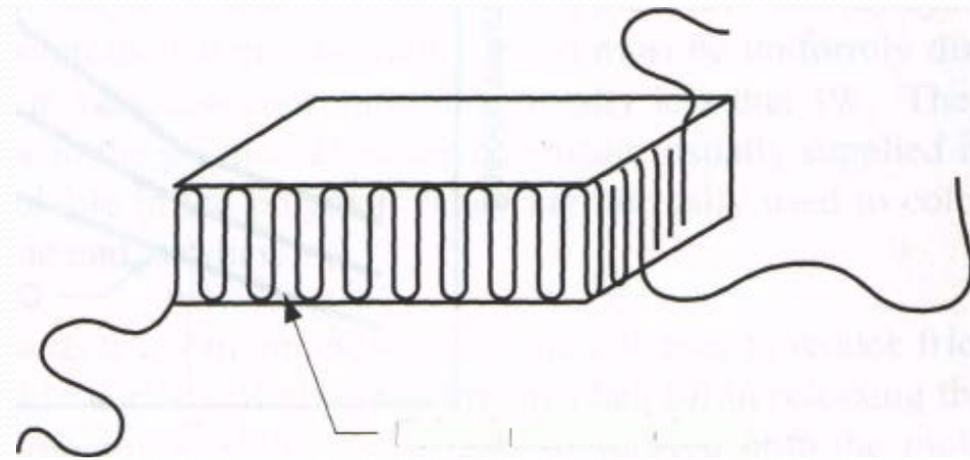
Table 2 Comparison of Low- and High-density Polyethylene

Polyethylene type	Low density	High density
Degree of crystallinity	55%	92%
Specific gravity	0.92	0.96
Modulus of elasticity	20,000 psi	100,000 psi
Melting temperature	115°C	135° C

Linear polymers consist of long molecules with thousands of repeated mers. Crystallization in these polymers involves the folding back and forth of the long chains upon themselves to achieve a very regular arrangement of the mers, as pictured in Figure 16(a). The crystallized regions are called *crystallites*. Owing to the tremendous length of a single molecule (on an atomic scale), it may participate in more than one crystallite. Also, more than one molecule may be combined in a single crystal region. The crystallites take the form of lamellae, as pictured in Figure 16(b), that are randomly mixed in with the amorphous material. Thus, a polymer that crystallizes is a two-phase system: crystallites interspersed throughout an amorphous matrix.



a) Crystallite



b) Folded molecule chains

Figure 16 Crystallized regions in a polymer: (a) long molecules forming crystals randomly mixed in with the amorphous material; and (b) folded chain lamella, the typical form of a crystallized region.

A number of factors determine the capacity and/or tendency of a polymer to form crystalline regions within the material. The factors can be summarized as follows:

- (1) as a general rule, only linear polymers can form crystals;
- (2) stereoregularity of the molecule is critical: isotactic polymers always form crystals; syndiotactic polymers sometimes form crystals; atactic polymers never form crystals;
- (3) copolymers, due to their molecular irregularity, rarely form crystals;
- (4) slower cooling promotes crystal formation and growth, as it does in metals and ceramics;
- (5) mechanical deformation, as in the stretching of a heated thermoplastic, tends to align the structure and increase crystallization; and
- (6) plasticizers (chemicals added to a polymer to soften it) reduce the degree of crystallinity.

Effects of crystallinity. The mechanical and physical properties of polymers are greatly influenced by the degree of crystallinity; as crystallinity increases, polymers become stiffer, harder, less ductile, more dense, less rubbery, and more resistant to solvents and heat (Figure 17). The increase in density with increasing crystallinity is caused by crystallization shrinkage and a more efficient packing of the molecules in the crystal lattice. For example, the highly crystalline form of polyethylene, known as high-density polyethylene (HDPE), has a specific gravity in the range of 0.941 to 0.970 (80% to 95% crystalline) and is stronger, stiffer, tougher, and less ductile than low-density polyethylene (LDPE), which is about 60% to 70% crystalline and has a specific gravity of about 0.910 to 0.925.

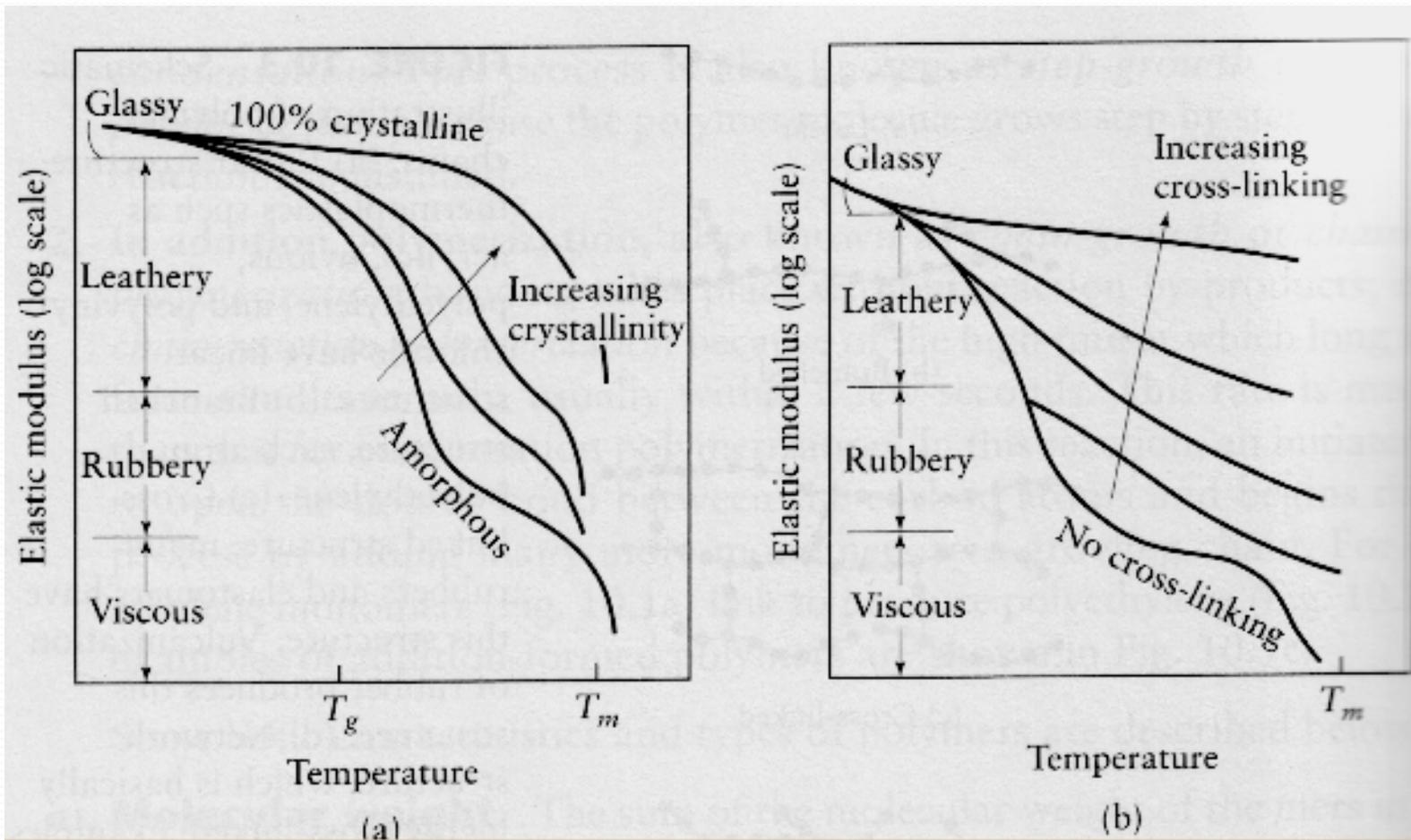


Figure 17 Behaviour of polymers as a function of temperature and (a) degree of crystallinity and (b) cross-linking



Optical properties also are affected by the degree of crystallinity. The reflection of light from the boundaries between the crystalline and amorphous regions in the polymer causes opaqueness. Furthermore, because the index of refraction is proportional to density, the greater the density difference between the amorphous and crystalline phases, the greater is the opaqueness of the polymer. Polymers that are completely amorphous can be transparent, such as polycarbonate and acrylics.



THE END OF SECOND LECTURE

Thermal Behavior of Polymers

The thermal behavior of polymers with crystalline structures is different from that of amorphous polymers. The effect of structure can be observed on a plot of specific volume (reciprocal of density) as a function of temperature, as plotted in Figure 18. A highly crystalline polymer has a melting point T_m at which its volume undergoes an abrupt change. Also, at temperatures above T_m , the thermal expansion of the molten material is greater than for the solid material below T_m . An amorphous polymer does not undergo the same abrupt changes at T_m . As it is cooled from the liquid, its coefficient of thermal expansion continues to decline along the same trajectory as when it was molten, and it becomes increasingly viscous with decreasing temperature. During cooling below T_m , the polymer changes from liquidity to rubbery. As temperature continues to drop, a point is finally reached at which the thermal expansion of the amorphous polymer suddenly becomes lower. This is the *glass-transition temperature*, T_g , seen as the change in slope. Below T_g , the material is hard and brittle.

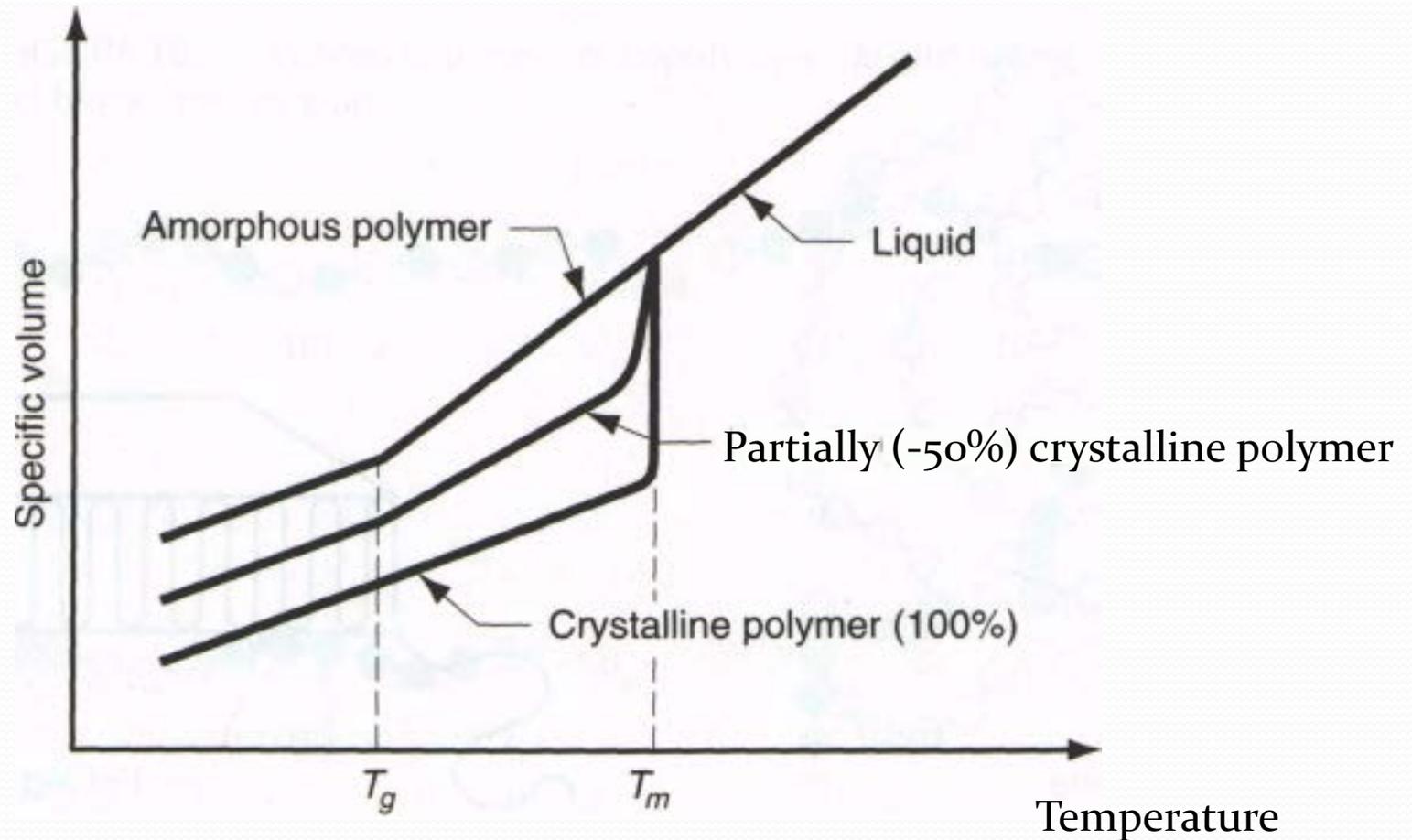


Figure 18 Behavior of polymers as a function of temperature.



A partially crystallized polymer lies between these two extremes, as indicated in the figure. It is an average of the amorphous and crystalline states, the average depending on the degree of crystallinity. Above T_m it exhibits the viscous characteristics of a liquid; between T_m and T_g it has viscoelastic properties; and below T_g it has the conventional elastic properties of a solid.

Material	T _g (°C)	T _m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene High density	-90	137
Polyethylene Low density	-110	115
Polymethylmethacrylate	105	
Polypropylene	-14	176
Polystyrene	100	239
Polytetrafluoroethylene (Teflon)	-90	327
Polyvinyl chloride	87	212
Rubber	-73	



What we have described in this section applies to thermoplastic materials, which can move up and down the curve of Figure 18 multiple times. The manner in which they are heated and cooled may change the path that is followed. For example, fast cooling rates may inhibit crystal formation and increase the glass-transition temperature. Thermosets and elastomers cooled from the liquid state behave like an amorphous polymer until crosslinking occurs. Their molecular structure restricts the formation of crystals. And once their molecules are cross-linked, they cannot be reheated to the molten state.



Additives The properties of a polymer can often be beneficially changed by combining them with additives. Additives either alter the molecular structure of the polymer or add a second phase to the plastic, in effect transforming a polymer into a composite material. Additives can be classified by function as (1) fillers, (2) plasticizers, (3) colorants, (4) lubricants, (5) flame retardants, (6) cross-linking agents, (7) ultraviolet light absorbers, and (8) antioxidants.

Fillers *Fillers* are solid materials added to a polymer usually in particulate or fibrous form to alter its mechanical properties or to simply reduce material cost. Other reasons for using fillers are to improve dimensional and thermal stability. Examples of fillers used in polymers include cellulosic fibers and powders (for example, cotton fibers and wood flour, respectively); powders of silica (SiO_2), calcium carbonate (CaCO_3), and clay (hydrous aluminum silicate); and fibers of glass, metal, carbon, asbestos, or other polymers. Fillers that improve mechanical properties are called *reinforcing agents*, and composites thus created are referred to as *reinforced plastics*, they have higher stiffness, strength, hardness, and toughness than the original polymer. Fibers provide the greatest strengthening effect.

Plasticizers Plasticizers are chemicals added to a polymer to make it softer and more flexible and to improve its flow characteristics during forming. The plasticizer works by reducing the glass-transition temperature to below room temperature. Whereas the polymer is hard and brittle below T_g , it is soft and tough above it. Addition of a plasticizer to polyvinyl chloride (PVC) is a good example; depending on the proportion of plasticizer in the mix, PVC can be obtained in a range of properties, from rigid and brittle to flexible and rubbery.

Colorants An advantage of many polymers over metals or ceramics is that the material itself can be obtained in almost any color. This eliminates the need for secondary coating operations. Colorants for polymers are of two types: (1) pigments and (2) dyes.

Pigments are finely powdered materials that are insoluble in and must be uniformly distributed throughout the polymer in very low concentrations, usually less than 1%. They often add opacity as well as color to the plastic.

Dyes are chemicals, usually supplied in liquid form, that are generally soluble in the polymer. They are normally used to color transparent plastics such as styrene and acrylics.

Other Additives *Lubricants* are sometimes added to the polymer to reduce friction and promote flow at the mold interface. Lubricants are also helpful in releasing the part from the mold in injection molding. Mold release agents, sprayed onto the mold surface, are often used for the same purpose.

Nearly all polymers burn if the required heat and oxygen are supplied. Some polymers are more combustible than others. *Flame retardants* are chemicals added to polymers to reduce flammability by any or a combination of the following mechanisms:

- (1) interfering with flame propagation,
- (2) producing large amounts of incombustible gases, and/or
- (3) increasing the combustion temperature of the material. The chemicals may also function to
- (4) reduce the emission of noxious or toxic gases generated during combustion.

We should include among the additives those that cause cross-linking to occur in thermosetting polymers and elastomers. The term *cross-linking agent* refers to a variety of ingredients that cause a cross-linking reaction or act as a catalyst to promote such a reaction. Important commercial examples are

- (1) sulfur in vulcanization of natural rubber,
- (2) formaldehyde for phenolics to form phenolic thermosetting plastics, and
- (3) peroxides for polyesters.

Many polymers are susceptible to degradation by ultraviolet light (for example, from sunlight) and oxidation. The degradation manifests itself as the breaking of links in the long-chain molecules. Polyethylene, for example, is vulnerable to both types of degradation, which lead to a loss of mechanical strength. *Ultraviolet light absorbers* and *antioxidants* are additives that reduce the susceptibility of the polymer to these forms of attack.



THE END OF THE CHAPTER



Maximum number of cavities in Injection Moulding

The maximum number of cavities can be determined according to the followings:

- 1) Shot capacity of the machine
- 2) Clamping capacity of the machine
- 3) Plastifying capacity of the machine
- 4) Cost of mould per cavity and cost of the total operation

1) Shot Capacity:

$$Q_1 = \frac{\frac{2}{3}S - W_r}{W_p}$$

where Q_1 : no. of cavities based on shot capacity
 S : shot capacity in weight
 W_r : weight of the sprue and runners
 W_p : weight of the piece

2) Clamping Capacity:

$$Q_2 = \frac{0,4C - A_r}{A_p}$$

where

Q₂: no. of cavities based on clamping capacity

C: clamping capacity (tons)

A_r: projected area of the sprue and runners

A_p: projected area of the piece

3) Plastifying Capacity:

$$Q_3 = \frac{0,00445PT - W_r}{W_p}$$

where

Q_3 : no. of cavities based on plastifying capacity

P : plastifying capacity of the heating cylinder (weight/hour)

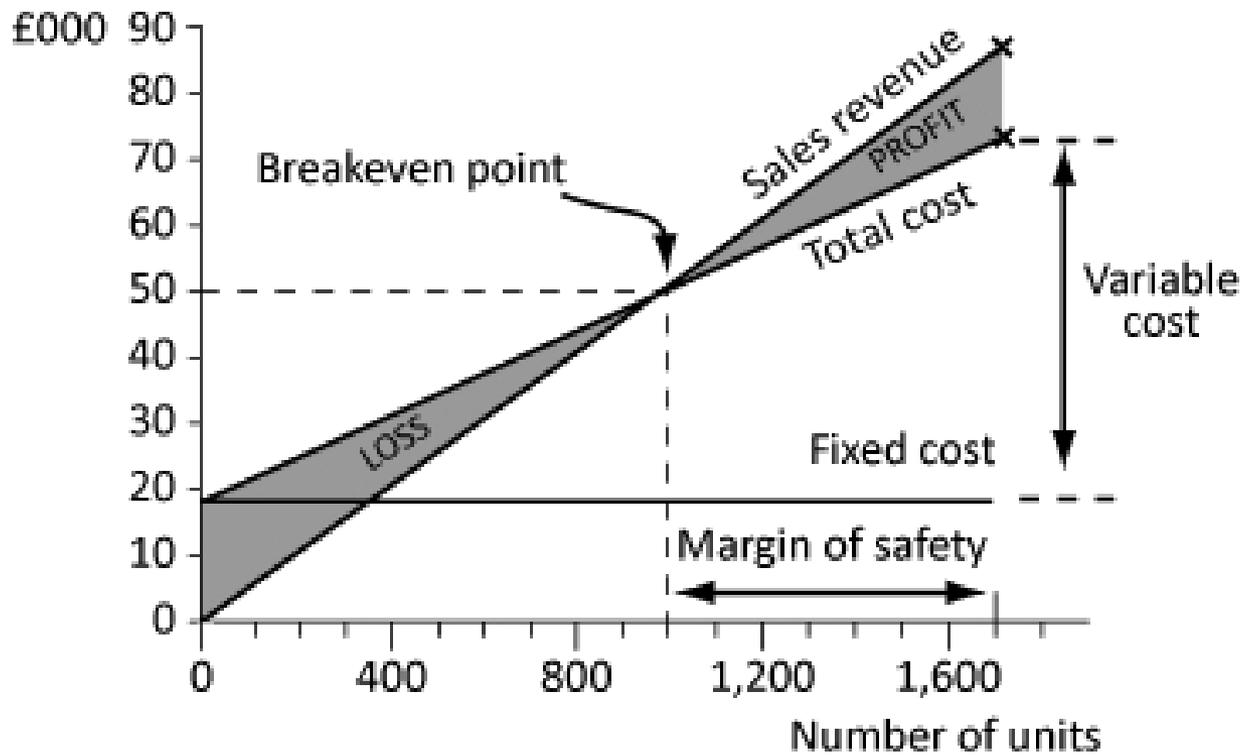
T : overall cycle time (second)

W_r : weight of the sprue and runners

W_p : weight of the piece

4) Cost Break-even Chart:

Final decision is to compromise of overall factors



MACHINING FROM STOCK

During machining of plastics the followings should be considered:

1. Low modulus of elasticity
2. High elastic recovery
3. Poor conduction of heat
4. Higher thermal expansion

Guidelines in specifying tool geometry:

- 1) Provide polished surfaces on those tool areas coming in contact with the work so as to minimize frictional drag and resulting heat generation
- 2) Design tools so that continuous type chips are produced. This involves the precaution of large rake angles. The rake angle will be dependent on the depth of cut, cutting speed, and the type of plastic material.
- 3) In drill design, the packaging of chips should be avoided by providing wide polished flutes and low helix angle.
- 4) In turning and milling, diamond tools provide the best accuracy, surface finish and uniformity. Surface speeds of 150-200 m/min with feeds of 0,05-0.10 mm are typical.





